Research Essentials

Innovative Solutions in Fluid-Particle Systems and Renewable Energy Management

Katia Tannous

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Innovative Solutions in Fluid-Particle Systems and Renewable Energy Management

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Biomass has attracted attention as a source of renewable energy. It is available in different forms such as lignocellulosic stalks of herbaceous and woody biomass. These forms of biomass should be prepared to go through bioconversion process or biofuel production. One of the major unit operations for preparation is size reduction, which increases the surface area available and breaks the structure of biomass. Size reduction is energy intensive and an expensive step of feedstock preparation. The characteristics of ground particles are the result of interactions between material properties and the modes of size reduction like shear, impact, and attrition. The fundamentals of size reduction of fibrous biomass are not well understood. This chapter summarizes the latest studies on modeling of size reduction of lignocellulosic and woody biomass.

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Steam explosion is a thermo-chemical pretreatment widely used to disrupt the ultra-structure of the cell wall of the ligno-cellulosic fiber to improve the fractionation of the major ligno-cellulosic components of the biomass for biochemical conversion. In recent years, steam explosion pretreatment has been applied on the fibers for improving the pellet quality of woody and agricultural biomass for thermo-chemical conversion. The improved qualities include high bulk density, low equilibrium moisture content, higher heating value, mechanical strength and moisture resistance. All of these desirable properties allow the steam exploded pellets to be handled and stored outdoors safely, similar to coal. This also raises lots of interests in considering pellets as preferable feedstock for the thermal power plant or bio-refinery facilities. In this chapter, the state of art of research findings on the effect of steam explosion on size reduction and pellet quality of woody and agriculture biomass will be discussed.

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The study of fluid dynamic and mixing characteristics of biomass particles in fluidized beds is fundamental for comprehension of thermal conversion processes. In this chapter a review of literature showed a large lacks of technical information about the quality of fluidization and representative models concerning binary mixtures (biomass and inert). A case study was presented involving Eucalyptus grandis wood and *tucumã* endocarp in order to obtain fluid dynamic parameters such as the characteristic fluidization, velocity and porosity, and the bed expansion. These parameters were more significant for mixtures with smaller diameter and mass fraction ratios, and sphericity ratio, due to the facility of beds to fluidize. A map was presented to identify the limits of effective mixtures considering four classes as a function of the complete fluidization Reynolds' and Archimedes' numbers. Empirical correlations have been proposed and showed a good agreement with the experimental work.

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The study of the kinetics involved in lignocellulosic biomass pyrolysis has received great attention in the last decades and different mathematical models have been derived. In this chapter, a literature review was performed in order to summarize the existing models that use thermogravimetric data to estimate the kinetic parameters, which are important to improve and optimize the process. Additionally, a case study was presented exemplifying the application of kinetic modeling for the residue of one Brazilian species (Brazil nut woody shell). The isoconversional models of Ozawa-Flynn-Wall, modified Coats-Redfern, and Friedman were applied, as well as three and four independent parallel reactions models. The four reactions model presented the best fit between experimental and theoretical data, providing a better representation of the biomass pyrolysis reaction.

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This chapter debates the potential of the biorefinery of biomass using microwave heating. First, the essential information regarding electromagnetic radiation is explained and the pros and cons of microwave heating versus conventional heating, especially in the thermochemical treatment of biomass, are discussed. Different methodologies for predicting and measuring the temperature gradient within a material subjected to electromagnetic waves are demonstrated. The chapter summarizes the key conclusions of various investigations regarding the effects of microwave heating on chemical reactions and presents how electromagnetic radiation can assist the biorefinery of biomass. Finally, the issues and limitations regarding scaling-up microwave heating are elucidated, along with possible solutions to these problems.

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Alberto Gonzalo Callejo, University of Zaragoza, Spain
Rolando Zanzi Vigouroux, Royal Institute of Technology, Sweden

In this chapter there is described a tentative of obtain and characterize pyrolysis liquids from cashew nut shell, using a suggested classification of tars. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture "tars" with a clear definition. And so, in order to facilitate the study of the evolution of liquid fraction composition, the compounds have been grouped according to their chemical nature, but differently from other works, it was extended the range of compounds in order to evaluate the influence of the reactor parameters in liquid fraction compositions. It is described, as well, the pyrolysis and gasification of cashew nut shell, that has been studied in a laboratory scale reactor. It was quantified and classified the production of liquids (tar) and evaluated the final temperature influence (800, 900 and 1000 °C) and the use of N_2 in pyrolysis case, and a mixture of N_2 and steam or air in the gasification case. Finally, it is described the identification and quantification of tar compositions, by CG-MS and CG-FID analyzes. Around 50 different compounds have been detected in the liquid fraction obtained, most of them being present at very low concentrations and it is observed that in the pyrolysis and gasification processes, phenol and benzene were the major chemical groups, and this fact agree with others works, presented here in a bibliographic revision.

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In recent years, attention has focused on exergy analysis, a type of thermodynamic analysis which is an important tool for the efficiency assessment and the processes optimization when dealing with energy conversion and, particularly, thermochemical processes such as gasification. Thus, this chapter aims to introduce the fundamental concepts of energy and exergy and describe the energy and exergy evaluation tools, elucidating its importance for calculations applied to gasification processes. A case study was performed to show the proposal of energy and exergy analysis. Therefore, a single global gasification chemical reaction was used to represent the gasification process. This analysis can provide a tool to assess and develop models, simulations, calculations, and to optimize real gasification processes. Information and experiences covered in this chapter help to be put into perspective the technology, research and overcoming of challenges.

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In this chapter sugarcane bagasse may be submitted to a biological route in which the technologies used to obtain lignocellulosic ethanol (2nd generation ethanol) from lignocellulosic materials involve pre-treatment and the hydrolysis of the polysaccharides in the biomass into fermentable sugars for subsequent fermentation. Taking into consideration the use of sugarcane bagasse as a raw material for 2nd generation ethanol, the acid hydrolysis / pretreatment of sugarcane bagasse could be more feasible that others, and must be evaluated in this context. On the other hand, from biomass is possible to obtain products with high added value and energy, mainly by the use of thermochemical processes (e.g. pyrolysis and gasification) and biochemical processes (e.g., fermentation and anaerobic digestion). However, the products obtained from the thermochemical processes can be used as raw material for biochemical processes which multiplies the quantity of products to be obtained from biomass.

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The management of projects regarding the use of biomass requires human resources with specific technical knowledge and tools to assess the real potential of raw materials within one or several production chains. Storage and transportation logistics, conservation and handling of the biomass, available technologies of transformation, and consumer market for the products are critical stages in the management process. The following chapter will present the technical, financial, and market criteria for managing production chains that use biomass as raw material in processes of fast pyrolysis.

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Chad Eugene Kruger, Washington State University, USA
Mark Raymond Fuchs, Washington State Department of Ecology, USA
Gloria Eileen Flora, U.S. Biochar Initiative, USA

The objective of this chapter is to review and discuss sustainability and techno-economic criteria to integrate pyrolysis, biochar activation, and bio-oil refining into sustainable business models. Several business models such as the production of biochar with heat recovery and bio-oil refining are discussed. Cost data needed by engineering practitioners to conduct enterprise-level financial analyses of different biomass pyrolysis economy models are presented. This chapter also reviews life cycle assessments of pyrolysis business models. If the feedstock used is produced sustainably and if the pyrolysis vapors are used for bio-oil or heat production, both, the production of biochar through slow pyrolysis and its use as a soil amendment to sequester carbon, and the production and refining of fast pyrolysis oils to produce transportation fuels could have a positive environmental impact.

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Foreword

The consumption of natural resources is experiencing an accelerated exponential rise, particularly during the last recent decades, due to the increasing demand of goods and services caused by the world's economic and demographic growth. The land-use change, waste products and industrial activity is increasingly threatening the ecosystems and current life support systems.

This fact is captured by global indicators such as the i) Living Planet Index, which measures more than 10,000 representative populations of mammals, birds, reptiles, amphibians and fish; ii) the Ecological Footprint, which represents the amount of biologically productive land and sea area necessary to supply the resources that a human population consumes, and to assimilate associated waste; or iii) the nine planetary boundaries—stratospheric ozone layer, biodiversity, chemicals dispersion, climate change, ocean acidification, freshwater consumption, land system change, nitrogen and phosphorous inputs to the biosphere and ocean and, atmospheric aerosol loading—within which humanity can continue to develop without provoking abrupt or irreversible environmental changes. Thus, during the period 1970-2010 the Living Planet Index (WWF, 2014) has declined by 52 per cent, i.e. in four decades population sizes of vertebrate species have dropped by half; the Ecological Footprint (WWF, 2014) has increased from 1 planet Earth area to 1,5 planets, i.e. for more than 40 years, humanity's demand has exceeded the planet's biocapacity—the amount of biologically productive land and sea area that is available to regenerate the consumed natural resources; and in 2009 was estimated that three—climate change, nitrogen input and biodiversity—of the nine planetary boundaries were already exceeded (Stockholm University, n.d.). These very global indicators are objective signs warning us that we are rapidly approaching the biophysical limits of our planet.

Moreover, demand of natural resources is unevenly distributed with people in industrial countries consuming resources at a much faster rate. And in this continuing overshoot, poverty is still widespread. About two thirds of world's population is living under the threshold of poverty. In other words, within this limited and somehow scarce availability of natural resources there is still about two thirds of world's population that has not covered yet their essential needs of food, water, clothes, education, health, housing, energy… And satisfying these essential needs requires massive extraction, processing and conversion of renewable and non-renewable natural resources, with its associated and unavoidable environmental impact.

In terms of energy, still nowadays there are more than 1 billion people without access to electricity (around 1.44 billion people [Lior, 2011] in 2009). On the other hand, world's energy demand is also experiencing an accelerated exponential growth, since several decades ago. Thus, it is expected that demand for electricity would require during the coming two decades the installation of as much power generation capacity as was installed in the entire 20th century (Lior, 2011). World's total primary energy supply doubled during the last four decades from 6101 Mtoe in 1973 to 13,371 Mtoe in 2012 (IEA, 2014). In this context, fossil fuels – one of the major contributors to the humanity's Ecological Footprint – still represented in 2012 more than 80% of primary energy supplied (IEA, 2014), with the environmental and socio-economic problems associated to their usage.

Fossil fuels are confined to limited regions of the planet and their supply is governed by dynamic political, economic and even environmental factors. Increased demand is placing more and more a higher pressure on non-renewable energy resources, thus boosting a very strong competition for the appropriation of these resources, which may contribute to a global instability. Thus, a new energy model with a consistent energy strategy addressing key aspects such as energy supply and demand, security of access, affordability and development issues, equity, market dynamics, efficiency and technological development, among others, is required. This is claimed more and more by worldwide renowned experts and decision makers, e.g. Maria van der Hoeven, Executive Director of the International Energy Agency.

Low carbon energy technologies provoking a low environmental impact and managed with sustainability criteria consist of new and innovative energy technologies in which renewable energy sources are essential.

Fortunately nature is providing to us with a huge amount of renewable high quality energy (exergy), i.e. renewable energies can satisfy at least two orders of magnitude more than the current world energy demand. Nevertheless they still represent a minority despite the already worldwide accepted need to accelerate the development of low-carbon energy technologies, which is being supported by important investments in renewable energy technologies. Thus, from the end of 2004, worldwide renewable energy capacity grew at rates of 10–60% annually for many technologies, and worldwide investments in renewable technologies amounted to more than US$ 214 billion in 2013, with China, USA, Japan and the European Union heavily investing in wind, solar, hydro and biofuels (REN21, 2014).

Biomass is nowadays the largest single renewable energy source providing 10% of global primary energy supply, about three times more than all other renewable energies together -hydro represents less than 2.5% and the rest (solar, wind, geothermal, etc.) about 1.1% (IEA, 2014). Currently biomass is widely used in many developing countries, where it provides basic energy for cooking and space heating but with inefficient technologies. It also plays an important role in some industrialized countries where biomass has a significant contribution in electricity and heat production as well as in biofuel production, as it is the case of bioethanol in Brazil.

It is foreseen in the short and mid-term a strong increase in bioenergy supply (REN21, 2014): providing flexible electricity; in the industry providing high temperature heat and replacing fossil fuels; in the residential sector, with the deployment of advanced biomass cookstoves and clean fuels heat production centralized and decentralized technologies; in the transport sector increasing very significantly the share of biofuels; and in the chemical industry providing not only energy but highly added value bioproducts and biochemicals.

Nevertheless, switching to a new sustainable energy model without the consumption of fossil fuels requires the massive usage of renewable energy resources, which involves very important technological challenges, e.g. dynamic and intermittent availability, low energy density requiring important surface area, quite often a mismatch between supply and demand, seasonal and weather dependent… Overcoming these difficulties requires rigorous and continued research accompanied with technological development and innovation.

In the particular case of biomass, its utilization at a large scale as an energy resource involves specific and complex challenges of different nature (environmental, social, technical) associated to biodiversity, food security risks and to the very specific features of the different climates with very different biological species. Due to the large variety of different feedstocks one of the main technological challenges is the efficient conversion of biomass either into different forms of energy (power or heat) or into bioproducts and biochemicals.

Efficient conversion of biomass involves, among others, milling, particulate size reduction, fluidization, chemical reactions, kinetics of chemical and energy conversion or thermochemical processes. This book envisages all these aspects presenting the updated state of the art of fluid particle system and biomass energy management, with a broad and applied perspective oriented to the identification of innovative particle treatment, energy efficient processes and production of marketable products with high added value and sustainability criteria.

Thus, in chapter 1 are presented the latest studies on modeling size reduction of lignocellulosic and woody biomass. Size reduction is an energy intensive and expensive unit operation of biomass preparation which is essential for an efficient biomass conversion. Recommendations about biomass size reduction operations depending on the end process are proposed based on the study and analysis of different fractionation mechanisms and models, in which the importance of moisture content and size characteristics on energy consumption are discussed.

Chapter 2 studies the state of art of research findings on the effect of steam explosion on size reduction and pellet quality of woody and agriculture biomass, allowing the steam exploded pellets to be handled and stored safely outdoor similar to coal and considering pellets as preferable feedstock for the thermal power plant or bio-refinery facilities. Steam explosion pretreatment of biomass prior to pelletization appears to be a promising technology to produce durable and hydrophobic pellets for safe handling, storage and conversion, allowing to reduce the high logistical cost of transportation and storage due to their higher bulk density and increasing its conversion efficiency by improving its physico-chemical characteristics, i.e lower equilibrium moisture content, higher heating value, improved mechanical strength and higher moisture resistance.

Chapter 3 is very useful to obtain higher efficiency in thermal conversion reactors improving the utilization of biomass as a renewable fuel. This is achieved through the study of a literature overview on fluid dynamic and mixing of biomasses associated to experimental studies, focusing in basic design parameters such as: characteristic fluidization velocities and porosities, and bed expansion in gas-fluidized beds. Furthermore is presented a case study in which are exemplified the differences between biomasses (Eucalyptus grandis and *tucumã* endocarp) including also recommendations to succeed the best mixtures with inert material (sand), and also suggesting empirical correlations of these parameters.

Pyrolysis is one of the most important ways to transform biomass into value added products (e.g., bio-char, bio-oil, fuels, synthesis gas, and chemicals) with several industrial applications, thanks to the conversion of solid biomass into liquid biofuels, presenting advantages in transport, storage, combustion, and flexibility in production and marketing. A deep understanding of the kinetics of pyrolysis of biomass is essential for the design industrial reactors, as well as to obtain important empirical parameters for process modeling and controlling. Thus, in Chapter 4 the study of the kinetics of the pyrolysis of biomass is performed, through a literature review to summarize the existing models that use thermogravimetric data to estimate the kinetic parameters, as well as through a case study exemplifying the application of kinetic modeling for the residue of one Brazilian species (Brazil nut woody shell).

Chapter 5 debates the potential of the biorefinery of biomass using microwave heating. Pros and cons of microwave heating versus conventional heating, especially in the thermochemical treatment of biomass, are discussed. Key conclusions regarding the effects of microwave heating on chemical reactions and how electromagnetic radiation can assist the biorefinery of biomass are presented. Furthermore, the issues and limitations regarding scaling-up microwave heating are elucidated, along with possible solutions to these problems.

Chapter 6 deals with the difficult and unsolved problem of obtaining and characterizing the liquid products obtained from biomass pyrolysis and gasification, which has long been a major difficulty for researchers. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture “tars” with a clear definition. Therefore, in this chapter is proposed a procedure for the capture and characterization of pyrolysis and gasification liquids based on the pyrolysis and gasification of cashew nut shell.

Chapter 7 presents a valuable tool for the energy analysis of complex systems, which is the exergy analysis. It is a powerful energy analysis tool locating and quantifying the degradation of the energy quality in energy conversion processes, e.g. biomass conversion processes. It provides their thermodynamic efficiency as a whole as well as the efficiency of each single process identifying the less efficient with higher potential of energy efficiency improvement. It is an excellent tool for appropriate energy process integration and energy efficient design of new biomass conversion systems.

Chapter 8 analyzes different processing routes for the sugarcane bagasse, which is already available in the production site. Thus, it is a renewable and economical alternative for the sustainable production of biofuels using the biological route and the hybrid biochemical - thermochemical routes, with the advantage that the sugarcane based process may share some of the available infrastructure for the first generation ethanol production. Alternatively, it is also analyzed how sugarcane bagasse can be used to obtain products with high added value and energy from the syngas and tar obtained by the combination of thermochemical and biochemical processes.

Chapters 9 and 10 address the technical, financial, and market aspects of biomass conversion processes. In chapter 9 these criteria for managing production chains that use biomass as raw material in processes of fast pyrolysis are presented, and it is shown how pyrolysis technology can promote changes in the structure of the existing market and creates a potential for the appearance of new models that will eventually change traditional models. Chapter 10 discusses sustainability and techno-economic criteria to integrate pyrolysis, bio-char activation, and bio-oil refining into sustainable business models.

Summarizing, this interesting book addresses key aspects of fluid particle system and biomass energy management that represent a valuable contribution to the challenging and very much needed task of promoting the efficient and sustainable use of the precious biomass resources given by our planet, contributing to build a future were society could live in harmony with nature.

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24 November 2014

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REFERENCES

IEA. (2014). *Key World Energy Statistics 2014*. Retrieved from http://www.iea.org/publications/freepublications/publication/KeyWorld2014.pdf

Lior, N. (2011). Sustainable energy development: The present situation and possible paths to the future. *Energy*, *43*(1), 174–191. doi:10.1016/j.energy.2011.11.038

REN21. (2014). *Renewables 2014: Global Status Report*. Retrieved from http://www.ren21.net/portals/0/documents/resources/gsr/2014/gsr2014_full%20report_low%20res.pdf

Stockholm University. (n.d.). *Planetary Boundaries Research*. Stockholm Resilience Centre. Retrieved from http://www.stockholmresilience.org/

WWF. (2014). Living [*Species and spaces, people and places*. Available at: http://wwf.panda.org/about_our_earth/all_publications/living_planet_report/]. *The Planetary Report*, *2014*.

Preface

INTRODUCTION

The fluid-particle systems and renewable energy cover larger engineering areas. There are several important and complex phenomena, and concepts involving milling, storage, traditional packed and fluidized bed reactors, alternative reactors (microwave), and transportation logistics, which resist understanding when approached in the thermochemical processes (e.g. pyrolysis and gasification) and biochemical processes (e.g. fermentation and anaerobic digestion).

The knowledge about these topics could be constructed by applying multiple perspectives and ways of thinking. Associating the academic and industrial experiences, this book provides materials and strategies to support the successful design for small and large scale chemical and energy plants using energy resources. Currently, the governments of different countries focus on the clean energy using residues and energetic biomasses for obtaining liquid, gaseous, and solid fuels. It is indispensable the development of new and innovative approaches to biomass supply chain for bioenergy production for growing national and international allowing competitions almost inexistent.

OBJECTIVES

The aim of this book is to present new phenomenological, experimental and theoretical experiences as well as financial, market criteria and business models concerning in fluid-particle systems focusing renewable energy resources. It was written for professionals who want to improve their understanding in the innovation of chemical processes (small and large scale-up) and sustainable development with reducing emissions of pollutants and greenhouse gases, as well as the reduction of agricultural, industrial and urban residues.

TARGET AUDIENCE

Academicians, researchers, students, and technology developers will find this book useful in furthering their own knowledge and researches in the pertinent topics of chemical, mechanical, food, agricultural, and biological engineering, and also areas correlated.

THE CHALLENGES

Biomass is abundant in the world with different spectra and should be treated with care and attention for sustainable production of biofuels and electricity. It can be classified in food crops (e.g., sugarcane bagasse, corn stover, and soybean); hydrocarbon-rich plants (e.g., latex-bearing species such as *Plumeria alba*, *Calotropis procera*, and *Euphorbia nerrifolia*); agricultural (e.g., straws, shells, husks, and endocarps), forestry (e.g., *Eucalyptus*, *Pinus*, poplar, and douglas-fir) and food wastes (e.g., solid waste); and energetic fast-growing crops (e.g., elephant grass, miscanthus, and switchgrass).

Lignocellulosic biomasses are mainly composed by hemicellulose, cellulose, and lignin as well as smaller amounts of extractives (e.g., resins, fats and fatty acids, phenolics, phytosterols, salts, minerals, and other compounds), moisture, and mineral (e.g., silicon, aluminum, calcium, magnesium, potassium, and sodium). Their compositions are dependents by several factors such as: type of biomass, genetics, environment, age, harvest timing, part of the plant, and transport and storage conditions (Lee, Owens, Boe, & Jeranyama, 2007; Vassilev, Baxter, Andersen, & Vassileva, 2010; White, Catallo, & Legendre, 2011).

Besides that, it is a potential source of several bio-based products according to the biorefinery approach. Currently, the interest of these products has increased because of rising barrel costs and an increasing concern about the depletion of the fossil resources (Carmo, 2013). The purpose of the biorefinery approach is the generation of energy and value-added chemical products from different biomass raw materials through the combination of different technologies (FitzPatrick, Champagne, Cunningham, & Whitney, 2010; Kajaste, 2014; Menon & Rao, 2012; Pippo, Luengo, Alberteris, Garzone, & Cornacchia, 2011). The conversion of this energy is mainly done by two technological routes: thermochemical processes (direct combustion, gasification and pyrolysis), characterized by moderate to high temperatures, and biochemical processes (fermentation and hydrolysis) (Nascimento, 2012).

The use of biomass as a source for obtaining energy, takes place the following benefits: 1) Biomass is a renewable source, sustainable and environmentally acceptable; 2) Fuels with negligible sulfur content, do not contributing to emissions of sulfur dioxide, which causes the acid rain formation; 3) Disposal of agricultural waste, and solid urban forest particularly in municipal areas; and 4) Internal resource that is not subject to fluctuations in world prices, and it does not cause market instabilities and uncertainties of supply from imported fuels (Saxena, Adhikari, & Goyal, 2007; Nascimento, 2012).

Any attempt to deal with the problem "biomass x bioenergy" demands an adequate understanding of the challenges that exist for the new generations in the worldwide. Innumerable challenges can be signaled, and some categories are considered relevant and pointed out below:

- The challenge of establishing a policy environment international for bioenergy and food production to coexist optimally, respecting growing global population.
- The challenge of establishing good practices for applying of crop residues as a nutrient source for the next crops than as bioenergy.
- The challenge of establishing appropriate technologies applying biomass (forest plantation) for electricity production, or processed to a liquid fuel like ethanol.
- The challenge of establishing appropriate infrastructure in small communities for obtaining their own electricity from food production reducing logistical cost of transportation and storage.
- The challenge of establishing technologies to develop of scale-up of equipment in a safe way and according to the international law.
- The challenge of establishing policies and procedures that manage new business processes, equalizing prices between biofuels, electricity and food production.

All these challenges and much more are periodically discussed all over the world looking for alternatives with sustainability to get an environmental equilibrium, social, cultural and economic.

SEARCHING FOR A SOLUTION

For the new millennium, innovative solutions to the problems of managing energy will lead to shifting in the emphasis from technology (small and large scale) to business and social projects with sustainability.

The main vector for development is through of the central agent "the entrepreneur" able to supply the market with new products or processes. The "entrepreneur" is anyone that has or shows initiative, resourcefulness, and makes decisions (e.g., scientists, engineers, and business man) concerning to the policies and regulations for a future establishment of the energy industry (Chung, 2013).

Developed countries and developing countries have their particular profile to find the best and success businesses in the transforming processes in bioenergy and biofuels. Three levels of studies can be found in the literature - experimental, modeling, and management and business- focusing the suitability of the biosphere.

Limitations of measurement techniques and the high costs of implementation lead to a give up of new experimental plans restricting in laboratorial study (small scale-up). The modeling is considered a tool for process optimization reducing the experimental costs, the time spent on development, and extending to a process scale-up. The models should be extended from pretreatment (grinding, drying kinetics, mixing process) to final products (biofuel or biochar), energetic balances, and kinetic mechanisms in diverse kind of reactors (traditional and alternatives). And finally, several business models related to the production of bioproducts with sustainability.

This book presents some solutions and recommendations involving storage and transportation logistics, conservation and handling (powder and pellets), pretreatment of biomass (physical, biological and thermal), fluid dynamics of mixtures in fluidized beds, pyrolysis in micro-scale regarding the kinetics of reaction, scale-up of pyrolysis processes (microwave), new analytical methodologies for obtaining products (char, tar, and gas) from pyrolysis and gasification processes, fundamental concepts and modeling of energy and exergy applied in the gasification processes, generation of new products from thermochemical (e.g., pyrolysis and gasification) and biochemical (e.g., fermentation and anaerobic digestion) routes for achieving high added value, technologies of transformation, market for the products, business models in the management pyrolysis process.

OVERVIEW OF THE BOOK

The book is organized into ten chapters. A brief description of each of the chapters follows:

Chapter 1 summarizes studies about the mechanisms and modeling of size reduction of lignocellulosic and woody biomasses in order to understand the energy consumption of feedstock preparation applied in bioconversion processes. The authors discuss the interactions between physical properties as moisture content and input particle size, and size reduction equipments and their performing based on shear, compression, impact, attrition and a combination of these forces to disintegrate the material. Besides that, presents the modeling of size reduction of biomass classified by the population balance and energy-particle size.

Chapter 2 presents the state-of-the-art of the researches related to steam explosion applied to bio-conversion of woody and agriculture biomass for production of bioethanol and biogas. The authors discuss the effect of steam explosion on size reduction and pellet quality including high bulk density, low equilibrium moisture content, higher heating value, mechanical strength and moisture resistance.

Chapter 3 reviews studies concerning to the fluid dynamic and mixing characteristics of various kinds of biomasses and inert in gas-fluidized beds using as alternative fuels for application in thermal conversion processes. The authors of this chapter discuss different methodologies and recommend them thought the study case to obtain of the basic operating parameters such as the characteristic fluidization, velocity and porosity, and the bed expansion. The lignocellulosic biomasses chosen to exemplify were based on the commercial and environmental appeals of different Brazilian regions. A map was presented to identify the limits of effective mixtures of particles. Empirical correlations have been proposed in order to optimize the experimental work.

Chapter 4 reviews from literature the kinetics modeling of lignocellulosic biomass pyrolysis applying the thermogravimetric analysis to estimate the kinetic parameters, which are very important to optimize the process. The authors present a case study in order to exemplify the application of isoconversional and independent parallel reactions models using a lignocellulosic residue from Amazon region.

Chapter 5 summarizes the main conclusions of various investigations regarding the effects of microwave heating comparative to conventional heating on chemical reactions and how electromagnetic radiation can assist the biorefinery of biomass. The authors compare the issues and limitations regarding scaling-up microwave heating are elucidated, along with possible solutions to these problems.

Chapter 6 analyses different compounds obtained from pyrolysis and gasification processes (char, tar, and gas) relating to their chemical structure, and evaluates the influence of the reactor parameters in the liquid fraction compositions. The authors present as a case study applying these processes using cashew nut shell as a lignocellulosic biomass.

Chapter 7 aims to introduce the fundamental concepts and modeling of energy and exergy applied in the gasification processes. Exergy is a type of thermodynamic analysis applied for the efficiency assessment and the processes optimization, especially concerning to the biomass conversion. The authors proposed a theoretical model relating energy and exergy balances characterizing a single global gasification chemical reaction exemplified by rice hull as a biomass.

Chapter 8 analyses the use of sugarcane bagasse as a raw material for obtaining 2nd generation ethanol applying acid hydrolysis/pretreatment and enzymatic hydrolysis, and compares the use of thermochemical (e.g. pyrolysis and gasification) and biochemical (e.g. fermentation and anaerobic digestion) routes for achieving products with high added value, and other biofuels (tar, char, and gases).

Chapter 9 presents the technical, financial, and market criteria for managing within one or several production chains that use biomass as raw material in processes of fast pyrolysis. The authors discuss about storage and transportation logistics, conservation and handling of the biomass, available technologies of transformation, and consumer market for the products critical stages in the management process.

Chapter 10 discusses biomass pyrolysis technologies, prospective business models and financial considerations for sustainable recovery of energy, carbon, nutrients, and products from lignocellulosic and organic wastes (biochar activation and bio-oil refining).

CONCLUSION

The biomass due to its potential in environmental preservation and energy generation can be considered a “gem” for all populations worldwide. We know that petroleum is in its advanced stage of lifetime and recent forecasts suggest a maximum half century of consumption of this fossil fuel. Therefore, we seek conciliation between technological development and a cleaner energy matrix, with power supply alternatives based on the most varied, such as agricultural, industrial and urban residues, energetic plantations, and forest plantations.

In this volume, experts in bioenergy and environment of many universities, institutions, and research centers have brought out different chain strategies as of quality of raw materials to new products depending to the processing adopted-leading to low costs operation.

They have shared their success and failure experiences and what solutions they adopted or recommended for their issues or challenges faced. I comprehend that such success or failure factors or solutions may be applicable for all situations in different countries as technological references. Of course the social context, environment, resources available and so forth can limit the application of renewable energy generation projects. But certainly case studies do provide learning opportunities for researchers, designers, and mainly governors to take note of others´ experiences critically and plan their own bioenergy production. Each chapter presented here does intend to focus in different part of productive chain substantiated in fundamental theories. My intention is to help the readers gain in insight into what makes and effective practice and solution in some aspect designs.

I hope that this volume would provide relevant insights into the approaches of sustainably and management of biofuels discussed all over the world and represented here from Brazil, Canada, Colombia, Spain, Sweden and the United State of America.

I am sure the rich experiences of the contributors of this volume would be beneficial to various researchers, institutions and governments to understand, examine, design, and select solutions to where bioenergy production can be best deployed.

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REFERENCES

Carmo, V. B. (2013). *Avaliação da eficiência energética renovável de biomassas alternativas para geração de eletricidade*. (Doctoral dissertation). University of Campinas, Campinas, Brazil. Retrieved from http://www.bibliotecadigital.unicamp.br/document/?code=000940097.

FitzPatrick, M., Champagne, P., Cunningham, M. F., & Whitney, R. A. (2010). A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technology, 101*(23), 8915-8922. doi:. 2010.06.12510.1016/j.biortech

Chung, J. N. (2013). Grand challenges in bioenergy and biofuel research: engineering and technology development, environmental impact, and sustainability. *Frontiers Energy Research, 1*, 1-4. doi: 10.3389/fenrg.2013.00004

Kajaste, R. (2014). Chemicals from biomass - managing greenhouse gas emissions in biorefinery production chains – a review. *Journal of Cleaner Production*, *75*, 1–10. doi:10.1016/j.jclepro.2014.03.070

Lee, D., Owens, V. N., Boe, A., & Jeranyama, P. (2007). *Composition of herbaceous biomass feedstocks.* Sun Grant Initiative, North Central Center, South Dakota State University. Retrieved from http://ncsungrant.sdstate.org/uploads/publications/SGINC1-07.pdf

Menon, V., & Rao, M. (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*, *38*(4), 522–550. doi:10.1016/j.pecs.2012.02.002

Nascimento, V. F. (2012). *Caracterização de biomassas amazônicas - ouriço de castanha do brasil, ouriço de sapucaia e caroço do fruto do tucumã - visando sua utilização em processos de termoconversão.* (Master dissertation). University of Campinas, Campinas, Brazil. Retrieved from http://www.biblioteca digital. unicamp.br/document/?code= 000881657

Pippo, W. A., Luengo, C. A., Alberteris, L. A. M., Garzone, P., & Cornacchia, G. (2011). Energy recovery from sugarcane-trash in the light of 2nd generation biofuels. Part 1: Current situation and environmental aspects. *Waste and Biomass Valorization*, *2*(1), 1–16. doi:10.1007/s12649-010-9048-0

Saxena, R., Adhikari, D., & Goyal, H. (2009). Biomass-based energy fuel through biochemical routes: A review. *Renewable & Sustainable Energy Reviews*, *13*(1), 167–178. doi:10.1016/j.rser.2007.07.011

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913–933. doi:10.1016/j.fuel.2009.10.022

White, J. E., Catallo, W. J., & Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 1–33. doi:10.1016/j.jaap.2011.01.004

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The world's energy consumption has been growing and the search for new energy sources and processing technologies are emergencies. Many institutions and organizations in the world are engaged in developing new technologies to attend the needs of their own populations. International interactions and collaborations with colleagues leaded to present new sources (biomasses), process designing, developing, and modeling in order to understand the phenomena and harnessing of these raw materials for energy generation. Their experiences are shared in this book as a compendium between theory and practice (case studies) of successes and recommendation of news methodologies and technologies.

This book has been a rewarding experience for me, as I express my heartfelt thanks and gratitude to all authors for their excellent contributions and insights. During the course of development of this book, some reviewers could not submit their work on time due their other engagements. I thank them also for their association, encouragement and support provided for this work.

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Chapter 1

Modeling Size Reduction and Fractionation for Cellulosic Feedstock

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ABSTRACT

Biomass has attracted attention as a source of renewable energy. It is available in different forms such as lignocellulosic stalks of herbaceous and woody biomass. These forms of biomass should be prepared to go through bioconversion process or biofuel production. One of the major unit operations for preparation is size reduction, which increases the surface area available and breaks the structure of biomass. Size reduction is energy intensive and an expensive step of feedstock preparation. The characteristics of ground particles are the result of interactions between material properties and the modes of size reduction like shear, impact, and attrition. The fundamentals of size reduction of fibrous biomass are not well understood. This chapter summarizes the latest studies on modeling of size reduction of lignocellulosic and woody biomass.

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INTRODUCTION

The form of biomass and the nature of end processes have a major impact on the selection of equipment, thus making design and selection of efficient equipment a challenge for engineers.

Woody biomass can be available in the form of logs and logging residues, sawdust and shavings, or short rotation fast growing trees. Logging residues consist of different parts of trees such as branches and leaves. Sawdust and shavings are often leftovers from wood working operations. Examples of short rotation trees include willows and poplars, all of which have a high rate of growth and can be harvested in a short time. Bulk density increases during grinding. This increase has major impact on transportation efficiency. In most grinding scenarios, the first step of size reduction happens in field to produce material with higher density and improve transportation efficiency. Esteban and Carrasco (2006) reported that initial bulk density of poplar chips and pine chips was 148.75 kg/m^3 and 258.25 kg/m^3, respectively. Bulk density of poplar chips and pine chips increased to 225.64 kg/m^3 and 328.76 kg/m^3, respectively, after grinding.

Lignocellulosic stalks (also known as herbaceous biomass) come from agricultural residues like corn stover, wheat straw, rice, and cotton. The stalks can also come from crops like switchgrass, miscanthus, giant reed and sorghum. These crops are cultivated for a specific application like bioenergy or feedstock for animal bedding.

Size reduction of biomass often occurs in more than one step, depending on the final use of ground biomass. The position of the steps of size reduction in the sequence of preparation processes of biomass for downstream process can have a major impact on the cost of preparation. Sokhansanj and Turhollow (2004) reported that moving the grinding operation to the field reduces the cost of cubing of grasses and stover.

Previous studies show woody and herbaceous biomass require different energy input during grinding. Each species differs in mean and distribution of size when ground in the same grinder set up (Mani, Tabil, & Sokhansanj, 2004; Esteban et al., 2006; Bitra et al., 2009; Adapa, Tabil, & Schoenau, 2011). Factors such as moisture content, input particle size, and mechanism of grinding affect size reduction energy consumption.

Every conversion process needs its specific biomass particle size to operate efficiently. The effects of particle size on various conversion processes are discussed in the following section.

Size reduction equipment are designed with a versatility such that to grind a wide range of feedstock for which little physical properties are known. Dimensions of biomass and its moisture content can be measured and somewhat controlled for predicting the performance of size reduction operation. However, inherent structural properties like toughness or hardness of a cellulosic biomass are not easily quantifiable.

A lack of knowledge of physical properties of biomass that influence size reduction is one reason that this area has remained empirical to date. Experienced operators are very much aware of empirical relationships between biomass properties and the performance of size reduction equipment. Much of this information is limited to a few locally grown biomass species, qualitative in nature and not transferable from one operation to the next or from one operator to the next.

BACKGROUND

Size reduction is one of the unit operations in biomass preparation that consumes a major amount of energy. Size reduction is also sensitive, as each end process needs a specific particle size to perform efficiently. The specific size needed for biomass refinery is summarized here.

Literature indicates that particles used for hydrolysis and subsequent fermentation should be around 2 mm (Van Draanen & Mello, 1997; Petersson et al., 2007). Wei et al. (2009) found that the size of a feedstock particle for hydrolysis ranges from 1 mm to a few centimeters. Dasari and Berson (2007) studied the impact of sawdust particle size (between 33 μm and 850 μm) on the rate of cellulose to glucose conversion and viscosity of wood particle slurries. Viscosity of wood particle slurries affects the reactor design, the power consumption and overall operating cost of the process. The results show that smaller particle sizes create slurries with lower viscosities and higher cellulose to glucose rate. A low slurry viscosity reduces the operating costs (Dasari & Berson, 2007).

According to Smook (1992), the ideal chip for pulping is about 20 mm long in the grain direction and 4-5 mm thick. In general chips 10-30 mm in length and 3-6 mm in thickness are acceptable for pulping.

Bridgwater, Meier, and Radlein (1999) reported that the maximum particle size for a circulating fluidized bed gasifier is 6 mm. The preferred size of particles for bio-oil production through pyrolysis is less than 1 mm. Bridgwater et al. (1999) also reported that particles less than 2 mm are suitable for fast pyrolysis in a fluidized bed and entrained flow reactors. For slow pyrolysis, like torrefaction and charcoal making, the size of particles can be as large as 50 mm because heat transfer is slow. For an efficient combustion using suspension burners, the content of very fine particles (smaller than 100 μm) should be higher than 10% by weight in order to achieve short ignition times (Esteban & Carrasco, 2006). Small particles size increase gas pressure drop across a gasifier therefore increase the required power to draw gas through the gasifier. Large pressure drops will lead to a reduction of the gas load in downdraft gasifiers, resulting in low temperature and increased tar production. Feedstocks possessing excessively large sizes give rise to reduced fuel reactivity, causing start-up problems and poor gas quality. Acceptable fuel sizes depend on the design of the gasifiers. In general, wood gasifiers work well on wood chips of 10 x 5 x 5 mm in size (Chandrakant, 1997). Nexterra requires particle sizes less than 75 mm for the optimum operation of their updraft gasifier. Nexterra specifies that total mass of particles with sizes less than 6 mm should not constitute more than 25% of the total mass of the biofuel feedstock when fed to their updraft gasifier (Nexterra, 2012).

Badger (2002) specified the optimum particle size for biomass combustion boilers between 6 and 60 mm. Pulverized fuel burners suitable for biomass usually require the biomass fuel to meet certain particle size specifications. In general, burners burning biomass powders require particle sizes below 1 mm (Andrel, Mory, & Zotter, 2000; Freeman et al., 2000; Kastberg & Nilsson, 2002), while particle sizes of coal in pulverized coal burners are below 0.1 mm (Siegle et al., 1996; Freeman et al., 2000). The small particle sizes of pulverized coal permit complete combustion after approximately half a second in the furnace. Biomass particles with sizes below 1.0 mm (Kastberg & Nilsson, 2002) have similar residence times, and this is the reason for considering the finely ground biomass as a pulverized feedstock.

Pellet plants use a screen size of less than 6 mm in hammer mill to produce small particles for making pellets. The target size range is 1-3 mm. The graph in Figure 1 shows the mass of remaining material on each screen size for three samples collected from an industrial wood pellet mill in British Columbia. Sawdust and shavings are two traditional sources of raw material for the pellet manufacturing industry. The sample labelled as blend in the graph is ground biomass fed to the pelletizing press. About 25% of the mass of sawdust and shavings were larger than 4 mm and roughly 25% were less than 1 mm. The remaining particle sizes were between 1 and 4 mm. After grinding and blending sawdust and shavings, the mean particle size was 1.0-1.4 mm. The fraction of small particles in the pan increased from less than 2-4% for sawdust and shavings to more than 10% for the blend material.

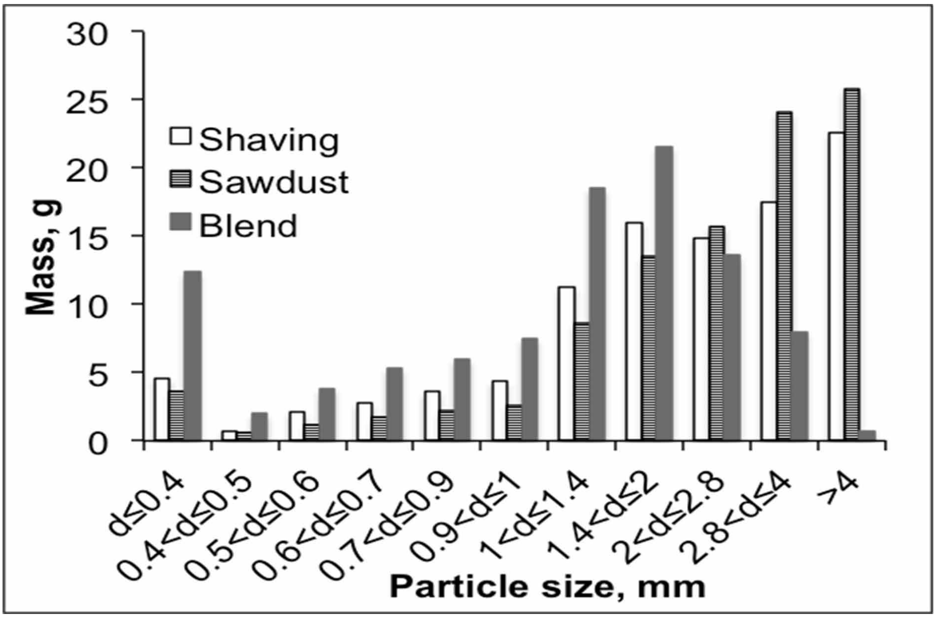
There are three ways that can be considered to reduce the energy consumption of size reduction at the same time meet the need of end process.

As it was shown particle size has a major role in each conversion process. Fractionation can be performed before grinding in order to bypass particle with small sizes that is not needed to go through size reduction.

Ground particle size is the result of interaction between material and grinding equipment.

It is important to identify the properties of the material that have major impact on size reduction.

Figure 1. Mass fractions of 100 g of sawdust and shavings before hammer milling and of their blend after hammer milling



As of grinding equipment there are two ways to reduce the energy consumption of size reduction:

1. Choosing the optimum screen size and size reduction mechanism;
2. Controlling the residence time of biomass in the grinder;

This chapter aimed at presenting the recent studies on fractionation and size reduction of biomass. Literature review is presented to show the importance of moisture content and size characteristics on energy consumption of size reduction. The chapter followed by introducing the empirical equations developed for biomass size reduction. Modeling size reduction to predict the energy consumption of grinding based on particle size is discussed.

FRACTIONATION

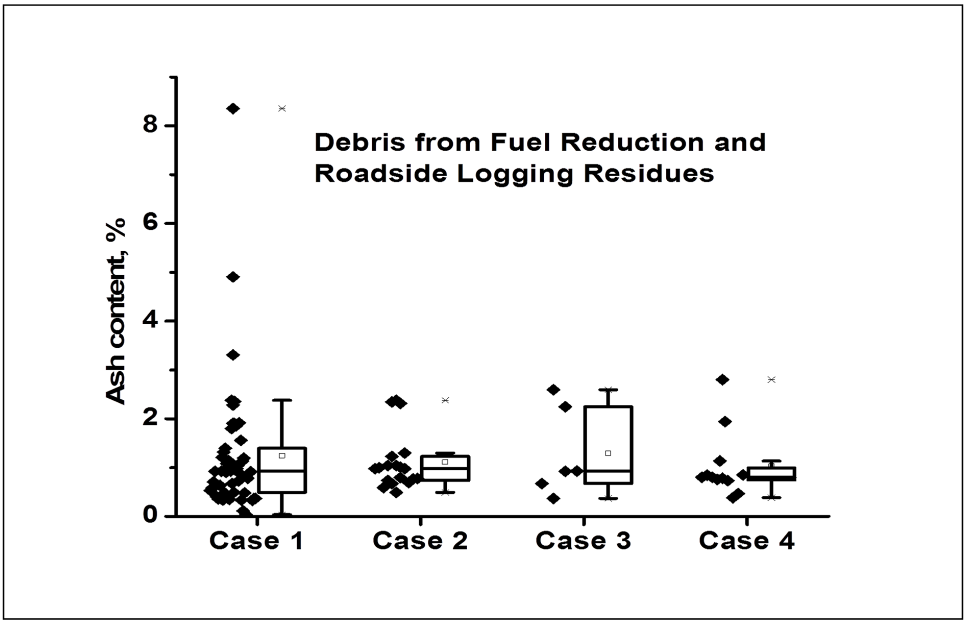
Fractionation is performed for three main purposes: It is performed before size reduction to remove the impurities such as sands and dirt to reduce the damage to the grinder parts such as knives and hammers therefore reduce the cost of maintenance of grinder.

Fractionation is performed after grinding to reduce the ash content. Ash content causes slagging and fouling problems during combustion (Baxter et al., 2012). In biochemical conversion specific constituents of ash can inhibit the fermentation depending on the microorganism tolerance.

Size distribution of ground particles shifts to smaller size range as the residence time of biomass inside the grinder increases. The mean size of ground particles is controlled by the screen size inside the grinder. A study on grinding particles by knife mill showed the geometric mean size of particle are around one-fourth of the screen size inside the grinder (Naimi et al., 2013). Population balance modeling predicts how particles are reduced in size and move to smaller range of particles during grinding (Naimi et al., 2011). The modeling applied the principal of population balance modeling on grinding switchgrass by knife mill. It can predict the optimum residence time of particles to reach the need of the down stream process. It also suggests that after a certain time fractionation and bypassing the big particles instead of keeping the grinder running might save energy.

Example or ash reduction by fractionation. Dry fractionation by sieving can reduce the ash content of biomass significantly. Figure 2 demonstrated the variability of ash content for four cases of biomass collected from field (Naimi et al., 2012). Ash content of samples from Case 1 was variable between 0.2 to 8%. Dry

Figure 2. Variability of ash content for woody residuals



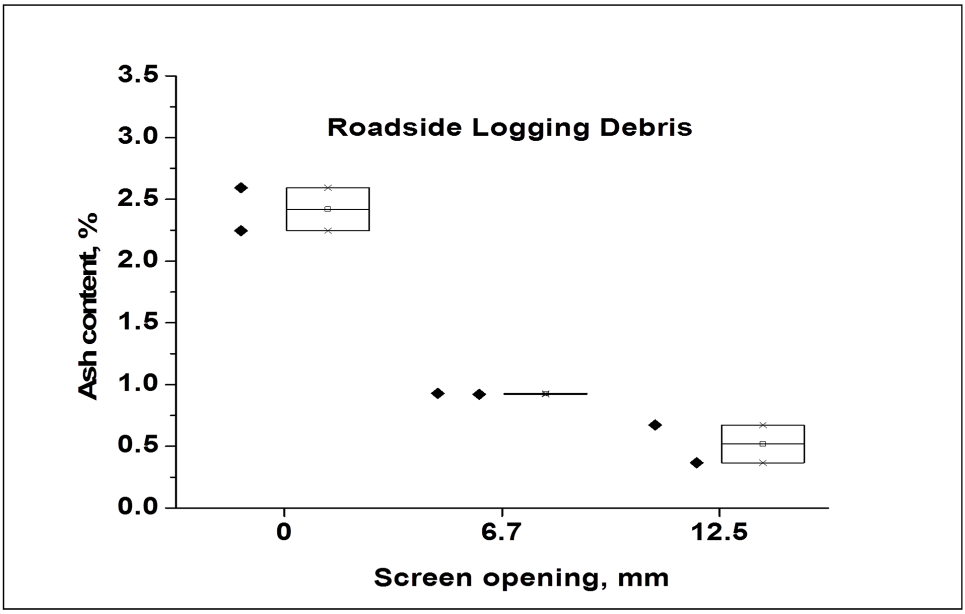
fractionation is performed on one sample of woody biomass. Figure 3 shows the impact of particle size on ash content of the sample. It shows that by dry fractionation using two screens plus pan a fraction with 1.9% ash content can be removed. The ash content of sample after fractionation is reduced to 0.5%.

Moisture Content

The water appears in the biomass structure in two forms: dissolved in the cell walls (bound water) and free liquid in the lumen (free water). Lumen is the empty space between the cell walls. The moisture content of a growing tree can vary in the range of 60-200% dry basis (Ketunnen, 2006). It's easy for wood to lose free water but difficult to lose bound water. In agricultural material with high water content, the cells behave in a nearly elastic manner (Morrow & Mohsenin, 1966), which impact the behavior of material under shear and impact forces.

Many studies are available on the impact of moisture content on density and mechanical properties of wood and herbaceous biomass. Average dry matter density of corn silage increased as the moisture content decreased (Zhang, Sword, Buckmaster, & Cauffman, 2003). Maximum shear stress of wheat straw stem increases as the moisture content increases from 0 to 20% but stayed constant as the moisture content

Figure 3. Impact of dry fractioantion on ash content of woody residuals



increases. Maximum bending stress decreases as the moisture content increases from 0 to 20% and stayed constant as the moisture content increases (Annoussamy, Richard, & Guerif, 2000).

Depending on grinder type and configuration there is a limit for moisture content of the material that a grinder can handle. Moisture content of 15 to 20 percent is the limit for wood chips and wood residual that a 1.5 kW knife mill can handle. Pieces of wood with different sizes entangle together, cause problems in feeding devices, and become stuck in grinding chamber when they are above this moisture content limit. It is hard to control moisture content of raw material on an exact number. This is the reason many researchers try to prepare raw material with a range of moisture content.

Igathinathane (2008) studied size reduction characteristics of corn stalks and switchgrass using a knife. The effect of high (51.1% ±4.1% wb) and low (9% ±0.5% wb) moisture contents were investigated. High moisture material requires significantly greater stress and energy (1.3 times) than low moisture material.

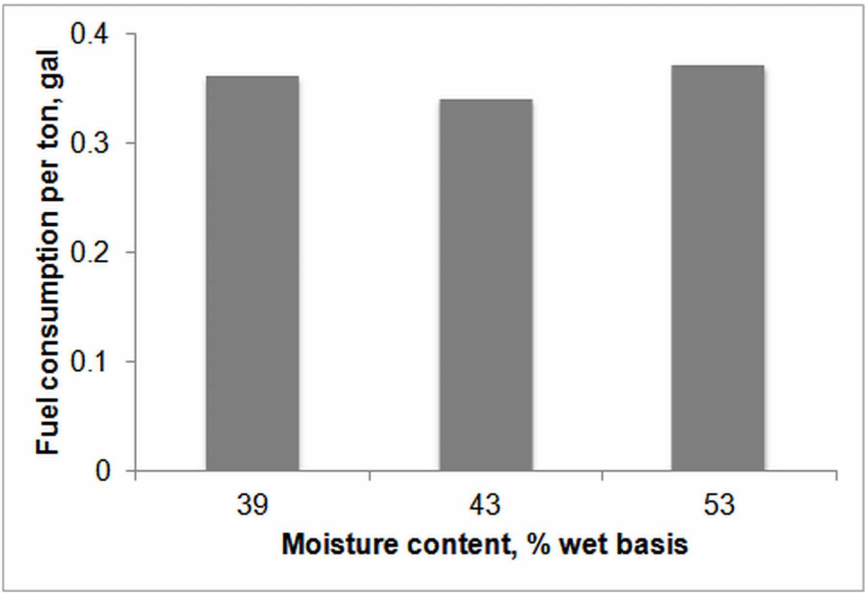
Analysis showed that the ground particle size distribution shifted to larger size range of particles with an increase in moisture content (Naimi et al., 2011). A larger fraction of particles collected in the pan for ground particles that was produced from feed material with 4% moisture content than particles that were produced from feed materials with 15% moisture content. The knife mill stopped working as the moisture content of the wood chips exceeds 20% wet basis.

Study shows that moisture content decreases during grinding. Moisture content is measured before and after grinding by hammer mill (Gil, Gonzalez, & Gil, 2008). The results showed that during grinding corn stover and pine chips, the moisture content decreased 2-3 and 3-5.2%, respectively. Moisture content of wood decreases during comminution process. Esteban and Carrasco (2006) studied different scenarios for grinding poplar chips, and pine chips. Initial moisture content was 11.89% and 14.25% (w.b) for poplar chips and pine chips, respectively. The decrease of moisture content observed was 31.62% and 34.18% for poplar chips and pine chips, respectively. They argued that this difference was due to higher initial moisture content for pine chips and lower throughputs in the hammer mills. They believed that long residence time of particles inside grinder increase the moisture content loss during grinding.

Cutshall, Greene, Baker, and Mitchell (2011) studied the impact of wood moisture content on fuel consumption of a drum chipper for grinding loblolly pine. Figure 4 shows that in the range of 39 to 53% moisture content the fuel consumption of loblolly pine ranged between 0.34 to 0.37 gal per ton. Pine with 43% moisture content has the minimum fuel consumption of 0.34 gal per ton.

Specific energy consumption of grinding dry and green slash by tub grinder on different screen sizes was studied (Arthur, Kepner, Dobie, Miller, & Parsons, 1982).

Figure 4. Relationship between fuel consumption of drum chipper for grinding loblolly pine and moisture content. Sample with 53% moisture content represent the green wood (Cutshall et al., 2011)



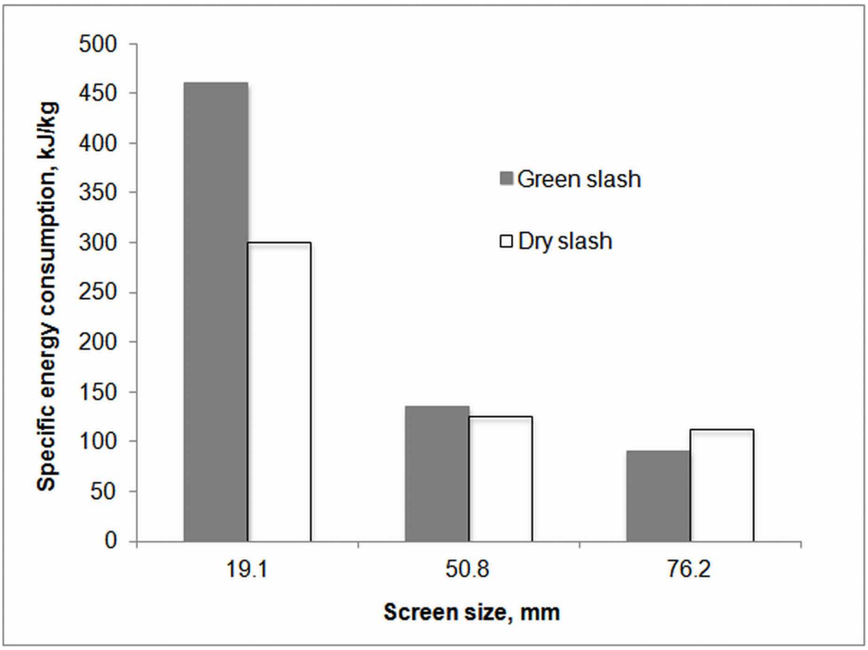
The results are depicted in Figure 5. The specific energy consumption of grinding dry slash was less than grinding green slash at 50.8 and 19.1 mm screen size. At 76.2 mm screen size the specific energy consumption of grinding was smaller for green slash comparing to dry slash.

Size Reduction Mechanism

Size reduction equipment are available in a variety of configurations. The equipment uses shear, compression, impact, or a combination of these forces to deconstruct the material. The application of compressive forces is in crushers, impact forces in hammer mills, and shear forces in knife mills and attrition mills. The following is a brief discussion of the equipment that are most widely used for disintegrating biomass.

Hammer mills. The equipment crush the material by impact using a high-speed rotor that carries loose swinging or fixed hammers on its periphery. The grinding chamber that houses the rotor may have a serrated plate and/or a screen. The process inside the grinding chamber may also include shearing, which improves the efficiency of grinding. The size of the average ground particles depends on the size of the perforations on the screen. Hammer mills are general-purpose devices capable of grinding seeds and fibres. Because of this versatility they are widely used in

Figure 5. Relation between specific energy consumption of tub grinder and screen size for dry and green slash (Arthur et al., 1982)



biomass applications where the characteristics of feed material vary. Large motors are placed on hammer mills to deal with unknown materials.

The hammers wear excessively and require regular resurfacing or replacement. Contaminants in forest residues (e.g. sands and stones) cause the sharp blades and knives to become blunt. Hammer mills avoid this problem by using blunt hammers. Hammer mills are sensitive to biomass moisture. High moisture (usually >20%) do not cut easily and tend to block the holes in the screen that surround the rotating hammers. Low moisture less than 5-7% tends to shatter and generate fine particles including dust.

Tub grinders. These are basically hammer mills with a large tub designed to receive straw bales or woody branches. The material is fed into a large rotating tub where it falls by way of gravity. The spinning action of the tub brings the unground material in contact with hammers, to cut and forces the biomass into a rectangular opening and finally into the path of swing hammers. The hammers pass over a series of screens or fixed anvils of various opening which control the final particle size. Models which are not equipped with their own loading facility, like a belt are usually fed with a front-end loader. Tub grinders are capable of processing a variety of feedstocks ranging from demolition wood, grass and leaves, pallets, square and round biomass bales. The grinder energy required to process materials decreases as the moisture content decreases.

Forage choppers. These are similar to hammer mills, but instead of hammers, fixed knives are mounted on a rotor. In forage choppers, the length of cut can be adjusted by changing the speed of the feed rolls, or by adjusting the number of knives on the periphery of the chopper head. The length of cut and the uniformity of cut length can be controlled using a screen with square, round or oblong holes placed around the chopper head.

Disk and drum chippers. These types of grinders are mainly used for cutting woody materials. The basic cutting device in chippers can be a disk or a drum to which cutting knives are attached. In drum chippers the knives are attached radially or spirally to a rotating cylinder. Drum chippers are of side-feed or end-feed types depending on feeding mechanism. In comparison with disk chippers drum chippers are heavier and more expensive but the feeding process is easier. Drum chippers can handle a wider size range of raw material than disk chippers.

Size Reduction Modeling

Empirical equations are also developed for grinding woody and herbaceous biomass. Mani et al. (2004) and Adapa et al. (2011) developed models for specific energy consumption of grinding biomass based on screen size inside the grinder. Bitra et al. (2009) and Miao, Grift, Hansen, and Ting (2011) developed models for specific energy consumption of grinding based on the geometric size of the feed and ground particles. Table 1 summarized the results of previous studies on modeling energy consumption of grinding vs particle size.

The table lists the form of preparation before grinding for each study. The moisture content of test samples have been reported between 8-15%. All the studies were conducted on hammer mill except Miao et al. (2011), which is on knife mill. The independent variable in the models are either screen size or geometric mean size of the particles except the study by Miao et al. (2011) which is not only screen size and geometric mean size of the particles but also grinding ratio. d_{gw} is to the power of 0.69-1.12 in the study by Bitra et al. (2009) and to the power of -1.6 to 1.5 in the study by Miao et al. (2011).

Disk Chipper. Major parameters affecting a disc chipper throughput are the power available to the chipper (the size of the chipper), diameter at breast height (DBH) fed to the chipper (Stokes, Watson, & Sirois, 1987), the dimensions of the chips (regular chips or micro chips). Other factors that have been correlated with the chipper productivity are the diameter of the stems, the species of trees (softwood,

Table 1. A summary of the studies on modeling specific energy of size reduction

Researcher	Biomass	Feed Particle Size	Grinder	MC	Equation Fitted
Mani et al. (2004)	Corn stover, swithgrass, and wheat straw	Pre-ground in knife mill with 25.4 mm screen	Hammer mill	8 and 12%	$E = k_1 + k_2 S$ $E = k_1 + k_2 S + k_2 S^2$ $IV^{(1)}$ screen size
Bitra et al. (2009)	Switchgrass, wheat straw, and corn stover	Pre-ground in knife mill with 25.4 mm screen	Hammer mill	9%	$E = K \Delta d_{gw}$ $K = f(N)$ $IV : d_{gw}$
Adapa et al. (2011)	Barley straw, canola straw, oat straw, and wheat straw	Chopped in a forage chopper	Hammer mill	12-16%	$E = k_1 S^{-k_2}$ IV : screen size
Miao et al. (2011)	Miscanthus, switchgrass, energy cane, and willow tree	Cut manually or chipped in a wood chipper	Knife mill	15% and air dried	$E = ax^b$ IV : screen size grinding ratio, or d_{gw}

[1] Independent Variable

hardwood), moisture content, and the size or design of the chipper (Watson, Sabo, & Stokes, 1986). However to the knowledge of author a model that includes all of the foregoing factors is not available in literature.

To model the chipper capacity as a function of chip size and power input, the published data from chipper technical data are used (LINDANA, 2008). The equation 1 is fitted to the data:

$$\begin{aligned} P_C &= 73.76 - 4.10 Z_C + 4.10 Q_C - 0.06 Q_C Z_C \\ R^2 &= 0.27 \end{aligned} \tag{1}$$

P_C is the chipper power (kW), Z_C is chip size (mm), Q_C is throughput volume in (m^3/h). This volume is estimated from measuring the volume of a box filled with chips per unit time. The last term represent the interaction of capacity and chop size. As noted in R^2, equation has poor fit to the data.

To analyze the sensitivity of throughput to chip size equation 1 was rearranged to solve for throughput as a function of given power and chip size.

$$Q_C = (P_C - 73.76 + 4.1 Z_C)/(4.1 - 0.06 Z_C) \tag{2}$$

Q_C is in m^3/h, Z_C is chipper size in mm, P_C is in kW. The productivity of the chipper then can be estimated from estimating the density of green chips,

$$M_C = [(Q_C/\rho_C)/(E_C*k_C*1000)] \tag{3}$$

M_C is the chipper productivity in t/h, ρ_C is the density of the green chips (kg/m^3) E_C is efficiency of the chipper, k_C characteristics of the material (k_C=1.0).

Stokes et al. (1987) found that power requirement of a chipper (69 cm capacity opening and 447 kW) increases with an increase in diameter at breast height and number of stems in the chipper. An equation was developed relating the power requirement of a chipper as a function of *DBH* (diameter at the breast height) and number of stems in the chipper.

$$\begin{aligned} P_C &= 1.45 + 0.875DBH + 0.126DBH * NS_C \\ R^2 &= 0.7 \end{aligned} \tag{4}$$

P_C power is in kW, *DBH* is in cm, and NS_C is the number of stems fed to the chipper (at once).

Table 2. lists available data on disk chipper performance. As is noted, the chipper performance in tons/PMH (Productive Machine Hour) decreases when the chip size decreases (Thompson & Sprinkle, 2013).

Drum chipper. Figure 6 shows the impact of species on power requirement of a drum chipper with two knives, 122 cm diameter and 550 rpm (Hakkila, 1989). The feed rate was 30 m/min and the feed consists of fresh single logs. The figure shows that as the log diameter increases the power requirement also increases. The figure also shows that the power is higher for true hickory and post oak, which are the hardwoods, comparing to Douglas-fir which is the softwood.

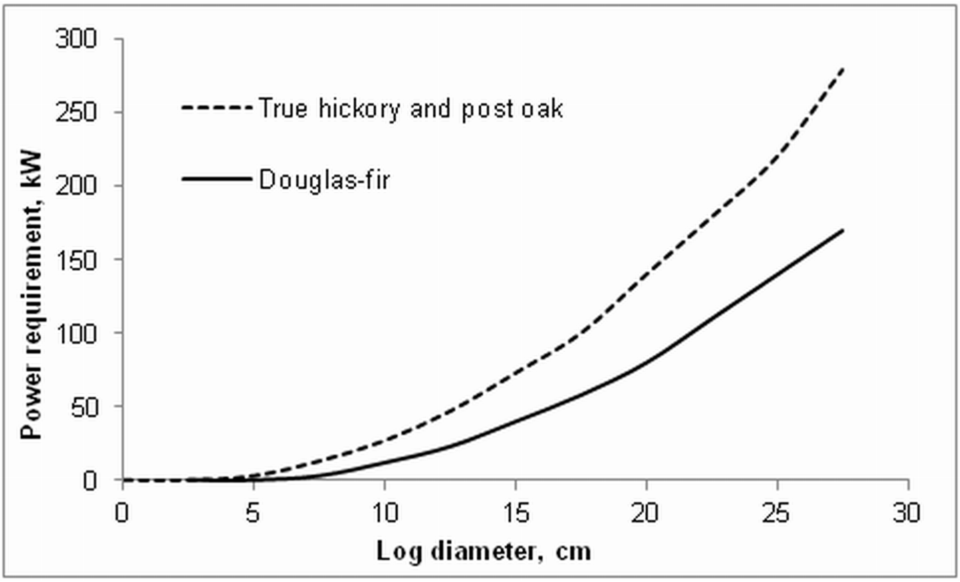
Tub Grinder- Four models of tub grinders are used to grind agricultural biomass (http://pami.ca/). All four models are designed to grind loose, stalked or baled straw

Table 2. Production data for disk chipper

	Tons/PMH		**Fuel (gal/ton)**		**Moisture content (wb)**	
	Regular	**Microchip**	**Regular**	**Microchip**	**Regular**	**Microchip**
Min	76.14	54.77			0.44	0.46
Max	82.89	84.16			0.54	0.56
Avg.	79.52	69.37	0.24	0.28	0.47	0.50

Source: Thompson and Sprinkle (2013)

Figure 6. The impact of species and log diameter on power requirement of a drum chipper (Adapted from Hakkila, 1989)



and hay. They are portable power take-off driven hammer mills with rotary feed tub. The manufacturer recommends use with tractors from 75 to 187 kW at 1000 rpm power take-off speed. They are designed to be batch fed with a suitably equipped front-end loader. Variable speed tub regulates the feed to the hammer mill. Fineness of grind is determined by the size of screen used below the hammer mill. Ground material falls through the screen onto conveyors which deliver it.

The four models are explained as below:

Model I- This model (Bearcat Model 4200) is a hammer mill. A tractor with 112 kW (150 hp) at 1000 rpm power is used to move the grinder around. The hammer mill has two rows of 12 and two rows of 14 swinging hammers. Screen size of 51 mm is used.

Model II- This model (Haybuster Model C-9) is a hammer mill with eight rows of swinging hammers. Four rows have eight hammers and four rows have seven hammers, recommended to use with tractors up to 187 kW at 1000 rpm power take-off speed. The hydraulically driven, variable speed tub regulates feed to a belt driven hammer mill. A hydraulic governor automatically controls the tub speed and stops tub rotation when the tractor speed drops below a preset level. Ground material falls through the screen onto two chain-driven screw conveyors which deliver it to an adjustable, slatted, rubber belt conveyor.

Model III- This grinder (Farmhand F-890) is recommended to use with tractors up to 75 kW at 1000 rpm power take-off speed. An attachment is available to convert the 1000 rpm gearbox for use at 540 rpm. The hydraulically driven, variable speed tub regulates feed to a gear driven hammer mill. A hydraulic governor automatically controls the tub speed and stops tub rotation when the tractor speed drops below a preset level. Ground material falls through the screen onto an apron chain conveyor which delivers it to a side mounted, slatted rubber belt elevating conveyor.

Model IV- This model (New Holland Model 379 Tub Grinder) is a hammer mill with four rows of swinging hammers. Each row has 12 hammers.

The maximum grinding rate for a tub grinders depends on the type of agricultural residues being ground, whether the hay is baled or loose, its moisture content and temperature, the screen size used, and the available tractor power. In general, grinding rates are higher at very low temperatures as hay becomes more brittle at reduced temperatures.

Specific capacity is a measure of how efficiently a machine performs a task. A high specific capacity indicates efficient energy use while a low specific capacity indicates inefficient operation. Tub grinders, in general, are inefficient machines.

The impact of four factors of biomass species, form of collection, screen size and tub grinder model on the grinding energy consumption and ground material size distribution are summarized.

The performances of the four Models are listed in Table 3.

Throughput and specific energy of four farm tub grinders are tested. The range in throughput is due to the form of biomass. Throughput was higher for alfalfa loose (stacked) hay than alfalfa-baled hay. For barley straw throughput was lower for loose straw than for baled straw.

Table 3. Screen size and throughput for alfalfa and straw for four tub grinder models

Biomass	**Screen size**	**Throughput, specific energy**	**Model**			
			I	**II**	**III**	**IV**
Alfalfa	51	t/h	3.7-11	4.5-4.8	4.2-5.4	6.5-8.0
		t/kWh	0.16	0.37	0.36	0.32
	25	t/h	1.9-5.5	2.2-2.4	2.1-2.7	-
		t/kWh	0.08	0.19	0.18	-
Barley straw	51	t/h	7.5-7.8	5.7-7.9	2.8-3.7	6.5-7.6
		t/kWh	0.08	0.15	0.08	0.08
	21	t/h	3.8-3.9	2.8-3.9	1.4-1.9	-
		t/kWh	0.04	0.08	0.04	-

Figures 7 to 9 show the power consumption of grinding two species of barley straw and alfalfa. Two forms of biomass collections are considered: round bale and stacked. The screen size inside the grinder was 51 mm. The linear regression of the data shows that Models I and II showed higher slopes comparing to Models III and IV.

Knife mill. Three equations of Rittinger, Kick, and Bond were tested on grinding Douglas-fir and hybrid willow (Naimi et al., 2013). The wood chips were pre-ground in a hammer mill. Figure 11 is a plot of mass fraction of ground particles of Douglas-fir and hybrid willow prepared by crushing wood chips in the hammer mill equipped with 25.4 mm screen. It was noted that Douglas-fir particles after hammer mill were smaller than the hammer milled hybrid willow particles. The pan mass fraction was 31% for Douglas-fir, whereas the pan mass fraction was 22% for willow. The fraction of large particles resting on 4-mm screen was 6% for Douglas-fir but 18% for hybrid willow. The geometric mean size was 1.73 mm for Douglas-fir and 2.23 mm for hybrid willow particles.

The pre-ground particles then were ground in a Retsch knife mill Model SM100 (Retsch Inc. Newtown, PA). Increasing feed rate from 1.7 g/s to 2.1 g/s showed a decrease in specific energy consumption for hybrid willow. The feeding rate was controlled by the feeder tray and is depended on particle density. Grinding Douglas-fir was not possible with the knife mill at feeding rates more than 2 g/s at 2 mm screen size. The grinder chamber was filled with material and grinder stopped working after a while. Grinding hybrid willow was not successful with 1-mm screen

Figure 7. Power consumption of grinding round barley straw bales at different grinding rates by the four models of tub grinder

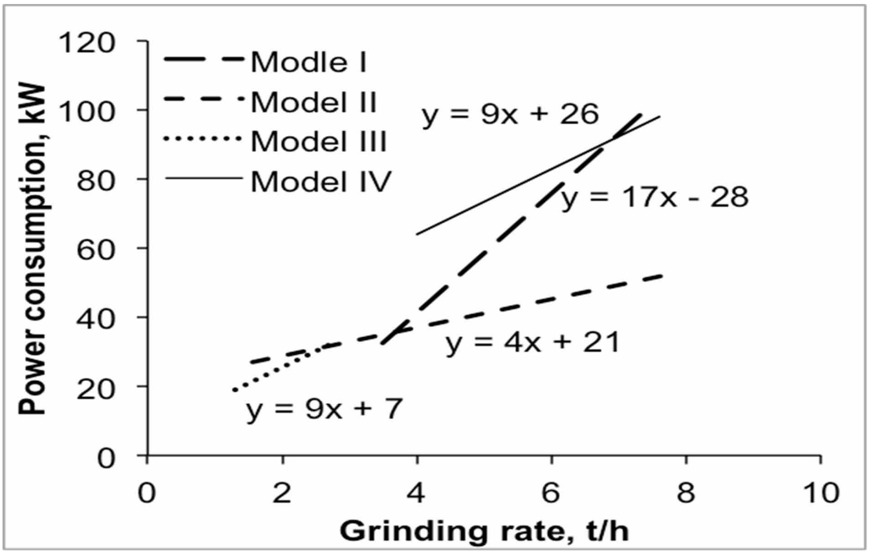


Figure 8. Power consumption of grinding barley straw stacks at different grinding rates by the four models of tub grinder

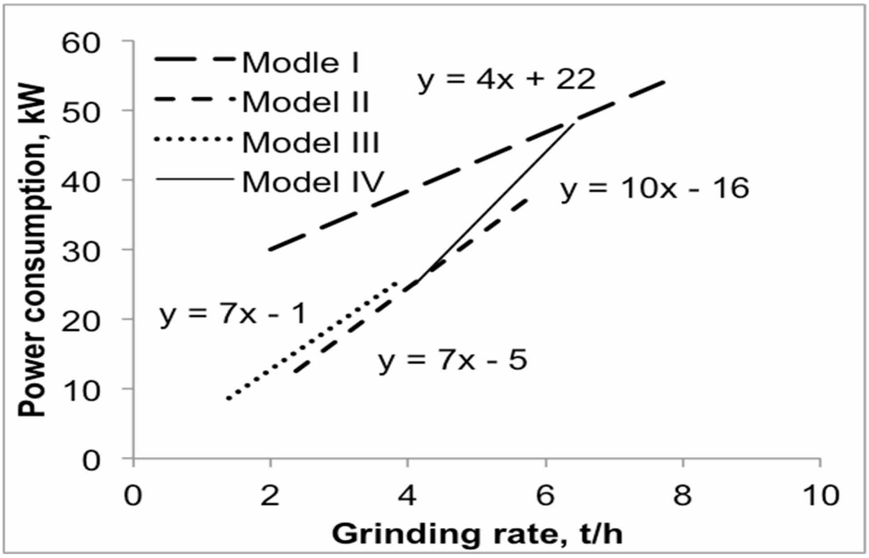


Figure 9. Power consumption of grinding round alfalfa hay bales at different grinding rates by the four models of tub grinder

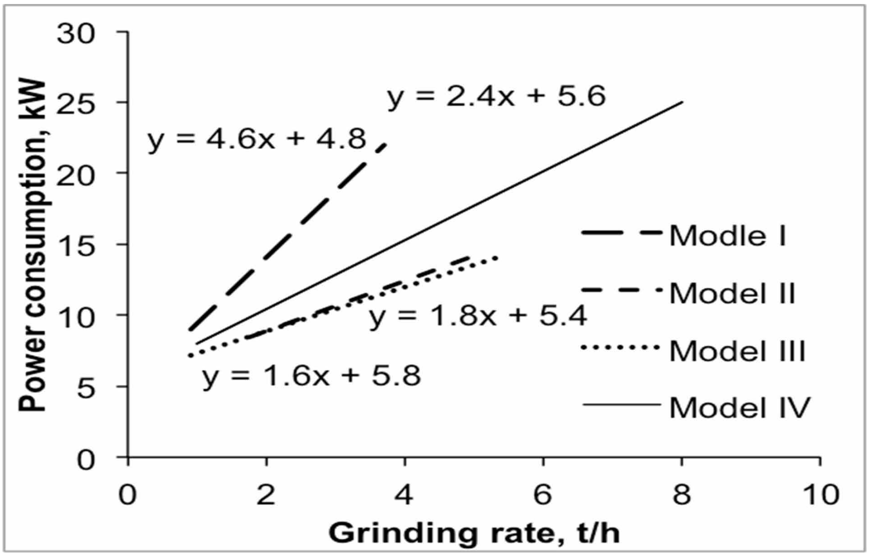


Figure 10. Power consumption of grinding alfalfa haystack at different grinding rates by the four models of tub grinder

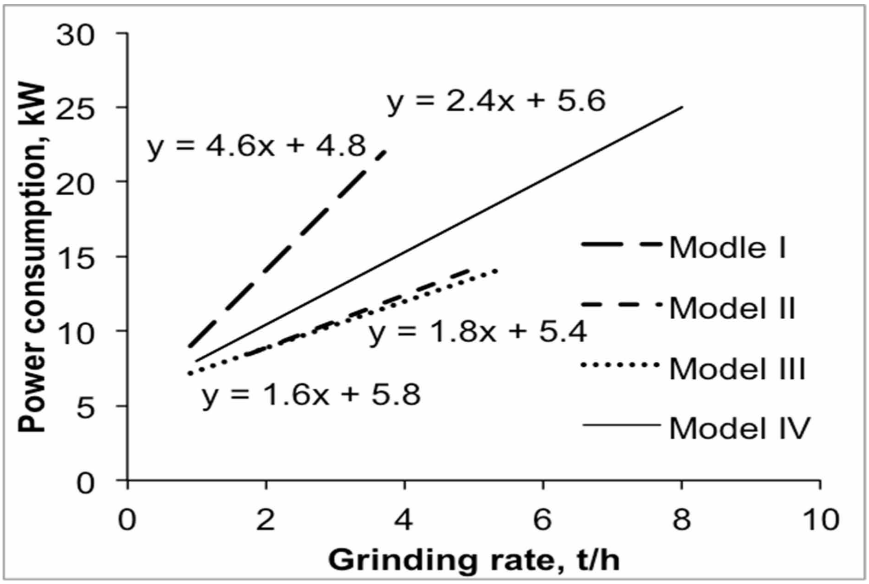
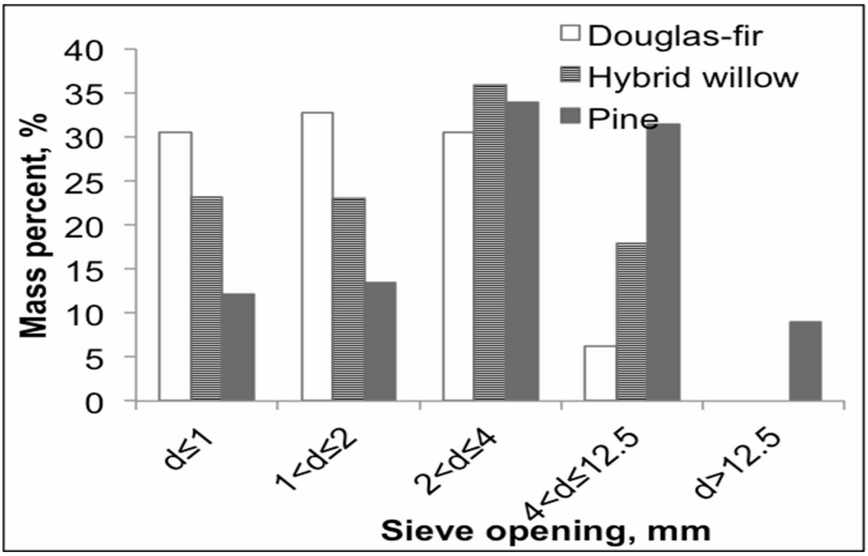


Figure 11. Size distribution of hammer-milled wood chips of hybrid willow and Douglas-fir on Gilson sieve shaker and pine wood chips as-received (PWC), sieve size 0 is the pan



installed in the knife mill. In order to maintain a constant feeding rate for both species on the three screens of 2, 4, and 6 mm, feeding rate was maintained at 1.7 g/s in all experiments.

The average geometric mean size of ground particles from the 2.38 mm infeed was larger for Douglas-fir (1.3 mm) compared to that of hybrid willow (1.2 mm). This observation is not consistent with products from the hammer mill in which mean size for hybrid willow particles was slightly higher than Douglas-fir. This result showed that the mechanisms of grinding: shear (knife mill) and impact (hammer mill) interact with wood species and creates different size distributions of ground particles.

The Rittinger equation has the best fit to the data and has the general form of equation 5:

$$E = K_R[(1/L_P) - (1/L_F)] \tag{5}$$

where, E is specific energy of grinding, L_F is the geometric mean size of feed particles and L_p is the geometric mean size of product particles. Table 4 lists the constants and coefficients of determination for each of the two species and three grinding equations. The values of coefficient of determination for fitting a straight line through the intercept for Rittinger and Bond were small with the intercepts near zero. Only the Rittinger equation gave a positive intercept for Douglas-fir. Comparing R^2 values, Rittinger's equation had a better fit to the data than other two equations. The last two rows in Table 4 represent pooled grinding data from the two species. The degree of fit decreases when data are pooled.

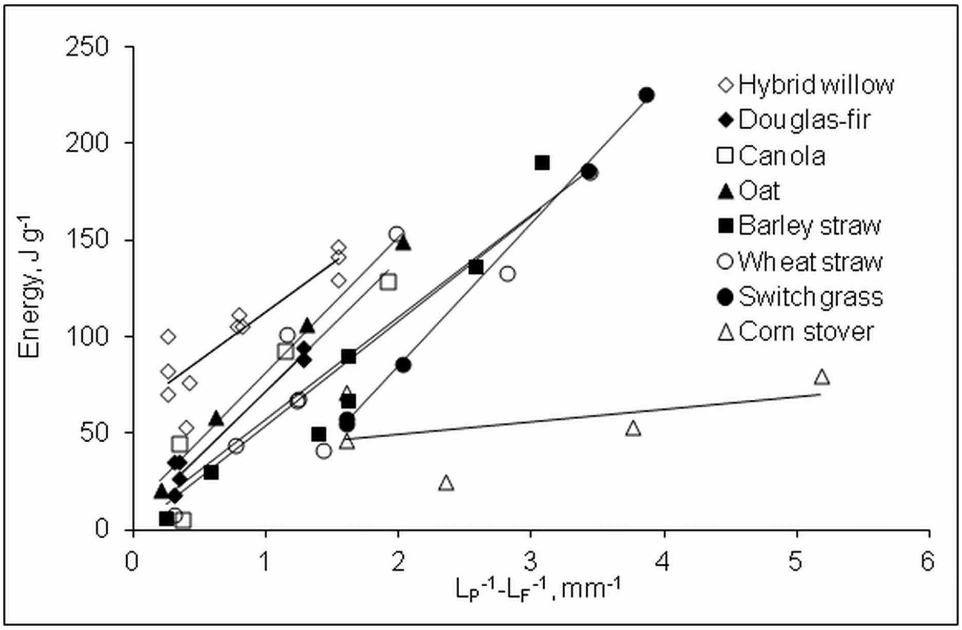
Table 4. Constants and coefficients of determination for Rittinger equation fitted to the grinding data of knife mill. The second line for each species is for a line passed through origin (intercept k_2=0)

	Rittinger		
	$(1/L_P)$ - $(1/L_F)$		
	k_1	k_2	R^2
Hybrid willow	48.9	64.2	0.79
	106.4	0.0	0
Douglas-fir	67.2	3.9	0.97
	71.1	0.0	0.97
Composite of two species	60.5	35.7	0.57
	93.6	0.0	0.33

Figure 12 plots specific energy versus Rittinger's parameters for the data from this study, and those extracted from Mani et al. (2004) for corn stover, wheat straw, switchgrass, and barley straw, from Bitra et al., (2009) for switchgrass, corn stover, and wheat straw, and from Adapa et al. (2011) for barley straw, wheat straw, canola, and oat. The geometric mean size of particles (ASAE Standard S319.3, 2001b) was used as the representative particle size. The slopes of the lines related to Douglas-fir, oat straw, switch grass and canola straw are similar and highest among the slopes. The slopes decreased for hybrid willow, barley straw and wheat straw, which have similar slopes. Corn stover has the lowest slope among all. The specific energy of corn stover was the lowest followed by straw and switchgrass. The specific energy data for grinding canola and oat reported by Adapa et al. (2011) were higher than other agricultural residues, but lower than the specific energy measured in this study for hybrid willow. Visual observations indicate that a line allowing for a non-zero intercept represented adequately the data by the Rittinger equation.

Hammer mill. Gil et al. (2008) studied the grinding of corn stover and pine chips by hammer mill. The hammer mill had a combination of fixed cutting blades

Figure 12. Specific energy vs. Rittinger's grinding equation parameter for the data from this study, and those extracted from Mani et al. (2004), Bitra et al., (2009), Adapa et al. (2011), and Miao et al. (2011). (Adapted from Naimi et al. 2013)



and floating hammers. The biomass has moisture content between 10-16% wet basis. The screen sizes of 2 and 5 mm inside hammer mill are tested. The results of energy consumption of grinding are depicted in Figure 13.

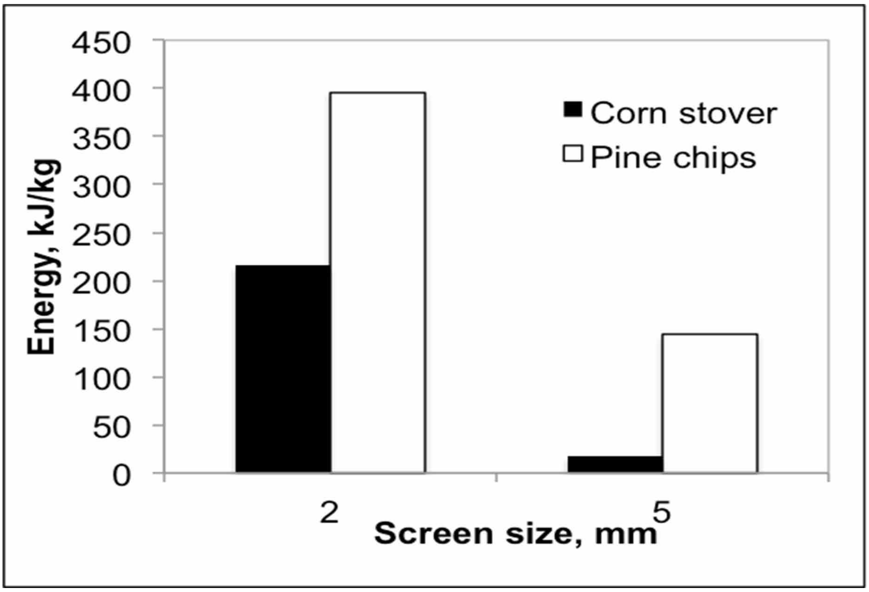
Pine wood chips (PWC) were pre-ground in six size categories by hammer mill (GlenMills Inc., Clifton, NJ) (Collard, 2012). The six size categories include: as-received (PWC), 3.13, 6.25, 10, 12.7, and 25.4 mm.

The specific energy increases from 5.2 J/g to 90.4 J/g when the screen size decreases from 25.4 mm to 3.1 mm. The specific energy standard deviation increases as the screen size decreases. PWC ground on 25.4 mm screen has the highest CV. That is because the mean of specific energy is the lowest when PWC is ground to 25.4 mm screen size. Coefficient of variations varies between 0.03 to 0.1 for all the other tests.

SOLUTIONS AND RECOMMENDATIONS

It is recommended that depending on the conversion process or biofuel production process one or a few steps of fractionation implemented before grinding step. The steps depend on the nature and cleanness of the biomass. The fractionation can be separating different parts of plant such as stems form leaves or sieving with one screen.

Figure 13. Energy consumption of grinding corn stover and pine chips by hammer mill. (Gil et al., 2008)



The validity of Rittinger equation should be tested on laboratory and industrial mills for grinding agricultural and woody biomass. Having such equation can help industries and engineers to predict the energy needed for grinding a specific ground particle size. It helps to choose an optimized size and mechanism of grinder for a species and particle size needed.

The modeling should be extended to grinders operated under different mechanisms and a wider range of input and output sizes using different species of woody and agricultural biomass.

Herbaceous and woody biomass collected from field has significant size and form variation. A method needs to be identified to give a size factor to a collected feedstock. This size factor can then be used as the initial size to test the applicability of Rittinger's equation on grinding feedstock collected from field.

CONCLUSION

Fractionation can improve the quality of biomass depending the end process. For example ash content can be reduced by dry fractionation and prevent the damages it might have on grinder. Ash reduction also prevents the impact of ash on inhibiting the fermentation depending on the microorganism tolerance.

Development of a model for energy consumption and size of particles is crucial to help choosing an efficient screen size inside the grinder to reach the particle size needed for downstream process. Material characteristics and grinder mechanism and size have impact on energy consumption and size distribution of ground particles.

Three well-known industrial equations: Kick, Rittinger, and Bond that relate specific energy to a characteristic particle dimension before and after size reduction fitted to the experimental data. The results of the studies show that Rittinger's equation is the best-fit equation to grinding biomass.

REFERENCES

Adapa, P., Tabil, L., & Schoenau, G. (2011). Grinding performance and physical properties of non-treated and steam exploded barley, canola, oat and wheat straw. *Biomass and Bioenergy*, *35*(1), 549–561. doi:10.1016/j.biombioe.2010.10.004

Andrel, H., Mory, A., & Zotter, T. (1999). Gasification of biomass and co-combustion of the gas in a pulverized-coal burner. *Proceeding of the 15th International Conference on Fluidized Bed Combustion*. Savannah, Georgia: ASME.

Annoussamy, M., Richard, G., & Guerif, J. (2000). Change in mechanical properties of wheat straw due to decomposition and moisture. *Applied Engineering in Agriculture*, *16*(6), 657–664. doi:10.13031/2013.5366

Arthur, J. F., Kepner, R. A., Dobie, J. B., Miller, G. E. & Parsons, P. S. (1982). Tub grinder performance with crop and forest residues. *Transactions of the ASABE, 25*(6), 1488-1494. doi:.3375110.13031/2013

Bitra, V. S. P., Womac, A. R., Chevanan, N., Miu, P. I., Igathinathane, C., Sokhansanj, S., & Smith, D. R. (2009). Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions. *Powder Technology*, *193*(1), 32–45. doi:10.1016/j.powtec.2009.02.010

Bridgwater, A. V., Meier, D., & Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, *30*(12), 1479–1493. doi:10.1016/S0146-6380(99)00120-5

Chandrakant, T. (1997). *Biomass gasification. Technology and Utilization*. ARTES Institute, University of Flensburg, Flensburg, Germany. Retrieved from http://members.tripod.com/~cturare/bio.htm

Collard, F. (2012). *Development of size reduction equations for calculating energy iput for grinding woody biomass with hammer mill. Internship Report*. Vancouver, Canada: Chemical and Biological Engineering Department. University of British Columbia.

Cutshall, J., Greene, D., Baker, S., & Mitchell, D. (2011). *Transpirational drying effects on energy and ash content from whole-tree chipping operations in a southern pine plantation. Paper presented at the 34th Council on Forest Engineering*. Quebec City, Canada.

Dasari, R. K., & Berson, R. E. (2007). The effect of particle size on hydrolysis reaction rates and rheological properties in cellulosic slurries. *Applied Biochemistry and Biotechnology*, *136-140*(1-12), 289–299. doi:10.1007/s12010-007-9059-x PMID:18478396

Earle, R. L., & Earle, M. D. (1983). *Unit Operations in Food Processing*. NZIFST(Inc) The web Edition. Retrieved from http://www.nzifst.org.nz/unitoperations

Esteban, L. S., & Carrasco, J. E. (2006). Evaluation of different strategies for pulverization of forest biomasses. *Powder Technology*, *166*(3), 139–151. doi:10.1016/j.powtec.2006.05.018

Freeman, M. C., O'Dowd, W. J., Brown, T. D., Hargis, R. A. Jr, James, R. A., Plasynski, S. I., & Battista, J. J. Jr et al.. (2000). Pilot-scale air toxics R&D assessment of creosote-treated and PCP-treated wood cofiring for pulverized coal utility boiler applications. *Biomass and Bioenergy*, *19*(6), 447–456. doi:10.1016/S0961-9534(00)00055-6

Gil, M., Gonzalez, A., & Gil, A. (2008). Evaluation of milling energy requirements of biomass residues in a semi-industrial pilot plant for co-firing. In *Proceedings of 16th European Biomass Conference and Exhibition*. Retrieved from: http://teide.cps.unizar.es:8080/pub/publicir.nsf/ codigospub/0497/$FILE/cp0497a.pdf

Hakkila, P. (1989). *Utilization of residual forest biomass*. Heidelberg, Berlin: Springer-Verlag. doi:10.1007/978-3-642-74072-5

Kettunen, P. O. (2006). *Wood, Structure and Properties*. Zuerich, Switzerland: Trans Tech Publications Ltd.

LINDANA. (2008). *TP Wood Chippers for Work in Green Areas*. Retrieved from http://www.machinerie.com/FedereePamphlet/Linddana/eNGLbrochure.pdf

Mani, S., Tabil, L. G., & Sokhansanj, S. (2004). Grinding performance and physical properties of wheat and barley straws, corn stover, and switchgrass. *Biomass and Bioenergy*, *27*(4), 339–352. doi:10.1016/j.biombioe.2004.03.007

Miao, Z., Grift, T. E., Hansen, A. C., & Ting, K. C. (2011). Energy requirement for comminution of biomass in relation to particle physical properties. *Industrial Crops and Products*, *33*(2), 504–513. doi:10.1016/j.indcrop.2010.12.016

Morrow, C. T., & Mohsenin, N. N. (1966). *Food engineering. Principles and selected applications*. New York: Academic Press.

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C., Womac, A. R., Lau, A., & Melin, S. (2011). Development of population balance model to simulate fractionation of ground switchgrass. *Transactions of the ASABE*, *54*(1), 219–227. doi:10.13031/2013.36239

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C. J., Lau, A., Melin, S., & Pelz, S. et al. (2012). Size reduction and fractionation to reduce the ash content of biomass. In the *62nd Chemical Engineering conference*. Vancouver, BC, Canada.

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C. J., Womac, A. R., Lau, A. K., & Melin, S. (2013). Development of size reduction equations for calculating energy input for grinding lignocellulosic particles. *Applied Engineering in Agriculture*, *29*(1), 93–100. doi:10.13031/2013.42523

Nexterra. (2012). *UBC biomass fuel specification for i.c. engine systems*. Nexterra Corp.

Petersson, A., Thomsen, M. H., Hauggaard-Nielsen, H., & Thomsen, A. B. (2007). Potential bioethanol and biogas production using lignocellulosic biomass form winter rye, oilseed rape and fababean. *Biomass and Bioenergy*, *31*(11-12), 812–819. doi:10.1016/j.biombioe.2007.06.001

Siegle, V., Schweitzer, B., Splethoff, H., & Hein, K. R. G. (1996). Preparation and co-combustion of cereals with hard coal in a 500 kW pulverized-fuel test unit. In *Proceedings of the 9th European Bioenergy Conference*, Vol. II, Elsevier Oxford, UK, 1027-1032.

Smook, G. A. (1992). *Handbook for Pulp and Paper Technologists*. Vancouver, BC: Angus Wilde Publication.

Sokhansanj, S., & Turhollow, A. F. (2004). Biomass densification – Cubing operations and costs for corn stover. *Applied Engineering in Agriculture*, *20*(4), 459–499. doi:10.13031/2013.16480

Stokes, B. J., McDonald, T. P., & Kelley, T. (1993) Transpirational drying and costs for transporting woody biomass - a preliminary review. IEA/BA Task IX, Activity 6: Transport and Handling. New Brunswick, CN: IEA pp. 76-91.

Stokes, B. J., Watson, W. F., & Sirois, D. L. (1987). Factors affecting power requirements for chipping whole trees. Paper No. 87-6012. *American Society of Agricultural Engineers Summer Meeting*, Baltimore, Maryland.

Thompson, J., & Sprinkle, W. (2013). Production, cost and chip characteristics of in-wood microchipping. In *2013 Council on Forest engineering Annual Meeting. Missoula, Montana, USA*.

Van Dranen, A., & Mello, S. (1997). *Production of ethanol from biomass*. U.S. Patent No. 5677154.

Watson, W. F., Sabo, R. F., & Stokes, B. J. (1986). Productivity of in-woods chippers processing understory biomass. In *Proceedings of the Council on Forest Engineering, Improving Productivity through Forest Engineering*. Academic Press.

Wei, L., Prodesimo, L. O., Igathinathane, C., & Batchelor, W. D. (2009). Process engineering evaluation of ethanol production from wood through bioprocessing and chemical catalysis. *Biomass and Bioenergy*, *33*(2), 255–266. doi:10.1016/j.biombioe.2008.05.017

Zhang, M., Sword, M., Buckmaster, W. D., & Cauffman, D. R. (2003). Design and evaluation of a corn silage harvester using shredding and flail cutting. *Transactions of American Society of Agricultural and Biological Engineers*, *46*(6), 1503–1511. doi:10.13031/2013.15633

ADDITIONAL READING

Morey, R., Kaliyan, N., Tiffany, D. G., & Schmidt, D. R. (2010). A corn stover supply logistics system. *Applied Engineering in Agriculture*, *26*(3), 455–461. doi:10.13031/2013.29946

Schell, D. J., & Harwood, C. (1994). Milling of lignocellulosic biomass. *Applied Biochemistry and Biotechnology*, *45/46*(1), 159–168. doi:10.1007/BF02941795

KEY TERMS AND DEFINITIONS

Wood Basic Density: In wood science wood basic at any moisture content is defined as the mass of oven-dry over the volume at moisture content.

Chapter 2

Effect of Steam Explosion Pretreatment on Size Reduction and Pellet Quality of Woody and Agricultural Biomass

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ABSTRACT

Steam explosion is a thermo-chemical pretreatment widely used to disrupt the ultra-structure of the cell wall of the ligno-cellulosic fiber to improve the fractionation of the major ligno-cellulosic components of the biomass for biochemical conversion. In recent years, steam explosion pretreatment has been applied on the fibers for improving the pellet quality of woody and agricultural biomass for thermo-chemical conversion. The improved qualities include high bulk density, low equilibrium moisture

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content, higher heating value, mechanical strength and moisture resistance. All of these desirable properties allow the steam exploded pellets to be handled and stored outdoors safely, similar to coal. This also raises lots of interests in considering pellets as preferable feedstock for the thermal power plant or bio-refinery facilities. In this chapter, the state of art of research findings on the effect of steam explosion on size reduction and pellet quality of woody and agriculture biomass will be discussed.

INTRODUCTION

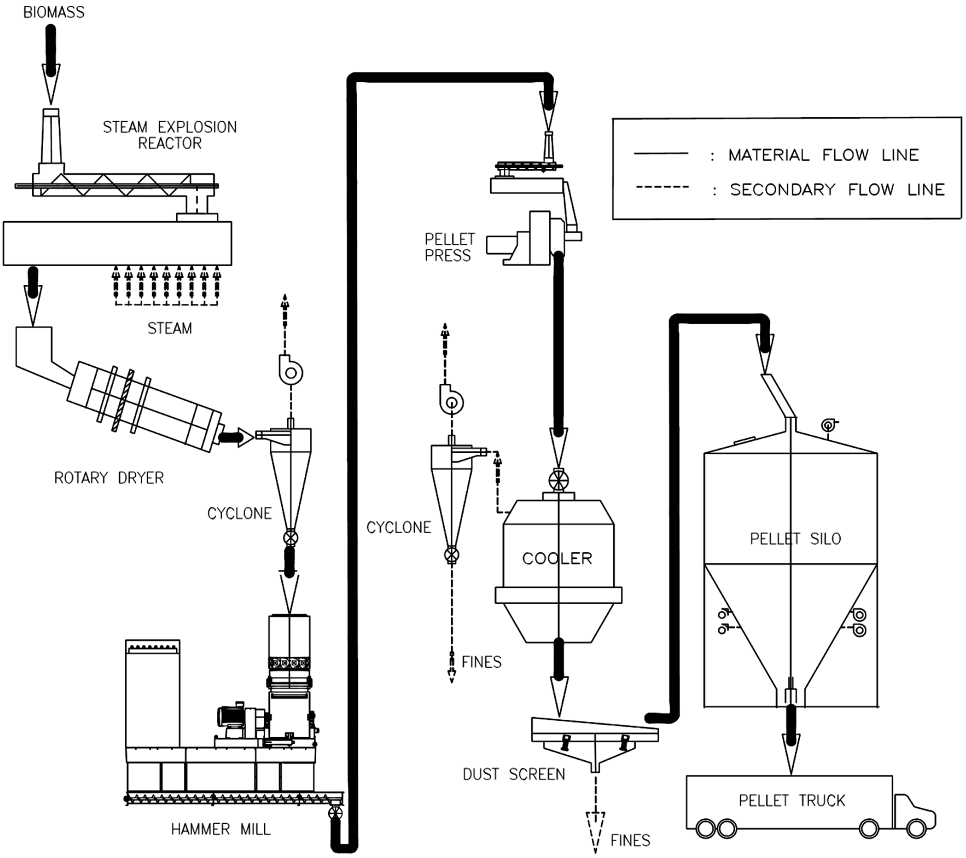
The global climate change has resulted in increasing the occurrence of natural catastrophes in recent decade, e.g. prolong winter storm with extremely low temperature and frequent rain storm flooding in summer in north eastern part of North America. It is noticeable that the glaciers in North and South Pole are melting rapidly due to global warming. The major cause is the increasing concentration of greenhouse gases (GHGs) in the atmosphere (U.S. Environmental Protection Agency, 2014). The major composition of GHGs are carbon dioxide (CO_2), methane (CH_4), tropospheric ozone (O_3), chlorofluorocarbon (CFC) and nitrous oxide (N_2O). The GHGs warm the lower atmosphere and surface of the planet by absorbing and emitting infrared radiation from the gases. The global average surface temperature has increased over 20th century by about 0.6ºC (IPCC, 2001).

Among different energy production technologies, fossil fuel burning has produced about three-quarters of the increase in CO_2 from human activity over the past 30 years (IPCC, 2001). Estimates of global CO_2 emissions in 2011 from fossil fuel combustion, including cement production and gas flaring, was 34.8 billion tonnes, an increase of 54% above emissions in 1990 (Le et al., 2011). Coal burning was responsible for 43% of the total emissions, oil 34%, gas 18%, cement 4.9% and gas flaring 0.7%. Therefore, it is of utmost importance to reduce the net emissions of GHGs caused by human activities by adopting renewable and sustainable energy.

Biomass is a promising coal replacement for combined heat and power generation. Unlike coal, biomass has a short life cycle and therefore considered as a carbon neutral fuel. In theory, biomass can be planted at a rate as they burned to produce emission. Biomass sequesters CO_2 in the atmosphere and converts them into oxygen and carbohydrates by photosynthesis. As a result, this helps to maintain a net carbon cycle in the atmosphere. Biomass is dispatchable which can be burnt more to meet high power output demand in winter. However, one of the major disadvantage of using biomass as feedstock for power generation is their high logistical cost of transportation and storage due to their low bulk density (Mobini et al., 2013). For woody biomass, the bulk densities of wood chips and wood sawdust are around 200 and 300 kg/m^3, respectively. It is even lower for the agricultural biomass. For example, the bulk density of switchgrass is between 60 – 250 kg/m^3 depending on moisture content (Lam et al., 2008). In addition, the as-harvested biomass are wet and with rock or metals. Therefore, the biomass requires to be pre-processed with drying, size reduction, pelletization and engineered into pellet form and potentially install with pretreatment unit prior to drying (Figure 1). The as-received biomass can be in wood chips, sawdust or shavings.

Wood pellets are with higher bulk density of 600 – 750 kg/m^3 and lower moisture content between 3 – 5% (w.b.). This is a preferable choice as feedstock for power stations. Besides, the biomass pellets with regular dimension with length up to 30 mm and diameter around 6.4 mm is eligible for using the same handling facilities of coal for the existing thermal power station. Although biomass pellets are promising solid fuel as coal replacement, their low binding ability between particles and high moisture absorption affinity impose lots of challenges of handling and storage issue of pellets (Danish Technological Institute, 2012). These issues lead to self-

Figure 1. A typical pellet plant with steam explosion pretreatment



heating and ignition (Guo, 2013), off-gassing formation (He et al., 2014) and oxygen depletion (Yazdanpanah et al., 2013) and dust explosion (Oveisi, et al., 2013). During the transportation of wood pellets in conveyors or bucket elevators, the mechanical forces introduced by the impact force of inter-pellets and the gravitational force during loading of pellets into the silos cause fractures and breakage and resulting in fines and dust formation (Danish Technological Institute, 2012; Oveisi et al., 2013). Dust formation is an inevitable issue during wood pellet handling in the pellet manufacturing facility and power plant, even there are standards proposed by EN standard (EN- 14961-1) to restrict the quality of pellets for safe handling. For storage, the freshly made wood pellets continued to emit flammable gases such as CO, H_2 and CH_4 during storage and handling (Yazdanpanah et al., 2013). It is reported that the composition of the gas mixture did not reach flammable concentrations for the stored wood pellets at 25, 40 and 60°C for a period of 9 weeks. However, the concentration of off-gasses increased tremendously for stored pellets with moisture content higher than 20%. As the biomass pellets are sensitive to moisture uptake, they swell and lose mechanical strength when exposed to rain (Lam et al., 2011). Therefore, wood pellets required closed silo for storage and cannot store outdoor as piles as coal.

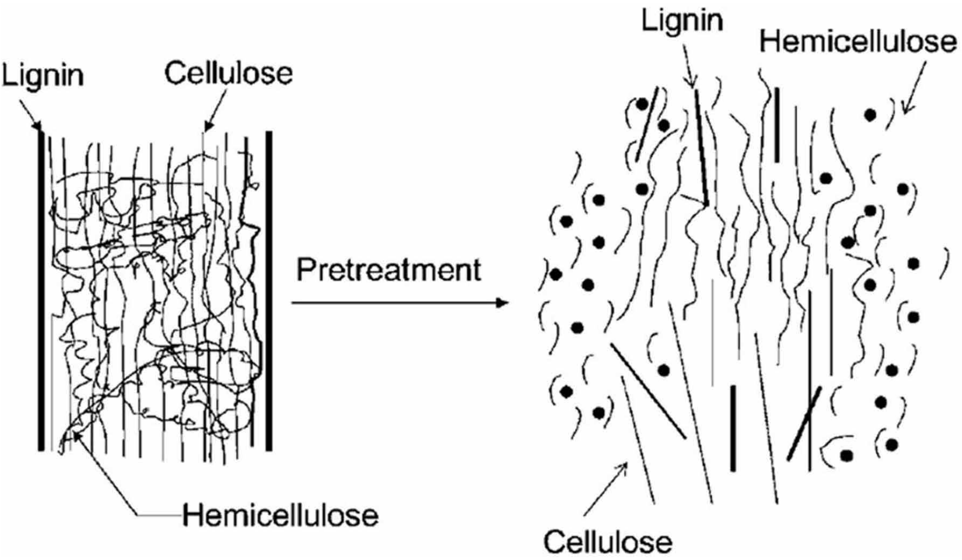
To overcome these issues, applying steam explosion pretreatment of biomass prior to pelletization appears to be a promising technology to produce durable and hydrophobic pellets for safe handling, storage and conversion. The steam exploded biomass pellets were also reported to be an excellent candidate as coal replacement for thermochemical conversion facilities as well as have a good potential as a feedstock for bioethanol refinery (Kumar et al., 2012a, 2012b).

BACKGROUND OF STEAM EXPLOSION PRETREATMENT

Steam explosion has been widely used as a physicochemcal pretreatment for lignocellulosic biomass for bioethanol production (Martin-Davison et al., 2015). The goal of the pretreatment is to fractionate the complex structure of cellulose, hemicellulose and lignin into simple units for recovery for fuels and chemicals conversion (Figure 2). It is a promising hydrothermal pretreatment for biorefinery as it has a lower environmental impact with less chemical used and mild pretreatment conditions compared to other pretreatment technologies (Mosier et al., 2005).

The process of steam explosion pretreatment involves three steps: autohydrolysis, physical defibrillation due to sudden decompression and impacts on wood particles (Muzamal et al., 2014). The biomass is first subjected to high pressure

Figure 2. Fractionation effect of steam explosion pretreatment on ligno-celluosic biomass fiber (Mosier et al., 2005)



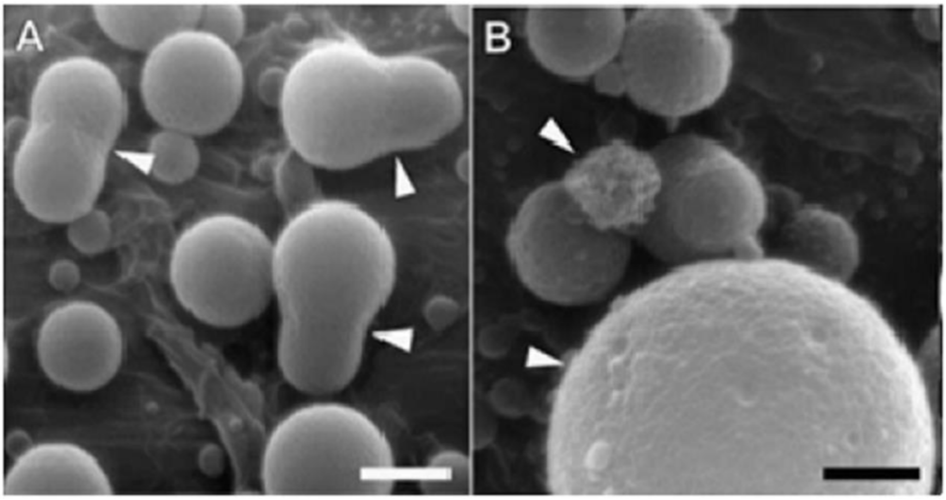
saturated steam between 180 – 240 ºC for 5 to 15 minutes depending on the treatment severity. The operating pressure ranges between 150 – 500 PSI (Lam, 2011). The severity of steam explosion pretreatment can be described by eq. (1.) developed by Overend et al. (1987):

$$R_0 = \int_0^t exp^{\left(\frac{(T-100)}{14.75}\right)} dt' \tag{1}$$

where R_0 is the severity factor (dimensionless), T is the reaction temperature (ºC) and t is the reaction time (min).

The initial high pressure steaming facilitates the hydrolysis of hemicellulose and lignin to form acetic acid and low molecular weight mono-saccharides and lignin. This weakens the bonding between the polysaccharides and lignin (Ramos et al., 2003; Muzamal et al., 2015). Some of the mono-saccharides dehydrate into the degraded components (e.g. furfural and 5-hyroxylmethyfurfural) at high temperature above 200 ºC. At the same time, lignin undergoes self-condensation and re-polymerization reaction with degraded components from mono-saccharides by

Figure 3. Lignin Coalescence caused by Hydrothermal Pretreatment (Donohoe et al., 2008). (A): Three pairs of droplets that appear to be fusing (Arrowheads) to form larger droplets. (B): Spherical droplets with a rough, coated surface (Arrowheads). The droplets in A and B are naturally redeposited on the cell wall surface following dilute acid pretreatment. Scale Bars = 0.5 μm.



dehydration (Li et al., 2007; Lam, 2011). Donohoe et al. (2008) visualizes the lignin droplets coalescence and migration through cell walls when the hydrothermal treatment temperature is above the phase transition temperature of lignin (Figure 3). This movement of lignin blocks the pores between the cellulose and hemicellulose fibers which inhibits the enzymes accessing the sugar for hydrolysis. However, this lignin droplets may act as binding agent for improving the mechanical strength of the steam exploded pellets (Lam, 2011).

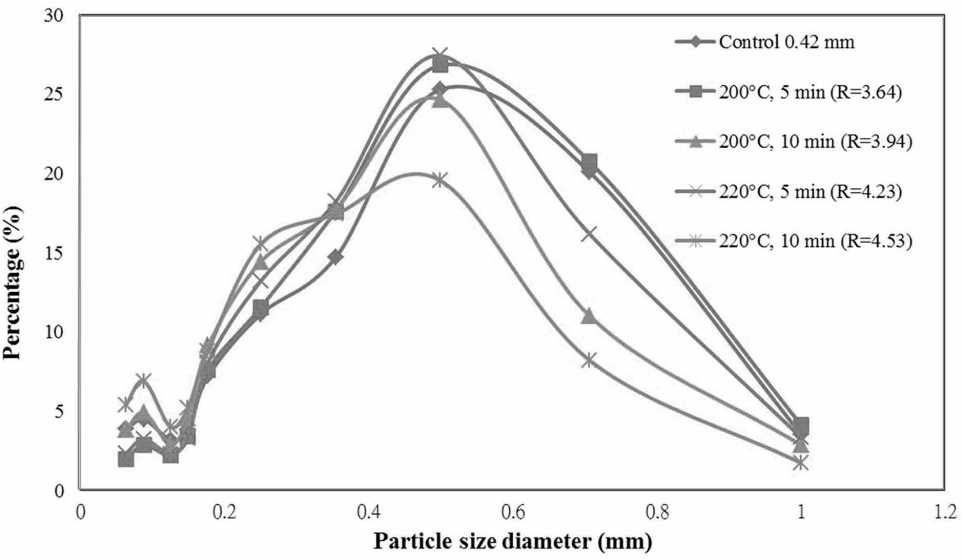
Steam explosion cleaves the linkage between the polysaccharides and lignin of the biomass, increasing the porosity of the ligno-cellulosic fibers to allow enhanced enzyme digestion of the biomass fibers (Ramos et al., 2003). Martin-Davidson et al. (2015) investigated the temperature effect of steam explosion on poplar hybrids with different lignin content in bioethanol production and reported that the highest enzymatic hydrolysis yield of 79% was obtained for the hybrid poplar with the lowest lignin content. A recent study reported steam explosion at 190 °C and 5 min without acid catalyst achieved the best enzymatic hydrolysis of spruce bark to recover the highest yield of sugars for fermentation (Kemppainen et al., 2012).

STEAM EXPLODED WOOD PELLET

Size Reduction Effect

Steam explosion had an energy saving in size reduction of steam treated samples (Lam, 2011). The particle size of steam treated material decreased from 0.42 to 0.35 mm with increasing treatment severity from 3.64 to 4.53 (Lam, 2011; Lam et al., 2012a). Figure 4 shows that the normal size distribution of the samples of 1.7 mm ground untreated particles with 10% m.c. (w.b.) and respective steam exploded fir particles under different severities. The fragmentation of the particles can be described by the formation of two peak regions for increasing treatment severity, i.e. fine particles and larger particles. This can be explained by the fragmentation due to pressure drop by explosion. It was speculated that the fine particles were disintegrated from the surface of the wood particles due to explosion effect and gradually formed two groups of particles. A recent research reported that the sudden decompression during steam explosion is not responsible for the disintegration of the wood particles into fragments but changes the porosity profiles of the tracheids (Muzamal et al., 2015). Instead, the disintegration occurs due to impact of softened wood chips.

Figure 4. Particle size distribution of untreated and steam exploded wood particles at different severity (R is severity factor) (Lam, 2011)



Owing to the size reduction effect by steam explosion, less energy was consumed to grind the steam exploded wood particles to a target particle size for pelletization. When the energy saving in size reduction is considered, the direct energy input to the size reduction per unit pellets decreased from 0.36 to 0.29 MJ/kg with increasing treatment severity (Lam, 2011). Furthermore, thermally treated wood particles were reported to have less energy consumption for grinding (Holtzapple et al., 1989; Govin et al., 2009). Torrefied spruce wood chips at 180 ºC were reported to have energy consumption of grinding dropped off by 40% compared to untreated one (Govin et al., 2009). This was due to the increase in brittleness of the materials. It was expected that steam exploded wood particles would have similar characteristics as torrefied wood particles which require less grinding energy (Repellin et al., 2010; Phanphanich et al., 2011).

Scanner imaging method is also a popular characterization method to measure the particle size distribution compared to the traditional gravitational sieving method (Tannous et al., 2013). The scanner imaging method allows to measure two dimension (i.e. length and width) of the particle which allows to estimate the particle shape of the ground wood particles. The geometric mean diameter of the particles determined by using the gravitational sieve is limited by the width of the particle and may not be a true representative of the particle size and shape for the correlation to their other physical properties (e.g. bulk density and flowability). These parameters are also important for reactor design (e.g. fluidized bed) and processing units of the wood particles (e.g. pneumatic conveyor).

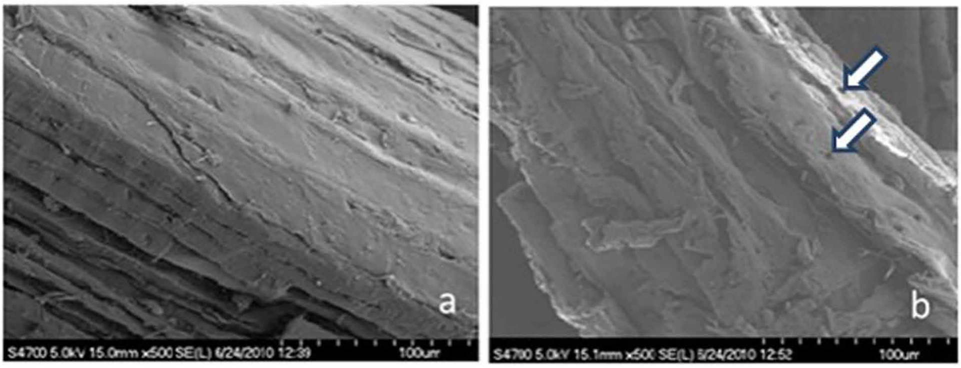
Lam (2011) investigated the particle length and width of the untreated wood particles and that of steam exploded wood particles treated at different severities by scanner imaging method and scanning electron microscope. For each imaging trial using scanner, it was about 100 – 300 particles to be measured and average values of dimensions were reported (Table 1). For untreated wood powder, the average length ranged between 3.14 – 4.22 mm and the average width ranged between 0.89 – 1.12 mm. From the image analysis, both the relative length and width of the steam exploded wood particles at four different treatment severities were smaller than the untreated particles.

In particular, the relative length and width of the steam exploded particles increased from 0.85 at a severity of 3.64 to 0.9 at severity of 3.94. The initial increase of relative dimensions of steam exploded wood particle treated at treatment severity of 4.23 may be due to the devolatilization during steaming. The particle swelled, expanded and released volatiles during steaming. This introduced the pores on the particle surfaces which was observed under SEM (Figure 5). Further particle dimensions reduction with increasing treatment severity was due to the fines formation by fragmentation and pores shrinkage upon heating.

Table 1. Physical dimensions analysis of untreated and steam exploded wood particles at different treatment severities using imaging scanner method (Lam, 2011)

Temperature (ºC)	**Time (min)**	**Severity**	**Trials**	**Number of particles**	**Length (mm)**		**Width (mm)**		**Aspect ratio**	
					Average	**SD**	**Average**	**SD**	**Average**	**SD**
Untreated			1	131	3.52	1.63	0.90	0.44	4.42	2.12
			2	108	4.22	1.91	1.12	0.49	4.22	2.11
			3	128	3.14	1.38	0.89	0.52	4.23	2.31
200	5	3.64	1	137	3.67	1.47	0.93	0.44	4.59	2.38
			2	302	2.27	1.19	0.62	0.37	4.26	2.40
			3	195	3.42	1.75	0.85	0.46	4.74	2.83
200	10	3.94	1	179	3.41	1.52	0.91	0.46	4.29	2.22
			2	329	3.10	1.61	0.84	0.42	4.11	1.97
			3	205	3.40	1.78	0.91	0.48	4.22	2.08
220	5	4.23	1	297	3.25	1.54	0.85	0.40	4.38	2.41
			2	367	2.45	1.23	0.68	0.35	4.17	2.16
			3	213	3.04	1.43	0.78	0.37	4.52	2.73
220	10	4.53	1	196	2.59	1.30	0.71	0.31	4.11	2.66
			2	204	2.32	1.07	0.70	0.33	3.85	2.44
			3	217	2.16	1.00	0.66	0.32	3.88	2.46

Figure 5. Particle surface under SEM: (a.) ground untreated particles by hammermill with 1.7 mm screen and (b.) uncatalyzed steam exploded wood particles at 220ºC for 10 minute



Potential Applications of Steam Exploded Wood Pellet

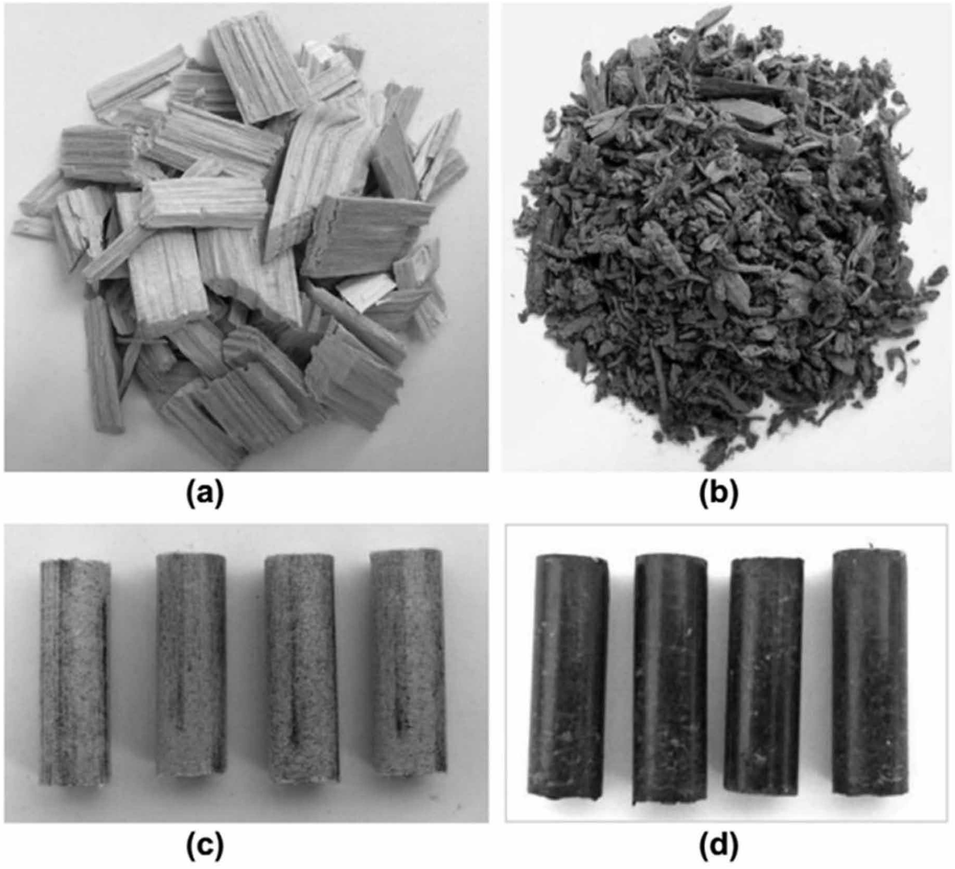
Steam explosion is an efficient pretreatment method for bio-conversion of wood chips to produce bioethanol (Kang et al., 2013) and biogas production (Horn et al., 2011). The major focus of steam explosion pretreatment is overcoming the lignin recalcitrance of softwood and facilitating effective enzymatic access to released cellulosic mono-sugar from auto-hydrolysis during steam treatment (Kumar et al., 2010, 2012a). Some of the studies reported the use of SO_2 as a catalyst during steam explosion is an efficient pretreatment method for softwood (Tooyserkani et al., 2013; Kang et al., 2013). Since densification brings merit in reducing the supply logistic cost of the biomass feedstock for bio-conversion, steam exploded wood pellet was also recently being evaluated for its potential application for their bio-conversion (Kumar et al., 2012b; Tooyserkani et al., 2013). Figure 6 shows the pellets made from wood chips and SO_2 catalyzed steam exploded wood pellets.

Kumar et al. (2012b) concluded that a single step of steam explosion pretreatment allows to facilitate both pelletization (i.e. size reduction to produce suitable particle size for pelletization) and subsequent enzymatic hydrolysis without the need for a further pretreatment step for bioconversion. Tooyserkani et al. (2013) reported that SO_2 catalyzed steam explosion pretreatment produced suitable particle size (i.e., less than 6 mm geometric mean diameter) from wood chips for pelletization by rapid decompression (Figure 7). The pelletization process did not affect the carbohydrate recovery yield from pellets and that was comparable to that of steam exploded wood chips. In general, the SO_2 catalyzed steam exploded wood pellets exhibits their potential suitability for biochemical conversion.

Apart from bioconversion application, steam exploded wood pellets were evaluated for their thermal conversion performance, e.g. production of syngas by gasification (Gunarathne et al., 2014) and heat and power production by combustion (Biswas et al., 2011a; Biswas et al., 2011b). Gunarathne et al. (2014) reported that steam gasification of steam exploded wood pellets favors the formation of the syngas with lower heating value of 10.6 MJ/Nm^3, however the syngas is with high concentration of CO and low concentration of H_2. This was due to the removal of –OH groups during steam explosion pretreatment.

A Swedish giant utility, Vattenfall evaluated the handling, storage, combustion and emissions performance of steam exploded wood pellets (also called as black pellets) in lab scale and in commercial scale (Dusan, 2011). They found steam exploded wood pellets could be a good candidate as coal replacement for thermal plant in addition to their merit of low dust formation than the untreated wood pellets (Figure 8) and lower greenhouse gases emission.

Figure 6. Appearance of raw material and pellets: (a) original Douglas fir wood chips, (b) SO_2-catalyzed steam treated and dried wood chips, (c) pellets made from untreated particles and (d) pellets made from SO_2-steam exploded particles (Tooyserkani et al., 2013).



Physical Properties

It was reported that the steam exploded wood pellets had higher mechanical strength and hydrophobicity compared to the untreated wood pellets (Lam, 2011; Lam et al., 2011; Lam et al., 2013; Tooyserkani et al., 2012; Tooyserkani et al., 2013). Lam et al. (2011) reported that the pellets made from non-catalyzed steam exploded wood at 200 – 200 °C and 5 – 10 min (Figure 9). They had a maximum breaking strength 1.4 – 3.3 times than that of the untreated wood pellets under the same pelletization

Figure 7. Particle size distribution for untreated (gray) and SO_2 -catalyzed steam exploded substrates (dark) before pelletization (Tooyserkani et al., 2013).

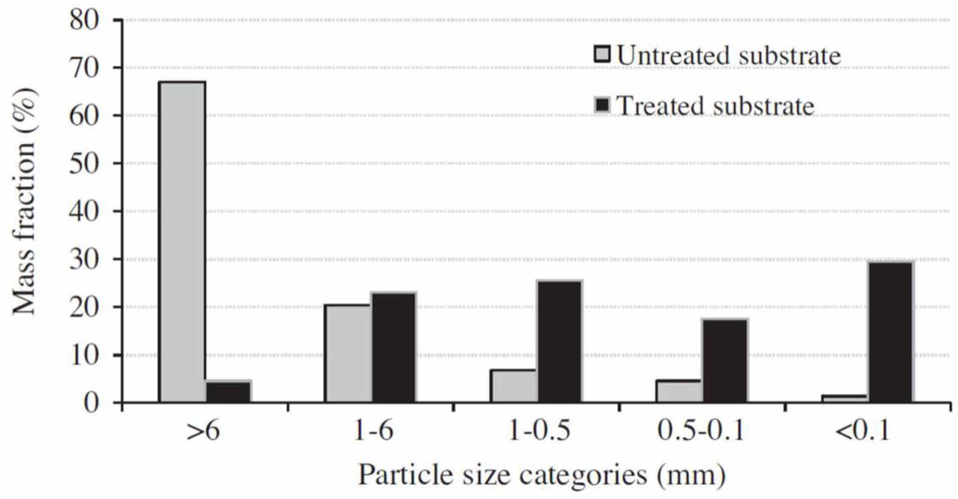
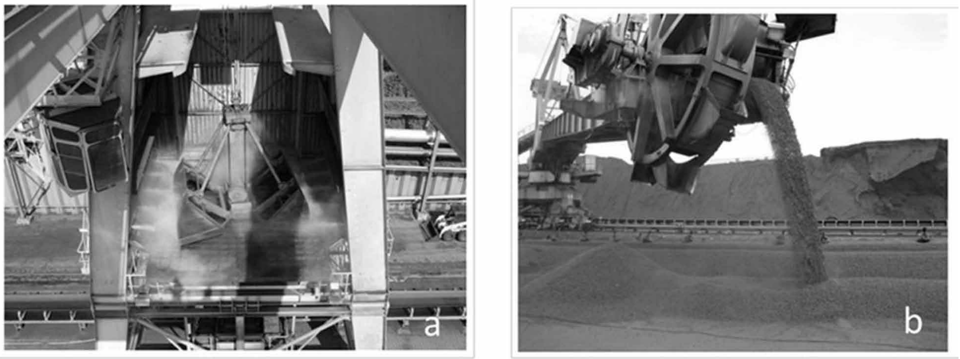
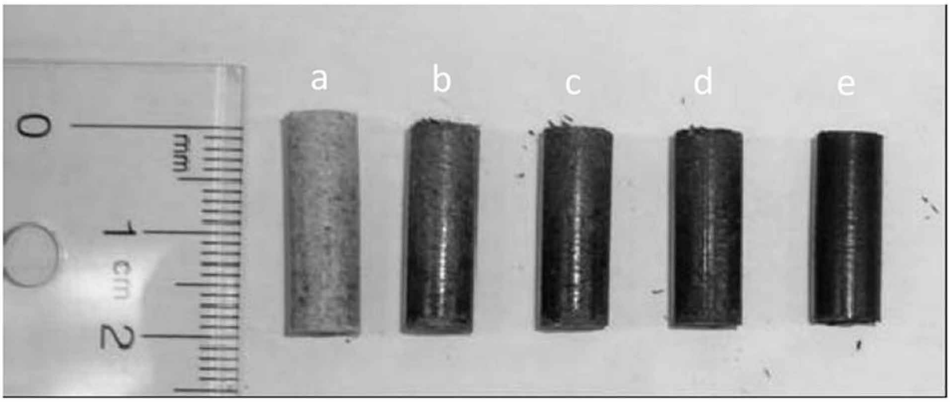


Figure 8. Unloading of steam exploded wood pellets with water dispersion system (a) and reclaimer (b) in commercial scale coal yard (Dusan, 2011)



condition. The pseudolignin may act as a natural binder that being activated during steam explosion pretreatment to enhance the binding strength between wood fibers for producing strong wood pellets. Meanwhile, the non-catalyzed steam exploded wood pellet showed an increase of high heating value from 18.94 to 20.09 MJ/kg with increasing treatment severity. The non-catalyzed steam exploded pellets also showed a reduced equilibrium moisture content of 2 – 4% (w.b.) and its moisture adsorption behaviour is well described by GAB model (Lam et al., 2012b).

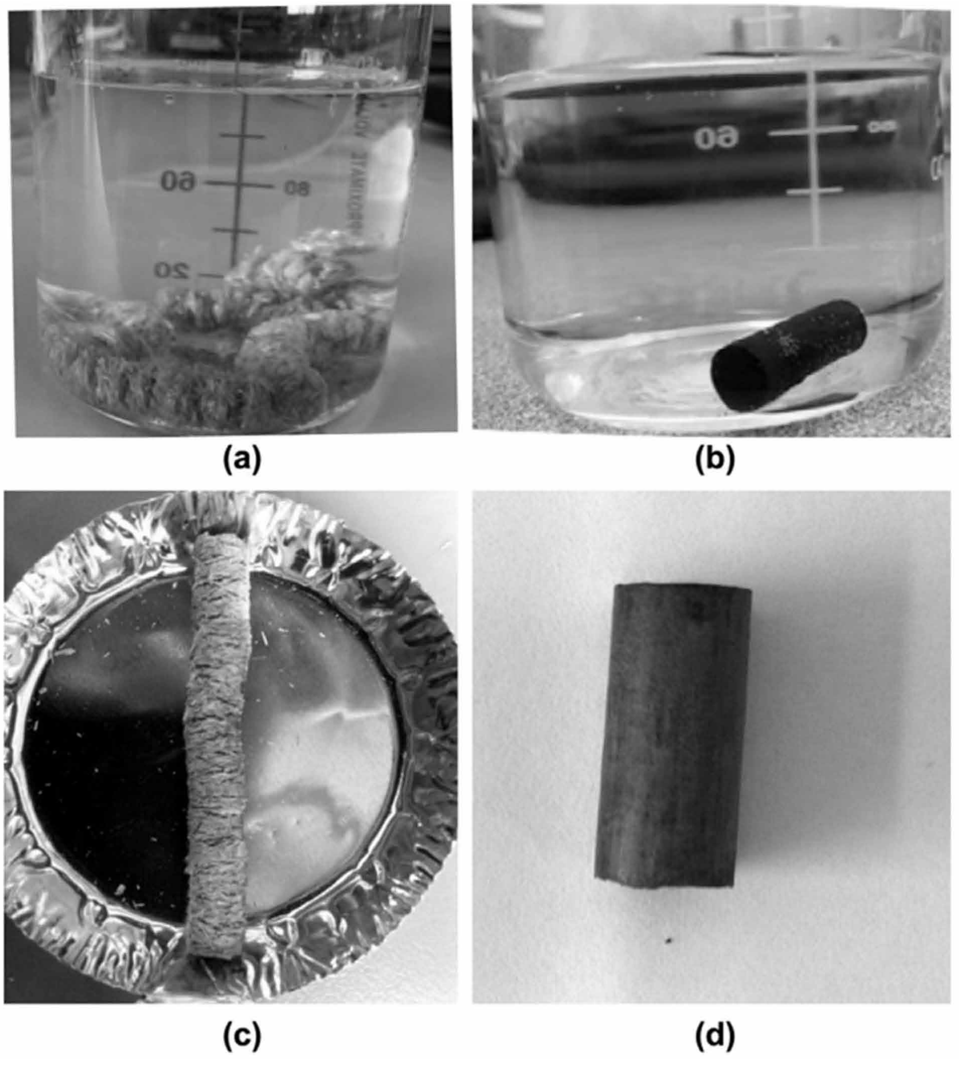
Figure 9. Physical appearance of wood pellets made from untreated and steam exploded Douglas fir at different steam explosion conditions: (a.) untreated, (b.) 200 °C-5 min, (c.) 200 °C-10 min, (d.) 220 °C-5 min, (e.) 220 °C-10 min (Lam et al., 2011).



Tooyserkani et al. (2013) reported that the SO_2 catalyzed steam exploded wood pellets were with high pellet density of 1.34 g/cm^3 while that of untreated pellets were with 1.21 g/cm^3. The required maximum breaking force to break the SO_2 catalyzed steam exploded wood pellet was about two times than that of untreated wood pellets made at the same pelletization condition. Meanwhile, the SO_2 catalyzed steam exploded wood pellet was found with more hydrophilic in nature. From the moisture adsorption test, the SO_2 catalyzed steam exploded wood pellets had a higher equilibrium moisture content (20.6% d.b.) than that of the untreated wood pellet (9.2% d.b.) and that of non-catalyzed steam exploded wood pellet (5.9% d.b.). It was deduced that SO_2 catalyst led to "open up" the ligno-cellulosic matrix more severely during steam treatment and resulted in more accessible area of the cellulose to adsorb the moisture. In addition, the SO_2 catalyst facilitates faster hydrolysis rate of the hemi-cellulose during steam treatment. Therefore, more soluble sugars were formed and adsorbed the moisture from the surrounding.

Although the SO_2 catalyzed steam exploded wood pellet shows more hydrophilic nature than the untreated pellet, their water moisture absorption was better than the untreated wood pellet from the water immersion test. The SO_2 catalyzed steam exploded wood pellet remained intact without any disintegration after one week immersing in water (Figure 10b). In contrast, the untreated wood pellet (Figure 10a) disintegrated completely right after immersing in water.

Figure 10. Moisture sorption tests: (a) untreated pellet right after immersing in water, (b) SO_2 catalyzed steam exploded pellet after one week immersing in water, (c) appearance of an untreated pellet reached to equilibrium moisture content in humid chamber (30 ºC – 90% RH) after 4 h and (d) unchanged appearance of a treated pellet reached to equilibrium moisture content after 24 h (Tooyserkani et al., 2013).



STEAM EXPLODED PELLETS FROM OIL PALM RESIDUES

Background of Oil Palm Residues

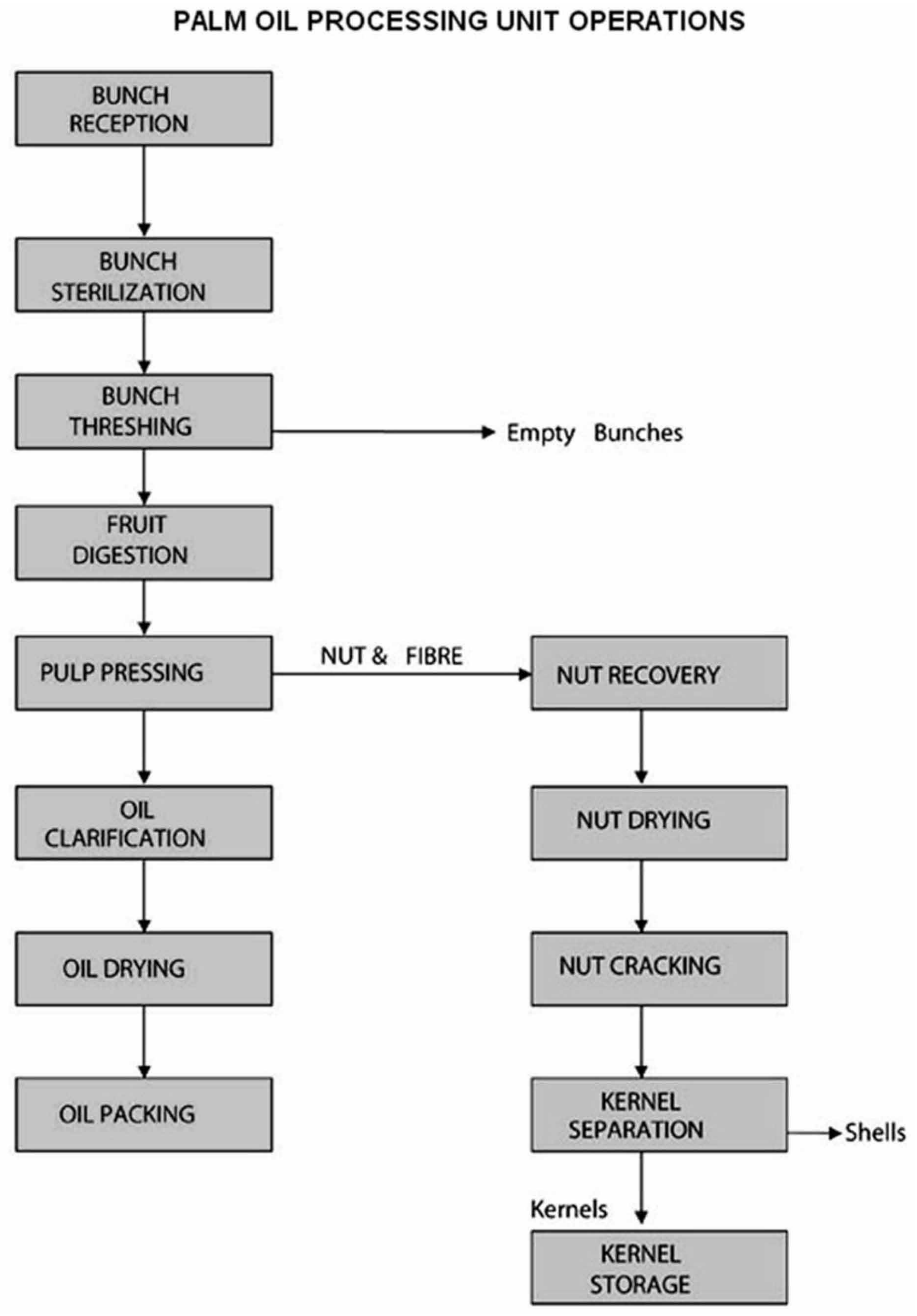
Palm oil is an essential food product, which accounts for one third of the world's vegetable oil market in 2007 (Timms, 2007). In Southeast Asia, approximately 85% of palm oil is produced in Malaysia and Indonesia. Palm oil is refined by mechanical pulping from the oil palm bunches (Figure 11). During the palm oil extraction process, the oil palm brunches are initially sterilized by low pressure steam 0.28 MPa at 140 °C, followed by threshing the palm oil from the fruit bunches (Shamsudin et al., 2012). Threshing is a process of which a rotary drum or a fixed drum equipped with rotary beater bars to detach the fruit from bunches. The residue produced during the threshing is the empty fruit bunch (EFB). The fruit bunch is further digested by steaming at 80 to 90 °C for breaking down the oil bearing cells (Kasim, 2009). The pure palm oil is then obtained by pulp pressing on the digested mixture and followed by clarification, drying and storage. Meanwhile, the palm kernel shell (PKS) is extracted as a by-product. It was reported that there were 232 million bone dry tonnes of oil palm residues produced from these process (Menon et al., 2003; Wan Rosli et al., 2004).

Current Applications of Oil Palm Residues

Disposal of substantial amount of agricultural residues is an urgent and critical issue for the palm oil mills. Currently, the residues are decomposed in open fields when open incineration is not applicable as an available disposal method. It is questionable how to utilize these abundant oil palm residues effectively by converting EFB and PKS into useful bio-fuel. EFB and PKS are agricultural residues with similar chemical composition and with high heating value (HHV) around 18 - 19 MJ/kg (Lam, 2013). It is expected that they can be burnt to recover energy similar to the woody biomass, especially when the shortage supply of wood pellets occurs.

According to the life cycle analysis (LCA) of different potential applications by using EFB for energy production in Malaysia, the most attractive and promising application is 100% firing EFB and PKS in combined heat and power (CHP) (Chiew et al., 2013). However, the bulky and wet nature of raw EFB makes EFB difficult to be combusted or gasified with high efficiency and low emissions. Similar to the pretreatment of woody biomass, pelletization of these oil palm residues

Figure 11. Unit operations of palm oil process



helps to eliminate these problems, for instance, the feeding performance of these residue to the downdraft gasifier or combustion unit is significantly improved due to their lower moisture content and uniform particle size (Salomon et al., 2013). EFB pellets exhibit three times higher bulk density. The pellets also demonstrate lower moisture content and the reductions of particle sizes compared to their raw materials, which are highly compatible for combustion to produce heat and power (Kerdsuwan et al., 2011). Gasification of wood pellets results in a richer producer gas while EFB pellets give a poorer one with higher contents of non-combustible compounds (Erlich et al., 2011). Another barrier of using EFB and PKS as bio-fuel for combustion is that they have a higher ash content between 2 – 5 wt.% (Lam, 2013) than woody biomass (around < 0.2 wt %) (Lam, 2011). This may impose a significant ash handling, slagging and fouling problems during combustion. Applying water leaching prior to pellet production would be recommended to prepare a good quality feedstock by reducing ash production in a power generator (Lam, 2013; Lam et al., 2014).

At present, there are limited literatures reporting the mechanical properties of pellets made from oil palm residue (Husain et al., 2002; Sing et al., 2012; Liu et al., 2014). For instance, it was demonstrated that a PKS briquette blended with palm fiber and using waste paper as binding agent gave the best mechanical properties (Sing et al., 2012). However, the briquettes produced solely of PKS without binders were easy to be disintegrated in the hardness test. In light of this issue, the poor binding quality of PKS suggests that there is a need of steam explosion pretreatment to enhance the pellet strength of oil palm residues.

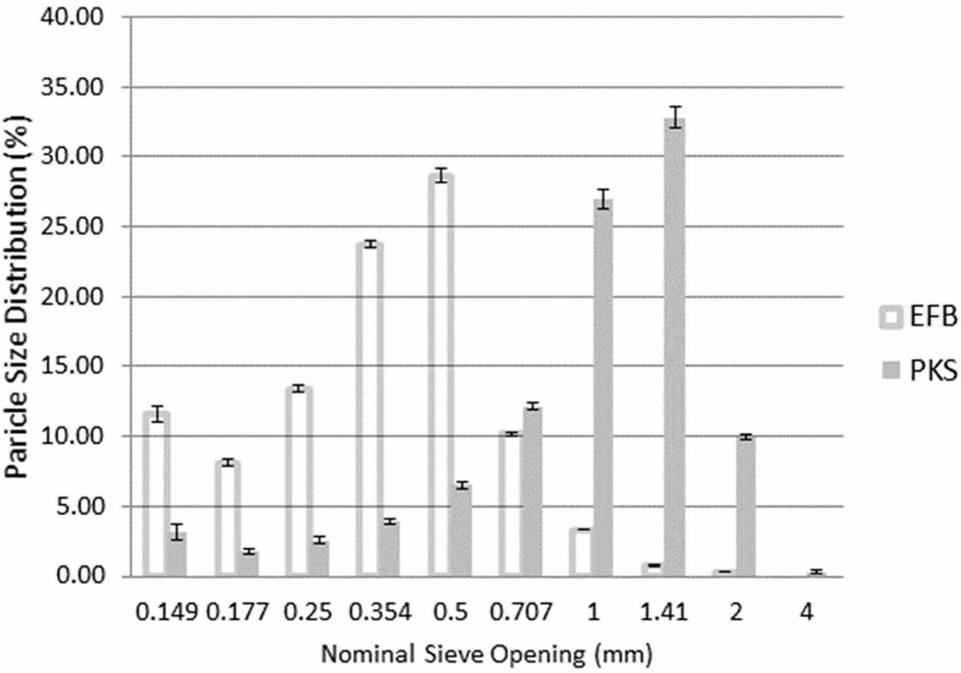
Physical Characterization of Pellets Made From Oil Palm Residue

Figure 12 shows the test samples after grinding, non-catalyzed steam explosion treatment and pelletization. For untreated ground particles, EFB has a slightly less dark color compared to PKS and with a smaller particle size distribution with a geometric mean diameter 0.31 mm (Figure 13). In contrast, the geometric mean particle diameter of untreated PKS ground particle is 0.72 mm. However, the EFB powder showed a darker color than that of PKS with steam explosion pretreatment at 220 °C for 5 minute. Similar to steam exploded wood, the dark color of the steam exploded EFB may be attributed to the caramelization of hemicellulose (i.e. Maillard reaction) and the degradation of extractives (Lam et al., 2012a). EFB has a higher hemicellulose and lower lignin content compared to softwood. Due to a lower recalcitrance of EFB, EFB is an excellent potential raw material for fuel ethanol production (Piarpuzan et al., 2011).

Figure 12. Physical appearance of untreated and steam exploded EFB and PKS in ground particles and pellets

Material	Untreated	Steam treated	Untreated	Steam treated
EFB				
PKS				

Figure 13. Particle size distribution of the ground particles of EFB (Left) and PKS (Right)



The increase in darkness of the steam exploded EFB pellet was highly correlated with an increase in its high heating value (HHV) from 18.54 to 22.42 MJ/kg (wet basis). This corresponds to an increase of 12% of HHV in dry basis by removing the moisture and volatiles with low heating value during steam explosion pretreatment. Surprisingly, this value was much higher than the increase in HHV of fir with 2.6%. For PKS, steam explosion did not have a significant effect on the changes of high heating values with a P-value < 0.05. Although steam explosion increases the high heating value of EFB by 21%, there was a considerable trade off that the ash content also increased from 5.5 – 8.1%. This was a reasonable result as there was a loss of volatiles during steam treatment. However, it is questionable whether the ash would be exposed more on the EFB particle surface were easier to be removed or leached by downstream pretreatment process.

The EFB and fir pellets did not show a significant change of pellet density after steam explosion and were 1.14 and 1.08 g/cm^3, respectively (Table 2). This is different from the previous report on increasing pellet density of other agriculture species: barley, canola, oat and straw, by steam explosion pretreatment (Adapa et al., 2010). However, steam explosion pretreatment improved the pellet density of PKS from 1.13 to 1.21 g/cm^3 and with a reduction of porosity from 17.9 to 10.1%. This may attribute to the rapid volatilization of extractives during high pressure steaming and led to the shrinkage of macro-pore of the PKS fibers. For the EFB and softwood fir, they exhibited a very small change of porosity within 1% after steam explosion pretreatment.

Table 2. Physical properties of untreated and steam exploded EFB, PKS and fir

	Powder						Pellet				
Biomass	**Moisture content[1] (%)**		**High heating value[1] (MJ/kg)**		**Ash content[1] (%)**		**Pellet density[2] (g/cm^3)**		**True density[2] (g/cm^3)**		**Porosity (%)**
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	
Untreated											
EFB	13.5	0.7	18.54	0.80	5.47	0.08	1.14	0.02	1.40	0.00	19.0
PKS	13.5	0.3	21.51	1.14	1.35	0.22	1.13	0.03	1.37	0.03	17.9
Fir	6.9	0.1	18.82	0.30	0.27	0.02	1.09	0.04	1.43	0.00	23.8
Steam exploded											
EFB	7.3	0.4	22.42	0.91	8.08	0.27	1.13	0.03	1.37	0.03	17.9
PKS	6.7	0.3	21.99	0.20	1.85	0.21	1.21	0.03	1.35	0.00	10.1
Fir	6.0	0.2	19.50	0.05	0.52	0.09	1.08	0.04	1.42	0.00	24.0

[1]: Number of measurements: n = 3

[2]: Number of measurements: n = 5

For the mechanical strength of the steam exploded pellets, the maximum breaking strength of EFB and PKS were increased by 63 and 45%, respectively (Table 3). Similar percentage increase was also observed for the Meyer hardness. Although there is a noticeable increase in mechanical strength of the steam exploded EFB and PKS pellets, their degree of percentage increase is not as much as the softwood fir with an increase in 230% in maximum breaking strength and 312% in Meyer hardness. Lam et al. (2013) reported that pseudolignin activated by steam explosion pretreatment was accounted for improving the binding ability of the softwood fibers to form durable pellets. In this case, it is less pronounced to improve the strength of pellets made from oil palm residue (Lam et al., 2015). This is because the native lignin content of the untreated EFB and PKS is low with 16.04 and 20.41%, respectively, when compared to the native lignin content of fir with 28%.

CONCLUSION

Steam explosion is a promising pretreatment technology to enhance the mechanical strength and moisture adsorption resistance of the biomass pellets. It improves the pellet quality which allows safe handling and storage. By pelletizing the steam exploded biomass, the raw biomass from field transforms to pellets with homogeneous physical and chemical properties and are ready at the gate of bio-conversion and thermochemical conversion facilities. Steam explosion not only changes the

Table 3. Mechanical properties and energy input for pelletization of untreated and steam exploded EFB, PKS and fir

Biomass	Meyer hardness^3 (N/mm^2)		Maximum breaking strength^3 (MPa)		Asymptotic modulus^3 (GPa)		Compression energy^3 (J/g)		Extrusion energy^3 (J/g)	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
Untreated										
EFB	1.82	0.68	57.71	21.62	0.72	0.06	30.15	1.51	0.99	0.10
PKS	1.35	0.23	42.70	7.23	0.62	0.02	32.61	1.04	3.95	1.51
Fir	1.60	0.20	18.00	4.00	1.33	0.03	20.45	1.67	0.49	0.03
Steam exploded										
EFB	2.97	0.23	94.06	7.30	0.51	0.03	44.50	4.56	5.81	1.34
PKS	1.95	0.89	61.83	28.20	0.59	0.04	31.81	1.38	5.16	0.45
Fir	6.60	2.10	59.30	11.10	1.19	0.01	36.25	4.78	1.17	0.14

^{3}: Number of measurements: n = 5

chemical structure of the ligno-cellulosic biomass fiber, but also changes their particle size and shape due to attrition between particles during rapid decompression. Future research interest could focus on understanding the effect of steam explosion conditions on the particle size distribution of different biomass feedstock considering the optimization of energy usage and carbon footprint. Different modes of size reduction could be investigated and correlated to the steam explosion process conditions. This is important for designing, controlling and optimizing the steam exploded pellets production process, as well as provide specification for designing handling equipment and reactors.

REFERENCES

Adapa, P. K., Tabil, L. G., & Schoenau, G. J. (2010). Compression characteristics of non-treated and steam-exploded barley, canola, oat and wheat straw grinds. *Applied Engineering in Agriculture*, *26*(4), 617–632.

Biswas, A. K., Umeki, K., Yang, W., & Blasiak, W. (2011a). Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment. *Fuel Processing Technology*, *92*(10), 1849–1854.

Biswas, A. K., Yang, W., & Blasiak, W. (2011b). Steam pretreatment of Salix to upgrade biomass fuel for wood pellet production. *Fuel Processing Technology*, *92*(9), 1711–1717. doi:10.1016/j.fuproc.2011.04.017

Chiew, Y. L., & Shimada, S. (2013). Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer – A case study of Malaysia. *Biomass and Bioenergy*, *51*, 109–124. doi:10.1016/j.biombioe.2013.01.012

Danish Technological Institute. (2012). *Guideline: Handling and Storage of Wood Pellets. Resultat Kontrakt Report*. Denmark: Taastrup.

Donohoe, B. S., Decker, S. R., Tucker, M. P., Himmel, M. E., & Vinzant, T. B. (2008). Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatement. *Biotechnology and Bioengineering*, *101*(5), 913–925. doi:10.1002/bit.21959 PMID:18781690

Dusan, S. (2011). *Black pellets verification programme*. Retrieved June 9, 2014, from http://www.solandersciencepark.se/sites/default/files/media/pdf_filer_sv/stefandusan.pdf

Erlich, C., & Fransson, T. H. (2011). Downdraft gasification of pellets made of wood, palm oil residues respective bagasse: Experimental study. *Applied Energy*, *88*(3), 899–908. doi:10.1016/j.apenergy.2010.08.028

Govin, A., Repellin, V., Rolland, M., & Duplan, J. (2009). Effect of torrefaction on grinding energy requirement for thin wood particle production. Presented at Nicolas Roche. *XII ° Congrès de la Société Française de Génie des Procédés Pour relever les défis industriels du XXI° siècle A la croisée des Sciences et des Cultures*, Marseille, France.

Gunarathne, D. S., Mueller, A., Fleck, S., Kolb, T., Chmielewski, J. K., Yang, W., & Blasiak, W. (2014). Gasification characteristics of steam exploded biomass in an updraft pilot scale gasifier. *Energy*, *71*, 496–506. doi:10.1016/j.energy.2014.04.100

Guo, W. (2013). *Self-heating and spontaneous combustion of wood pellets during storage*. (Doctoral dissertation). Available from The University of British Columbia, Vancouver.

He, X., Lau, A. K., Sokhansanj, S., Lim, C. J., Bi, X. T., & Melin, S. (2014). Investigating gas emissions and dry matter loss from stored biomass residues. *Fuel*, *134*, 159–165. doi:10.1016/j.fuel.2014.05.061

Holtzapple, M. T., Humphrey, A. E., & Taylor, J. D. (1989). Energy requirements for the size reduction of Poplar and Aspen wood. *Biotechnology and Bioengineering*, *33*(2), 207–210. doi:10.1002/bit.260330210 PMID:18587902

Horn, S. J., Estevez, M. M., Nielsen, H. K., Linjordet, R., & Eijsink, V. G. H. (2011). Biogas production and saccharification of *Salix* pretreated at different steam explosion conditions. *Bioresource Technology*, *102*(17), 7932–7936. doi:10.1016/j.biortech.2011.06.042 PMID:21727002

Husain, Z., Zainac, Z., & Abdullah, Z. (2002). Briquetting of palm fibre and shell from the processing of palm nuts to palm oil. *Biomass and Bioenergy*, *22*(6), 505–509. doi:10.1016/S0961-9534(02)00022-3

IPCC. (2001). *Summary for policymakers, concentrations of atmospheric greenhouse gases*. Retrieved June 10, 2014, from http://www.grida.no/climate/ipcc_tar/wg1/006.htm

Kang, Y., Bansal, P., Realff, M. J., & Bommarius, A. S. (2013). SO_2- catalyzed steam explosion: The effects of different severity on digestibility, accessibility, and crystallinity of lignocellulosic biomass. *Biotechnology Progress*, *29*(4), 909–916. doi:10.1002/btpr.1751 PMID:23749425

Kasim, N. B. (2009). *Separation technique of crude palm oil at clarification area via optimum parameters* (Bachelor of Chemical Engineering Thesis). Available from Universiti Malaysia Pahang, Malaysia.

Kemippainen, K., Inkinen, J., Uusitalo, J., Setala, T. N., & Siika-aho, M. (2012). Hot water extraction and steam explosion as pretreatments for ethanol production from spruce bark. *Bioresource Technology*, *117*, 131–139. doi:10.1016/j.biortech.2012.04.080 PMID:22613888

Kerdsuwan, S., & Laohalidanond, K. (2011). Renewable energy from palm oil empty fruit bunch. In M. Nayeripour & M. Kheshti (Eds.), *Renewable energy – trends and applications* (pp. 123–150). Croatia: InTech. doi:10.5772/25888

Kumar, L., Arantes, V., Chandra, R., & Saddler, J. (2012a). The lignin present in steam pretreated softwood binds enzymes and limits cellulose accessibility. *Bioresource Technology*, *103*(1), 201–208. doi:10.1016/j.biortech.2011.09.091 PMID:22047660

Kumar, L., Chandra, R., Chung, P. A., & Saddler, J. (2010). Can the same steam pretreatment conditions be used for most softwoods to achieve good, enzymatic hydrolysis and sugar yields? *Bioresource Technology*, *101*(20), 7827–7833. doi:10.1016/j.biortech.2010.05.023 PMID:20570139

Kumar, L., Tooyserkani, Z., Sokhansanj, S., & Saddler, J. (2012b). Does densification influence the steam pretreatment and enzymatic hydrolysis of softwoods to sugars? *Bioresource Technology*, *121*, 190–198. doi:10.1016/j.biortech.2012.06.049 PMID:22858485

Lam, P. S. (2011). *Steam explosion of biomass to produce durable wood pellets* (Doctoral dissertation). Available from The University of British Columbia.

Lam, P. S., Lam, P. Y., Sokhansanj, S., Bi, X. T., & Lim, C. J. (2013). Mechanical and compositional characteristics of steam-treated Douglas fir (*Pseudotsuga menziesii L.*) during pelletization. *Biomass and Bioenergy*, *56*, 116–126. doi:10.1016/j.biombioe.2013.05.001

Lam, P. S., Lam, P. Y., Sokhansanj, S., Lim, C. J., Bi, X. T., Stephen, J. D., & Mabee, W. E. et al. (2015). Steam explosion of oil palm residues for the production of durable pellets. *Applied Energy*, *141*, 160–166. doi:10.1016/j.apenergy.2014.12.029

Lam, P. S., Sokhansanj, S., Bi, X. T., & Lim, C. J. (2012a). Colorimetry applied to steam-treated biomass and pellets made from western Douglas fir (Pseudotsuga Menziesii L.). *Transactions of the ASABE*, *55*(2), 673–678. doi:10.13031/2013.41368

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., & Larsson, S. H. (2012b). Drying characteristics and equilibrium moisture content of steam-treated Douglas fir (*Pseudotsuga menziesii L.*). *Bioresource Technology*, *116*, 396–402. doi:10.1016/j.biortech.2012.03.093 PMID:22542137

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., & Melin, S. (2011). Energy input and quality of pellets made from steam-exploded Douglas fir (*pseudotsuga menziesii*). *Energy & Fuels*, *25*(4), 1521–1528. doi:10.1021/ef101683s

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., Naimi, L. J., Hoque, M., & Ye, X. P. et al. (2008). Bulk Density of wet and dry wheat straw and switchgrass particles. *Applied Engineering in Agriculture*, *24*(3), 351–358. doi:10.13031/2013.24490

Lam, P. Y. (2013). *Steam pre-treatment and leaching for the production of high quality oil palm residue pellets* (Master dissertation). Available from The University of British Columbia, Vancouver.

Lam, P. Y., Lim, C. J., Sokhansanj, S., Lam, P. S., Stephen, J. D., Pribowo, A., & Mabee, W. E. (2014). Leaching characteristics of inorganic constituents from oil palm residues by water. *Industrial & Engineering Chemistry Research*, *53*(29), 11822–11827. doi:10.1021/ie500769s

Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., & House, J. I., … Zeng N. (2012). The global carbon budget 1959–201. *Earth System Science Data Discussions*, *5*(2), 1107–1157.

Li, J., Henriksson, G., & Gellerstedt, G. (2007). Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion. *Bioresource Technology*, *98*(16), 3061–3068. doi:10.1016/j.biortech.2006.10.018 PMID:17141499

Liu, Z., Quek, A., & Balasubramanian, R. (2014). Preparation and characterization of fuel pellets from woody biomass, agro-residues and their corresponding hydrochars. *Applied Energy*, *113*, 1315–1322.

Martin-Davison, J. S., Ballesteros, M., Manzanares, P., Sepulveda, P. X., & Fernandez, A. V. (2015). Effects of temperature on steam explosion pretreatment of Poplar Hybrids with different lignin contents in bioethanol production. *International Journal of Green Energy*, *12*(8), 832–842. doi:10.1080/15435075.2014.887569

Menon, N. R., Rahman, Z. A., & Bakar, N. A. (2003). Empty fruit brunches evaluation: Mulch in plantation vs. fuel for electricity generation. *Oil Palm Industry Economic Journal*, *3*, 15–20.

Mobini, M., Sowlati, T., & Sokhansanj, S. (2013). A simulation model for the design and analysis of wood pellet supply chains. *Applied Energy*, *111*, 1239–1249. doi:10.1016/j.apenergy.2013.06.026

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, *96*(6), 673–686. doi:10.1016/j.biortech.2004.06.025 PMID:15588770

Muzamal, M., Gamstedt, E. K., & Rasmuson, A. (2014). Modeling wood fiber deformation caused by vapor expansion during steam explosion of wood. *Wood Science and Technology*, *48*(2), 353–372. doi:10.1007/s00226-013-0613-0

Muzamal, M., Jedvert, K., Theliander, H., & Rasmuson, A. (2015). Structural changes in spruce wood during different steps of steam explosion pretreatment. *Holzforschung*, *69*(1), 61–66. doi:10.1515/hf-2013-0234

Oveisi, E., Lau, A., Sokhansanj, S., Lim, C. J., Bi, X. T., Larsson, S. H., & Melin, S. (2013). Breakage behavior of wood pellets due to free fall. *Powder Technology*, *235*, 493–499. doi:10.1016/j.powtec.2012.10.022

Overend, R. P., Chornet, E., & Gascoigne, J. A. (1987). Fractionation of lignocellulosics by steam aqueous pretreatments. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, *321*(1561), 523–536. doi:10.1098/rsta.1987.0029

Phanphanich, M., & Mani, S. (2011). Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology*, *102*(2), 1246–1253. doi:10.1016/j.biortech.2010.08.028 PMID:20801023

Piarpuzan, D., Quintero, J. A., & Cardona, C. A. (2011). Empty fruit bunches from oil palm as a potential raw material for fuel ethanol production. *Biomass and Bioenergy*, *35*(3), 1130–1137. doi:10.1016/j.biombioe.2010.11.038

Ramos, L. P. (2003). The chemistry involved in the steam treatment of lignocellulosic materials. *Quimica Nova*, *26*(6), 863–871. doi:10.1590/S0100-40422003000600015

Repellin, V., Govin, A., Rolland, M., & Guyonnet, R. (2010). Energy requirement for fine grinding of torreifed wood. *Biomass and Bioenergy*, *34*(7), 923–930. doi:10.1016/j.biombioe.2010.01.039

Salomon, M., Gomez, M. F., Erlich, C., & Martin, A. (2013). Pelletization: An alternative for polygeneration in the palm oil industry. *Biomass Conversion and Biorefinery*, *3*(3), 213–229. doi:10.1007/s13399-013-0075-5

Shamsudin, S., Shah, U. K. M., Zainudin, H., Aziz, S. A., Kamal, S. M. M., Shirai, Y., & Hassan, M. A. (2012). Effect of steam pretreatment on oil palm empty fruit bunch for the production of sugars. *Biomass and Bioenergy*, *36*, 280–288. doi:10.1016/j.biombioe.2011.10.040

Sing, C. Y., & Aris, M. S. (2012). An experimental investigation on the handling and storage properties of biomass fuel briquettes made from oil palm mill residues. *Journal of Applied Science*, *12*(24), 2621–2625. doi:10.3923/jas.2012.2621.2625

Tannous, K., Lam, P. S., Sokhansanj, S., & Grace, J. R. (2013). Physical properties for flow characterization of ground biomass from Douglas fir wood. *Particulate Science and Technology*, *31*(3), 291–300. doi:10.1080/02726351.2012.732676

Timms, R. (2007). Palm oil – The oil for the 21st century? *European Journal of Lipid Science and Technology*, *109*(4), 287–288. doi:10.1002/ejlt.200700047

Tooyserkani, Z., Kumar, L., Sokhansanj, S., Saddler, J., Bi, X. T., Lim, C. J., & Melin, S. et al. (2013). SO_2- catalyzed steam pretreatment enhances the strength and stability of softwood pellets. *Bioresource Technology*, *130*, 59–68. doi:10.1016/j.biortech.2012.12.004 PMID:23347905

Tooyserkani, Z., Sokhansanj, S., Bi, X. T., Lim, C. J., Saddler, J., Lau, A., & Kumar, L. et al. (2012). Effect of steam treatment on pellet strength and the energy input in pelleting of softwood particles. *Transactions of the ASABE*, *55*(6), 2265–2272. doi:10.13031/2013.42484

U.S. Environmental Protection Agency. (2014). *Climate change indicators in the United States, 2014. 3rd edition. EPA 430-R-14-004*. Retrieved April 7, 2015, from www.epa.gov/climatechange/indicators

Wan Rosli, W. D., Law, K. N., Zainuddin, Z., & Asro, R. (2004). Effect of pulping variables on the characteristics of oil palm frond fiber. *Bioresource Technology*, *93*(3), 233–240. doi:10.1016/j.biortech.2003.11.016 PMID:15062817

Yazadanpanah, F., Sokhansanj, S., Lim, C. J., Lau, A., Bi, X. T., Lam, P. Y., & Melin, S. (2013). Potential for flammability of gases emitted from stored wood pellets. *Canadian Journal of Chemical Engineering*, *92*(4), 603–609. doi:10.1002/cjce.21909

KEY TERMS AND DEFINITIONS

DF: Douglas fir – softwood abundant in BC, Canada.
EFB: Empty Fruit Bunch – an agricultural biomass abundant in South East Asia.
PKS: Palm Kernel Shell – an agricultural biomass abundant in South East Asia.

Chapter 3

Fluid Dynamic and Mixing Characteristics of Biomass Particles in Fluidized Beds

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ABSTRACT

The study of fluid dynamic and mixing characteristics of biomass particles in fluidized beds is fundamental for comprehension of thermal conversion processes. In this chapter a review of literature showed a large lacks of technical information about the quality of fluidization and representative models concerning binary mixtures (biomass and inert). A case study was presented involving Eucalyptus grandis wood and tucumã endocarp in order to obtain fluid dynamic parameters such as the characteristic fluidization, velocity and porosity, and the bed expansion. These parameters were more significant for mixtures with smaller diameter and mass fraction ratios, and sphericity ratio, due to the facility of beds to fluidize. A map was presented to identify the limits of effective mixtures considering four classes as a function of the complete fluidization Reynolds' and Archimedes' numbers. Empirical correlations have been proposed and showed a good agreement with the experimental work.

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INTRODUCTION

The social requirement for sustainability has conducted researches to study the use of renewable energy sources in replacement of fossil fuels (non-renewable and highly polluting), widely applied in recent centuries. Among the alternatives available, biomass is the one to be considered. In Brazil, among the numerous sources, agricultural and industrial residues play an important role in the energy matrix (Brazilian Energy Balance, 2014).

Renewable fuels can be obtained through different equipments, and among them fluidized beds are highlighted. The development of these kinds of technologies over the years has allowed achieving higher efficiency levels reducing emissions and increasing fuel flexibility, which are keys to the current global market and environmental conditions (Peña, 2011). The products obtained from these technologies are: solid fuels (biochar) produced by pyrolysis, gases by gasification, and liquid after the synthesis of these gases. The fluidized bed design and the success of the scale-up applying biomass depend strictly of the best operating conditions and the fluid dynamic behavior of particles in the bed.

This chapter will present an overview from literature about fluid dynamic and mixing of biomasses associated to experimental studies, focusing in basic design parameters such as: characteristic fluidization velocities and porosities, and bed expansion in gas-fluidized beds. Besides that, a case study will exemplify the differences between biomasses (*Eucalyptus grandis* and *tucumã* endocarp) showing recommendations to succeed the best mixtures with inert material (sand), and also to propose empirical correlations of these parameters. This work can be useful for researchers of academy and industry to obtain better efficiency in their thermal conversion reactors improving the utilization of biomass as a renewable fuel.

BACKGROUND

Despite the efforts in developing technologies to convert biomass into energy employing fluidized beds, few authors have attempted to understand the fluidization mechanics of biomass or it mixture with an inert (Cui & Grace, 2007). Generally, it is assumed that the design and operation of equipment involving biomass can be based on the conventional knowledge of fluidization. The use of fluidized beds stands out with numerous advantages such as: high heat transfer, uniform and controllable temperatures, and efficient gas-solid contact. However, for it occur effectively, the ideal operating conditions and choice of materials must be performed carefully (Basu, 2010; Cui & Grace, 2007; Gómez, Mesa-Pérez, & Brossard-Perez, 2008).

As noted in several studies in subsequent years, biomass does not fluidize or fluidize with low quality without the presence of an inert. The fluidized beds operating conditions for mixtures of biomass and inert particles are classified differently of homogeneous particles. This work will present a literature review and recommendations for readers in order to facilitate fluidized bed designs applying heterogeneous particles (binary mixtures) regarding their fluid dynamic behavior patterns.

Particle Classification and Terminology

The fluid dynamic behaviors of homogeneous and heterogeneous particles in gas-fluidized beds were defined in the 1970's, when scientists (Geldart, 1973; Rowe, Nienow, & Agbim, 1972) related them with the physical properties, diameter and density of particles. In practical situations, it is known that the particle shape is also fundamental for these equipment designs, however is not included in those terminologies (Mano & Rosendahl, 2010; Tannous, Lam, Sokhansanj, & Grace, 2012).

Geldart (1973) addressed the classification for homogeneous particles in a simple way, emphasizing the particle and fluid properties. It is still the current and the most applied due to the simplicity among different behavior patterns in the gas-solid systems. Based on ambient conditions, four groups were defined as: C, A, B and D. In the group C (e.g., cement), the particles are cohesive and extremely difficult to fluidize, since their interparticle forces are stronger than the forces exerted by the fluid. The group A (e.g., alumina) corresponds to the aeratable particles, where the interparticle forces are moderated, and the bed expansion is considerable after the minimum bubbling velocity. In the group B (e.g., sand), the particles are fluidizable, the interparticle forces are negligible and the bubbles appear when the fluidization begins. And finally, in the group D (e.g., biomass), the particles are spoutable and large bubbles are observed near the distributor crossing the bed like complete slugs.

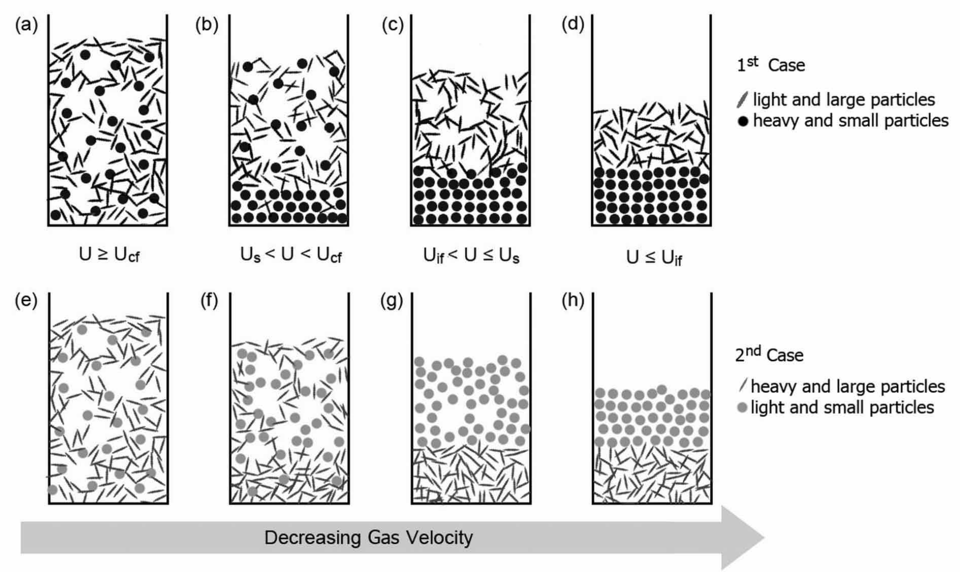
For heterogeneous particles (binary particles), Rowe et al. (1972) defined a terminology relating physical properties of each component of mixtures and their behavior under the fluidization process, according to heavy and light densities, small and big sizes, and also packing and fluid particles which fluidize above or below minimum fluidization velocity of mixture. In addition, the authors defined two terms, jetsam and flotsam, to identify these particles in the mixtures. Therewith, heavier or bigger particles that are prone to sink into the bed were called jetsam. On the other hand, particles which have a tendency to float generally smaller in size or with lower density were designated as flotsam. This terminology has been applied during many years for different materials such as: corundum, glass, iron, polyethylene, and sand (e.g., Baleato, 1986; Santos, 1997), and currently for biomasses such as: rice husk, wood, and walnut (e.g., Lourenço, 2012; Basu Paudel, 2011).

Description of the Fluidization Phenomenon

Heterogeneous particles are susceptible to the mixing and segregation phenomena in gas-fluidized beds (Rowe et al., 1972) considering: particles having different densities but same diameter; particles having the same density but different diameters, and particles varying in both diameter and density, as well as the initial arrangement of particles in the bed (completely segregated or mixed).

Two representative cases of mixtures in a fluidized bed initially well-mixed, in a decreasing gas velocity are schematized in Figure 1. In Figures 1(a) to 1(d), the first case is presented for a bed composed by light and large particles mixed with heavy and small particles, usually, applied for biomass and inert mixtures. In the second case, the Figures 1(e) to 1(h) present beds with heavy and large particles mixed with light and small particles. In Figures 1(a) and 1(e) show beds well-mixed considered by the differences in size and density of particles. The Figures 1(b) and 1(f) evidence the partial segregation of particles, in which heavier and larger particles move to the bottom of the beds, respectively. Figures 1(c) and (g) show an effective separation with stratification with lighter and smaller particles moving to the top of the beds, respectively. And finally, all particles are fixed in their respective priority (Figures 1d and 1h). These behaviors can be influenced by increasing of mass fraction of biomass in the mixture.

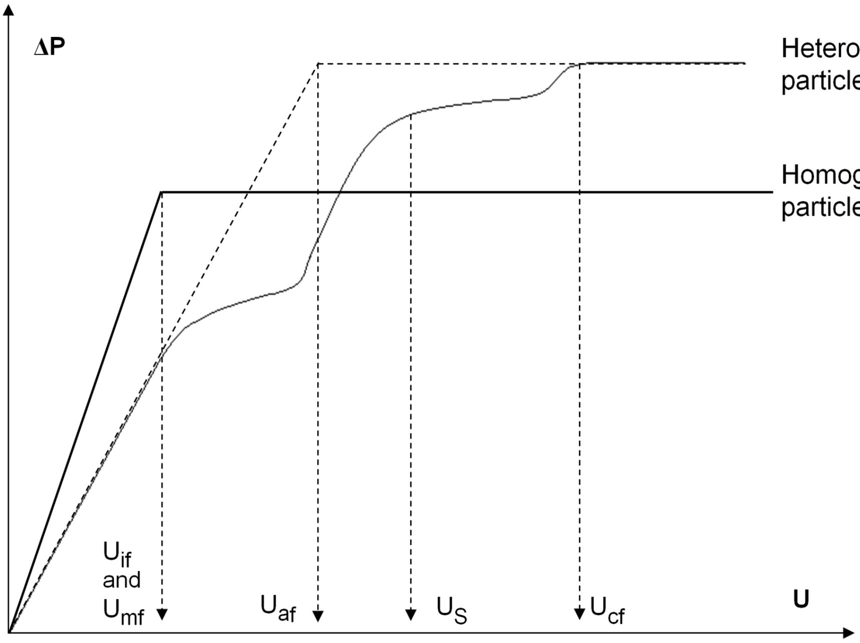
Figure 1. Arrangement of particles in a fluidized bed initially well-mixed



The mixture and segregation regions of binary particles (Figure 1) are easily identifiable by different methodologies, determining the transition boundaries defined by their characteristic fluidization velocities. The traditional method considers the total pressure drop of the bed as a function of the decreasing superficial gas velocity. This pressure drop reduces smoothly with the gas velocity, triggering the separation of materials due to their differences, until they reach the stagnation point of the bed. Chiba, Chiba, Nienow, and Kobayashi (1979) identified the minimum fluidization velocity of jetsam and flotsam particles of well-mixed and segregated and partially segregated beds.

In subsequent years, other definitions of velocity have emerged applying the same method for different materials such as: inert (e.g., Formisani, Girimonte, & Longo, 2008; Tannous, Hemati, & Laguerie, 1998), food (e.g., Mourad, Hemati, & Laguerie, 1994), and biomass (e.g., Aznar, Garcia-Gorria, & Corella, 1992a, b; Rao & Bheemarasetti, 2001; Tannous & Mizonov, 2009; Mitri, Lourenço, & Tannous 2011; Lourenço, 2012). These velocities were defined to characterize the fluid dynamic of the fluidized beds through the pressure drop as a function of decreasing superficial gas velocity (Figure 2), namely: (a) initial fluidizing velocity (U_{if}), corresponding to the beginning of the bed motion, predominantly inert particles, without signifi-

Figure 2. Evolution of pressure drop as a function of decreasing gas velocity for homogeneous and heterogeneous particles (binary mixture)



cant pressure fluctuations. Below this velocity, the pressure drop decreases linearly with the gas velocity; (b) apparent fluidization velocity (U_{af}), commonly defined as the minimum fluidization velocity of the mixture, and graphically identified by the intersection between fixed and fluidized states, as denoted for homogeneous particles (U_{mf}). In exceptional cases, the passage of these states is not effective because it is in a segregation region; (c) segregation velocity (U_S), corresponding to the totally defluidized zone on the upper/lower layer of the bed (Figure 1c and 1g), and characterize the limit between the total and partial segregation states. For biomass, the particles with lower density can segregate at the upper layer of the bed with the higher mass fraction in the mixture. This phenomenon indicates the beginning of an abrupt reduction in the total pressure drop; (d) complete fluidization velocity (U_{cf}), defined as one in which the pressure drop is quite constant and equal to the apparent weight of the bed per unit cross-sectional area of the column, corresponding to complete suspension of the particles in the bed.

Extending these definitions and identifying them in new methods, the evolution of the standard deviation of pressure fluctuations and bed expansion as a function of superficial gas velocity have been frequently used. The first approach was initially proposed by Punčochář, Drahoš, Čermák, and Selucký (1985) for homogeneous particles, and later applied to polydisperse particles by Tannous et al. (1998). The second method was defined by the ratio between the void volume and the total volume of the mixture. In both cases, the U_{if} is not well-defined due to the absence of pressure fluctuations, and in some cases it can be the same U_{af} (e.g., Lourenço, Mitri, & Tannous, 2012; Tannous & Mizonov, 2009).

Other techniques can be found in the literature to analyze the hydrodynamic behaviors of fluidized beds such as pressure fluctuation and fast Fourier transform (Kunii & Levenspiel, 1991), however there are frequently used for homogeneous particles and limited for binary particles due the interferences of one particle to another one.

Influences of Different Parameters on the Characteristic Velocities

Depending on the thermal process in the fluidized bed (e.g., drying, torrefaction, pyrolysis, and gasification), various control parameters and types of solids and gases generated can be influenced by the flow dynamics and efficiency of mixing using biomass as a feedstock. These entails the variation of temperature within the reactor, the variation in the gas velocity relative to the minimum fluidization conditions, the changes of porosity and bed expansion, and the mass particle distribution within the bed (Santos, 2010).

The literature have presented new information about the alternative raw materials for energy and their fluid dynamic studies considering mixtures with inert, catalysts and minerals and biomasses (Lourenço, 2012). Then, in this section some influences that affect the mixing quality will stand out such as: the biomass/inert mass fraction and diameter ratios, and also the column settings (diameter, height, and geometry), the most part are related to our case study.

Influence of Mass Fraction Ratio

Aznar et al. (1992a, b) showed the importance of this issue analyzing the fluid dynamic properties, apparent (U_{af}) and complete fluidization (U_{cf}) velocities for mixtures of agricultural and forest residues (cereal straw, pine sawdust, wood chips, and *Cynara carduncculus*) with different inert materials (sand, dolomite, and FCC). The diameters (A to D groups of the Geldart classification) and shapes of both materials were very broad. These works have discussed the effect of the volume fraction ratio of biomass (0-97.5 v%) in the mixtures. The authors concluded that both fluidization velocities increased with the increasing volume fraction ratios being more pronounced for U_{cf}. The biomass fractions added in the mixtures with sand varied for each species and the fluidizable limits used were 60 v%, 80 v%, 65 v%, and 75 v%, respectively, for the biomasses cited above. For mixtures of cereal straw and wood chips with FCC, the quantity of biomass was 70 v% and 65 v%, respectively, because above that the elutriation of the inert was observed in attempt to fluidize the particles. The sawdust and dolomite mixture was tested and all velocities increased with the increasing biomass fractions up to 70 v%, obtaining U_{cf}/U_{af} maximum of 1.7.

The mixtures evaluated by Rao and Bhemarasetti (2001) were rice husk, sawdust, and peanut shell (2x1x10 mm; -1000+800 mm; -1200+800 μm, respectively) with two diameter ranges of sand (-600+355 μm and -355+250 μm) with densities of 2500-2700 kg/m^3. The authors revealed that for all biomasses, there were an increase in U_{af} with the increasing biomass fractions in the mixtures (2-15%), being 4-fold more pronounced for the smallest inert diameter.

Ramakers, Ridder, and Kerkhof (2004) analyzed U_{af} in mixtures of *Fagus sylvatica* (d_p=7900 μm) and sand with different diameter ranges (100-500 μm, 400-600 μm and 800-1200 μm) and biomass mass fractions of 10-33 wt%. The authors observed an increase in U_{af} with the increasing of biomass fractions, which was more significant for the largest inert diameter. The best mixtures were comprised by smaller diameter of inert and biomass fractions up to 10 wt%.

Considering further studies with rice husk, Tannous and Mizonov (2009) analyzed the mass fraction ratios (2.5-15 wt%) on the characteristic velocities (U_{if}, U_{af}, and U_{cf}) for two diameters of biomass (1436.98-1979.50 μm) in the mixtures with alumina (81.8 μm and 3900 kg/m^3, and 364 μm and 3975.1 kg/m^3). For smaller alumina particle diameter, the apparent and complete velocities were practically constant up to 7.5 wt%, and increased to 15 wt%, while for medium particles these parameters increased significantly up to the limit of 10 wt%. In agreement with this work, Oliveira and Tannous (2009) realized experiments with mixtures with sand (358 µm) for the same diameters of rice husk, where all velocities gradually increased up to 10 wt% fraction ratio.

Mitri et al. (2011) have studied binary particles of wood residues of *Cariniana legalis* (Martius) Kuntze (494-2008 µm) and sand (336 µm), considering mass fraction ratios between 2.5-15 wt%. The authors observed that U_{if}, U_{af}, and U_{cf} increased with the increasing of mass fraction ratios, except for the smaller diameter of biomass, where U_{if} and U_{af} decreased further 10 wt%. This behavior was due to the inversion of particles in the bed, where the wood particles were deposited on the surface, preventing the movement of the mixture. Also, they concluded that for below to 10 wt%, the beds behaved as effective mixtures.

Basu Paudel (2011) analyzed the influence of mass fraction ratios on U_{af} from 0 to 100 wt% for mixtures of walnut (100 µm, 1200 kg/m^3) and corn cob (1040 µm, 1080 kg/m^3) with sand (240.8 µm, 2630 kg/m^3). According to the authors, for both mixtures, the U_{af} increased a maximum of 8-fold considering 0 wt% as a reference.

Influence of Diameter Ratio

In this section, the same researches presented in the subsection "Influence of mass fraction ratio" will be discussed, therefore we will restrict it to their conclusions about the influence of biomass/inert diameter ratio.

Aznar et al. (1992a, b), considering mixtures with sawdust (d_p=507 µm) and sand (-200 +125 µm, -297 +200 µm, -400+297 µm, -500+400 µm), observed an increase in the U_{af} and U_{cf} with the increasing inert diameters for biomass fractions up to 50 v%, and then rising sharply, keeping the U_{cf}/U_{af} ratio of 2. For mixtures with cereal straw and *Cynara carduncululs*, the increase of biomass or inert diameter also caused an increase on the mixture velocity, and the increasing of U_{cf} was most significant than for U_{af}.

Rao and Bhemarasetti (2001) evaluated the fluid dynamics of mixtures with two diameter ranges of sand (- 600 + 355 µm and -355 + 250 µm) and biomasses (rice husk, sawdust, and peanut shells). The authors concluded that the U_{af} increased almost 100% with the increase of inert diameter for fractions up to 10 wt%. Above this mass fraction, the velocity was practically constant (3%) for mixture with sawdust and peanut husk and inert. However, for rice husk, this velocity was more influenced with an increase between 14-88% with the inert diameter, depending on the biomass fraction used. Rao and Reddy (2010) evaluated the same biomasses but with different inert diameters (400 µm, 660 µm and 930 µm), and concluded that the U_{af} increased with the increasing of these diameters for all mixtures proposed. For the rice husk and sawdust, the authors observed that the sand diameter of 400 μm is more suitable to get better mixtures avoiding preferential channels, and consequently have lower U_{af}. For the groundnut shells mixtures, all diameters of sand particles were fairly good, but the authors recommended the intermediate diameter (660 μm) for better mixing.

Tannous and Mizonov (2009) studied the influence of two diameters of rice husk and alumina in mixtures considering the diameter ratios of 5.4, 17.6, and 24.2, for mass fraction ratios up to 15 wt%. It was found that with increasing diameter ratios, between 5.4 and 24.1, with predominance of alumina in the mixture, U_{if}, U_{af}, and U_{cf} decreased considerably up to 10 wt% due to formation of large voids in the bed. Regarding the increase of the diameter ratio between 17.6 and 24.1, with predominance of biomass, the U_{af}, and U_{cf} were quite constant between 5-15 wt%. In this case only the U_{if} presented a reduction of fractions up to 10 wt%, and an increasing thereafter. Using the same biomass, Oliveira and Tannous (2009) analyzed other diameter ratios (4.7 and 6.4) using sand as inert material, and observed that those three velocities were higher for smaller diameter ratios. The authors do not discuss the reason for this behavior, but this can be attributed to the better mixing of the bed.

Ramarkers et al. (2004) also observed the same increasing trend for the three diameters of sand (fine, medium and coarse) and wood chips (7900 μm), where the U_{af} increased 3.5-5.5-fold with increasing inert diameters.

For Mitri et al. (2011), the U_{if} and U_{af} increased with the diameter ratio of *Cariniana legalis* (1.5 and 3) up to 15 wt%, but the velocities decreased to the highest biomass diameter ratio (6) up to 10 wt% (operating limit). On the other hand, the U_{cf} was constant for the smallest diameter (D=1.5) and increased from D=3 to 6. According to the authors, depending on the diameters ratios, U_{af} can be in the highest segregation zone.

Influence of Bed Configuration

There are a few concerns in the literature about bed configuration and mixture of particles. It is known that for large homogeneous particles (B and D group), the bed height and column diameter do not influence significantly the minimum fluidization conditions and bed expansion (Tannous, Hemati, & Laguerie, 1994).

Aznar et al. (1992a, b) discussed the effect of the bed diameter (14 cm and 30 cm) and the bed height/diameter ratio (1 and 2) on the U_{af} and U_{cf} for sawdust/sand mixtures, and no effect was observed. Analyzing the effect of the column diameter, for larger size, the velocities were 10-20% higher due to the bad distribution of fluidizing air across the column.

Tannous and Mizonov (2009) analyzed two bed geometries, cylindrical (ID=0.092 m) and conical (ID=0.053 m, 71° of angle), considering rice husk and alumina mixtures with mass fraction ratios between 2.5-15 wt%, and diameter ratios of 5.4-24.2. The cylindrical bed promoted the formation of slugs into the bed conducting higher velocities (U_{if}, U_{af}, and U_{cf}) mainly the U_{cf}. However, the conical geometry was more conducive for mixing, leading to lower velocities to reach the complete fluidization.

Empirical Correlations for Characteristic Velocities

Since the 70's, the majority of studies in fluidization technology seeks to establish empirical models representing the initial process operation, such as the minimum fluidization velocity of binary mixtures of solids or apparent fluidization velocity (U_{af}). The most of published works applied homogeneous particles correlations (e.g., Grace, 1982; Lucas, Arnaldos, Casal, & Puigjaner, 1986; Tannous et al., 1994) adapted for binary particles using specific settings like the effective diameter and density (e.g., Goossens, Dumont, Spaepen, & 1971; Rao & Bheemarasetti, 2000), and the bed porosity (e.g., Rasul & Rudolph, 2000).

Some of them are also accounted for binary mixtures (e.g., Chiba et al., 1979; Mourad et al., 1994; Thonglimp et al., 1984). These equations were derived according to the fluid and solid properties, bed characteristics (mass fraction and minimum operating conditions for each component). In general, they are related by dimensionless numbers such as Reynolds' and Archimedes', representative of inertial to viscous forces ratio, and gravitational to viscous forces ratio, respectively.

In the case of mixtures containing biomass, there is a lack in the literature of empirical correlations for determining the characteristic velocities such as: initial fluidization velocity (U_{if}), apparent fluidization velocity (U_{af}), segregation velocity (U_S), and complete fluidization velocity (U_{cf}). This is due to the scattering of experimental data caused by the different biomass species, mass fractions and diameter ratios in the mixtures. Aznar et al. (1992a, b) and Ramarkers et al. (2004) explicitly discouraged the development of mathematical model for the determination of apparent fluidization velocity. Nonetheless, a few correlations were found and they will be discussed in this section.

Rao and Bheemarasetti (2001) defined an equation for the determination of U_{af} considering the original equation of Wen and Yu (1966) for a Reynolds number less than 20 (Kunii & Levenspiel, 1991). Two new parameters, the effective diameter and density, were introduced. The effective diameter is a function of the parameter k' dependent upon the inert diameter. Moreover, it depends on the individual physical properties. The effective density was obtained by the weighted average relating the mass and density of each component of the mixture.

Mitri et al. (2011) proposed two empirical correlations for the determination of the U_{af} using Reynolds' and Archimedes' numbers obtained by adjusting of a power-law series. The effective diameter and density applied were defined according to Goossens (1971). It is important to remark that the authors used the true density instead of the particle density, leading to the overestimated values. Following the same proposal, Basu Paudel (2011) suggested two correlations relating the same dimensionless numbers for pure biomass (corn cob and walnut), and another adapted for mixtures applying the mass fractions of biomass particles between 0 wt% to 100 wt%.

Bilbao, Lezaun, and Abanades (1987) presented a correlation that characterizes the U_{cf}. According to the authors, this velocity is dependent on the minimum fluidization velocity of the jetsam (inert) and flotsam (biomass) particles, being determined empirically and experimentally, respectively. In addition, the equation is also dependent on the inert fraction (jetsam) in the mixture.

Bed Porosity at Apparent and Complete Fluidization Velocities

The characteristic porosity terminology, apparent (ε_{af}) and complete (ε_{cf}), is sparingly seen in the literature and no empirical correlations were found. These porosities regard to the void volume at the beginning of the particles motion at the top of the bed associated to the apparent fluidization velocity (U_{af}), and when the bed is totally suspended by the gas related to the complete fluidization velocity (U_{cf}), respectively. The mass fraction and diameter ratios as well as the bed configurations can influence these parameters.

Ramarkers et al. (2004) observed that the ε_{af} increased with biomass (wood chips) fractions above 20 wt%, 5 wt% and 5 wt% for the three diameters of sand (100-500 µm, 400-600 µm and 800-1200 µm), respectively. Above these fractions, the porosity showed a reduction, attributed possibly to the filling of voids by the presence of inert among wood particles, resulting in better mixtures. Regarding the effect of the diameter ratio, the authors did not observe a clear trend in their experiments.

Tannous & Mizonov (2009) evaluated two diameters of rice husk and alumina (D=5.4-24.2), observing that the increase in the ε_{af} was gradual with increasing mass fraction ratios (2.5-15 wt%) in a maximum variation of 37%. However, concerning the increase of the diameter ratios, this porosity was less influenced with a maximum variation of 20%. Comparatively to the same biomass and applying sand as an inert (306.93 µm), Oliveira & Tannous (2009) also observed an increase of ε_{af} with mass fraction ratios (max. of 44%), but it was almost constant for D=4.6-6.4 up to 10 wt%.

Mitri et al. (2011) studied wood/sand mixtures obtaining the ε_{af} and ε_{cf} for mass fraction ratios up to 15 wt% and diameter ratios between 1.5 and 6. It was observed that the ε_{af} increased significantly (15-30%) with the increase of mass fraction ratio, but it was quite constant for higher than 7.5 wt%. For ε_{cf} it was more significant with a reduction of 34% for D=1.5. In addition, no agreement was observed in the effect of diameter ratio, because the mixtures up to D=3 showed an increase of ε_{af} (62%), and for higher diameters (D=6) it decreased. No significant effect was observed in the ε_{af} and ε_{cf} up to D=3.

Concerning the influence of bed configuration on ε_{af}, the only work found was from Tannous and Mizonov (2009), analyzing two bed geometries (cylindrical and conical) considering mixtures of rice husk and alumina. The conical bed geometry promoted better mixtures leading to a low variation (27%) regarding all fractions ratios.

Bed Expansion

The bed expansion (ε) is an important parameter for designing the fluidized bed height required to an industrial plant. In general, it is expressed by a relation between the bed height (for any velocity) and the height at the apparent velocity, or even between the void volume and the total volume of the bed. None empirical equation was found so far in the literature regarding mixtures of biomass/inert.

Rao and Reddy (2010) analyzed the effect of inert diameter (sand, 440 μm, 660 μm, and 930 μm) in mixtures with rice husk (2094 μm), sawdust (578 μm), and groundnut shell (878 μm) considering different mass ratios (1:13, 1:5 and 1:12), respectively. The authors observed that the bed height presents a reduction close to the minimum fluidization of biomass for the rice husk and ground shells mixtures for sand diameters. For the mixture of sawdust and sand (930 μm) the expansion was always crescent. The authors concluded that the best mixtures were: rice husk and sawdust using smaller inert diameter, and groundnut shells using medium inert diameter.

Basul Paudel (2011) concluded that for mixtures of walnut and corn cob with sand the bed expansions increased linearly with the increase of the superficial velocity while it decreased with increasing of effective density, due to the weight of the bed. Furthermore, the authors noted that the increase in the particle density has greater influence on the bed expansion than the particle diameter.

Mitri et al. (2011) and Lourenço, Mitri, and Tannous (2012) studied the expansion of *Cariniana legalis* particles (493.5-2008.0 μm) with sand (331.6 μm) for biomass mass fractions of 2.5% to 15% and diameter ratios between 1.5 to 6.0. It was observed a variation more significant between U_{af} and U_{cf} for D= 1.5 and 3.0 of around 38% with increasing of biomass mass fraction. The variation of increasing of diameter ratio is quite irregular, but can reach 52% between the highest diameter ratios (3 and 6). Besides that, from U_{cf}, the curves tended to overlap for both effects of mass fraction and diameter ratios. For all gas velocity ranges (0-0.8 m/s), it was verified that the expansion increased more significantly for smaller diameter ratio (1.5) and lower biomass mass fraction (2.5 wt%).

CASE STUDY OF FLUID DYNAMIC AND MIXING BEHAVIORS OF *EUCALYPTUS GRANDIS* AND *TUCUMÃ* ENDOCARP WITH INERT PARTICLES

A comparative study was performed to evaluate the fluid dynamics of binary mixtures considering two kinds of biomasses and one inert in order to improve the fluidized bed configuration commonly used in the thermal conversion processes.

Experimental Setup

The experiments were performed in a fluidized bed in an acrylic column of 0.092 m of internal diameter and a perforated plate distributor (fraction of open area of 5.9%). A radial blower (Elétrica Ampéres S.A, S1SSM2, Brazil) was used to introduce compressed air into the column and the air temperature was reduced through the shell-and-tube heat exchanger using water as refrigerant fluid. The measures of temperature and humidity were obtained through a digital thermo-hygrometer (Incoterm, 9680, Brazil). The volumetric flow rates were controlled by rotameters in the range of 0-100 Nm^3/h (Omel S.A., Brazil). The differential pressure measurements were performed by pressure transmitters, XLDP models from Ashcroft (Dresser Instruments, USA) with a maximum of 12 kPa. The delivery of signals was analyzed by a data acquisition system (Easyest LX, Keithley, USA) at a frequency of 200 Hz. From the 1024 pressure signals registered, the mean pressure differentials (ΔP) and standard deviation (σ) of pressure fluctuations were calculated according to equations (1) and (2), respectively:

$$\Delta P = (1 / N)\sum_{1}^{N} \Sigma(DP_i) \tag{1}$$

$$\sigma = \left[1 / (N - 1)\sum_{1}^{N} (\text{”}P_i - \text{”}P)^2 \right]^{1/2} \tag{2}$$

where, N and ΔP_i are the number of sampling points and the instantaneous differential pressure, respectively.

The packed bed height/column diameter ratio was between 1.1 and 2.0. All experiments were performed by the average of three replicates for each superficial gas velocity.

Materials and Properties

The solid materials selected were *Eucalyptus grandis* W. Hill ex Maiden (eucalyptus) and *Astrocaryum aculeatum* Meyer (*tucumã* endocarp) as biomasses, and quartz sand as inert. The eucalyptus wood and *tucumã* endocarp (residue) were accessed, respectively, in *Itapetininga* city (23°36'25.1"S × 48°04'31.5"W), São Paulo State, and in *Parintins* city (-2°40'42.34"S × -56°46'32.35"W), Amazon State.

The biomasses were ground in a hammer mill (Tiger S.S., CV2, Brazil) during 21 s (17 g) and 46 s (70 g), for eucalyptus and *tucumã* endocarp, respectively. The granulometric distribution of particles were determined by screening, in triplicate, using sieves of the Tyler series (Granutest, Brazil) with opening ratio of 1.41.The sieves were placed in a shaker (Produtest, n. 4063, Brazil) with a vibration level 9 for 15 minutes. Considering the mass fraction retained on each sieve and the arithmetic mean diameter between two consecutive sieves, the mean Sauter diameters (d_p) chosen were between 500-2000 µm for the biomasses and 331 µm for the sand (Table 1).

The determination of sphericity (ϕ) was performed by a pachymeter (Digimess, 100174, China) for eucalyptus, and by image capture (HP Scanjet 3800, China) in which it was processed through the software APOGEO (Silva & Tannous, 2012) for *tucumã* endocarp. The sphericity of eucalyptus (rectangle parallelepiped) and *tucumã* endocarp and sand (irregular) particles was calculated by Wadell (1935) and Riley (1941) equations. A hundred particles for each material were considered as representative samples (Table 1).

The biomass and inert particle densities (ρ_p) were determined using a mercury porosimeter (Aminco, N.5-7118, USA) and picnometry method based on the displacement water volume (Santos, 1997), respectively. The true density (ρ_s) was determined by helium gas picnometry (Micromeritics, AccuPyc 1330, USA, 1997). The measurements were performed in triplicates (Table 1).

The bed fluid dynamic behavior was initially evaluated considering 800 g of sand mass and subsequently 40 g to 160 g of biomasses were added, leading to different mass fraction ratios (χ) of 5 wt%, 10 wt%, 15 wt%, and 20 wt%. The three particle diameters of eucalyptus (508 µm, 986 µm, and 1993 µm), and *tucumã* endocarp (502 µm, 1017 µm and 2017 µm) and one sand diameter (331 µm) conducting to the diameter ratios (D) of mixture of 1.5, 3 and 6. The effective density (ρ_M) and diameter (d_M) were determined by equations (3) and (4) according to Goossens (1971):

Table 1. Physical properties of homogeneous particles and their fluid dynamic parameters

	Physical properties				Fluid dynamic parameters			
Material	d_p **(μm)**	ρ_p**(kg/m³)**	ρ_s **(kg/m³)**	**ϕ (-)**	$U_{mf,calc}$[1]**(m/s)**	$U_{t,calc}$[2]**(m/s)**	$\varepsilon_{mf,calc}$[3]**(-)**	**Geldart groups**
Sand	331±1.10	2636.0±115.5	2656.7±0.85	0.85±0.11	0.10 (*exp*)	2.82	0.42 (*exp*)	B (fluidizable)
Tucumã endocarp	502±1.68	1115.0	1564.6 ± 4.00	0.81±0.04	0.13	2.25	0.45	B (fluidizable)
	1017±0.97		1569.6 ± 3.73	0.85±0.01	0.36	3.93	0.43	
	2017±7.36		1553.4 ± 5.10	0.89±0.01	0.67	5.96	0.41	D (spoutable)
Eucalyptus	508±2.29	394.9	1442.6±1.77	0.36±0.13	0.09	0.48	0.73	A (aeratable)
	986±4.50		1428.3±0.70	0.41±0.13	0.26	0.77	0.69	B (fluidizable)
	1993±9.89		1424.6±0.66	0.50±0.07	0.52	1.32	0.62	D (spoutable)

Sources: [1]Lucas et al. (1986); [2]Haider and Levenspiel (1989); [3]Foust et al. (1982)

$$1/\rho_M = w_b/\rho_b + w_i/\rho_i \quad (3)$$

$$1/(d_M\rho_M) = w_b/(d_b\rho_b) + w_i/(d_i\rho_i) \quad (4)$$

where, $w_{i,b}$ are the mass fractions with mean diameter $d_{i,b}$ and density $\rho_{i,b}$ of the biomass and inert particles, respectively.

Methodology

All experiments considering homogeneous particles (only inert) and heterogeneous particles (binary particles) were quantitatively analyzed through three methods in the defluidization process, total pressure drop, standard deviation of the pressure fluctuations and bed expansion. Also, the experiments were qualitatively analyzed by visual observations using image registration (digital camera). The runs were operated in the bubbling and slugging regimes (Lourenço, 2012).

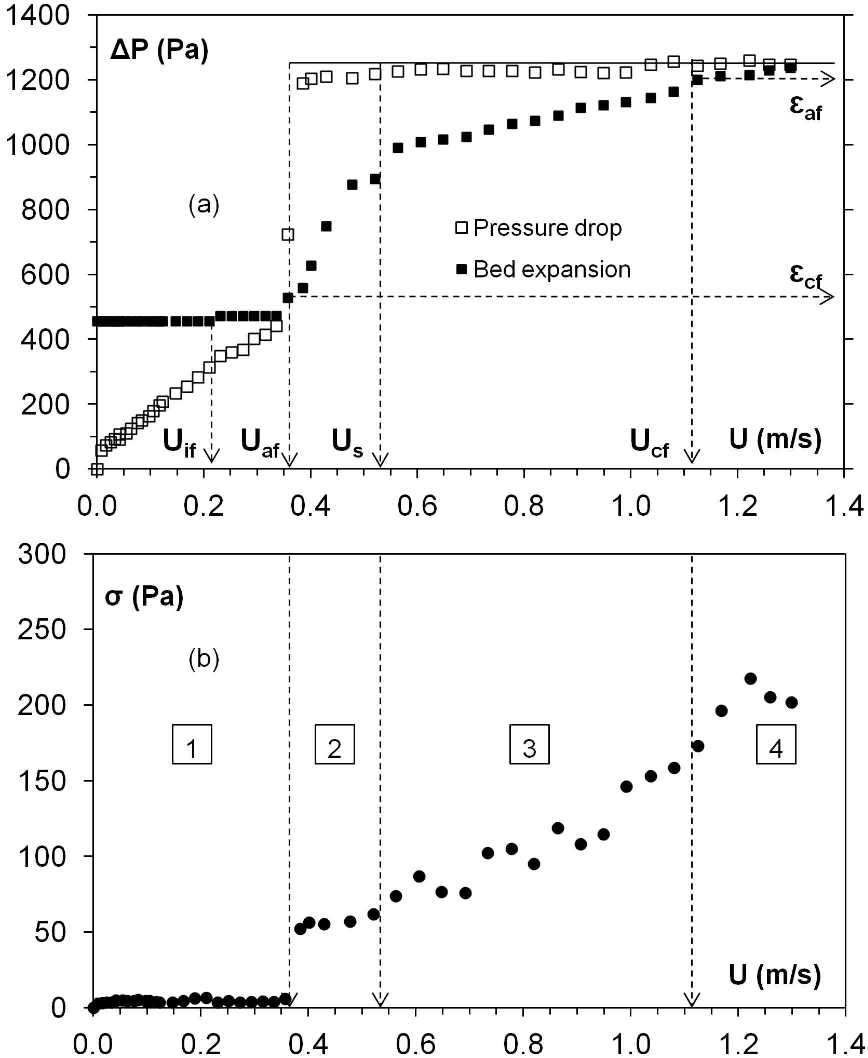
For homogeneous particles, the minimum fluidization velocity (U_{mf}) and the porosity (ε_{mf}) were determined only experimentally for sand. For biomass, this velocity was determined by Lucas et al. (1986) equations considering $0.1<\varphi<0.5$ (eucalyptus) and $0.8<\varphi<1.0$ (tucumã endocarp). The ε_{mf} was determined graphically relating the bed porosity and the sphericity of particles (Foust, Clump, & Wenzel, 1982). The U_t was calculated by Haider and Levenspiel (1989) equation.

For heterogeneous particles, the initial fluidization velocity (U_{if}), the apparent fluidization velocity (U_{af}), the segregation velocity (U_S), and the complete fluidization velocity (U_{cf}) were considered (Figure 3).

The evolution of total pressure drop (method 1) refers to the measurement of the mean differential pressure between two pressure taps, close to the distributor and in the column exit, as a function of the decreasing superficial gas velocity for a bed initially well-mixed (Figure 3a). The evolution of the standard deviation of the pressure fluctuations (method 2) as a function of the decreasing superficial gas velocity (Figure 3b) was also applied. Four zones were defined considering three main characteristic velocities by the slope of the curve characterized through the bubble types presenting the bed:

- Fixed bed, $U<U_{if}$ (zone 1): the pressure drop decrease linearly with gas velocity (Figure 3a) because no pressure fluctuation are presented and, consequently, the standard deviation is zero (Figure 3b);
- Total segregation, $U_{if}<U<U_S$ (zone 2): corresponds to the appearance of a higher concentration of biomass at the top of the bed, consisting essentially

Figure 3. Methodologies for the determination of characteristic parameters as a function of the superficial gas velocity (a) total pressure drop, (b) standard deviation of pressure fluctuations - eucalyptus/sand mixture (D=6.0 and χ=20%)



of larger diameters and light density (1st case, Figure 1). This phenomenon indicates the beginning of an abrupt reduction of the total pressure drop (Figure 3a), but dependent of conditions of mixture, this arrangement can have smooth increasing fluctuations (Figure 3b). The apparent fluidization velocity (U_{af}), defined graphically by the intersection between fixed and fluidized states, as denoted for homogeneous particles (U_{mf}).

- Partial segregation, $U_S<U<U_{cf}$ (zone 3): The pressure drop increase smoothly and closer to the complete mixture (Figure 3a), correspondent to the suspension of biomass particles by the bubble flow of inert particles in the lower layers of the bed (Figure 3b).
- Complete fluidization, $U>U_{cf}$ (zone 4): the biomass is completely supported and mixed with inert particles, and drop pressure is equal to the apparent weight of the bed per unit cross-sectional area (Figure 3a). Also, the fluctuations increase considerable characterizing large bubbles in the bed and, consequently, the increasing standard deviation (Figure 3b).

The bed expansion, ε (method 3), shown in Figure 3(a), was determined by the relation between the void volume relating biomass and inert, and the total volume of the mixture (equation 5) as function of the superficial gas velocity (Lourenço, 2012). The minimum and maximum bed heights were measured using a millimeter scale fixed to the column wall.

$$\varepsilon=1-\{[1/(A_c H)][(m_b/\rho_b)+(m_i/\rho_i)]\} \tag{5}$$

where, A_c is the cross-sectional area of the bed; H is the arithmetic mean of bed heights (maximum and minimum) for each superficial gas velocity; and m_b and m_i are the biomass and inert masses, respectively.

In the Figure 3(a), the apparent porosity (ε_{af}) and complete porosity (ε_{cf}) were determined taking into account the characteristic fluidization velocities.

Statistical Criteria

The comparisons between the experimental and calculated data for different correlations were based on statistical criteria according to the equations (6) to (8):

Relative error (E_1)

$$E_1 = 100(1/N)\sum_{1}^{N}(x_{exp} - x_{calc})/(x_{exp}) \tag{6}$$

Absolute relative error (E_2)

$$E_2 = 100(1/N)\sum_{1}^{N}\left|(x_{exp} - x_{calc})\right|/(x_{exp}) \tag{7}$$

Root Mean Square Error (E_3)

$$E_3 = \left[(1/N) \sum_{1}^{N} (x_{exp} - x_{calc})^2 \right]^{1/2} \tag{8}$$

where, x_{exp} represents an experimental value; x_{calc}, the calculated value by correlation, and N is the number of experimental points.

RESULTS AND DISCUSSION

Table 1 shows the results obtained of the fluid dynamic parameters, minimum fluidization velocity (U_{mf}) and porosity (ε_{mf}), and terminal velocity (U_t) for homogeneous particles. For heterogeneous particles (binary mixtures), the bed behavior was evaluated through the characteristic velocities and porosities considering the influences: nature of biomass, biomass/inert mass fraction ratio (χ), and biomass/inert diameter ratio (D). The results are shown in Table 2. The results of characteristic velocities for the two methods applied, total pressure drop and standard deviation of pressure fluctuations had a good agreement (std. deviation of 0.05). It is noteworthy that, for the mixture of eucalyptus/sand of D=3 and χ=20 wt% was not well succeed making unfeasible the mixing to obtain U_{if}.

Characteristic Fluidization Velocities

Influence of the Nature of Biomass

Due to the diversity of biomass samples, two physical properties could aid in the interpretation of the fluid dynamic behavior of mixtures: particle density and shape. The *tucumã* endocarp density is almost 3-fold the eucalyptus density (Table 1) and closer to the inert density. These differences in densities (Table 2) lead to the reduction of stratification zone (U_{cf}-U_{if}) of about 4.8-fold (0.20-0.95 m/s) for eucalyptus/sand to 2.2-fold (0.14-0.31m/s) for *tucumã*/sand mixtures.

Regarding to the geometry of particles (Table 1), *tucumã* endocarp and sand, also contributed to the mixture because both materials have irregular shapes and closer sphericity, 0.85 and $0.81<\phi<0.89$, respectively. The low sphericity of eucalyptus ($0.36 <\phi<0.50$) may have promoted its separation from the inert, due to the low contact area between the particles. From visual observations, it was also noted that the mixture of eucalyptus/sand presented poorer quality (Figure 4) than the *tucumã*/sand mixtures (Figure 5). As can be seen in Figure 4(b) and 4(c), the bed presented high concentration of eucalyptus deposited on the surface while the inert remained on the bottom layer. Also, a very interesting event happened for D=6 and

Table 2. Experimental results from the fluid dynamic parameters for Eucaliptus grandis/sand and tucumã endocarp/sand mixtures

Solid	d_p (μm)	D	χ (wt%)	U_{if} (m/s)	U_{af} (m/s)	U_S (m/s)	U_{cf} (m/s)	U_{cf}/U_{if} (-)	U_{cf}/U_{af} (-)	U_{cf}/U_S (-)	$U_{cf}-U_{if}$ (m/s)	$U_{cf}-U_{af}$ (m/s)	ε_{af} (-)	ε_{cf} (-)
Eucalyptus/ sand	508	1.5	5	0.10	0.11	0.23	0.30	3.05	2.77	1.36	0.20	0.20	0.45	0.63
			10	0.11	0.13	0.29	0.42	3.82	3.36	1.45	0.30	0.30	0.47	0.71
			15	0.11	0.13	0.30	0.47	4.27	3.62	1.57	0.34	0.34	0.48	0.71
			20	0.13	0.14	0.34	0.56	4.31	4.15	1.65	0.43	0.43	0.55	0.82
	986	3.0	5	0.13	0.15	0.24	0.40	3.08	2.76	1.67	0.27	0.26	0.42	0.68
			10	0.12	0.14	0.30	0.50	4.17	3.70	1.67	0.38	0.37	0.41	0.71
			15	0.13	0.17	0.41	0.68	5.23	4.69	1.66	0.55	0.54	0.42	0.79
			20	-	0.41	0.56	0.98	-	2.39	1.75	-	0.57	0.58	0.83
	1993	6.0	5	0.11	0.12	0.27	0.43	3.91	3.74	1.62	0.32	0.32	0.41	0.71
			10	0.11	0.14	0.31	0.50	4.08	3.64	1.67	0.39	0.37	0.40	0.72
			15	0.12	0.24	0.34	0.80	6.66	3.33	2.00	0.68	0.56	0.39	0.77
			20	0.17	0.34	0.40	1.12	6.59	3.11	2.09	0.95	0.78	0.48	0.80
Tucumã endocarp/ sand	502	1.5	5	0.08	0.08	0.12	0.22	2.75	2.75	1.69	0.14	0.14	0.39	0.64
			10	0.07	0.07	0.14	0.23	3.29	3.29	1.70	0.16	0.16	0.40	0.64
			15	0.07	0.07	0.13	0.23	3.29	3.29	1.77	0.16	0.16	0.40	0.64
			20	0.08	0.08	0.13	0.27	3.38	3.38	2.08	0.19	0.19	0.43	0.65
	1017	3.1	5	0.11	0.11	0.20	0.27	2.45	2.45	1.35	0.16	0.16	0.40	0.61
			10	0.10	0.10	0.21	0.27	2.80	2.80	1.37	0.17	0.18	0.40	0.61
			15	0.10	0.10	0.20	0.29	2.90	2.90	1.45	0.19	0.19	0.40	0.63
			20	0.11	0.11	0.20	0.32	2.95	2.95	1.67	0.21	0.22	0.37	0.67
	2017	6.1	5	0.10	0.10	0.18	0.28	2.80	2.80	1.56	0.18	0.18	0.37	0.65
			10	0.11	0.11	0.19	0.32	2.91	2.91	1.68	0.21	0.21	0.38	0.66
			15	0.11	0.11	0.20	0.35	3.18	3.18	1.75	0.24	0.24	0.38	0.67
			20	0.11	0.13	0.21	0.42	3.82	3.23	2.00	0.31	0.29	0.38	0.72

χ=20 wt%, where the bed collapsed in the U_{af} (Figures 3 and 4a). For all *tucumã*/ sand mixtures high homogeneity with a few suspended particles on the bed surface (Figure 5c) were observed.

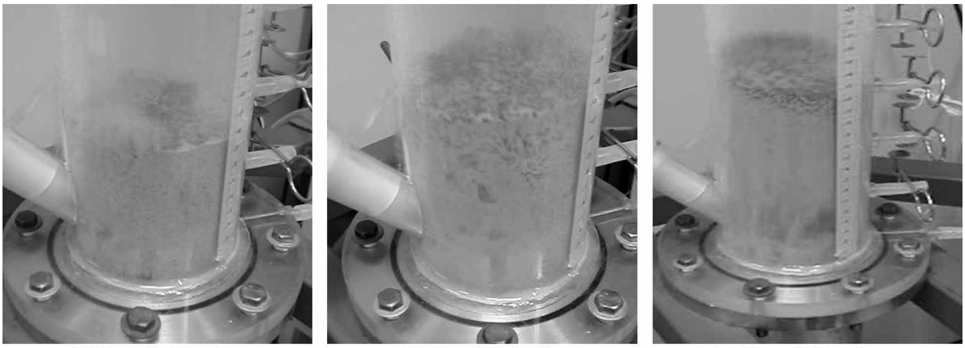
Influence of the Mass Fraction Ratio

The results of characteristic velocities for both biomasses considering the mass fraction ratios between 5-20 wt% are shown in the Table 2. Concerning the eucalyptus/ sand mixtures, all fluidization velocities (U_{if}, U_{af}, U_S, and U_{cf}) increased with the

Figure 4. Images of the fluid dynamic behaviors of mixtures of eucalyptus/sand (D=6, χ=20%) and its characteristic velocities (a) apparent (b) segregation, and (c) complete fluidization

(a) U_{af} = 0.36 m/s **(b) U_S = 0.54 m/s** **(c) U_{cf} = 1.12 m/s**

Figure 5. Images of the fluid dynamic behaviors of mixtures of tucumã endocarp/ sand (D=6, χ=20%) and its characteristic velocities (a) apparent (b) segregation, and (c) complete fluidization



(a) U_{af} = 0.13 m/s **(b) U_S = 0.21 m/s** **(c) U_{cf} = 0.42 m/s**

increasing mass fraction ratios. It is noteworthy that, for the largest mass fraction and diameter ratios (D=3, χ=20 wt%, and D=6, χ=15-20 wt%), the beds were more expressive in the slugging regime promoting a fair increase of velocities.

The segregation regions (U_{cf}–U_{if}) were influenced progressively by diameter ratios increasing up to 2-fold (D<3.0) and 3-fold (D=6.0). In this case, U_{if} and U_{af} were almost equal, and both velocities can be used as a reference for the segregation range. This rising is also evident for the other ranges, U_{cf}/U_{if} and U_{cf}/U_{af}, with exception of 15 wt% (D=3.0) and 20 wt% (D=3-6), where these ratios are decreasing due the low mixture quality. It is observed that for both cases, the fluidization were difficult to maintain the mixture causing the bed collapse and a considerable drop pressure (Figure 6a). For other experiments, the mixtures were more effective considering the pressure drop profiles of mixtures are similar to the profile of sand particles (Figure 6).

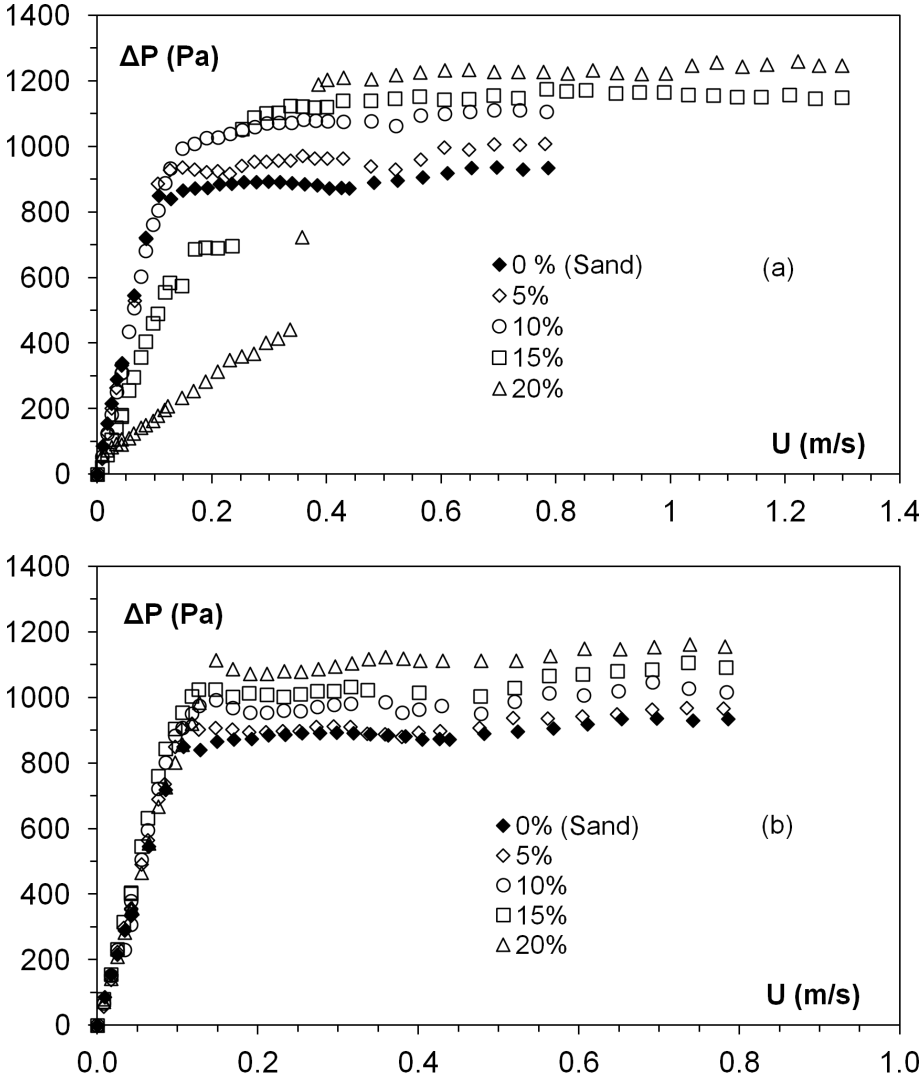
For U_{cf}/U_S, the increasing was gradual for D=1.5 (variation of 20%), however for D=3 (<15 wt%) and 6 (<10 wt%) this region remained constant and close to 1.7. Comparatively, the U_{cf}/U_{af} for eucalyptus was higher than for *Cariniana legalis* (Mitri et al., 2011) due to the higher difference between densities of biomass (394.92 kg/m^3) and sand (2636 kg/m^3). However, the maximum mass fraction ratio applied in the mixtures for D=6 was 20 wt% and 12.5 wt%, respectively, where the segregation of biomass occurs on the bottom of the bed.

Considering the *tucumã*/sand mixtures (Table 2), the U_{if} and U_{af} were practically the same, where for D=1.5, the velocities were slightly slower than the minimum fluidization velocity of sand, suggesting an increase of the apparent porosity of bed (ε_{af}). The segregation and complete velocities increased progressively leading to a larger region of segregation (U_{cf}–U_{if}), up to 70%. In this region, it was observed a higher concentration of *tucumã* endocarp in the upper layer of the bed. The U_{cf}/U_{if}, U_{cf}/U_{af}, and U_{cf}/U_S presented a significant increase (~40%) for D=1.5 and 20 wt%. None work has been found in the literature to compare our results.

Evolution of the Total Pressure Drop and the Standard Deviation of Pressure Fluctuation

Figure 6 shows the evolution of the total pressure drop as a function of the superficial gas velocity for eucalyptus/sand (a) and *tucumã*/sand (b) considering diameter ratio of 6 and mass fraction ratios of 0-20 wt%. For gas velocities faster than U_{cf}, the total pressure drop through the bed tends to a constant value between 890-1270 Pa, respectively. The profiles followed a trend of a homogeneous behavior in all mass fraction ratios for *tucumã* (Figure 6b). The same effect was observed for mixtures with smaller diameter ratios (D=1.5), up to 15 wt%, to the intermediate diameter ratio (D=3), and up to 10% for the larger ratio (D=6) of eucalyptus (Figure 6a).

Figure 6. Evolution of the total pressure drop as a function of the superficial gas velocity - Influence of mass fraction ratio for D=6 (a) Eucalyptus/sand and (b) Tucumã endocarp/sand



Above these conditions, the pressure drop profiles were quite different, presenting an abrupt region close to U_{af} due to difficulties in keeping the bed in fluidized state. The separation of particles occurred (U_S), when the eucalyptus particles moved to the bottom and the sand moved to the top of the fluidized bed through the preferential channels (Figure 6a). The higher the mass fraction ratio, the higher the deposition of solid is on the bottom of the bed, making the pressure drop decreased abruptly.

For the *tucumã*/inert mixtures, a high bubbling led to the uniform mixing and a thin layer of biomass on the surface (Figure 6b). The movement of particles into the bed makes the pressure drop move up and down. Below U_{if} velocity, the linear decrease in the pressure drop was considered as fixed bed with a predominance of viscous forces ($1.84<Re_p<16.68$).

Comparatively, the Figure 7 shows the evolution of the standard deviation of pressure fluctuations as a function of the superficial gas velocity. The fluctuations were influenced by the mass fraction ratio of the mixture of eucalyptus/sand (Figure 7a). For the case of higher mass fraction ratio (20%), there was a significant reduction of the amplitude of the standard deviations in comparison to 5 wt%, due to the increase of the biomass volume into the bed, blocking the air passage, and thereby impairing the homogeneity of the mixture. However, for the *tucumã*/sand mixture there was an increase in the standard deviation between the fluidization regions and a slight increase with the mass fraction ratios (5-20 wt%) due to the increase in the total mass of the bed, without losing the homogeneity of the mixture. This is explained by the formation of bubbles into the bed. In addition, the profiles followed the trend of homogeneous behavior until a mass fraction ratio of 10 wt% for the three diameter ratios (Figure 7b).

Influence of the Diameter Ratio

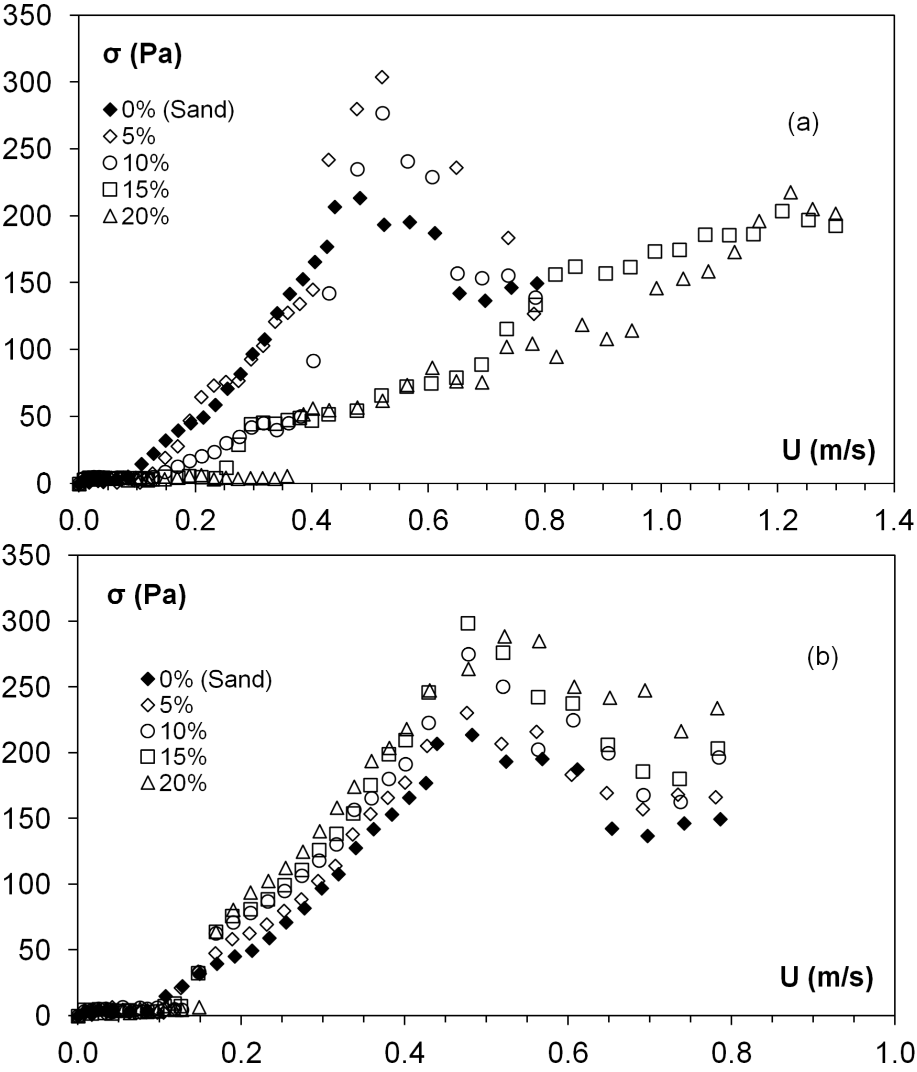
The results of the fluid dynamic parameters concerning the influence of the diameter ratio (1.5-6.0) are shown in Table 2. For the case of eucalyptus/sand mixture, there is a slight increase in the U_{if}, U_{af}, and U_S with the increase of D, which is more significant (70-100%) for the U_{cf} for 15-20 wt% of mass fraction ratios. For smaller diameters ($D<3$) and fractions (5-15 wt%), it was observed that the U_{if}, U_{af}, and U_S tend to constant values. In the case of the mixture *tucumã*/sand, it was observed that with an increase of D, there was a similar increasing trend of all fluidization velocities being more significant for U_{af} and U_S (35-62%). It is important to highlight that for diameter ratios of 3 and 6, the velocities are closed, due their fluid dynamic characteristics (bubbling regime).

Criteria for Fluidization Quality and Mixing of Beds

Although researchers still apply the concept of U_{af} as reference of particle mixtures, this parameter is not adequate to represent the fluidized state. In the case of perfect mixing, U_{cf} is more appropriate, since the pressure drop remains constant symbolizing the force equilibrium of particles.

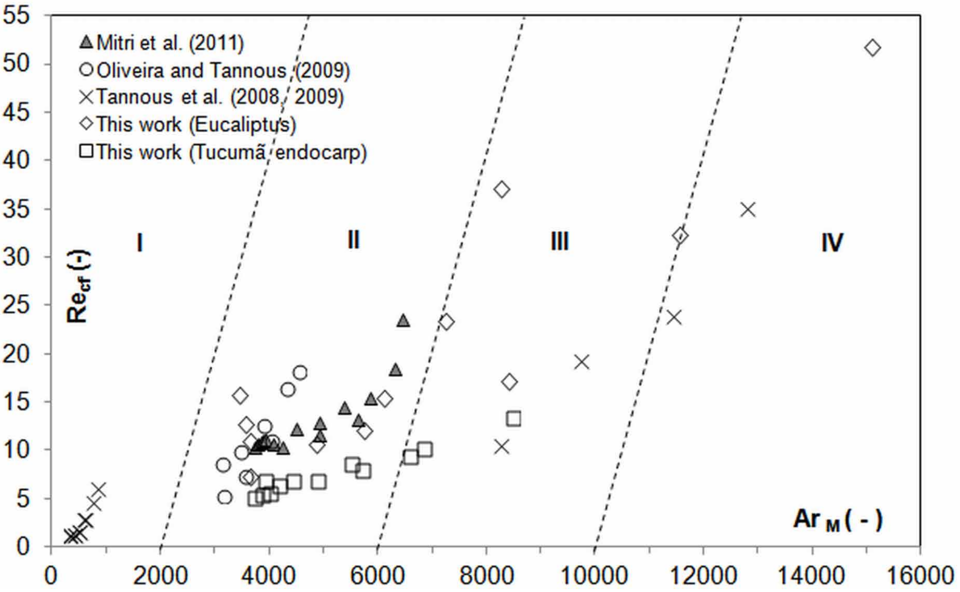
Considering the literature data from Oliveira and Tannous (2009), Tannous and Mizonov (2009), and Mitri et al. (2011) as well as our experimental data, it was

Figure 7. Evolution of the standard deviation of the pressure fluctuations as a function of the superficial gas velocity - Influence of mass fraction ratio for D=6 (a) Eucalyptus/sand and (b) Tucumã endocarp/sand



established some boundaries that can assist the fluidized bed designs. In Figure 8 the limits of the Reynolds' number for complete fluidization ($1 < Re_{cf} < 55$) as a function of Archimedes' number of mixtures ($200 < Ar_M < 16000$) are shown taking into account the effective diameter and density according to equations (3) and (4). All mixtures were considered fluidizable.

Figure 8. Diagram for identification of complete fluidization according to the Reynolds' number as a function of the Archimedes' number of mixtures considering different classes (I-IV)



Four classes were categorized to identify the quality of mixture with predominance of some features:

- Class I – predominance of diameter ratio (11-16); particle density ratio constant (4); acceptable mass fraction ratio up to 15%;
- Class II – predominance particle density ratio (2-7); diameter ratio variable (1.5-6); acceptable mass fraction ratio up to 20% for the smaller diameters;
- Class III – predominance particle density ratio (2-7); diameter ratio variable (3-6), and mass fraction ratio variable between 2.5-20%;
- Class IV – predominance of particle density ratio (4-7); diameter ratio constant (6); mass fraction ratio variable between 8-20%.

Establishment of New Correlations

The empirical correlations related to U_{af} are not frequently founded in the literature due the complexity of mixtures between biomass and inert. However, our experimental results were compared with different empirical correlations for binary inert mixtures (Thonglimp et al., 1984) and binary mixtures (Rao and Bhemarasetti, 2000;

Basu Paudel, 2011; Mitri et al., 2011). The results were not predictive with relative errors of 41%, 63%, 43%, and 82%, respectively. Mitri et al. (2011) equation was elaborated using the true density as the reference, overestimating the velocities.

For this reason, empirical correlations (Table 3) were proposed for the four fluidization velocities applying the power law and the modified Ergun's equation (1952), relating to the Reynolds' (Re) and Archimedes' (Ar_M) numbers according to equations (9) and (10), respectively. The effective density (ρ_M) and diameter (d_M) in these equations were calculated using equations (3) and (4), U is the superficial gas velocity for each characteristic velocity, and ρ_g and μ_g are the density and viscosity of gas.

$$Re=d_M U \rho_g/\mu_g \text{ for } U=U_{if},\ U_{af},\ U_S,\ or\ U_{cf} \tag{9}$$

$$Ar_M=d_M^{\,3}\rho_g(\rho_M-\rho_g)g/\mu_g^{\,2} \tag{10}$$

Due to the availability of experimental data of U_{if}, U_{af}, and U_{cf}, the works of Basu Paudel (2011), Karmakar, Haldar, and Chatterjee (2013), Mitri et al. (2011), Oliveira and Tannous (2009), Rao and Bheemarasetti (2008), Si and Guo (2008), and Tannous and Mizonov (2009) were considered into the empirical correlations. Besides that, the U_S equation was elaborated only with our data because it is the first proposal found in the literature for biomasses.

Table 3. New empirical correlations for characteristic fluidization velocities

Correlations	**Errors**		
	E_1 (%)	E_2 (%)	E_3 (-)
Initial fluidization velocity			
$Re_{if} = [15.8^2+0.019Ar_M]^{1/2}-15.8$ (11) valid for $0.2< Re < 7$ and $400< Ar_M < 1.5\ 10^4$	3.74	16.73	0.64
Apparent fluidization velocity			
$Re_{af} = [33.9^2+0.051Ar_M]^{1/2}-33.9$ (12) valid for $1.4< Re < 14$ and $340< Ar_M < 2.1\ 10^4$	2.73	23.54	2.76
Segregation velocity			
$Re_S = 0.0008Ar_M^{\,1.04}Mv^{-0.45}$ (13) valid for $1.2 < Re < 35$ and $340< Ar_M <1.5\ 10^4$	1.69	25.26	0.097
Complete fluidization velocity			
$Re_{cf}=0.0123Ar_M^{\ 0.8086}$ (14)	-3.18	20.71	3.59
valid for $1 < Re < 52$; $340 < Ar_M <1.5\ 10^4$ and $1\ 10^3 <Mv < 3.0\ 10^3$			

The relative error (E_1), absolute relative error (E_2), and root mean square error (E_3) are also presented in Table 3 according to the equations (6), (7) and (8), respectively. It is observed that each velocity follow a specific profile showing different tendencies of fluid dynamic behavior.

Bed Porosity at Apparent and Complete Fluidization Velocities

In Table 2 is presented the bed porosities, apparent (ε_{af}) and complete (ε_{cf}) concerning the effects of mass fraction and diameter ratios for eucalyptus/sand and *tucumã*/sand, respectively. For eucalyptus/sand, it was observed that the ε_{af} and ε_{cf} are more influenced by the increasing of the mass fraction ratio than the diameter ratio (Table 2). Considering the diameter ratio ranges (1.5-6), the maximum increase for the porosities were 19% and 13%, respectively. For the mass fraction ratio range (5-20 wt%), the increasing of 41% for ε_{af}, and of about 200% for ε_{cf}, were obtained. These behaviors can be attributed to the gradual presence of slugs in the bed for high biomass fractions with the increasing gas velocity required to completely fluidize these mixtures.

There is an agreement with Ramarkers et al. (2004) and Mitri et al. (2011) works shown in the Background in the subsection "Bed Porosity at Apparent and Complete Fluidization". Looking at the similar ranges of mass fraction of biomass in the mixtures, the authors found an increase in ε_{af} of up to 12% and 30% for sand diameters around of 100-500 µm and around 330 µm, respectively.

For the *tucumã* (Table 2), the ε_{af} and ε_{cf} increased 16.2% and 10.8%, respectively, with the increasing mass fraction ratio, whereas the ε_{af} decreased 5.1% and ε_{cf} increased in 10.8% for the highest diameter ratios. These values are indicative of low influence exerted by *tucumã* in the mixture, considering the beds with characteristics of homogeneous particles. Moreover, these mixtures are far below of those founds for the eucalyptus, due of particle densities is closer.

Establishment of New Correlations

None empirical correlation for binary mixtures applying biomass and inert was found in the literature to determine the characteristic porosities, ε_{af} and ε_{cf}. Therefore, equations (15) and (16) represent empirically our experimental data and from the literature (Mitri et al., 2011; Oliveira & Tannous, 2009).

$$\varepsilon_{af} = 0.07 Re^{0.43} Ar_M^{0.5} Mv^{-0.4} \quad E_1=5.03\%;\ E_2=21.35\%;\ E_3=0.12 \tag{15}$$

valid for $1.6 < Re_{af} < 18$, $3.1\ 10^3 < Ar_M < 1.5\ 10^4$, and $1.0\ 10^3 < Mv < 2.1\ 10^3$.

$$\varepsilon_{cf} = 0.07 Re^{0.4} Ar_M^{0.5} Mv^{-0.4} \quad E_1 = 7.94\%;\ E_2 = 18.75\%;\ E_3 = 0.14 \tag{16}$$

valid for $10 < Re_{cf} < 52$, $3.7\ 10^3 < Ar_M < 1.5\ 10^4$, and $1.0\ 10^3 < Mv < 2.1\ 10^3$.

$$Mv = (\rho_M - \rho_g)/\rho_g \tag{17}$$

Bed Expansion

Evaluating the overall mixtures, the bed expansion was more significant for the smallest diameter and the highest mass fraction ratios due to the facility in mixing through the growth of bubbles and the intensity burst at the bed surface. As an example, Figures 9 and 10 show the evolution of the bed expansion as a function of the superficial gas velocity for eucalyptus/sand (a) and *tucumã*/sand (b) for different mass fraction and diameter ratios, respectively.

Remarking that the expansions of the eucalyptus/sand mixtures (Figure 9a), the slower velocities, the closer was U_{if}, exhibited for the same tendency up to 15 wt% (0.40-0.42). Between U_{if} and U_{cf}, it can be observed a large deviation between the mass fraction ratios and this gap is increasing with the diameter ratio (Figure 10a). The most pronounced expansion decay was observed for 20 wt%. In addition, for U_{cf} higher than 0.8 m/s, overlapping curves were noted. For *tucumã*/sand mixtures, the expansions were quite similar conducting low effect of mass fraction ratio (Figure 9b).

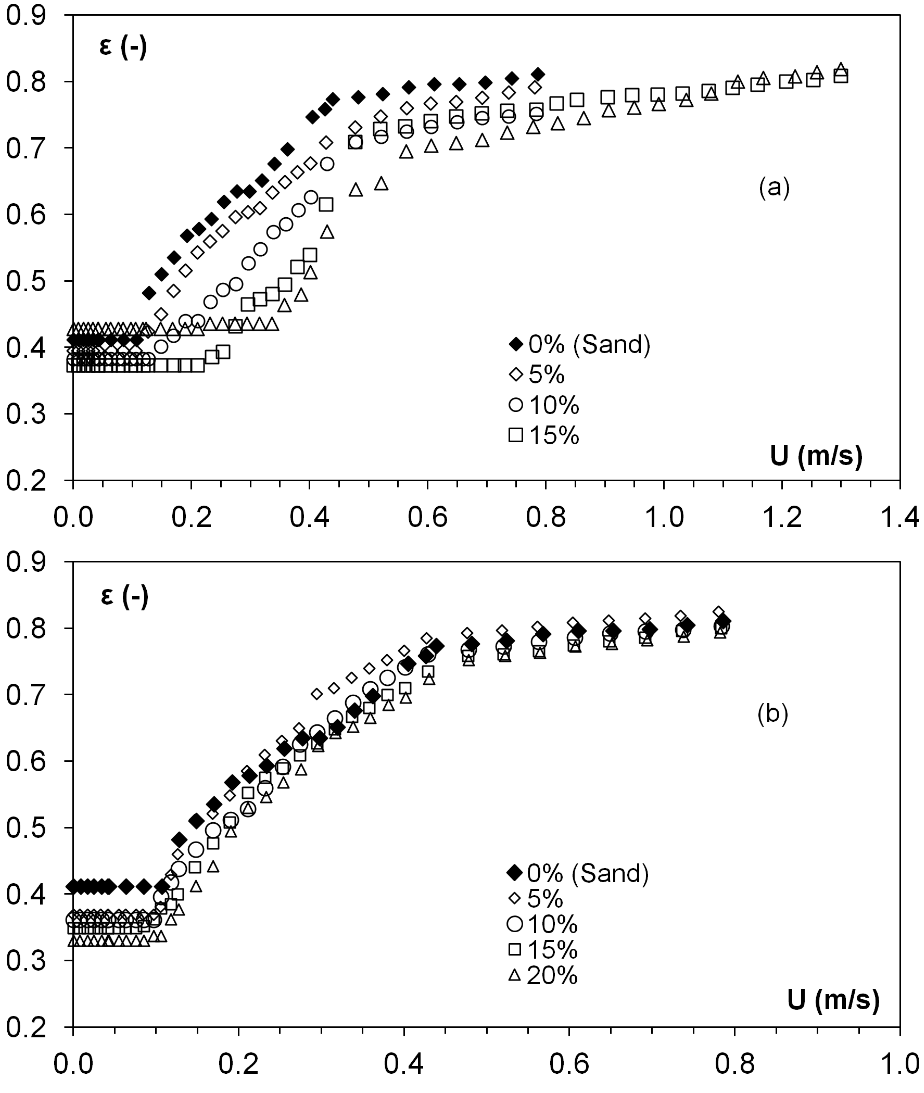
Regarding the influence of the diameter ratio, the bed expansions for eucalyptus/sand mixtures were more significant for the smallest diameters as shown in the Figure 10a. The expansions increased rapidly between U_{if} (or U_{af}) and $U_{cf,}$ and after that, it was observed an abrupt increase due to the presence of slugs. With respect to *tucumã* endocarp (Figure 10b), it was observed that the expansions was little influenced but accentuated in D=1.5.

Establishment of New Correlations

None empirical correlation for binary mixtures applying biomass and inert was found in the literature to determine the bed expansion. Therefore, the equation (18) was proposed considering our experimental data and from the literature (Mitri et al., 2011; Oliveira & Tannous, 2009), the equations (9) to (10), and superficial gas velocity up to1.4 m/s:

$$\varepsilon = 0.67 Re^{0.43} Ar_M^{-0.22} Mv^{0.12} \quad E_1 = 3.84\%;\ E_2 = 8.65\%;\ E_3 = 0.076 \tag{18}$$

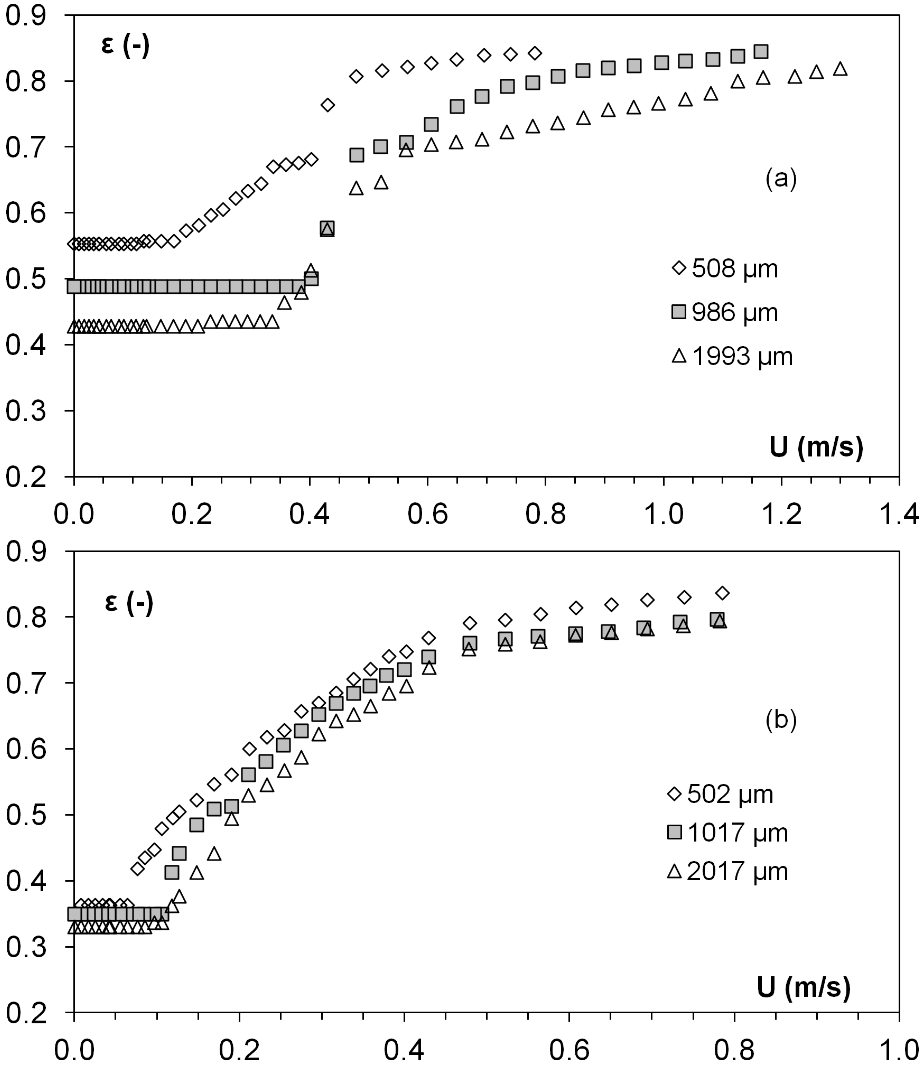
Figure 9. Evolution of the bed expansion as a function of the superficial gas velocity - Influence of mass fraction ratio for D=6 (a) Eucalyptus/sand and (b) Tucumã endocarp/sand



valid for $10 < Re < 60$, $3.1\ 10^3 < Ar_M < 1.5\ 10^4$, and $1.0\ 10^3 < Mv < 2.1\ 10^3$.

The comparison between calculated and experimental results is shown in Figure 11, and it translates in a good agreement. The maximum relative error was between 15-20%, mainly for the highest mass fraction ratios (χ=20%) and superficial gas velocities.

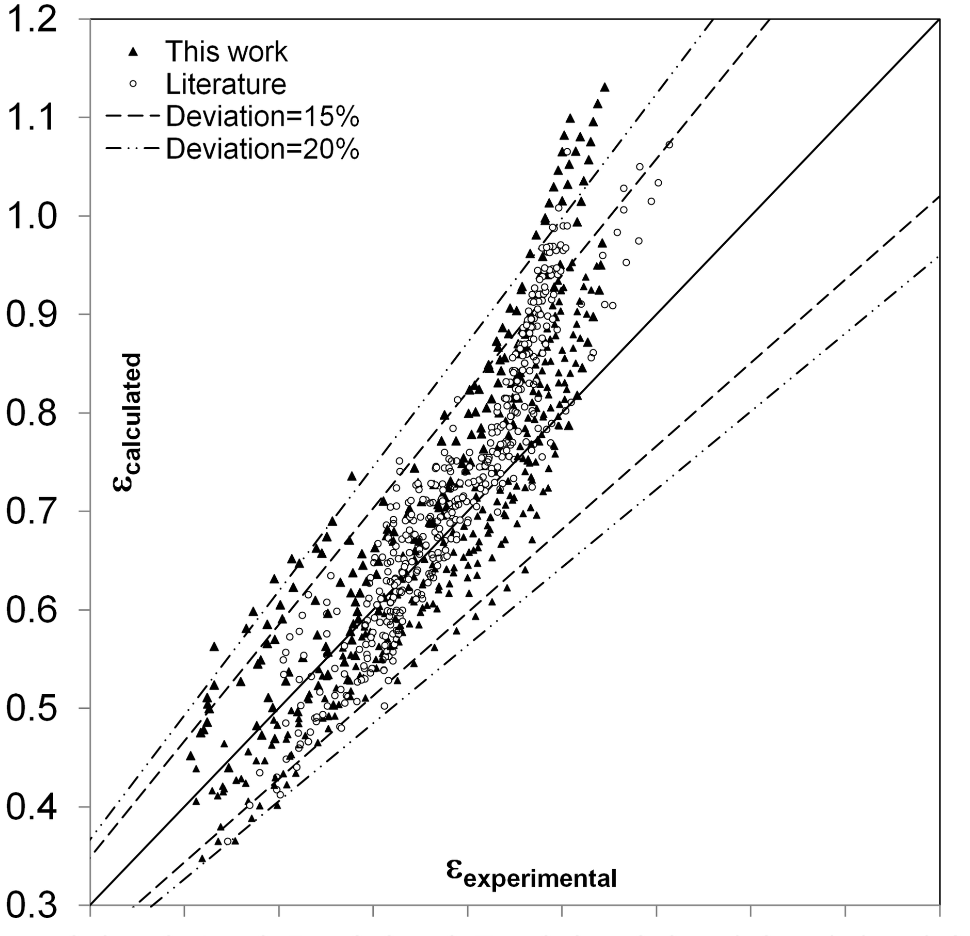
Figure 10. Evolution of the bed expansion as a function of the superficial gas velocity - Influence of diameter ratio for χ=20% (a) Eucalyptus/sand and (b) Tucumã endocarp/sand



FUTURE RESEARCH DIRECTIONS

This study is considered rather complex by researchers, in an operational standpoint, due to the feedstock, biomass. Their physical characteristics can result in inefficient processes concerning their mixing quality in beds compounded of inert materials. Finding the ideal point of mixing between these features is a new challenge and deserves attention from researchers. It requires carrying out studies of biomass concentration profiles along the bed, in the mixing and segregation states, in order to confront the characteristics velocities and thus to recommend experimental conditions to obtain the perfect mixture. Other fundamental aspect is the scale-up in order to ascertain the fluid dynamic behavior providing a guarantee of its stability. Limitations of measurement techniques and the high costs of implementation lead to a dropout of new experimental setups. This is extended when it comes to thermochemical processes where physical, chemical, thermal and reactive effects happen simultaneously in order to generate products with high value-added. Mathematical modeling can assist in determining new parameters without experimental studies.

Figure 11. Comparison between calculated and experimental data of bed expansion for various biomasses



CONCLUSION

In this chapter, experimental fluid dynamic characteristics and mixtures with biomass particles in gas-fluidized beds were discussed, focusing their applications in thermal conversion processes. It was observed a large lack in the literature about the diversity of biomasses in order to understand the mechanisms of mixtures. In the case of biomass, there is an agreement that the presence of an inert can easily lead to the best quality of fluidization. Eucalyptus and *tucumã* endocarp were studied in a case study as options of renewable sources. Characteristic velocities and fluid dynamic states were defined, in which the segregation and complete velocities represent the effective separation and perfect mixture conditions, respectively. The segregated state depends strongly on the solid physical properties, mass fraction ratios, and superficial gas velocity. Concerning the influence of mass fraction and diameter ratios, the characteristic fluidization velocities increased been more expressive for eucalyptus/sand at $D=6$ and $\chi=20\%$. The *tucumã*/sand mixtures showed to be favorable to a better quality of mixtures. In addition, it was observed that the apparent and complete porosities and bed expansions were more significant for the smaller diameter and mass fraction ratios, due to the facility of beds to fluidize with lighter mixtures. A diagram to identify the quality of mixtures considering four classes as a function of the complete fluidization Reynolds' and Archimedes' numbers was proposed. Empirical correlations for characteristic velocities and porosities, as well as the bed expansion showing a good agreement with the available experimental data were proposed.

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REFERENCES

Abdullah, M. Z., Hussain, Z., & Yin Pong, S. L. (2003). Analyses of cold flow fluidization test results for various biomass fuels. *Biomass and Energy*, *24*(6), 487–494. doi:10.1016/S0961-9534(02)00150-2

Aznar, M. P., Garcia-Gorria, F. A., & Corella, J. (1992a). Minimum and maximum velocities for fluidization for mixtures of agricultural and forest residues with a second fluidized solid. I. Preliminary data and results with sand-sawdust mixtures. *International Chemical Engineering*, *32*(1), 95–102.

Aznar, M. P., Garcia-Gorria, F. A., & Corella, J. (1992b). Minimum and maximum velocities for fluidization for mixtures of agricultural and forest residues with a second fluidized solid. II. Experimental results for different mixtures. *International Chemical Engineering*, *32*(1), 103–113.

Baleato, F. Z. (1986). *Analyse des phénomènes de mélange et de ségrégation de deux populations différentes de particules solides dans un lit fluidisé par un gaz* (Unpublished Doctoral Dissertation). National Polytechnic Institute of Toulouse, Toulouse, FR.

Basu, P. (2010). *Biomass gasification and pyrolysis - Practical design and theory*. Burlington, MA: Academic Press.

Basu Paudel, B. E. (2011). *Experimental Study on Fluidization of Biomass, Inert Particles, and Biomass/Sand Mixtures*. (Master's thesis, University of North Texas, Denton, USA). Retrieved from http://digital.library.unt.edu/ark:/67531/metadc84265/

Bilbao, R., Lezaun, J., & Abanades, C. (1987). Fluidization velocities of sand/straw binary mixtures. *Powder Technology*, *52*(1), 1–6. doi:10.1016/0032-5910(87)80001-3

Brazilian Energy Balance Year 2013. (2014). Retrieved from https://ben.epe.gov.br/downloads/S%C3% ADntese%20do%20Relat%C3%B3rio%20Final_2014_Web.pdf

Chiba, S., Chiba, T., Nienow, A. W., & Kobayashi, H. (1979). The minimum fluidization velocity, bed expansion and pressure-drop profile of binary particle mixture. *Powder Technology*, *22*(2), 255–269. doi:10.1016/0032-5910(79)80031-5

Cui, H., & Grace, J. R. (2007). Fluidization of biomass particles: A review of experimental multiphase flow aspects. *Chemical Engineering Science*, *62*(1-2), 45–55. doi:10.1016/j.ces.2006.08.006

Ergun, S. (1952). Fluid flow through packed columns. *Chemical Engineering Progress*, *48*(2), 89–94.

Formisani, B., Girimonte, R., & Longo, T. (2008). The fluidization process of binary mixtures of solids: Development of the approach based on the fluidization velocity interval. *Powder Technology*, *185*(2), 97–108. doi:10.1016/j.powtec.2007.10.003

Foust, A. S., Clump, C. W., & Wenzel, L. A. (1982). *Princípio das operações unitárias*. Rio de Janeiro, BR: Livros Técnicos e Científicos Press.

Geldart, D. (1973). Types of gas fluidization. *Powder Technology*, *7*(5), 285–292. doi:10.1016/0032-5910(73)80037-3

Gómez, E. O., Mesa-Pérez, J. M., & Brossard-Perez, L. E. (2008). Pirólise rápida de materiais lignocelulósicos para a obtenção do bioóleo. In L. A. B. Cortez, E. O. Gómez, & E. E. S. Lora (Eds.), *Biomassa para energia* (pp. 395–396). Campinas, BR: University of Campinas Press.

Goossens, W. R. A., Dumont, G. L., & Spaepen, G. L. (1971). Fluidization of binary mixtures in the laminar flow region. *Chemical Engineering Progress Symposium Series*, *67*(116), 38–45.

Grace, J. R. (1982). Fluidized-bed hydrodynamics. In G. Hetsroni (Ed.). Handbook of multiphase systems (pp. 8: 5-64). Washington, US: Hemisphere Publishing.

Haider, A., & Levenspiel, O. (1989). Drag coefficient and terminal velocity of spherical and non-spherical particles. *Powder Technology*, *58*(1), 63–70. doi:10.1016/0032-5910(89)80008-7

Karmakar, M. Kr, Haldar, S., & Chatterjee, P. Kr. (2013). Studies on fluidization behaviour of sand and biomass mixtures [Special issue]. *International Journal of Emerging Technology and Advanced Engineering*, *3*(3), 180–185.

Kunii, D., & Levenspiel, O. (1991). *Fluidization Engineering*. Newton, MA: Butterworth-Neinemann Ltda Press.

Lourenço, J. B. (2012). *Estudo das características fluidodinâmicas de misturas da madeira de eucalipto e do caroço do fruto do tucumã com inerte visando aplicação em processos de termoconversão.* (Master's thesis). Retrieved from Acervus Unicamp Dissertations and Theses database. (T/UNICAMP L934e)

Lourenco, J. B., Mitri, A. G., & Tannous, K. (2012). Fluid dynamic and mixing characteristics in fluidized beds of inerts and biomass - *Eucalyptus grandis* and *Cariniana legalis*. In *Proceedings of the 3nd International Symposium on Gasification and Its Applications ISGA-3* [CD]. Vancouver, CA.

Lucas, A., Arnaldos, J., Casal, J., & Puigjaner, L. (1986). High temperature incipient fluidization in mono and polydisperse systems. *Chemical Engineering Communications*, *41*(1-6), 121–132. doi:10.1080/00986448608911715

Mando, M., & Rosendahl, L. (2010). On the motion of non-spherical particles at high Reynolds number. *Powder Technology*, *202*(1), 1–13. doi:10.1016/j.powtec.2010.05.001

Mitri, A. G., Lourenço, J. B., & Tannous, K. (2011). Comportamento fluidodinâmico e velocidades características de misturas binárias de biomassa (C*ariniana legalis*) e areia. In *Proceeding of the XXXV Congresso Brasileiro de Sistemas Particulados* (pp.100-109) [CD]. Vassouras, BR.

Mourad, M., Hemati, M., & Laguerie, C. (1994). Hydrodynamique d'un séchoir à lit fluidisé à flottation: Détermination dês vitesses caractéristiques de fluidisation de mélanges de maïs et de sable. *Powder Technology*, *80*(1), 45–54. doi:10.1016/0032-5910(94)87004-7

Oliveira, C. R. M., & Tannous, K. (2009). Fluidodinâmica de biomassa em leito fluidizado gasoso. In *Proceedings of the VIII Congresso Brasileiro de Engenharia Química* [CD]. Uberlândia, BR. Retrieved from http://www.cobeqic2009.feq.ufu.br/uploads/media/84220321.pdf

Penã, J. A. P. (2011). Bubbling fluidized bed (BFB), when to use this technology? In *Industrial Fluidization South Africa* (pp. 1–12). Johannesburg, South Africa: The Southern African Institute of Mining and Metallurgy.

Punčochář, M., Drahoš, J., Čermák, J., & Selucký, K. (1985). Evaluation of minimum fluidization velocity in gaz fluidized bed from pressure fluctuations. *Chemical Engineering Communications*, *35*(1-6), 81–87. doi:10.1080/00986448508911219

Ramakers, B. J., Ridder, R., & Kerkhof, P. J. A. M. (2004). Fluidization behavior of wood/sand mixtures. *Maderas. Ciencia y Tecnología*, *6*(2), 145–153. doi:10.4067/S0718-221X2004000200005

Rao, K. V. N. S., & Reddy, G. V. (2010). Cold flow studies of rice husk, sawdust, and groundnut shell fuels in a fluidized bed. *Energy Source Part A: Recovery, Utilization, and Environmental Effects*, *32*(18), 1701–1711. doi:10.1080/15567030902882893

Rao, T. R., & Bheemarasetti, J. V. R. (2001). Minimum fluidization velocities of mixtures of biomass and sands. *Energy*, *26*(6), 633–644. doi:10.1016/S0360-5442(01)00014-7

Rasul, M. G., & Rudolph, V. (2000). Fluidized bed combustion of Australian bagasse. *Fuel*, *79*(2), 123–130. doi:10.1016/S0016-2361(99)00144-1

Riley, N. A. (1941). Projection sphericity. *Journal of Sedimentary Research*, *11*(2), 94–95.

Rowe, P. N., Nienow, A. W., & Agbim, A. J. (1972). A preliminary quantitative study of particle segregation in gas fluidized beds – Binary systems of near spherical particles. *Transactions of the Institution of Chemical Engineers*, *50*, 324–333.

Santos, E. S. (1997). *Estudo dos fenômenos de mistura e segregação em leitos fluidizados de partículas polidispersas*. (Master's thesis). Retrieved from Acervus Unicamp Dissertations and Theses database. (T/UNICAMP Sa59e)

Santos, F. J. (2010). Fluidodinâmica do leito fluidizado aplicada à gaseificação. In C. G. Sánchez (Ed.), *Tecnologia da gaseificação de biomassa* (pp. 263–275). Campinas, BR: Átomo Press.

Si, C., & Guo, Q. (2008). Fluidization characteristics of binary mixtures of biomass and quartz sand in an acoustic fluidized bed. *Industrial & Engineering Chemistry Research*, *47*(23), 9773–9782. doi:10.1021/ie801070z

Silva, F. S., & Tannous, K. (2012). *APOGEO - Analisador de Partículas e Formas Geométricas* [Computer software and manual]. Rio de Janeiro, BR: Brazilian National Institute of Industrial Property.

Tannous, K., Hemati, M., & Laguerie, C. (1994). Caractéristiques au minimum de fluidisation et expansion des couches fluidisées de particules de la catégorie D de Geldart. *Powder Technology*, *80*(1), 55–72. doi:10.1016/0032-5910(94)02841-9

Tannous, K., Hemati, M., & Laguerie, C. (1998). Hydrodynamic characteristics of fluidized beds containing large polydispersed particles. *Brazilian Journal of Chemical Engineering*, *15*(1), 67–76. doi:10.1590/S0104-66321998000100007

Tannous, K., Lam, P. S., Sokhansanj, S., & Grace, J. R. (2013). Physical properties and flow characterization of ground biomass from Douglas fir wood. *Particulate Science and Technology. International Journal (Toronto, Ont.)*, *31*(3), 291–300. doi:10.1080/02726351.2012.732676

Tannous, K., & Mizonov, V. (2009). Comportamento da biomassa na fluidodinâmica em leitos fluidizados cônico e cilíndrico. In *Proceedings of the XXXIV Congresso Brasileiro de Sistemas Particulados* (pp. 171-181) [CD]. Campinas, BR.

Thonglimp, V., Hiquily, N., & Laguerie, C. (1984). Vitesse minimale de fluidisation et expansion de couches de mélanges de particules solides fluidisés par un gaz. *Powder Technology*, *39*(2), 223–239. doi:10.1016/0032-5910(84)85040-8

Wadell, H. (1935). Volume, shape and roundness of quartz particles. *The Journal of Geology*, *43*(3), 250–280. doi:10.1086/624298

Wen, C. Y., & Yu, Y. H. (1966). Mechanics of fluidization. *Chemical Engineering Progress Symposium Series*, *62*(62), 100-111.

ADDITIONAL READING

Cortez, L. A. B., Gómez, E. O., & Lora, E. E. S. (2008). *Biomassa para energia*. Campinas, BR: University of Campinas Press.

Geldart, D. (1986). *Gas fluidization technology*. Chichester, ENG: John Wiley & Sons Ltd. NREL - National Renewable Energy Laboratory. *Learning about renewable energy*. Retrieved April 10, 2012 from http://www.nrel.gov/learning/ re_biomass.html

Sánchez, C. G. (2010). *Tecnologia da gaseificação de biomassa*. Campinas, BR: Átomo Press.

Yang, W. C. (2003). *Handbook of fluidization and fluid-particle systems*. New York, US: Marcel Dekker Press. doi:10.1201/9780203912744

KEY TERMS AND DEFINITIONS

Bed Expansion: When the superficial gas velocity increases through the bed after apparent fluidization, the height of the solid layers increases creating voids (bubbles or slugs). It is related to the void volume and the total bed volume.

Bed Porosity: Bed volume fraction occupied by empty spaces related to the apparent and complete velocities.

Bubbling Bed: Flow regime in which small bubbles appear close to the distributor and growth vertically with the excess of gas velocity.

Characteristic Fluidization Velocity: Transition velocities, initial, apparent, segregation, and complete, which characterize the fluid dynamic behaviors of a binary mixture.

Empirical Correlation: Equations developed from experimental data using significant parameters seeking the representation of the physical process involved.

Fluidized Bed: Equipment used in physical, chemical, and thermal processes in which solid particles are suspended by a gas providing a larger contact area and improving the heat and mass transfer processes.

Homogeneous Particles: One solid particle with the same physical properties (size, density and sphericity).

Heterogeneous Particles: Two or more solid particles with different physical properties (size, density and sphericity).

Segregation: Total or partial separation of particles into the bed, due to the differences in density and/or diameter, mass fraction as well as the superficial velocity.

Slugging Bed: Flow regime characterized by the growth and horizontal coalesce of bubbles along the bed reaching the entire cross-sectional area of the column.

Chapter 4

Modeling the Kinetics of Lignocellulosic Biomass Pyrolysis

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ABSTRACT

The study of the kinetics involved in lignocellulosic biomass pyrolysis has received great attention in the last decades and different mathematical models have been derived. In this chapter, a literature review was performed in order to summarize the existing models that use thermogravimetric data to estimate the kinetic parameters, which are important to improve and optimize the process. Additionally, a case study was presented exemplifying the application of kinetic modeling for the residue of one Brazilian species (Brazil nut woody shell). The isoconversional models of Ozawa-Flynn-Wall, modified Coats-Redfern, and Friedman were applied, as well as three and four independent parallel reactions models. The four reactions model presented the best fit between experimental and theoretical data, providing a better representation of the biomass pyrolysis reaction.

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INTRODUCTION

Pyrolysis is a thermochemical process that involves the heating of materials in the absence of oxidizing agents. The heating process can use isothermal or constant heating rate conditions to reach a maximum pyrolysis temperature. The nature of the obtained products depends on different factors, including the temperature, heating rate, condensation temperature, and particle size.

Pyrolysis is one of the most important ways to transform biomass into value added products (e.g., bio-char, bio-oil, fuels, synthesis gas, and chemicals) with several industrial applications. This process is attractive because solid biomass can be readily converted into liquid biofuels, presenting advantages in transport, storage, combustion, and flexibility in production and marketing.

In order to design industrial reactors, as well as to obtain important empirical parameters for process modeling and controlling, the kinetics involved in biomass pyrolysis should be well understood. This not only allows the estimation of kinetic parameters, but also the simulations beyond the tested temperature range. Experimentally, thermogravimetric analysis (TGA) is the commonly applied procedure to study the pyrolysis kinetics.

TGA is a technique that consists in monitoring the mass of a solid sample as a function of temperature or time, as it is subjected to a specific temperature program in a controlled atmosphere. This analysis has been used to investigate the degradation kinetics of different materials such as polymers since the 1960's by many researchers.

These researchers developed diverse mathematical models that allow the determination of the kinetic parameters (activation energy, pre-exponential factor, and reaction order) considering a global reaction scheme (single-step reaction). These models are considered a tool for process optimization, since they reduce the experimental costs, and the time spent on development, leading to an easier process scale-up.

Over the years more sophisticated kinetic models were derived, so that, different more complex materials, such as biomass, could be modeled. Initially, models taking into account multistep reaction schemes, such as consecutive or parallel reactions were developed. This consideration greatly enhanced the fitting quality, mainly because it regards: the process temperature, extend of conversion, and the biomass composition. Despite that, due to changes in the activation energy of biomass during the course of reaction, models that regarded a distributed profile for the activation energy were obtained. Although these distributed models present an enhanced fitting quality, its practical use is sometimes unadvisable because of the mathematical complexity inherent to its application.

The main goal of this chapter is to present the theoretical fundamentals of the kinetic modeling of biomass pyrolysis, discussing its complexities in the application of global and independent parallel reaction schemes. The kinetics of biomass pyrolysis is strongly dependent on the fractions of its main pseudo-components (hemicellulose, cellulose, and lignin) and therefore their separate contributions are also discussed. In order to apply the theory, a comparative case study is presented using thermogravimetric experimental data of one biomass from the Brazilian Amazon rainforest, Brazil nut woody shell (*Bertholletia excelsa* Humboldt & Bonpland), providing the analytical methodology of pyrolysis kinetics. This research provides ways to estimate the kinetic parameters, which are important variables in the process control, optimization and development, especially in an industrial scale.

BACKGROUND

The growing concern about the mitigation of pollutants emissions and the search for renewable and sustainable sources of fuels (especially in liquid form), have brought new attention to biomass and its utilization as a feedstock for obtaining biofuels. The balance between carbon dioxide emissions and fixation presented by photosynthesizing biomasses, as well as the great availably (especially regarding agricultural residues), have shown the great potential of biomass in becoming a widespread source of fuels and chemicals (Abbasi & Abbasi, 2010).

Biomass is a generic term that refers to every organic non-fossilized animal, vegetable or microbiological raw materials that can be converted into chemicals and fuels (Vassilev, Baxter, Andersen, & Vassileva, 2010). Special focus has been given to vegetable and microbiological biomasses, or simply *phytomass* (Abbasi & Abbasi, 2010). This kind of biomass is represented by an abundant and diverse spectrum comprising: food crops-to-energy (e.g., sugarcane, corn, and soybean); hydrocarbon-rich plants (e.g., latex-bearing species such as *Plumeria alba*); agricultural (e.g., straws, shells, and endocarps), forestry (e.g., leaf litter, and sawmill waste) and food wastes (e.g., biomass components of municipal solid waste); and, energetic fast-growing crops and woody species (e.g., poplar, pine, and switchgrass).

Due to its composition, phytomass is usually referred as a lignocellulosic material. Lignocellulosic biomasses are mainly composed by hemicellulose, cellulose, and lignin as well as smaller amounts of extractives (e.g., essential and fatty oils, terpenes, phenolic compounds, and resins), moisture, and inorganic matter (White, Catallo, & Legendre, 2011). Vassilev et al. (2010) pointed out that great variability has been observed in lignocellulosic biomass composition, depending on a diversity of factors such as: type of biomass, plant species, part of the plant, growing conditions, age, transport and storage conditions, and harvesting time.

Biomass is the main renewable raw material to be used in sustainable biorefineries, integrating processes for the production of food, biofuels, chemicals, biomaterials, electricity, and heat. Biomass structure can be decomposed using technologies such as pyrolysis and gasification to generate a variety of value-added products (Kajaste, 2014; Menon, & Rao, 2012; Pippo, Luengo, Alberteris, Garzone, & Cornacchia, 2011).

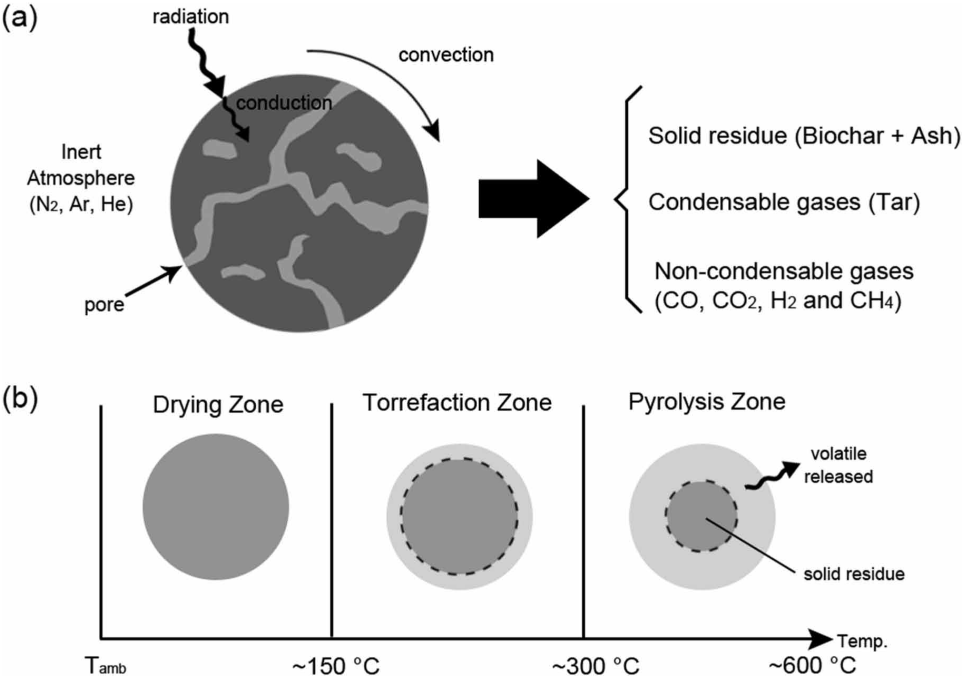
The conversion of biomass generates different energetic products, such as ethanol, biodiesel, biogases, bio-oil, and biochar, depending on the conversion technique applied. These products can be directly burned, or used in engines, turbines, and fuel cells to obtain electricity, heat, and power (Basu, 2010). There are mainly three ways to convert biomass into fuels, the thermochemical, biochemical, and mechanical routes. Among these, the thermochemical route presents some advantages over the others, such as lower pollutants emission, faster reaction times, and lower generation of by-products (Demirbas & Balat, 2007).

In thermochemical processes, lignocellulosic biomass is integrally converted into energetic products through combustion, torrefaction, liquefaction, gasification, or pyrolysis. Among this, pyrolysis is considered promising in obtaining biofuels because it can convert solid biomass into easily transportable liquids (with a higher energy density) in a rapid and efficient manner (Mettler, Vlachos, & Dauenhauer, 2012). This reaction involves the thermal degradation of biomass in an inert atmosphere (Figure 1), e.g., nitrogen (N_2), argon (Ar), and helium (He), using either isothermal or non-isothermal heating programs to reach temperatures of about 600°C. It is recommended the use of argon (Ar) as inert atmosphere instead of nitrogen, especially when one desires to perform the quantitative analysis of the gases produced after pyrolysis, since carbon monoxide (CO) is undistinguishable from nitrogen (N_2), for both present the same atomic mass (Pella & Colombo, 1973).

Figure 1. (a) describes the heat transfer mechanisms of a biomass particle subjected to pyrolysis. The main products are solid residues and gas. Some of the gases are readily condensed while the remaining gas is mainly constituted by carbon monoxide (CO) and dioxide (CO_2), hydrogen (H_2), and methane (CH_4). The thermal decomposition of a biomass particle as a function of temperature is presented in Figure 1(b). The first step is the drying, which can reach temperatures up to 150 °C, depending on the biomass nature. The second step is the torrefaction process, occurring between 150 – 300 °C, where the thermal stage corresponds to the biomass exothermic decomposition into low molecular gases (CO and CO_2). The final step takes place between 300 – 600 °C, where a high amount of volatiles is released as condensable gases (vapors and precursors of the liquid fraction), non-condensable gases, and char (Basu, 2010).

According to Mettler et al. (2012) the main difficulties involved in pyrolysis are the complex and multiscale nature of biomass feedstock, and also to obtain a mathematical model that describes, firstly, the reaction kinetics, and secondly, the transport phenomena (heat, mass, and momentum transfer).

Figure 1. Heat and mass transfer of a biomass particle submitted to pyrolysis (a), and particle decomposition as a function of temperature (b)



As a consequence of biomass complex composition and heterogeneity, its kinetic behavior under pyrolysis is difficult to describe (Van de Velden, Baeyens, Brems, Janssens, & Dewil, 2010). The kinetic modeling of biomass pyrolysis aims to obtain equations that represent the behavior of biomasses in a wide range of experimental conditions, providing a deeper insight into the reactions occurring during pyrolysis, and reveling similarities and differences among biomasses (Várhegyi, Antal, Jakab, & Szabó, 1997)

The study of kinetics involved in biomass pyrolysis is relevant, firstly, because the complex interdependence between kinetic and transport phenomena makes the kinetic modeling an indispensable step to pyrolysis practical use (Mettler et al., 2012). Secondly, because it provides means to: simulate complete conversion-time curves, control and optimize the process parameters (Sbirrazzuoli, Vincent, Mija, & Guigo, 2009), and design industrial reactors.

Experimentally, the kinetic analysis pyrolysis is associated with thermoanalytical data from differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and its first derivative (DTG) (Sbirrazzuoli et al., 2009) or differential thermal analysis (DTA) (White et al., 2011). According to White et al. (2011) the use of TGA is the most common procedure in solid-phase thermal degradation studies, being specially and widely applied in the study of biomass pyrolysis.

In TGA measurements, the remaining mass at a specific heating rate is registered as a function of time or temperature, while DTG provides the reaction rate (White et al., 2011). There are two kinds of TGA, isothermal and non-isothermal. In the first one, a constant specific temperature is used in the analysis, while in the second the temperature is gradually increased by a linear heating rate. Both techniques have been employed in the kinetic modeling of pyrolysis (Vyazovkin et al., 2011).

Nevertheless, all experimental techniques present some limitations. In the TGA, as well as other techniques such as DSC, DMA and DTA, the limitations arise from effects caused by intra- and inter-particle transport phenomena. The intra-particle heat and mass transfer effects are mainly influenced by the particle diameter, sample mass and heating program.

The diameter affects the particles internally, since large particles tend to develop a temperature gradient with external temperatures higher than the center temperature. It was observed that for particle diameters higher than 0.5 mm, the established temperature profile induces the generation of composition gradients, due to the different reactions velocities in different temperatures (Nascimento, 2012).

The inter-particle heat and mass limitations strongly depend on the sample mass used in the analysis. In TGA experiments, the sample is inserted in, generally, a metallic pan forming a packed bed with small dimensions (Becidan, Várhegyi, Hustad, & Skreiberg, 2007). Therefore, if higher amounts of mass are used, temperature profiles can also be formed in this small dimension bed, where the particles of the external layer will be at a higher temperature than those at the center of the sample bed, also inducing the development of a composition gradient. In order to avoid this kind of experimental limitations, the literature recommends the use of sample mass lower than 10 mg. Although, depending on the biomass density, which is greatly variable, previous mass influence studies must be performed in order to obtain the least variable decomposition profile (Nascimento, 2012).

Another parameter that affects the decomposition by thermogravimetry is the heating rate. If heating rates faster than 20 °C/min are used, the reacting time will be shortened in such a manner that some of the reactions steps will fail to be registered by the equipment, diminishing the experimental reliability (Rueda-Ordóñez, Olivares-Gómez, & Tannous, 2013). Lisbôa and Watkinson (1999) investigated the influence of the particle diameter (<0.074 mm and <0.250 mm), gas flow rate (62-300 mL/min), and sample mass (5.81-20.9 mg) on the pyrolysis of oil shale by thermogravimetry, using heating rates of 50 °C/min and 70 °C/min. The authors observed that is possible to avoid the thermal lag effects using particle diameter, gas flow rate, and sample mass lower than 0.25 mm, 100 mL/min, and 20 mg, respectively. However, as the biomass compositional and physicochemical properties are variable, one is advised to perform a set of preliminary experiments in order to define the best conditions, and having Lisbôa and Watkinson's values as a reference.

This chapter presents general information about the kinetics of lignocellulosic biomass pyrolysis. The role of biomass main pseudo-components (hemicellulose, cellulose, and lignin) is discussed relating the specificities of the mathematical models commonly applied in pyrolysis kinetics. This work is to be an initial guide to biomass pyrolysis modeling, a topic that has not yet presented a general consensus by the scientific community.

Biomass Composition and Pyrolysis Kinetics

As aforementioned, biomass presents a complex and variable composition. In this context, Vassilev, Baxter, Andersen, Vassileva, and Morgan (2012) presented an overview of organic and inorganic composition of 93 biomasses including wood and woody biomass, herbaceous and agricultural biomass, animal, and contaminated biomass. A great diversity has been observed in the fractional composition of biomass pseudo-components. For example, the mean weight percentages of woody biomass pseudo-components on a dry ash-free basis were 34.5%, 39.5%, and 26.0% for hemicellulose, cellulose, and lignin, respectively, whilst for shells and husks these percentages change to 27.4%, 40.0%, and 32.6%, respectively.

The hemicelluloses are natural highly branched polymers composed by several monomeric polysaccharides such as xylose, mannose (prevalent in hardwoods), glucose, galactose, arabinose (prevalent in softwoods), and other polysaccharides (Lanzetta & Di Blasi, 1998) with a random and amorphous structure (Vassilev et al., 2012). The hemicellulose bonds non-covalently to the cellulose microfibrils and is thermally less stable than cellulose. It undergoes dehydration at temperatures below 280 °C, forming anhydride fragments, water soluble acids, char, gases, and water. At higher temperatures, it depolymerizes yielding volatile organics, levoglucosan and other anhydrohexoses, levoglucosenones, and furans (Van de Velden et al., 2010).

Celluloses are natural polymers formed by anhydroglucose units connected by glycosidic bonds. It is the main component of the plant cell wall and its decomposition is the mostly investigated and well understood (Van de Velden et al., 2010). The long linear chains formed in this polymer are bond to one another by a network of hydrogen bonds (Vassilev et al., 2012), what makes cellulose thermally more stable than hemicellulose. At temperatures below 350 °C it goes through dehydration where the water and volatile matter contents are released, and there is a large decrease in the degree of polymerization (Van de Velden et al., 2010). Between 300 – 450 °C the depolymerization to levoglucosan and other primary anhydrosugars is dominant, while the fragmentation takes place at around 600 °C, forming hydroxy-acetaldehyde, 5-hydroxymethyl-furfural, methanol, acetaldehyde, and carbon monoxide and dioxide as the main products (Ranzi et al., 2008; Van de Velden et al., 2010).

Lignins are three-dimensional, highly branched, polyphenolic polymers, formed by three main phenylpropane units, namely p-coumaril, coniferyl, and sinapyl. It is an amorphous cross-linked resin that forms an irregular array of hydrogen bonds. Lignin thermal decomposition occurs in a broad temperature range, as a result of its high thermal stability. It is mostly responsible for char and volatiles of low molecular mass formation (Liu, Zhong,Wang, & Luo, 2011; Várhegyi, Antal, Jakab, & Szabó,1997). At temperatures lower than 500 °C dehydration is dominant and a diversity of products is released, while higher temperatures lead to the formation of a variety of lignite monomers such as catechols, vanillins, and aromatic carbohydrates. Above 700 °C these monomers are decomposed and released to the vapor phase (Van de Velden et al., 2010).

As lignocellulosic biomass is mainly composed by a complex mixture of hemicellulose, cellulose, and lignin, its behavior under pyrolysis is influenced by the contents of each pseudo-component (Van de Velden et al., 2010). To date, most devolatilization schemes consider that the different volatiles released during biomass pyrolysis are related to the three main components separately. The sum of these individual devolatilization rates, weighted according to their initially present percentage in the unreacted biomass, gives the total devolatilization process rate (White et al., 2011). Therefore, the study of the individual pseudo-components thermal degradation and kinetics under pyrolysis provides ways of understanding the expected reaction pathway in biomass degradation (Várhegyi, Antal Jr., Szekely, & Szabó, 1989).

In a review published by Di Blasi (2008) considering a wide number of studies on wood and biomass pyrolysis, the author observed that the mean temperature range for low heating rates in which hemicellulose, cellulose, and lignin present the higher decomposition rates were 225 – 325 °C, 325–375 °C, and 250 – 500 °C, respectively. Di Blasi also stated that during thermal conversion, as the heating rate increases, the temperature range of the components degradation becomes narrower.

In biomass decomposition, as even with the use of slow heating rates (< 20 °C/min), hemicellulose and cellulose decompose at a very close temperature range, there is still an overlapping of their degradation zones and usually two distinct peaks cannot be clearly observed in the derivative of the TGA curve (DTG). In these curves, hemicellulose usually represents a shoulder in the cellulose peak, which occurs at approximately 350 °C. Due to the aforementioned complexities, lignin presents a wide and flat DTG peak, overlapped by the cellulose and hemicellulose peaks, reaching also low (< 10%) and high (> 80%) conversions (Parthasarathy & Narayanan, 2014).

In order to understand the thermal decomposition of biomass main pseudo-components various authors studied the pyrolysis of commercially available forms of hemicellulose, cellulose, and lignin, and also of different biomasses regarding the effects of each component (Anca-Couce, Berger, & Zobel, 2014; Branca & Di Blasi, 2013; Orfão, Antunes, & Figueiredo, 1999; Várhegyi et al., 1989; Várhegyi et al., 1997; White et al., 2011). A wide spectrum of models, biomasses and experimental conditions were applied, resulting in a scatter of the estimated kinetic parameters.

White et al. (2011) reviewed the pyrolysis of different nutshells and presented a case study based on sugar cane bagasse slow and fast pyrolysis, under oxidative and non-oxidative media. Most researches used a three-step parallel reaction model considering first-order mechanisms for a variety of heating rates, particle sizes, temperature range, and sample masses. In slow pyrolysis under inert atmosphere, the values of activation energy (E) for the hemicellulose, cellulose, and lignin ranged between 105.0 – 253.5 kJ/mol, 194.0 – 250.0 kJ/mol, and 26.0 – 60.0 kJ/mol, respectively. The values of log of pre-exponential factor (A) for the hemicellulose, cellulose, and lignin ranged between 15.43 – 17.71 s^{-1}, 7.43 – 18.0 s^{-1}, and 0.78 –2.58 s^{-1}, respectively.

Anca-Couce et al. (2014) reviewed the pyrolysis of twelve lignocellulosic biomasses (e.g., pine wood, eucalyptus, pine barks, cotton, beech wood, olive husks, hazelnut shells, and corn-cobs), and estimated the kinetic parameters of other four (three beech woods and one pine wood) with a three-step parallel reaction scheme. The researchers have observed that, considering the reviewed and estimated values, the E for cellulose presents the narrowest observed range (190 – 250 kJ/mol). Hemicellulose normally presents lower values of E (75 – 220 kJ/mol) than cellulose, while the values for lignin are fairly low (25 – 200 kJ/mol) and usually do not exceed 100 kJ/mol. These values show there is a lack of consistency among different estimations for the pyrolysis kinetic parameters of biomass pseudo-components.

Biomass Kinetic Modeling

In the first attempt to understand biomass thermal behavior and kinetics, were considered the classical mathematical methods developed in the 1960's. They assumed that the thermal decomposition could be well described by a single-step reaction (Coats & Redfern, 1965; Flynn & Wall, 1966; Horowitz & Metzger, 1963; Kissinger, 1957).

The primary aim of pyrolysis kinetic modeling is to obtain the kinetic parameters, activation energy (E), pre-exponential factor (A) and the reaction mechanism, $f(\alpha)$, which may include other parameters, such as the reaction order (n). Equation (1) represents the conversion rate ($d\alpha/dt$), where k is the reaction rate constant (Van Krevelen, Van Heerden, & Huntjens, 1951).

$$d\alpha/dt=[k(T)][f(\alpha)] \tag{1}$$

The conversion, α, is a dimensionless measurement of the amount of reactants that has been converted into products. The mathematical representation of conversion can be expressed by two relations (equations 2a and 2b). The first is presented in equation (2a), being m_0 the initial mass of the sample, and m_t is the mass at a certain decomposition time, and is used when it is necessary to perform a quantitative simultaneous comparison between thermogravimetric curves (TG) obtained at different heating rates. This kind of comparison is necessary when isoconversional methods are applied, since the differences observed in the experimental final residue amounts can only be described by the kinetic model if just the initial mass is used as a normalized standard.

$$W=1-\alpha = 1-[(m_0-m_t)/m_0] \tag{2a}$$

The second mathematical representation of conversion is presented in equation (2b), in which the difference lays in the relation (m_0-m_f) in the denominator, being m_f the mass at the end of the main decomposition considered. Equation (2b) is commonly encountered in literature (e.g., Anca-Couce et al., 2014; Órfão et al., 1999) and it is used when the thermogravimetric curves are analyzed separately. The separate analysis of each TG results obtained at different heating rates is necessary when multiple reactions are considered in the kinetic scheme and, as the calculations are performed separately, the difference between the initial and the final mass is used as a normalized standard, without losing any experimental information.

$$\alpha = (m_0-m_t)/(m_0-m_f) \tag{2b}$$

The reaction rate constant is given by equation (3), deduced experimentally by Arrhenius, where R is the universal gas constant and T is the absolute temperature.

$$k(T)=A[\exp(-E/RT)] \tag{3}$$

Combining equation (1) and equation (3), one obtains equation (4), which represents the reaction rate in terms of the kinetic parameters.

$$d\alpha/dt=A[f(\alpha)][\exp(-E/RT)] \tag{4}$$

In solid-state kinetics, many models have been proposed being generally classified based on the graphical shape of their curves of α versus time (t) or ($d\alpha/dt$) versus α, and on their mechanistic assumptions. It should also be noted that as biomass pyrolysis usually proceeds via a complex arrangement of reactions, where each one of these reactions have its own activation energy, it is common the use of an average, apparent activation energy to describe the overall process (White et al., 2011).

Model-free methods refer to equations in which a reaction mechanism assumption is not necessary to obtain E. Although no assumptions are needed to perform a complete kinetic analysis, the definition of some reaction mechanism is mandatory to estimate the pre-exponential factor. Among these, there are the isoconversional methods, which can be mainly divided into two categories, integral and differential (Flynn & Wall, 1966).

Depending on the mathematical resolution applied to equation (4), differential or integral methods arise. When differential methods are applied, the direct use of classical numerical methods generates an approximated solution within the mathematical method and experimental errors. Since there is no analytical solution to the integrated form of equation (4), integral methods are based on approximations given by different authors to the temperature integral.

As no assumption is made over the kinetic models, differential isoconversional methods are prone to be more accurate than integral methods. However, this accuracy is diminished by difficulties on the baseline experimental definition and when there is a dependence of E on heating rates. Thus, differential methods cannot be considered necessarily more precise than integral methods, and kinetic modeling with both methods is advised (Vyazovkin et al., 2011).

Integral Methods

Acording to Sbirrazzuoli et al. (2009), when non-isothermal analysis is employed, the process temperature is controlled by a constant heating rate β, which is represented by a variation of temperature with time, $\beta = dT/dt$. Reaction rates as a function of temperature (Doyle, 1961) can be formulated through equation (5).

$$d\alpha/dt = (d\alpha/dt)(dT/dT) = (d\alpha/dT)(dT/dt) = (d\alpha/dT)\beta \tag{5}$$

Then, the conversion rate can be defined as a function of temperature with an expression of the rate law for non-isothermal conditions, which can be obtained by substituting equation (5) into equation (4). Therefore, equation (6), expresses the non-isothermal conversion rate.

$$d\alpha/dT = (A/\beta)[f(\alpha)][exp(-E/RT)] \tag{6}$$

The integral approach assumes that the apparent activation energy (E) remains constant throughout the entire reaction, and that no reactions occur at low temperatures. Therefore, a value of zero is assumed for the initial conversion, related to an initial temperature. Additionally, as no reaction is observed for low values of temperature, the lower integration limit for this variable is also zero. The integration of equation (6), from these initial parameters up to a specific conversion temperature, T_α, related to conversion α, gives the equation (7).

$$g(\alpha) = \int_0^\alpha d\alpha \,/\, f(\alpha) = A \,/\, \beta \int_0^{T\alpha} \exp(-E \,/\, RT) dT \tag{7}$$

In equation (7) $g(\alpha)$ is an integral function of the conversion, dependent on the reaction mechanism. The right side is the temperature integral, which the solution is represented by the function $p(x)$ (White, et al., 2011; Sanchez, Otero, Gómez, & Morán, 2009), defined in equation (8), where $x=-E/RT$:

$$g(\alpha) = (AE \,/\, \beta R)\{-[\exp(x) \,/\, x] + \int_{-\infty}^{x} [\exp(x) \,/\, x] dx\} = (AE \,/\, \beta R) p(x) \tag{8}$$

Depending on the approximate solution for the $p(x)$ function, different integral methods have been developed over the years. Table 1 shows a summary of the integral and differential isoconversional methods.

One of the first works dealing with an approximation for the temperature integral in equation (7) was presented by Van Krevelen, et al. (1951), in which a simple mathematical arrangement, presented in equation (15), was proposed, where T_{max} is the peak temperature in the conversion rate curve.

$$\exp(-E/RT)=[\exp(-T_{max}/T)]^{(E/RTmax)} \approx [0.368(T/T_{max})]^{(E/RTmax)} \tag{15}$$

The kinetic model developed by Van Krevelen et al. (1951) is presented in equation (9), Table 1. Flynn and Wall (1966) tested this model comparing it with theoretical curves, in which the kinetic parameters were known, and concluded that the method should be limited to cases with a previously defined reaction order.

Coats and Redfern (1965) proposed a solution of the $p(x)$ function based on an asymptotic expansion shown in equation (16), and the model proposed by them is presented in equation (10), Table 1. The authors observed that analyzing up to the second term of the expansion, acceptable results were obtained.

$$p(x)=\{[\exp(x)]/x^2\}\{1+(2!/x)+(3!/x^2)+(4!/x^3)+...+(n\,!/x^{(n-1)})\} \tag{16}$$

Table 1. Main features of integral and differential methods

Model	Graphic Representation	Parameter (E)	Observations	Reference
Integral models				
$\ln[g(\alpha)]=\ln\{[(AR)/(\beta E)]\{(0.386/T_{max})\text{^}[E/(RT_{max})]\}(T_{max}+1)\} + \{E/[R(T_{max}+1)\}\ln(T)$ (9)	$\ln[g(\alpha)]$ vs $\ln(T)$	mR	Fitting Model Non-isothermal Non-isoconversional	Van Krevelen et al. (1951)
$\ln[g(\alpha)/T^2]=\ln\{[(AR)/(\beta E)][1\text{-}(2RT/E)]\} - [E/(RT)]$ (10)	$\ln[g(\alpha)/T^2]$ vs $1/T$	mR		Coats and Redfern (1965)
$\log_{10}(\beta)=\{\log_{10}(AE/R) - \log_{10}[g(\alpha)] - 2.315\}\text{-}0.4567(E/RT)$ (11)	$\log_{10}(\beta)$ vs $1/T$	$mR/0.4567$	Free Model Non-isothermal Isoconversional	Doyle (1961) Ozawa (1965), Flynn and Wall (1966)
$\ln(\beta/T^2)=\ln\{[(AR)/(E)]\} - \ln[g(\alpha)] - [E/(RT)]$ (12)	$\ln(\beta/T^2)$ vs $1/T$	mR		Braun et al. (1991)
Differential models				
$\ln(\beta/ T^2_{m,i})=\ln\{[(AR)/(E)\, f'(\alpha)]\} - [E/(RT_{m,i})]$ (13)	$\ln(\beta/T^2_{m,i})$ vs $1/ T_{m,i}$	mR	Free Model Non-isothermal Non-isoconversional	Kissinger (1957)
$\ln[\beta_i(d\alpha/dt)_{\alpha,i}]=\ln\{[(A_\alpha)f(\alpha)]\} - [E_\alpha/(RT_{\alpha,i})]$ (14)	$\ln[\beta_i(d\alpha/dt)_{\alpha,i}]$ vs $1/T_{\alpha,i}$	$mRT_{\alpha,i}$	Free Model Non-Isothermal Isoconversional	Friedman (1964)

The definition of $g(\alpha)$ function in equation (7) is mandatory to apply the Coats and Redfern method, and its use is uncommon in the literature. Flynn and Wall (1966) compared the results obtained through this method with theoretical curves and concluded that it is only applicable for conversions lower than 0.3. Nevertheless, some recent studies (Tonbul, 2008, Lu, Song, & Lin, 2009) used this method to evaluate the combustion and pyrolysis kinetic parameters. Ebrahimi-Kahrizsangi and Abbasi (2008) used simulated TGA curves for different kind of reactions and compared with results obtained by this method, concluding that it is not accurate, and generates great deviation from the real values.

The Ozawa-Flynn-Wall (OFW) method was proposed independently by Ozawa (1965) and Flynn and Wall (1966), and derived based in equation (17), proposed by Doyle (1961).

$$\log_{10}[p(x)]=a+bx \tag{17}$$

The values a and b are constants determined by linear interpolation, for example, $a=-2.315$ and $b=-0.4567$ for $20 \leq x \leq 60$. The OFW method is presented in equation (11), Table 1. In this method application, it is necessary to use at least three different heating rates in the thermogravimetric analysis, and it is considered more reliable than the methods of Van Krevelen, and Coats and Redfern (Flynn & Wall, 1966).

According to White et al. (2011), OFW method introduces error, overestimating E. However, it is commonly used due to its easy application. Some recent works (e.g., Anca-Couce et al., 2014, Ceylan & Topçu, 2014; Ye, Li, Chen, Zhang, & Xu, 2010) employed this method to determine E of different biomasses in TGA experiments under nitrogen atmosphere.

Braun, Burnham, Reynolds and Clarkson (1991) used the asymptotic expansion previously presented by Coats and Redfern (1965), proposing a method that uses different heating rates to obtain E. This method is known as the modified Coats and Redfern (MCR) method. In addition, in the literature, the same mathematical relation is commonly referred as Kissinger-Akahira-Sunose (KAS) method.

The use of MCR in biomass analysis is very common, and the activation energies are lower than those determined by the Ozawa-Flynn-Wall method. Equation (11), Table 1, presents this method and its linearization form. White et al. (2011) point out that it can overestimate the kinetic values when applied in biomass investigations.

Other approaches have been proposed over the years and, with the computational advances, more accurate procedures emerged. Even so, these proposals, such as the methods of Starink (1996) and Tang, Liu, Zhang and Wang (2003) have been sparsely found in the literature.

Differential Methods

Differential isoconversional methods are not dependent on approximations for the temperature integral and, therefore, kinetic parameters can be straight calculated. Vyazovkin et al. (2011) point out that caution must be taken when using differential models, since its use introduces imprecision into the measured data, and also inaccuracy, when the data are smoothed. Moreover, when the activation energy (E) shows a clear dependency on the heating rate or on the conversion, the use of differential methods should be avoided (Sbirrazzuoli et al., 2009).

The most common differential method is the Friedman (FD) model (Friedman, 1964), shown in equation (14), Table 1. In this model, the reaction mechanism, $f(\alpha)$, was considered independent of temperature and dependent only on the remaining mass. In this model α represents each different conversions chosen to perform the calculations. For a non-isothermal linear condition the index i in equation (14) identifies a specific heating rate (Sbirrazzuoli et al., 2009).

Another widely used differential method was developed by Kissinger (1956). This method was based on the derivative of equation (4), shown in equation (18), in which the right hand term is zero when the reaction rate is maximum. The Kissinger method and its linearized form are presented in equation (13), Table 1.

$$d(d\alpha/dt)/\mathrm{dt}=\mathrm{d}\{A[f(\alpha)][\exp(-E/RT)]\}/\mathrm{dt} \quad (18)$$

As this method produces only a single set of kinetic parameters, it may not display the general tendency of E for complex kinetics since only one point from DTG data (peak) is considered (Yao, Wu, Lei, Guo, & Xu, 2008). This fact implies that the adequate determination of E can only be accomplished for single-step kinetics.

Reaction Mechanisms

During pyrolysis, physical and chemical phenomena occur simultaneously, but usually, only one of these steps controls the overall kinetics (Vyazovkin et al., 2011). Therefore, the form of the reaction mechanism function should be suitable for this controlling step.

Several different functions for the reaction mechanism of solid-state kinetics can be found elsewhere (Aboulkas & El Harfi, 2008; Lua & Su, 2006; Vlaev, Markovska, & Lyubchev, 2003;Vyazovkin et al., 2011). These functions present one of the four kinds of possible kinetic curve patterns (linear, accelerating, sigmoidal, and decelerating) (Vyazovkin et al., 2011), and can represent chemical reaction, random nucleation and nuclei growth, phase boundary reaction or diffusion phenomena (Vlaev et al., 2003).

According to White et al. (2011) when kinetic analysis is applied to biomass degradation, reaction-order models are frequently used, due to their simplicity and closeness to relations that are valid for homogeneous kinetics. This consideration is valid for biomass thermal decomposition when non-isothermal data is analyzed since sigmoidal patterns, arise from the variation of temperature and degree of conversion (Vyazovkin et al., 2011).

This way, the mechanism of n^{th} order presented in equation (19), was used in this work. This mechanism considers that the quantity or fraction of the remaining reactants is elevated to a particular power, which can be an integer or a fraction number, commonly known as the reaction order, n (White et al., 2011).

$$f(\alpha)=(1-\alpha)^n \tag{19}$$

Fitting Models

Fitting models are the most popular methods applied to evaluate solid-state kinetics, especially in non-isothermal experiments. Nonlinear least squares method is commonly used to fit biomass thermogravimetric and theoretical data, and to evaluate the Arrhenius parameters (White et al., 2011). Several numerical methods (e.g., Euler and Runge-Kutta) are frequently used to solve the conversion rate equation.

Equations (2) and (20) can be used to transform the TGA and DTG data to conversion and conversion rate, respectively. The kinetic parameters estimated are those which minimize the objective function (OF) given in equation (21).

$$d\alpha/dt=(-dm/dt)/(m_0) \tag{20}$$

$$OF=\sum_{i=0}^{N}[(d\alpha_i^{\exp}/dt)-(d\alpha_i^{calc}/dt)]^2 \tag{21}$$

According to Órfão et al. (1999) the fit between the experimental and theoretical data can be determined by equation (22), where N is the number of data points and $(d\alpha/dt)_{\max}$ is the highest decomposition rate observed in the DTG. The best fit is obtained when the sum of the weighted squares of the residuals is at minimum, i.e., a value closer to zero, presenting a smaller random error. The authors also stated that for 95% of confidence interval, a fit of 5% indicates there was a good agreement.

$$\text{Fit }(\%) = 100[(OF/N)^{0.5}/(d\alpha/dt)_{\max}] \tag{22}$$

Global Reaction Scheme (GRS)

The biomass pyrolysis involves several complex simultaneous reactions, forming different intermediate and final products. Thus, an exact kinetic model is extremely difficult to achieve (Yao et al., 2008). An easy way to obtain a first approach of the pyrolysis kinetics of biomass is to use a model considering a global or single-step reaction. The GRS considers biomass pyrolysis as a one-step reaction with a n^{th} order mechanism, as shown in Figure 2.

According to Cardoso, Miranda, Santos, & Ataíde (2011) the application of global models to thermogravimetric data of lignocellulosic biomass shows a wide divergence, related to the very complex composition. Since biomass DTG frequently presents more than one peak and/or shoulders, related to the main components decomposition, the fitting through a one-step global reaction usually cannot describe the process.

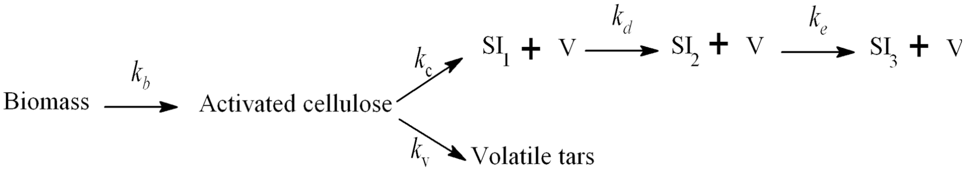
Mixed and Consecutive Reaction Schemes (MCRS)

Mixed and consecutive reaction schemes (MCRS) are usually derived directly from TGA and DTG data or theorized, as shown in Figure 3. To develop a new mechanism researchers analyze the different peaks and shoulders in thermoanalytical curves proposing different decomposition mechanism based on their observations. A variety of these mechanisms have been proposed over the years for organic-based compounds like polymeric resins, grain straws, woods, and walnut shells (Branca & Di Blasi, 2013; Chen, Liu, & Fan, 2006; Lanzetta & Di Blasi, 1998; Várhegyi et al., 1989; Yuan & Liu, 2007).

Figure 2. Biomass pyrolysis global reaction scheme

$$\text{Biomass} \xrightarrow{k} \text{Biochar} + \text{Gas (condensable vapours and non-condensable gases)}$$

Figure 3. Biomass pyrolysis consecutive reaction scheme



Although these mechanisms help to improve the fitting quality when compared to global schemes (Bradbury, Sakai, & Shafizadeh, 1979; Broido, 1976; Várhegyi, Jakab, & Antal Jr., 1994), the use of MCRS seems to be avoided because of the inherent specificity involved, generally, the form of these mechanisms is achieved from the analysis of experimental data considering some specific materials and experimental conditions.

Independent Parallel Reaction Scheme (IPRS)

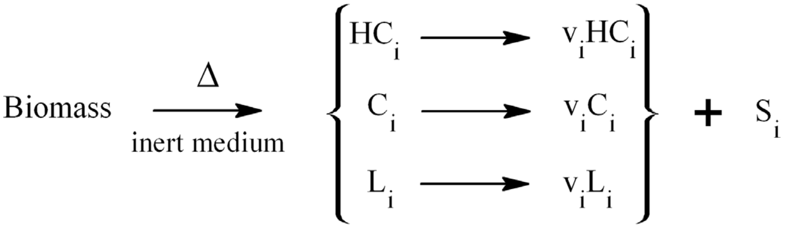
Considering the complexity of reactions that occur during biomass decomposition, researchers observed that is not possible to describe the entire phenomenon with a single reaction (Cai, Wu, Liu, & Huber, 2013; Grønli, Gábor & Di Blasi, 2002), and also that mixed and consecutive schemes tend to be too specific (Várhegyi et al., 1994).

The independent parallel reaction scheme (IPRS) assumes that each component reacts independently of the others in a certain temperature range, and the summation of the individual conversion rates represents the whole biomass kinetic behavior. The components normally are hemicellulose, cellulose, and lignin. The IPRS (Figure 4) also considers that there are no secondary reactions between the gaseous products (v_i) and the char (S_i) formed (Cai et al., 2013). However, few studies also take into account a higher number of reactions, such as the work of Becidan et al. (2007) who evaluated the fitting quality of different reaction orders and number of reactions, concluding that a four-reaction approach generates more accurate parameters.

Based on the conversion rate definition in equation (4), the overall conversion, regarding each pseudo-component, can be expressed by equation (23), where x_i is the mass fraction and j is the number of pseudo-components.

$$d\alpha \,/\, dt = -\sum_{i}^{j} x_i (d\alpha_i \,/\, dt) \tag{23}$$

Figure 4. Biomass pyrolysis independent parallel reactions scheme



The method of least squares is normally used to evaluate the kinetic parameters. Thus, the use of a three-step IPRS generates three sets of kinetic parameters (E_i, n_i, and k_i), which has been found to resemble the pure compounds activation energies (E) (Cardoso et al., 2011; Grønli et al., 2002; Orfão et al., 1999; Sánchez-Silva, López-González, Villaseñor, Sánchez, & Valverde, 2012; Vyazovkin et al., 2011).

However, it is important to emphasize that the use of a single heating rate is disapproved because it can generate inconsistent parameters. This fact is discussed by Anca-Couce et al. (2014) and White et al. (2011) that highlight the importance of using various heating rates in the kinetic estimations in order to satisfy an entire range of heating conditions.

Distributed Activation Energy Models (DAEM)

In order to account for the experimentally observed shift of activation energy (E) with the conversion, the distributed activation energy models (DAEM) were developed (Vyazovkin et al., 2011). The DAEM frequently considers various parallel reactions to provide a good fitting of the overlapping curves (Várhegyi, Czégény, Jakab, McAdamb, & Liu, 2009), where the distributed reactivity is usually approximated by a Gaussian distribution of E, but also, other distributions can be employed such as Weibull's distribution (Vyazovkin et al., 2011). A variety of studies present several approximations for the temperature integral and for the estimation methods, from which different DAEM arise (Cai et al., 2013; Fiori, Valbusa, Lorenzi, & Fambri, 2012; Güneş & Güneş, 2002; Wanjun, Cunxin, & Donghua, 2005).

Although DAEM has been considered the most accurate to study thermal decomposition of different biomasses, the inclusion of the distributed profile generates mathematical complexities that are not observed in mixed and consecutive reaction schemes (MCRS), for example (Várghegyi et al., 2009). Other disadvantages are the incapability of modeling the drying stages, and the complex or laborious mathematical manipulations that need to be applied (Cai et al., 2013; Chen, Zheng, & Zhu, 2013; Várghegyi et al., 2009). Among its advantages, DAEM avoids the underestimation of E, which is common when a global reaction scheme (GRS) is used to adjust the temperature dependency (Di Blasi, 2008).

Considering all the reviewed models, numerous studies have employed multiple heating rates experiments for a three-step independent parallel reaction scheme (IPRS), using different biomasses, heating rates, reaction mechanisms and temperature ranges. Other researches applied not only IPRS, but also DAEM, GRS, and MCRS to estimate parameters such as activation energy (E) and pre-exponential factor (A). Some of these took into account biomass pseudo-components and reaction orders (n) higher than first-order. In order to exemplify the biomass pyrolysis kinetic, Table 2 shows a compendium of models, TGA conditions, and evaluated kinetic parameters made in the last five years. The investigations presented in Table 2 have been performed using nitrogen as analysis gas with the exception of the work of Sánchez-Silva et al. (2012), which used helium.

Regarding the evolution of the schemes, the GRS represented the first attempts to model biomass pyrolysis. It uses a linear regression method to evaluate the kinetic parameters (Vyazovkin et al., 2011). The MCRS accounts for multistep kinetics using the same principles involved in GRS (Várhegyi et al., 1994). However, the inherent specificity involved in the derivation of such schemes is not interesting from a practical point of view.

Differently from other schemes, IPRS relates to the composition of the biomass and requires the use of non-linear regression methods with initial assumptions to perform evaluations. This method is mathematically more complex but shows great improvements in the fitting quality of biomass kinetics, providing a better understanding of the process in a microscopic scale (Anca-Couce et al., 2014). The DAEM can be seen as an extension of IPRS, where E is considered to be represented by a continuous distribution of activation energies, involving the application of extremely complex methods to optimize the kinetic parameters (Cai et al., 2013).

PYROLYSIS KINETICS OF AN AMAZONIAN BIOMASS: A CASE STUDY

Considering the lack of information about the kinetic behavior of Brazilian native biomasses under pyrolysis, the purpose of this case study is to apply the theoretical foundations presented in the "Background" section to Brazil nut woody shell. Through the use of thermogravimetric analysis, integral and differential global isoconversional methods, and also multistep fitting models (considering three and four independent reactions) will be applied.

This biomass was selected because its consumption in the Amazon region forms a great quantity of residues that are usually discharged as wastes and could be used to generate biofuels in isolated communities where this biomass is abundant and the energy supply is still unsound. Therefore, this case study provides ways to remedy a social impairment observed in a historically disadvantaged area, generating local income with reduced environmental impacts.

Materials and Properties

The Amazonian biomass selected for this work was *Bertholletia excelsa* Humboldt & Bonpland (Brazil nut) woody shell. As its nuts already present an established regional market, only the part that is considered an agricultural residue was used.

Table 2. Recent kinetics biomass studies considering TGA conditions, modeling and parameters

Reference	*TGA* conditions	Biomass	Model	Parameters	
	Sample mass Heating rate Temperature range			*E* (kJ/mol)	log A (s^{-1})
Becidan et al. (2007)	2.5-5 mg 5, 10 and 20 °C/min 23-600°C	Wood, coffee, and brewery grain wastes	1-step IPRS	76.0-206.0	2.5-16.4
			n-step IPRS	81.0-214.0	5.3-17.6
			3-step DAEM	175.0-236.0	12.6-20.9
Ye et al. (2010)	10 mg 10, 30 and 50 °C/min 25-800°C	Maize straw	KAS	130.1-156.0	14.2-23.7
			OFW	132.3-157.8	14.7-24.0
Cardoso et al. (2011)	6 mg 5, 10,15,20, 25,40, 50°C/min 100-900 °C	Tobacco waste Sorghum bagasse	Ozawa	77.7-132.0 80.5-138.4	- -
			n-step IPRS	39.7-272.0 35.7-220.0	5.2-36.8 6.7-32.1
Nascimento (2012)	2.5-10 mg 5, 10, 20, and 40°C/min 25-900 °C	Brazil nut woody shell *Sapucaia* nut woody shell *Tucumã* endocarp	Ozawa	129.9-143.6 96.6-150.2 129.1-158.2	14.9-19.0 11.7-21.7 16.5-21.3
			KS	131.3-138.9 135.1-142.9 128.5-142.7	15.4-20.1 17.5-20.8 15.4-20.1
Sánchez-Silva et al. (2012)	10 mg 5, 15, and 40 °C/min 25-900 °C	Fir wood *Eucalyptus* bark Pine bark	n-step IPRS	95.6-154.2 57.1-202.8 91.4-166.4	13.9-14.8 8.4-13.9 12.90-14.0
		Pure components		HC: 94.1-181.4 C: 191.3 L: 88.9-99.1	13.3-14.2 14.54 8.6-13.8
Cai et al. (2013)	5 mg 10 and 20 °C/min 25-900 °C	Rice straw	3-step DAEM	HC: 187.3 C: 204.4 L: 242.6	13.1 13.8 15.9
Anca-Couce et al. (2014)	3-20 mg 1, 2.5, 3, 5, 10,20, 80 and 108 °C/min 25-500 °C	Four different beech woods Three kinds of pine wood	KAS	145.6-203.9	-
			KS	127.0-313.9	-
			n-step IPRS	HC: 122.5-153.4 C: 178.6-190.2 L: 70.8-203.0	8.1-14.4 9.7-13.5 1.7-15.1
Ceylan and Topçu (2014)	10 mg 5, 10, and 20 °C/min 20-1000 °C	Hazelnut husk	KAS	95.0-162.0	4.8-22.8
			OFW	102.5-161.5	5.4-22.9

Brazil nut woody shell was obtained by Nascimento (2012) in *Aninga* community (–2°40’42.34” S × –56°46’32.35” W), located in *Parintins* city, Amazon State, Brazil. The main properties of the particles obtained by Nascimento (2012) are presented in the Table 3. The mean Sauter diameter selected was around 500 µm because it was considered small enough to avoid the effects of heat and mass transfer between particles (Cai et al., 2013).

The residue presented significant volatile matter content, which facilitates the overall biomass decomposition. Also, present low ash content, which is interesting when regarding thermal conversion processes since elevated contents of inorganics can cause operational inconveniences such as corrosion and fouling (McKendry, 2002). In addition, the samples presented a predominance of carbon and oxygen in their constitution, and lower (LHV) and higher heating values (HHV) up to 20 MJ/kg.

Table 3. Physical, chemical and thermal properties of the Brazil nut woody shell (adapted from Nascimento, 2012)

Properties	**Brazil nut woody shell**
Physical analyses	
Mean Sauter diameter (µm)	499±3.16
Apparent density (kg/m^3)	853.95
True density (kg/m^3)	1458.87±0.54
Sphericity	0.66±0.09
Moisture (wt% wet basis)	7.81 ± 0.01
Ultimate analysis **(wt% dry basis)**	
C	46.42±0.27
N	0.20±0.04
H	6.18±0.19
O	46.84±0.42
Proximate analysis **(wt% dry basis)**	
Volatile matter	86.27 ± 0.25
Ash	0.37 ± 0.06
Fixed carbon	13.36 ± 0.24
Heating value **(MJ/kg)**	
HHV	20.02±0.36
LHV	16.75±0.33

Experimental Set-Up

A thermogravimetric analyzer (Shimadzu Corp., TGA-50, Japan) was used by Nascimento (2012) to perform the thermal decomposition experiments with an uncertainty of 0.001 mg. The samples were placed in an open sample platinum pan (6 mm internal diameter and 2.5 mm depth) with initial masses of 10.06±0.04 mg.

The temperature was controlled from room temperature (~25 °C) up to 900 °C, at heating rates of

5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min. The remaining mass data was acquired with a time step of 5 seconds. High purity nitrogen (99.996%) at a flow rate of 50 mL/min was used. The equipment was purged with nitrogen 10 min before starting each run in order to avoid the samples oxidation.

Analysis and Data Processing

The thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) curves were analyzed using the TA-50WS software from Shimadzu Corporation (version 1.17). The mass data from TGA/DTG were normalized by equation (2a). The kinetic parameters, activation energy, pre-exponential factor and reaction order were calculated using the program MS Excel (version 2007, KB2887324 32-Bit Edition).

Kinetic Modeling

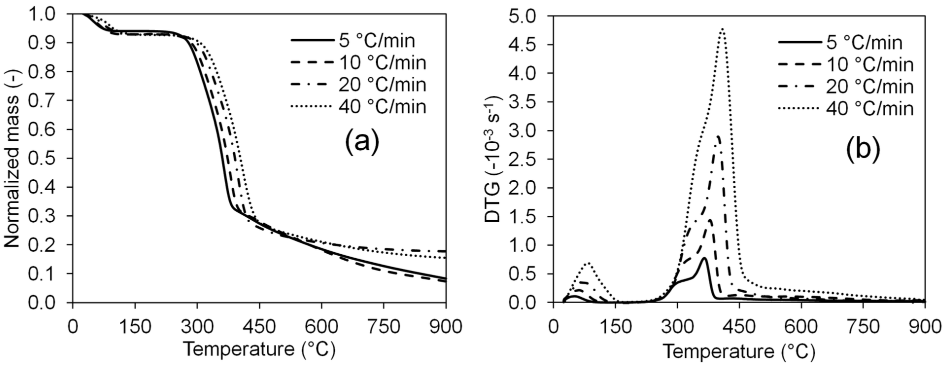
In this case study, two modeling approaches were used to estimate the kinetic parameters, isoconversional and independent parallel models. Firstly, the integral methods of Ozawa-Flynn-Wall (OFW) and modified Coats-Redfern (MCR), as well as the differential method of Friedman (FD) were applied. These isoconversional methods were selected due to their simplicity and their common adoption in the literature (see section "Biomass Kinetic Modeling"). Secondly, the parameters were also determined using three- and four-step independent parallel reaction schemes (see section "Fitting Models").

Results and Discussion

Thermal Analysis

Thermogravimetric (TGA) and the derivative thermogravimetric analysis (DTG) were used to investigate the thermal behavior and kinetics of the Brazil nut woody shell in an inert atmosphere, as shown in Figure 5 for four heating rates (5, 10, 20, and 40 °C/min).

Figure 5. Thermogravimetric analysis (a), and the derivative thermogravimetry (b) of the Brazil nut woody shell (adapted from Nascimento, 2012)



In the temperature interval between room temperature and 150 °C, in Figure 5(a), it was observed a decrease in the normalized mass of 6.0%, 7.16%, 7.11%, and 7.23% for the heating rates of 5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min, respectively. These results are attributed to the release of water and extractives, being also associated to the first peak in the DTG presented in Figure 5(b). In the temperature range of 150-230 °C, it was not registered a considerable decrease in the normalized mass (< 1%).

However, in Figure 5(a) it was observed the highest decrease in the normalized mass between 230 °C and 450 °C being related to the main decomposition of hemicellulose and cellulose, and part of the lignin (Di Blasi, 2008). In this temperature range, the mass released was 61.0%, 60.84%, 64.89%, and 62.77% for each increasing heating rates, respectively. The hemicellulose and cellulose decomposition reactions are characterized by a shoulder and a peak in the DTG curve, presented in Figure 5(b).

At temperatures above 400 °C the decomposition of more stable intermediates of lignin and also secondary reactions between phases occurred (gaseous, liquid and solid products), affecting the normalized mass at the end of analysis. The final residues in the thermogravimetric analysis (Figure 5a) were 8.42%, 7.39%, 17.82%, and 15.57% for the increasing heating rates, respectively.

Isoconversional Methods Application

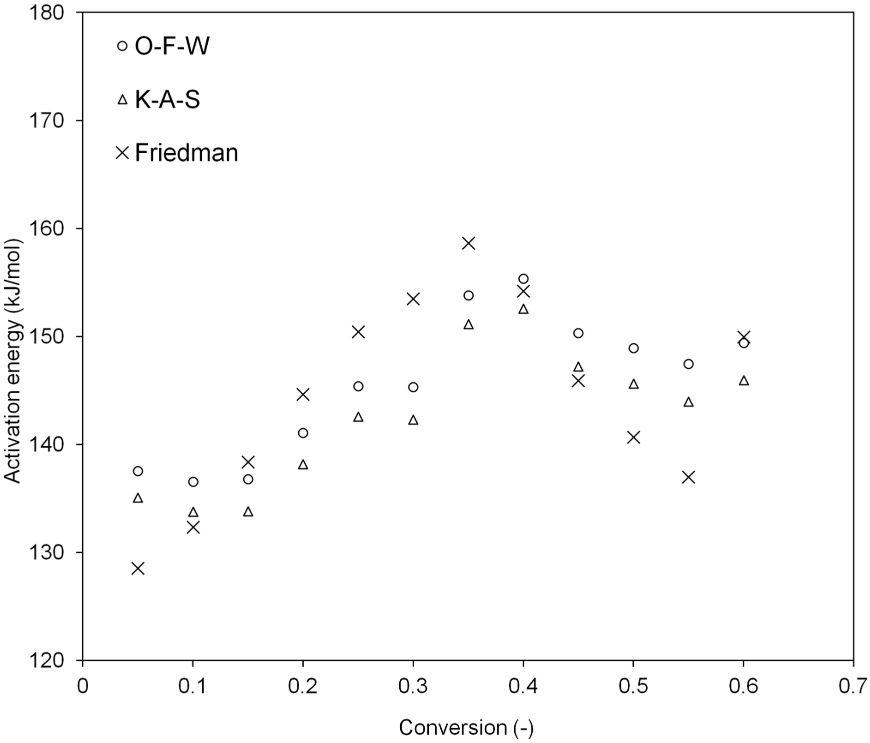
The isoconversional methods of Ozawa-Flynn-Wall (OFW), modified Coats-Redfern (MCR), and Friedman (FD) were used to estimate the apparent activation energy (E) through the linearization methods presented in Table 1. The remaining masses, W, from TGA curves, were normalized by equation (2a). The range of conversions between 0.05 and 0.6 was selected, relating to the main decomposition region. The conversions above 0.60 were related to the lignin decomposition, i.e., temperatures above 450°C.

$$W=1-\alpha=1-[(m_0-m_t)/m_0] \tag{2a}$$

The comparison of the results obtained by OFW, MCR and FD methods presented slight differences. The activation energies for the MCR method were lower than the obtained by OFW with differences of about 2 kJ/mol, as observed by Ceylan and Topçu (2014), Rueda-Ordóñez et al. (2013), Yao et al. (2008), and Ye et al. (2010). The activation energies obtained by the Friedman method presented low accuracy, since the derivative data was determined by numerical and smoothing methods that generated errors. Therefore, the FD results were not taken into account.

Figure 6. presents the E as a function of conversion (α) for Brazil nut woody shell. In order to analyze this dependency α was divided into three regions, $0.05 \leq \alpha_1 \leq 0.15$, $0.15 < \alpha_2 \leq 0.40$, $0.40 < \alpha_3 \leq 0.60$, respectively.

Figure 6. Apparent activation energy as a function of conversion for Brazil nut woody shell



The *E* for the first and third conversion ranges were practically constant. For the first range, the *E* values were 136.95±0.52 kJ/mol and 134.24±0.75 kJ/mol, for the OFW and MCR methods, respectively. The temperatures range associated with these conversions (280 – 320 °C) was attributed to the dominant reactions of hemicellulose. Considering the third range, the *E* values were 149.02±1.20 kJ/mol and 145.70±1.33 kJ/mol, for the OFW and MCR methods, respectively, and the associated temperature range (360 – 420 °C) was attributed mainly to the reaction of cellulose. In the second conversion range, the *E* is linearly dependent on α, as shown by Equation (25). The temperature range associated with these conversions (320 – 360 °C) was attributed to both hemicellulose and cellulose.

$$E=125.70+74.89\alpha \quad 0.15<\alpha_2\leq 0.40 \tag{25}$$

Equation (25) presents a correlation coefficient of 0.9497 and was determined using the values obtained by the OFW method, considered by the authors of this work as the most reliable isoconversional method. Furthermore, the MCR method follows the same trend; therefore, the slopes are practically the same for both methods.

As observed in the investigations of Cardoso et al. (2011), Rueda-Ordóñez et al. (2013), and Yao et al. (2008), the thermal degradation of lignocellulosic biomass is not well modeled by a global kinetic approach. The clear dependency of *E* on α indicates that the determined kinetic parameters can be considered just rough estimates, and that multistep kinetic models have to be considered in order to obtain values indeed representative.

Independent Parallel Reaction Scheme (IPRS) Method Application

This section was divided into two parts considering three and four independent parallel reactions, where the initial values were obtained using the Ozawa-Flynn-Wall method, considering hemicellulose and cellulose reactions (137 kJ/mol and 149 kJ/mol, respectively). The pre-exponential factor, reaction order and volatile fraction released here determined were assumed more as fitting variables rather than as physically meaningful values.

Three Reactions Approach

Three independent parallel reactions, one for each main biomass pseudo-component, hemicellulose (HM), cellulose (C), and lignin (L) were taken into account in this approach. All reactions were considered to be represented by an n^{th} order mechanism function and, as presented in the section "Reaction Mechanism", this function is the most commonly used to investigate biomass. The Euler's method was used to solve the conversion rate function presented in equation (4) and the data was fitted with the least square method.

Table 4. presents the kinetic parameters estimated by the independent parallel reaction approach using three- and four-reaction schemes. The kinetic parameters obtained with the three-reaction approach presented low variation among the heating rates. The fit was evaluated with the equation (22) and remained lower than 5%, as recommended by Órfão et al. (1999), with values of 2.88%, 2.90%, 3.83%, and 0.91% for the heating rates of 5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min.

The apparent activation energy (*E*) for hemicellulose remained 133.7 kJ/mol with variations lower than 0.1% between the results obtained at different heating rates. Cellulose presented the same behavior, for which the apparent activation energy was 149.79 kJ/mol, what is 15 kJ/mol higher than the *E* for hemicellulose. These parameters are in agreement with the investigation of White et al. (2011), who concluded that the hemicellulose and cellulose activation energies are in the range of 194.0 – 250.0 kJ/mol, and 105.0 – 253.5 kJ/mol, respectively. The activation energy for hemicellulose is lower than for cellulose due to its structure and intermolecular bonds, since the existence of amorphous regions causes the decomposition to carry on in a lower energy level. However, the *E* determined for lignin (147.79 kJ/mol) is almost as high as the *E* for cellulose (149.79 kJ/mol). Comparing this result with the one for pure lignin (89-99 kJ/mol) obtained by Sánchez-Silva et al. (2012), the activation energy is much superior, basically due to the chemical interactions among the main components. The pre-exponential factor (*A*), presented in logarithmic form, remained about 9 log s^{-1} for all pseudo-components, and the reaction order (*n*) remained about 1.0 for the hemicellulose and cellulose. Those

Table 4. Kinetic parameters determined using three- and four-step independent parallel reaction scheme

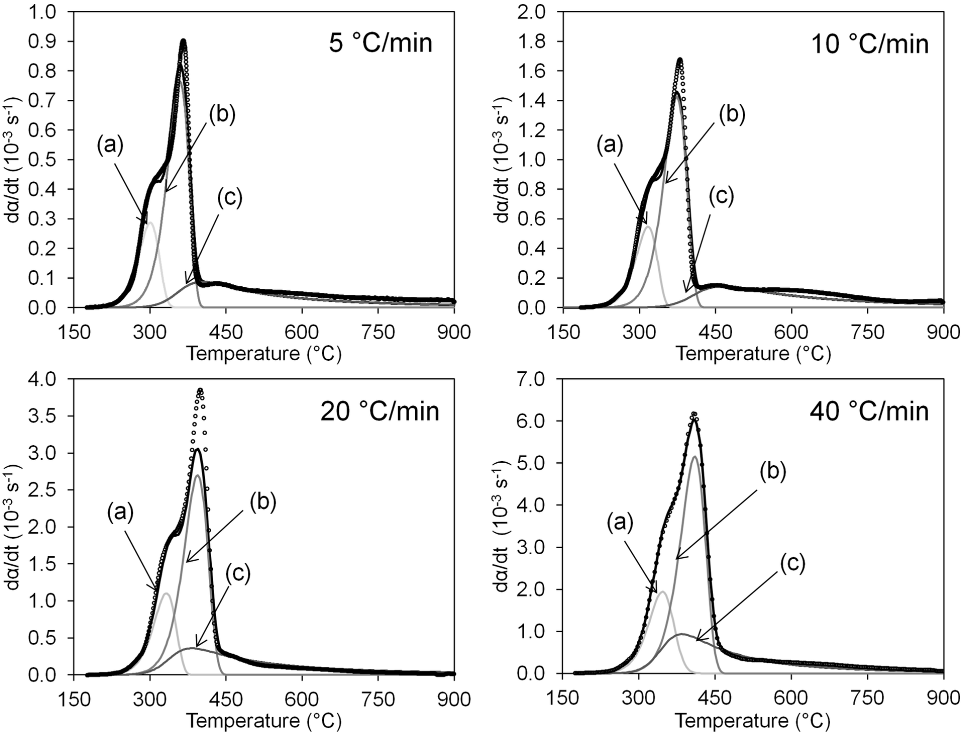
Component	E (kJ/mol)	log A (s^{-1})	n (-)	c (-)
Three reactions approach				
HC	133.69 ± 0.01	9.73 ± 0.04	1.06 ± 0.10	0.18 ± 0.01
C	149.79 ± 0.03	9.91 ± 0.06	1.00 ± 0.03	0.50 ± 0.01
L	147.79 ± 0.74	9.10 ± 0.96	9.13 ± 1.31	0.32 ± 0.01
Four reactions approach				
HC	133.70 ± 0.01	9.74 ± 0.04	1.03 ± 0.05	0.18 ± 0.01
C	149.79 ± 0.03	9.91 ± 0.06	1.00 ± 0.03	0.50 ± 0.00
L_1	79.80 ± 0.23	3.65 ± 0.63	1.87 ± 0.96	0.18 ± 0.01
L_2	148.50 ± 0.05	7.13 ± 1.50	5.33 ± 1.17	0.15 ± 0.02

values are in agreement with the literature, as shown in Table 2. Considering lignin, the *n* presented an oddly high value, indicating that this reaction may deviate from the experimental data.

The conversion rates as function of temperature, at all heating rates, are shown in Figure 7. The different shapes of the curves reflect the contents of each pseudo-component of biomass (Anca-Couce et al., 2014) and can also represent the occurrence of interactions, which-could affect the reaction pattern. These interactions were studied by Liu et al. (2011), who investigated the influence of different pseudo-components mass fractions in the pyrolysis (TGA), and its interactions for generic biomasses determined by a simplex-lattice design. The authors have observed that the interactions can modify *E*, providing different values for each generic biomass. The interactions between lignin and hemicellulose, and hemicellulose and cellulose fractions were found to be fairly intense.

In Figure 7, it is possible to observe that the overlapping of hemicellulose and cellulose reactions intersects at around 330 °C, forming a peak and a shoulder. As

Figure 7. Conversion rate curve of Brazil nut woody shell for n^th^ order three-step IPRS. Theoretical data as solid lines, experimental as symbols (o). Hemicellulose (a), cellulose (b), and lignin (c)



the heating rates increase, there is a shift of the overall conversion rate to the right. The curves at heating rates higher than 10 °C/min presented a displacement of the lignin peak to the left, curve (c), increasing the overlapping effect with cellulose. At all heating rates, the theoretical and experimental data are in agreement up to 300 °C while for higher temperatures the theoretical curves are clearly underestimated, indicating that this model was not the most accurate.

Concluding, the use of three-step IPRS model provided satisfactory results for the hemicellulose and cellulose fractions. Nevertheless, the lignin theoretical data was not in a good agreement with the experiments, and the simulated data was underestimated at temperatures higher than 500 °C. In order to obtain results with a better agreement, it was proposed to divide the lignin contribution in two separate reactions.

Four Reactions Approach

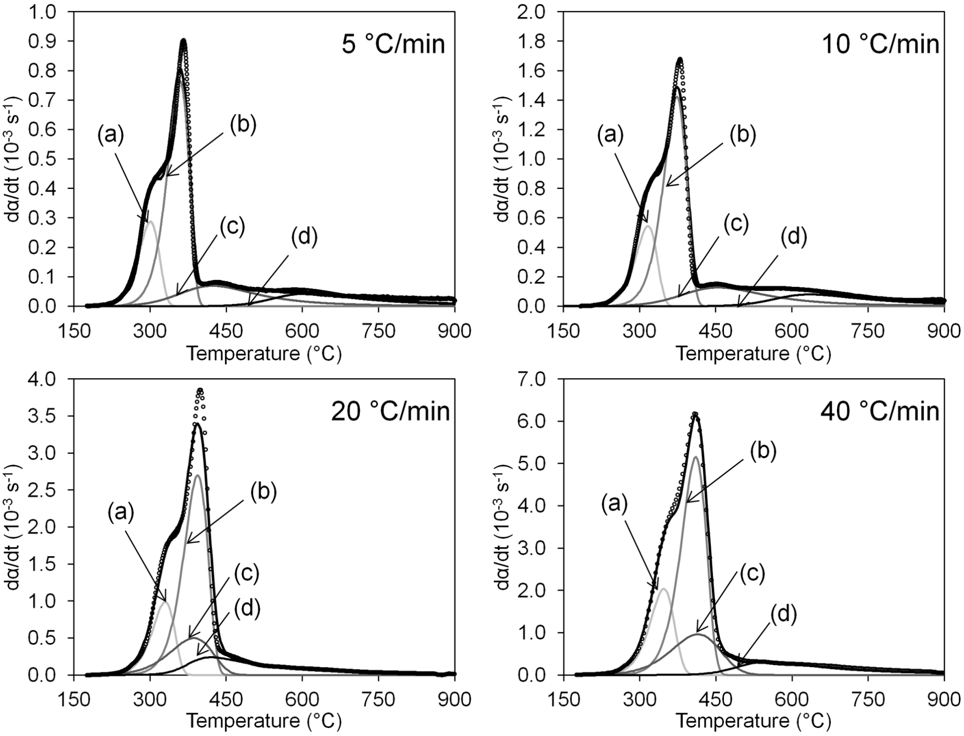
In the four-step IPRS, the lignin was considered to be represented by two distinct parallel reactions, namely L_1 and L_2. The new kinetic parameters are presented in the Table 4. The fit applying this approach were 2.72%, 2.67%, 2.66%, and 1.51% for the heating rates of 5 °C/min, 10 °C/min, 20 °C/min, and 40 °C/min.

The kinetic parameters related to hemicellulose and cellulose remained practically the same as the ones obtained with the three-step IPRS. The activation energy (*E)* for the L_1 reaction was approximately

80 kJ/mol. This value is in agreement with those of lignin activation energy commonly encountered in literature (Anca-Couce et al., 2014; Sánchez-Silva et al., 2012; White et al., 2011). However, the *E* for the L_2 reaction was approximately 150 kJ/mol and higher than the one evaluated with the three-step IPRS (Table 4). The pre-exponential factor (*A*) remained nearly the same for hemicellulose and cellulose, and was 3.65 log s^{-1} and 7.13 log s^{-1} for L_1 and L_2, respectively. The reaction order (*n*) oscillated between 1 and 2 for the hemicellulose, cellulose, and L_1 fractions, and for L_2 a fifth-order reaction was obtained. The conversion rates as a function of temperature, at all heating rates, are shown in Figure 8.

In Figure 8, in the temperature range between 150 – 400 °C, the behavior of the simulated curves at all heating rates was nearly the same observed in the three-step IPRS. In this range, hemicellulose and cellulose were almost completely decomposed. At temperatures above 400 °C, the reactions were mainly related to lignin. In addition, between 420 – 480 °C there is a slight underestimation of the theoretical data for lignin but, despite that, a much better agreement was obtained, comparatively to the same reaction in the three-step IPRS. As these differences were little representative, they were considered negligible, since the average deviation was lower than the obtained with the three reactions approach.

Figure 8. Conversion rate curve of Brazil nut woody shell for nth order four-step IPRS. Theoretical data as solid lines, experimental as symbols (o). Hemicellulose (a), cellulose (b), L_1 (c), and L_2 (d)



To summarize, the use of a four-step IPRS provided very good results, better than the ones obtained with the three-step IPRS, as reflected in the average deviation calculated for each pseudo-component. These results are in agreement with the obtained by Becidan et al. (2007).

FUTURE RESEARCH DIRECTIONS

Firstly, the TGA experiments at heating rates lower than 5 °C/min should be applied to biomass pyrolysis in order to improve the visibility of the remaining pseudo-components, with special consideration to the lignin fraction, which minimizes the overlapping effects. Secondly, it is suggested to evaluate other models, such as DAEM and IPRS with different reactions schemes balancing their complexity levels considering the lowest average deviations. These different schemes could be associated with the heat transfer, regarding the pyrolysis heat flow in a realistic manner analyzing the endothermic and exothermic reaction zones provided by DSC experiments. Furthermore, it is advisable to search new mathematical methods in order to determine parameters with the use of differential evolution algorithms with efficient and faster calculations. Finally, a parametric sensitivity analysis should be helpful in providing a wider perspective of the reaction mechanism.

CONCLUSION

The most relevant studies published concerning biomass pyrolysis kinetics were reviewed. Pyrolysis is a thermal process in which solid biomass is readily converted into biofuels with a higher energy density. The study of this process kinetics is important to optimize the process, to evaluate the energy requirement, and to design and operate industrial reactors. Experimentally, thermogravimetric analysis (TGA) and its derivative (DTG) are the most commonly analytical procedures used in kinetic evaluations.

Lignocellulosic biomass is the main renewable raw material to be used in sustainable bio-refineries, being mainly composed by variable quantities of hemicellulose (25–35%wt), cellulose (30–40%wt), and lignin (25–35%wt). These components present decomposition temperature ranges of 225 – 325 °C, 325 – 375 °C, and 250 – 500 °C, respectively. Nonetheless, with the use of TGA and DTG on kinetics research, studies of biomass pyrolysis determined activation energy (*E*) ranges for hemicellulose, cellulose, and lignin were 194.0 – 250.0 kJ/mol, 105.0 – 253.5 kJ/mol, and 26.0 – 60.0 kJ/mol, respectively.

In addition, no consensus has been reached about the most adequate kinetic model to be used. Among the most commonly reaction schemes encountered in the literature, the global and independent parallel schemes were most widely applied to calculate the kinetic parameters. However, because of the biomass complex structure, the parameters obtained by global models can only be used as initial approximations for subsequent calculations, what is necessary when more tangled models are used. The independent parallel reactions model is an example and considers separate reaction for each main component of biomass, generating accurate results and showing a versatility that allows its application to any kind of lignocellulosic material.

The Amazon rainforest is a rich region in terms of variety of biomass, as the Brazil nut woody shell. This biomass presents characteristics, such as availability, low ash content, low moisture content and other physical and thermal properties, which make it suitable for a thermal conversion process. In order to exemplify, a case study of the pyrolysis kinetics of Brazil nut woody shell was performed. The isoconversional models of Ozawa-Flynn-Wall, modified Coats-Redfern, and Friedman were applied as a first approach to provide the apparent activation energies used as initial values in the IPRS application. Handling the four-step IPRS reached accurate results throughout the entire experimental temperature range. Nonetheless, between 420 – 480 °C, it has been observed a negligible underestimation of the theoretical data. The four-step IPRS was found to be suitable for the kinetic description of different lignocellulosic residues submitted to pyrolysis, improving the understanding of this phenomenon.

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REFERENCES

Abbasi, T., & Abbasi, S. A. (2010). Biomass energy and the environmental impacts associated with its production and utilization. *Renewable & Sustainable Energy Reviews*, *14*(3), 919–937. doi:10.1016/j.rser.2009.11.006

Aboulkas, A., & El Harfi, K. (2008). Study of the Kinetics and Mechanisms of Thermal Decomposition of Moroccan Tarfaya Oil Shale and Its Kerogen. *Oil Shale*, *25*(4), 426–443. doi:10.3176/oil.2008.4.04

Anca-Couce, A., Berger, A., & Zobel, N. (2014). How to determine consistent biomass pyrolysis kinetics in a parallel reaction scheme. *Fuel*, *123*, 230–240. doi:10.1016/j.fuel.2014.01.014

Basu, P. (2010). *Biomass Gasification and Pyrolysis Practical Design and Theory. Elsevier* (pp. 1–364). Kidlington, Oxford: Academic Press.

Becidan, M., Várhegyi, G., Hustad, J. E., & Skreiberg, Ø. (2007). Thermal decomposition of biomass wastes. A kinetic study. *Industrial & Engineering Chemistry Research*, *46*(8), 2428–2437. doi:10.1021/ie061468z

Bradbury, A. G. W., Sakai, Y., & Shafizadeh, F. (1979). A kinetic model for pyrolysis of cellulose. *Journal of Applied Polymer Science*, *23*(11), 3271–3280. doi:10.1002/app.1979.070231112

Branca, C., & Di Blasi, C. (2013). Char structure and combustion kinetics of a phenolic-impregnated honeycomb material. *Industrial & Engineering Chemistry Research*, *52*(41), 14574–14582. doi:10.1021/ie402470z

Braun, R. L., Burnham, A. K., Reynolds, J. G., & Clarkson, J. E. (1991). Pyrolysis kinetics for lacustrine and marine source rocks by programmed micropyrolysis. *Energy & Fuels*, *5*(1), 192–204. doi:10.1021/ef00025a033

Broido, A. (1976). Kinetics of solid-phase cellulose pyrolysis. In F. Shafizadeh, K. V. Sarkanen, & D. A. Tillman (Eds.), *Thermal uses and properties of carbohydrates and lignins* (pp. 19–36). New York: Academic Press. doi:10.1016/B978-0-12-637750-7.50006-6

Cai, J., Wu, W., Liu, R., & Huber, G. W. (2013). A distributed activation energy model for the pyrolysis of lignocellulosic biomass. *Green Chemistry*, *15*(5), 1331–1340. doi:10.1039/c3gc36958g

Cardoso, C. R., Miranda, M. R., Santos, K. G., & Ataíde, C. H. (2011). Determination of kinetic parameters and analytical pyrolysis of tobacco waste and sorghum bagasse. *Journal of Analytical and Applied Pyrolysis*, *92*(2), 392–400. doi:10.1016/j.jaap.2011.07.013

Ceylan, S., & Topçu, Y. (2014). Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresource Technology*, *156*, 182–188. doi:10.1016/j.biortech.2014.01.040 PMID:24508656

Chen, D., Zheng, Y., & Zhu, X. (2013). In-depth investigation on the pyrolysis kinetics of raw biomass. Part I: Kinetic analysis for the drying and devolatilization stages. *Bioresource Technology*, *131*, 40–46. doi:10.1016/j.biortech.2012.12.136 PMID:23340100

Chen, H., Liu, N., & Fan, W. (2006). Two-step consecutive reaction model and kinetic parameters relevant to the decomposition of Chinese forest fuels. *Journal of Applied Polymer Science*, *102*(1), 571–576. doi:10.1002/app.24310

Coats, A. W., & Redfern, J. P. (1965). Kinetic parameters from thermogravimetric data. II. *Journal of Polymer Science. Part B: Polymer Letters*, *3*(11), 917–920. doi:10.1002/pol.1965.110031106

Demirbas, M. F., & Balat, M. (2007). Biomass pyrolysis for liquid fuels and chemicals: A review. *Journal of Scientific and Industrial Research*, *66*(10), 797–804.

Di Blasi, C. (2008). Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science*, *34*(1), 47–90. doi:10.1016/j.pecs.2006.12.001

Doyle, C. D. (1961). Kinetic Analysis of Thermogravimetric Data. *Journal of Applied Polymer Science*, *5*(15), 285–292. doi:10.1002/app.1961.070051506

Ebrahimi-Kahrizsangi, R., & Abbasi, M. H. (2008). Evaluation of reliability of Coats-Redfern method for kinetic analysis of non-isothermal TGA. *Transactions of Nonferrous Metals Society of China*, *18*(1), 217–221. doi:10.1016/S1003-6326(08)60039-4

Fiori, L., Valbusa, M., Lorenzi, D., & Fambri, L. (2012). Modeling of the devolatilization kinetics during pyrolysis of grape residues. *Bioresource Technology, 103*(1), 389–397. doi:. 09.11310.1016/j.biortech.2011

Flynn, J. H., & Wall, L. A. (1966). General Treatment of the Thermogravimetry of Polymers. *Journal of Research of the National Bureau of Standards*, *70*(6), 487–523. doi:10.6028/jres.070A.043

Friedman, H. L. (1964). Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *Journal of Polymer Science Part C: Polymer Symposia*, *6*(1), 183–195. doi:10.1002/polc.5070060121

Grønli, M. G., Várhegyi, G., & Di Blasi, C. (2002). Thermogravimetric analysis and devolatilization kinetics of wood. *Industrial & Engineering Chemistry Research*, *41*(17), 4201–4208. doi:10.1021/ie0201157

Güneş, M., & Güneş, S. (2002). A direct search method for determination of DAEM kinetic parameters from nonisothermal TGA data (note). *Applied Mathematics and Computation*, *130*(2-3), 619–628. doi:10.1016/S0096-3003(01)00124-2

Horowitz, H. H., & Metzger, G. (1963). A new analysis of thermogravimetric traces. *Analytical Chemistry*, *35*(10), 1464–1468. doi:10.1021/ac60203a013

Kajaste, R. (2014). Chemical from biomass-managing greenhouse gas emissions in biorefinery production chains-a review. *Journal of Cleaner Production*, *75*, 1–10. doi:10.1016/j.jclepro.2014.03.070

Kissinger, H. E. (1957). Reaction kinetics in differential thermal analysis. *Analytical Chemistry*, *29*(11), 1702–1706. doi:10.1021/ac60131a045

Lanzetta, M., & Di Blasi, C. (1998). Pyrolysis kinetics of wheat and corn straw. *Journal of Analytical and Applied Pyrolysis*, *44*(2), 181–192. doi:10.1016/S0165-2370(97)00079-X

Lisbôa, A. C. L., & Watkinson, A. P. (1999). Operating conditions for oil shale thermogravimetry. *Powder Technology*, *101*(2), 151–156. doi:10.1016/S0032-5910(98)00166-1

Liu, Q., Zhong, Z., Wang, S., & Luo, Z. (2011). Interactions of biomass components during pyrolysis: A TG-FTIR study. *Journal of Analytical and Applied Pyrolysis, 90*(2), 213–218. doi:. 2010.12.00910.1016/j.jaap

Lu, C., Song, W., & Lin, W. (2009). Kinetics of biomass catalytic pyrolysis. *Biotechnology Advances*, *27*(5), 583–587. doi:10.1016/j.biotechadv.2009.04.014 PMID:19393731

Lua, A. C., & Su, J. (2006). Isothermal and non-isothermal pyrolysis kinetics of Kapton® polyimide. *Polymer Degradation & Stability*, *91*(1), 144–153. doi:10.1016/j.polymdegradstab.2005.04.021

McKendry, P. (2002). Energy production from biomass (part 1): Overview of biomass. *Bioresource Technology*, *83*(1), 37–46. doi:10.1016/S0960-8524(01)00118-3 PMID:12058829

Menon, V., & Rao, M. (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*, *38*(4), 522–550. doi:10.1016/j.pecs.2012.02.002

Mettler, M. S., Vlachos, D. G., & Dauenhauer, P. J. (2012). Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy and Environmental Science, 5*(7), 7797–7809. doi: 79E10.1039/C2EE216

Nascimento, V. F. (2012). *Caracterização de biomassas amazônicas-ouriço de castanha do brasil, ouriço de sapucaia e caroço do fruto do tucumã-visando sua utilização em processos de termoconversão.* (Master dissertation). Retrieved from Acervus Unicamp dissertations and Theses database. (T/UNICAMP N17C)

Orfão, J. J. M., Antunes, F. J. A., & Figueiredo, J. L. (1999). Pyrolysis kinetics of lignocellulosic materials - three independent reactions model. *Fuel*, *78*(3), 349–358. doi:10.1016/S0016-2361(98)00156-2

Ozawa, T. (1965). A new method of analizing thermogravimetric data. *Bulletin of the Chemical Society of Japan*, *38*(11), 1881–1886. doi:10.1246/bcsj.38.1881

Parthasarathy, P., & Narayanan, S. K. (2014). Determination of kinetic parameters of biomass samples using thermogravimetric analysis. *Environmental Progress & Sustainable Energy*, *33*(1), 256–266. doi:10.1002/ep.11763

Pella, E., & Colombo, B. (1973). Study of carbon, hydrogen and nitrogen determination by combustion-gas chromatography. *Mikrochimica Acta*, *61*(5), 697–719. doi:10.1007/BF01218130

Pippo, W. A., Luengo, C. A., Alberteris, L. A. M., Garzone, P., & Cornacchia, G. (2011). Energy recovery from sugarcane-trash in the light of 2nd generation biofuels. Part 1: Current situation and environmental aspects. *Waste and Biomass Valorization*, *2*(1), 1–16. doi:10.1007/s12649-010-9048-0

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., & Sommariva, S. (2008). Chemical Kinetics of Biomass Pyrolysis. *Energy & Fuels*, *22*(6), 4292–4300. doi:10.1021/ef800551t

Rueda-Ordóñez, Y. J., Olivares-Gómez, E., & Tannous, K. (2013). Thermogravimetric study and kinetic analysis of sugarcane straw. In *Proceedings of the 22nd International Congress of Mechanical Engineering* (*COBEM, 2013*). Ribeirão Preto, SP, Brazil. ABCM.

Sanchez, M. E., Otero, M., Gómez, X., & Morán, A. (2009). Thermogravimetric kinetic analysis of the combustion of biowastes. *Renewable Energy*, *34*(6), 1622–1627. doi:10.1016/j.renene.2008.11.011

Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P., & Valverde, J. L. (2012). Thermogravimetric-mass spectrometry analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technology*, *109*, 163–172. doi:10.1016/j.biortech.2012.01.001 PMID:22297048

Sbirrazzuoli, N., Vincent, L., Mija, A., & Guigo, N. (2009). Integral, differential and advanced isoconversional methods - Complex mechanisms and isothermal predicted conversion–time curves. *Chemometrics and Intelligent Laboratory Systems, 96*(2), 219–226. doi:. 02.00210.1016/j.chemolab.2009

Starink, M. (1996). A new method for the derivation of activation energies from experiments performed at constant heating rate. *Thermochimica Acta*, *288*(1-2), 97–104. doi:10.1016/S0040-6031(96)03053-5

Tang, W., Liu, Y., Zhang, H., & Wang, C. (2003). New approximate formula for Arrhenius temperature integral. *Thermochimica Acta*, *408*(1-2), 39–43. doi:10.1016/S0040-6031(03)00310-1

Tonbul, Y. (2008). Pyrolysis of pistachio shell as a biomass. *Journal of Thermal Analysis and Calorimetry*, *91*(2), 641–647. doi:10.1007/s10973-007-8428-6

Van de Velden, M., Baeyens, J., Brems, A., Janssens, B., & Dewil, R. (2010). Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy*, *35*(1), 232–242. doi:10.1016/j.renene.2009.04.019

Van Krevelen, D., Van Heerden, C., & Huntjens, F. (1951). Physicochemical aspects of the pyrolysis of coal and related organic compounds. *Fuel*, *30*, 253–259.

Várhegyi, G., Antal, M. J. Jr, Jakab, E., & Szabó, P. (1997). Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *42*(1), 73–87. doi:10.1016/S0165-2370(96)00971-0

Várhegyi, G., Antal, M. J. Jr, Szekely, T., & Szabó, P. (1989). Kinetics of the thermal decomposition of cellulose, hemicellulose, and sugar cane bagasse. *Energy & Fuels*, *3*(3), 329–335. doi:10.1021/ef00015a012

Várhegyi, G., Czégény, Z., Jakab, E., McAdam, K., & Liu, C. (2009). Tobacco pyrolysis. Kinetic evaluation of thermogravimetric–mass spectrometric experiments. *Journal of Analytical and Applied Pyrolysis*, *86*(2), 310–322. doi:10.1016/j.jaap.2009.08.008

Várhegyi, G., Jakab, E., & Antal, M. J. Jr. (1994). Is the Broido-Shafizadeh model for cellulose pyrolysis true? *Energy & Fuels*, *8*(6), 1345–1352. doi:10.1021/ef00048a025

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913–933. doi:10.1016/j.fuel.2009.10.022

Vassilev, S. V., Baxter, D., Andersen, L. K., Vassileva, C. G., & Morgan, T. J. (2012). An overview of the organic and inorganic phase composition of biomass. *Fuel, 94*, 1–33. doi:. 2011.09.03010.1016/j.fuel

Vlaev, L. T., Markovska, I. G., & Lyubchev, L. A. (2003). Non-isothermal kinetics of pyrolysis of rice husk. *Thermochimica Acta*, *406*(1–2), 1–7. doi:10.1016/S0040-6031(03)00222-3

Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., & Sbirrazzuoli, N. (2011). ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica Acta*, *520*(1–2), 1–19. doi:10.1016/j.tca.2011.03.034

Wanjun, T., Cunxin, W., & Donghua, C. (2005). Kinetic studies on the pyrolysis of chitin and chitosan. *Polymer Degradation & Stability*, *87*(3), 389–394. doi:10.1016/j.polymdegradstab.2004.08.006

White, J. E., Catallo, W. J., & Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 1–33. doi:10.1016/j.jaap.2011.01.004

Yao, F., Wu, Q., Lei, Y., Guo, W., & Xu, Y. (2008). Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. *Polymer Degradation & Stability*, *93*(1), 90–98. doi:10.1016/j.polymdegradstab.2007.10.012

Ye, N., Li, D., Chen, L., Zhang, X., & Xu, D. (2010). Comparative studies of the pyrolytic and kinetic characteristics of maize straw and the seaweed *ulva pertusa*. *Journal PLOS ONE*, *5*(9), 1–6. doi:10.1371/journal.pone.0012641 PMID:20844751

Yuan, H. R., & Liu, R. H. (2007). Study on pyrolysis kinetics of walnut shell. *Journal of Thermal Analysis and Calorimetry*, *89*(3), 983–986. doi:10.1007/s10973-006-7688-x

ADDITIONAL READING

Babu, B. V., & Chaurasia, A. S. (2003). Modeling for pyrolysis of solid particle: Kinetics and heat transfer effects. *Energy Conversion and Management*, *44*(14), 2251–2275. doi:10.1016/S0196-8904(02)00252-2

Becidan, M., Skreiberg, Ø., & Hustad, J. E. (2007). Experimental study on pyrolysis of thermally thick biomass residues samples: Intra-sample temperature distribution and effect of sample weight ("scaling effect"). *Fuel*, *86*(17-18), 2754–2760. doi:10.1016/j.fuel.2007.03.007

Bridgwater, A. V. (2003). Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*, *91*(2–3), 87–102. doi:10.1016/S1385-8947(02)00142-0

Haseli, Y., van Oijen, J., & de Goey, L. (2011). Modeling biomass particle pyrolysis with temperature-dependent heat of reactions. *Journal of Analytical and Applied Pyrolysis*, *90*(2), 140–154. doi:10.1016/j.jaap.2010.11.006

Kim, S., & Eom, Y. (2006). Estimation of kinetic triplet of cellulose pyrolysis reaction from isothermal kinetic results. *Korean Journal of Chemical Engineering*, *23*(3), 409–414. doi:10.1007/BF02706742

Pimenidou, P., & Dupont, V. (2012). Characterisation of palm empty fruit bunch (PEFB) and pinewood bio-oilsand kinetics of their thermal degradation. *Bioresource Technology*, *109*, 198–205. doi:10.1016/j.biortech.2012.01.020 PMID:22297046

KEY TERMS AND DEFINITIONS

Conversion: Mass fraction of reactants that have been converted into products related to the initial reactant mass.

Isoconversional Methods: Methods that obtain the kinetic parameters (activation energy, pre-exponential factor and reaction order) of a solid-state reaction for each considered extent of reaction.

Lignocellulosic Biomass: Organic material basically composed by cellulose, hemicelulose and lignin.

Thermal Decomposition Kinetics: Define the reaction decomposition rate described by an Arrhenius expression, taking into account temperature and conversion dependence.

Thermogravimetric Analysis: Experimental technique that measures the remaining mass as function of temperature, in which the sample is submitted to a controlled temperature program.

Thermal Conversion: Processes that applies heat, pressure or catalysis to convert biomass into fuels to produce heat and power.

Woody Shell: It is a hard and fibrous outer layer, which covers the nuts, usually discharged as residues.

Chapter 5

Microwave Heating Assisted Biorefinery of Biomass

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ABSTRACT

This chapter debates the potential of the biorefinery of biomass using microwave heating. First, the essential information regarding electromagnetic radiation is explained and the pros and cons of microwave heating versus conventional heating, especially in the thermochemical treatment of biomass, are discussed. Different methodologies for predicting and measuring the temperature gradient within a material subjected to electromagnetic waves are demonstrated. The chapter summarizes the key conclusions of various investigations regarding the effects of microwave heating on chemical reactions and presents how electromagnetic radiation can assist the biorefinery of biomass. Finally, the issues and limitations regarding scaling-up microwave heating are elucidated, along with possible solutions to these problems.

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INTRODUCTION

Fundamentals of Electromagnetic Waves

Electromagnetic radiation behaves like waves moving at the speed of light and photons carrying radiated energy. Electromagnetic waves are comprised of both alternating electric and magnetic fields that are orthogonal to each other and propagate in the direction of oscillation, as shown in Figure *1*.

The history of electromagnetism dates back to 1831, when Michael Faraday discovered electromagnetic induction. Then, James Clerk Maxwell commenced working on Faraday's concept, and in 1864 presented a mathematical framing to explain the combined impact of electric and magnetic fields that later became known as the electromagnetic theory. In Maxwell's original paper, entitled "A Dynamical Theory of The Electromagnetic Field," published in 1865, electromagnetic theory was presented through 20 equations. Thereafter, these equations were simplified into the forms known today as "Maxwell's four equations". The differential and integral forms of these equations are expressed in Equations (1) to (4). Equation (1) is Gauss's law for an electric field, Equation (2) is Gauss's law for a magnetic field, Equation (3) is Faraday's law of induction, and Equation (4) is Ampere's law (Gupta & Eugene, 2007):

Differential form:

Integral form: $\nabla \bullet D = \rho$

$$\oint DdA = \int_V \rho dv \tag{1}$$

Differential form:

Integral form: $\nabla \bullet B = 0$

$$\oint BdA = 0 \tag{2}$$

Differential form:

Integral form: $\nabla \times E = - \partial B/\partial t$

$$\oint E \cdot dl = -\int_A (\partial B \,/\, \partial t) \cdot ndA \tag{3}$$

Differential form:

Integral form: $\nabla \times H = J + \partial D/\partial t$

$$\oint H \cdot dl = \int_{A} J \cdot n dA + \int_{A'} (\partial D / \partial t) \cdot n dA \tag{4}$$

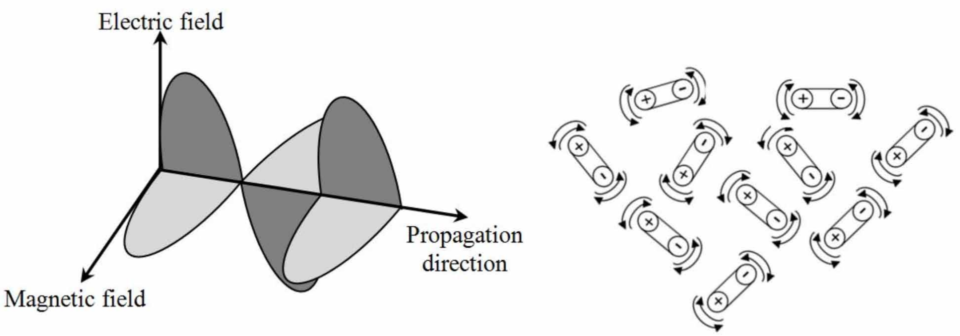
where E refers to the electric field strength [V/m], H the magnetic field strength [A/m], D the electric flux density [C/m^2], B the magnetic flux density [Wb/m^2], J the current density [A/m^2], v the velocity [m/s], and ρ the charge density [C/m^3].

An electromagnetic spectrum covers a wide range of frequencies and a corresponding range of wavelengths. Each of the electromagnetic applications (radio waves, microwaves, infrared, visible light, ultraviolet radiation, X-ray, and gamma ray) holds a specific frequency to avoid overlapping each other. As illustrated in Figure *2*, microwaves take a place in the electromagnetic spectrum, from 300 *MHz* to 300 *GHz* of frequency and from 1 m to 1 mm of corresponding wavelength. Throughout the 20th century, the rapid development of electromagnetic waves' technology has established microwaves in a number of implementations, such as communications, navigation, radar detection, power transmission, and microwave heating. Nowadays, microwave heating (MWH) is being widely implemented in both small scale applications, such as domestic microwave ovens, and large scale ones, as is evident in a number of industrial sectors. This is a consequence of the increased attention in research on microwave heating, which is manifest in the potential of publications in scientific literature. This chapter briefly presents several aspects, which are the result of replacing classical heating by electromagnetic radiation. If further details are needed, kindly refer to the additional readings at the end of this chapter.

Mechanism of Microwave Heating

In the absence of an external alternating electric field, materials that contain permanent dipole moments have randomly oriented molecules. As a result of there being no net, a dipole moment is presented. An external alternating electric field is merely applied and the molecules are aligned with the alternating field, which results in permanent dipoles parallel to the oscillating field. These aligned dipoles pursue the fluctuation of the applied electric field, i.e., they reorient themselves to try to be in phase with the alternating field, as depicted in Figure *1*. Since the agitated molecules do not possess the ability to reorient as rapidly as the field reversing, a phase shift is created between the orientation and the electric field. This phase shift creates random collisions between the oriented molecules and each other and, consequently, heat energy is released from the exposed material. In the case of an ideal dielectric material, the lag between the orientation and the alternating field does not exist,

Figure 1. Propagation of electromagnetic waves and molecular dipoles response



and therefore no heat energy is released. In conclusion, for non-magnetic materials, the dominant mechanism of microwave-induced heating involves the agitation of molecular dipoles due to the presence of an oscillating electric field. Accordingly, MWH is defined as "a volumetric energy conversion mechanism" for the conversion of electromagnetic energy to heat within the volume of the heated material.

Generally speaking, as depicted in Figure 3, materials can be classified into three main categories, depending on their interaction with electromagnetic waves:

Figure 2. Electromagnetic spectrum (Adapted from Gupta & Eugene, 2007)

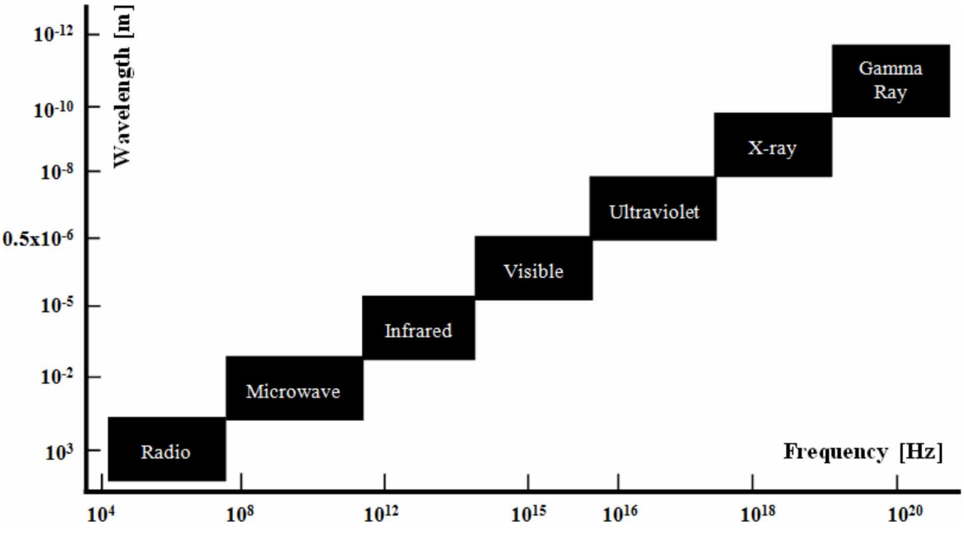
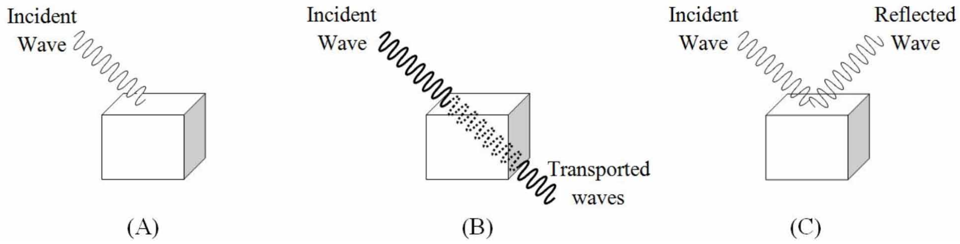


Figure 3. Material categories, based on the response to microwaves: (A) absorbing materials, (B) transparent materials, and (C) impermeable materials (Adapted from Durka et al., 2009)



1. Materials that absorb microwaves and convert them to heat energy are called “absorbing materials,” typically high-dielectric loss materials, e.g., silicon carbide and carbon;
2. Materials that allow electromagnetic waves, which are considered transparent electromagnetic waves, to pass through with little attenuation are called ”transparent materials,” and are typically insulating materials, e.g., ceramics, quartz, glass, and air; and
3. Materials that reflect electromagnetic waves are called “impermeable materials” and are typically highly conductive materials, e.g., metals.

Besides the above three categories, if the exposed material interacts with the magnetic component of the applied electromagnetic field, it is called “magnetic material,” typically ferrites. Absorbing materials have the highest response to electromagnetic radiation compared to the other categories. In order to perform MWH in a process, at least one of the heated materials in that process must involve the first category. Fortunately, most of the materials involved this category are relevant to microwave chemistry (Durka, Van Gerven, & Stankiewicz, 2009).

MAIN PARAMETERS DESCRIBING MICROWAVE HEATING

In MWH, the crucial parameters that describe electromagnetic propagation and the level of heat generation inside a microwave absorbent material are “complex permittivity” (ε) and “complex permeability” (μ) and can be expressed by Equations (5) and (6), respectively.

$$\varepsilon = \varepsilon' - j\,\varepsilon'' \qquad (5)$$

$$\mu = \mu^{/} \text{-} j\, \mu^{//} \qquad (6)$$

Complex permittivity represents the response of an exposed material to an alternating electric field, as it measures the ability of the material to absorb and store electric potential energy. The real part of the complex permittivity, $\varepsilon^{/}$, is called a "dielectric constant" and also known as "permittivity", which refers to the ability of a dielectric material to pass microwaves through it. $\varepsilon^{/}$ can be expressed as the product of the permittivity of free space (ε_o), 8.854×10^{-12} F/m, and the material relative permittivity ($\varepsilon^{/}_r$). The imaginary part of the complex permittivity, $\varepsilon^{//}$, is called the "dielectric loss factor," and it indicates the ability of the material to dissipate microwave energy; in other words, it measures the amount of electric energy that can be stored within the exposed material.

Another parameter commonly used to represent the response of a material to an alternating electric field is called "loss tangent" (tan δ). It describes the ability of the heated material to convert the absorbed microwave energy into heat energy. Loss tangent can be expressed by the ratio between $\varepsilon^{//}$ and $\varepsilon^{/}$ as in Equation (7):

$$\tan \delta = \varepsilon^{/} / \varepsilon^{//} \qquad (7)$$

where δ is the phase difference between the alternating applied electric field and the polarization of the exposed material (Durka et al., 2009).

Likewise, complex permeability represents the response of a material to an alternating magnetic field. The real part of complex permeability, $\mu^{/}$, is called "magnetic permeability." It represents the amount of magnetic energy that can be stored within the exposed material. $\mu^{/}$ can be expressed as the product of the permeability of free space (μ_o), $4\pi \times 1^{-7}$ F/m, and the relative permeability of the material ($\mu^{/}_r$). The imaginary part of complex permeability, $\mu^{//}$, refers to the amount of magnetic energy that can be converted into thermal energy. The ratio between $\mu^{//}$ and $\mu^{/}$ is called "magnetic loss tangent," and can be expressed by Equation (8).

$$\tan \delta_{\mu} = \mu^{/} / \mu^{//} \qquad (8)$$

For non-magnetic materials, since the effect caused by the magnetic field component is usually negligible, the parameter that describes the conversion of microwave into heat energy is tan δ.

For most of the conventional materials, $\varepsilon^{/}$, $\varepsilon^{//}$, and tan δ are well documented in the scientific literature. Table 1 represents the typical values of the selected materials. It should be noted that the dielectric properties of a material are affected by the frequency of the applied external electromagnetic waves and the exposed material's temperature (Motasemi, Afzal, Salema, Mouris, & Hutcheon, 2014; Salema et al.,

Table 1. Dielectric constant, dielectric loss, and loss tangent of selected materials

Material	$\varepsilon^{/}$	$\varepsilon^{//}$	tan δ	T [^oC]	f [GHz]
Vacuum[1]	1.00	0	0	25	na
Air[1]	1.0006	0	0	25	na
Glass (Pyrex)[1]	4.82	0.026	0.0054	25	3
Fused quartz	4	0.001	0.00025	20	2.45
Styrofoam[1]	1.03	0.0001	0.0001	25	3
PTFE[1]	2.08	0.0008	0.0004	25	10
Titanium oxide[1]	50	0.25	0.0050	25	na
Magnesium oxide[1]	9	0.0045	0.0005	25	na
Aluminum oxide[1]	9	0.0063	0.0007	25	na
Zinc oxide[1]	3	3	1.0000	25	na
Water, ice[2]	0.003	0.001	0.3333	-12	2.45
Water, distilled[2]	78	12	0.1538	25	2.45
Apple[2]	57	12	0.2105	19	2.5
Beef, frozen[2]	4.4	0.53	0.1205	-20	2.45
Beef, cooked[2]	30.5	9.6	0.3148	30	2.45
Potato[2]	15.7	0.27	0.0172	25	2.45
Paper[2]	2.7	0.2	0.0741	na	2.45
Paper[2]	2.8	0.2	0.0714	na	0.915
Polyethylene[2]	2.26	0.002	0.0009	na	0.915
Polyethylene[2]	2.3	0.001	0.0004	na	2.45
Methanol[1]	32.6	21.48	0.6589	25	2.45
Ethanol[1]	24.3	22.86	0.9407	25	2.45
Zirconium oxide[1]	20	2	0.1000	25	na

na: not avalible.
Adapted from (Durka et al., 2009) [1] *and (Gupta & Eugene, 2007)* [2]

2013). For instance, $\varepsilon^{/}$ and $\varepsilon^{//}$ of distilled water change from 78 and 12 to 0.003 and 0.001when the temperature changes from 25 ^oC to -12 ^oC, respectively. Therefore, the effect of these two factors must be taken into consideration.

Dissipated Power and Penetration Depth

Power dissipated within an exposed material, which also indicates the energy absorbed by the heated material, can be expressed via the summation of two terms. As shown in Equation (9), the first term indicates the converted energy due to the electric loss, whereas the other refers to the energy from the magnetic loss:

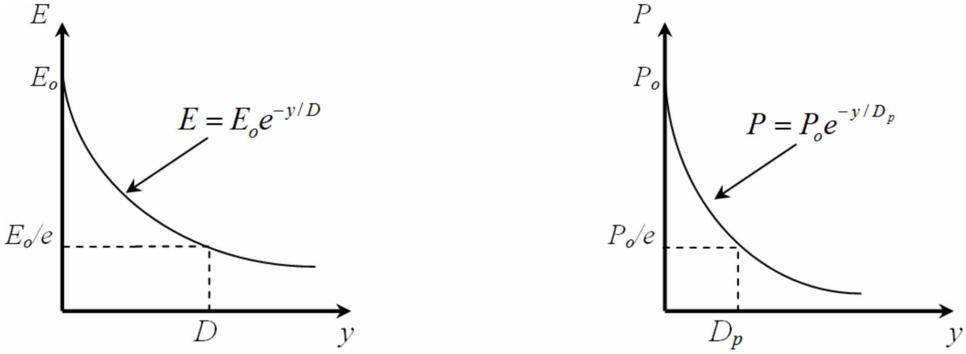
$$P_{av} = \omega\varepsilon_o\varepsilon^{//}_{eff}E^2_{rms}V + \omega\mu_o\mu^{//}_{eff}H^2_{rms}V \tag{9}$$

where P_{av} is the average absorbed power [W], ω is the angular frequency [s^{-1}] and equals 2π*f*. $\varepsilon^{//}_{\mathrm{eff}}$ refers to the effective dielectric loss factor [-] and equals the summation of the losses due to conduction ($\varepsilon^{//}_{\mathrm{cond}}$) and polarization ($\varepsilon^{//}_{\mathrm{polar}}$), such as dipolar, electronic, atomic, and interfacial polarization. Since it is difficult to distinguish between the losses due to conduction and the ones due to polarization, the summation of all losses can be expressed together by $\varepsilon^{//}_{\mathrm{eff}}$ as expressed in Equation (10) (Metaxas & Meredith, 2008). E_{rms} is the root mean square of the electric field [*V*/*m*], $\mu^{//}_{\mathrm{eff}}$, the effective magnetic loss factor [-], H_{rms}, the root mean square of the magnetic field [*A*/*m*], and *V,* the volume of the target material [m^3]. The product of ε_0 and $\varepsilon^{//}_{\mathrm{eff}}$ can be replaced by $\varepsilon^{/}$ tan δ.

$$\varepsilon^{//}_{\mathrm{eff}} = \varepsilon^{//}_{\mathrm{polar}} + \varepsilon^{//}_{\mathrm{cond}} \tag{10}$$

For non-magnetic materials, reducing the electric field/power along the exposed material can be expressed by a parameter that is called “penetration depth” or “skin depth” (*D*). In the case of *D,* which refers to the external electric field component, it is called “electric field penetration depth” (D_E), which represents the depth at which the magnitude of the electric field strength drops by a factor of 1/*e* (=1/2.7183) with respect to the incident value on the outer surface. On the other hand, when *D* refers to the dissipated/absorbed power inside the exposed material, it is called “power penetration depth” (D_p), which has the same definition as D_E, but it is related to the power density and equals to $D_E/2$, as illustrated in Figure ***4***A and Figure 4B, respectively.

Figure 4. Schematic representation of (A) electric field penetration depth and (B) power penetration depth (Adapted from Gupta & Eugene, 2007)



$$E = E_o e^{-y/D}$$

Electric field penetration depth and power penetration depth can be expressed as a function of another parameter called the attenuation factor (α), as presented in Equation (11) and Equation (12), respectively. The basic expression of α (assuming $\mu = \mu^{/}$) is expressed by Equation (13). Kindly refer to the book "*Industrial microwave heating*" by A.C. Metaxas and R.J. Meredito for the detailed derivation of P_{av} and α (Metaxas & Meredith, 2008).

$$D_E = 1/\alpha \tag{11}$$

$$D_p = 1/(2\alpha) \tag{12}$$

$$\alpha = \omega\left(\frac{\varepsilon_o \varepsilon^{/} \mu^{/} \mu_o}{2}\left[\left(1+\left(\varepsilon^{//}_{eff}/\varepsilon^{/}\right)^2\right)^{1/2} - 1\right]\right)^{1/2} \tag{13}$$

In the case of heating a highly loss medium (i.e., $\varepsilon^{//}_{\mathrm{eff}} >> \varepsilon^{/}$)), the expression $[(1+(\varepsilon^{//}_{\mathrm{eff}}/\varepsilon^{/})^2)^{1/2}-1]$ can be replaced by $\varepsilon^{//}_{\mathrm{eff}}/\varepsilon^{/}$ and Equation (13) can, therefore, be rewritten as a form of Equation (14) In contrast, in the case of a low loss medium (i.e., $\varepsilon^{//}_{\mathrm{eff}} << \varepsilon^{/}$), Equation (13) can be simplified into Equation (15), after submission of $\omega=2\pi f=2\pi c/\lambda_o$, where λ_o is the free space wavelength and *c* is the velocity of light (Gupta & Eugene, 2007; Metaxas & Meredith, 2008).

$$\alpha=\omega(\varepsilon_o\, \varepsilon^{//}_{\mathrm{eff}}\, \mu^{/}\mu_o /2)^{1/2} \tag{14}$$

$$\alpha=\pi\, \varepsilon^{//}_{\mathrm{eff}} /(\lambda_o(\varepsilon^{/})^{1/2}) \tag{15}$$

Substitution of Equation (15) in Equations (11) as well as (12) presents the final form of D_E and D_p, as expressed in Equations (16) and (17), respectively.

$$D_E=\lambda_o(\varepsilon^{/})^{1/2}/(\pi\, \varepsilon^{//}_{\mathrm{eff}}) \tag{16}$$

$$D_p=\lambda_o(\varepsilon^{/})^{1/2}/(2\pi\, \varepsilon^{//}_{\mathrm{eff}}) \tag{17}$$

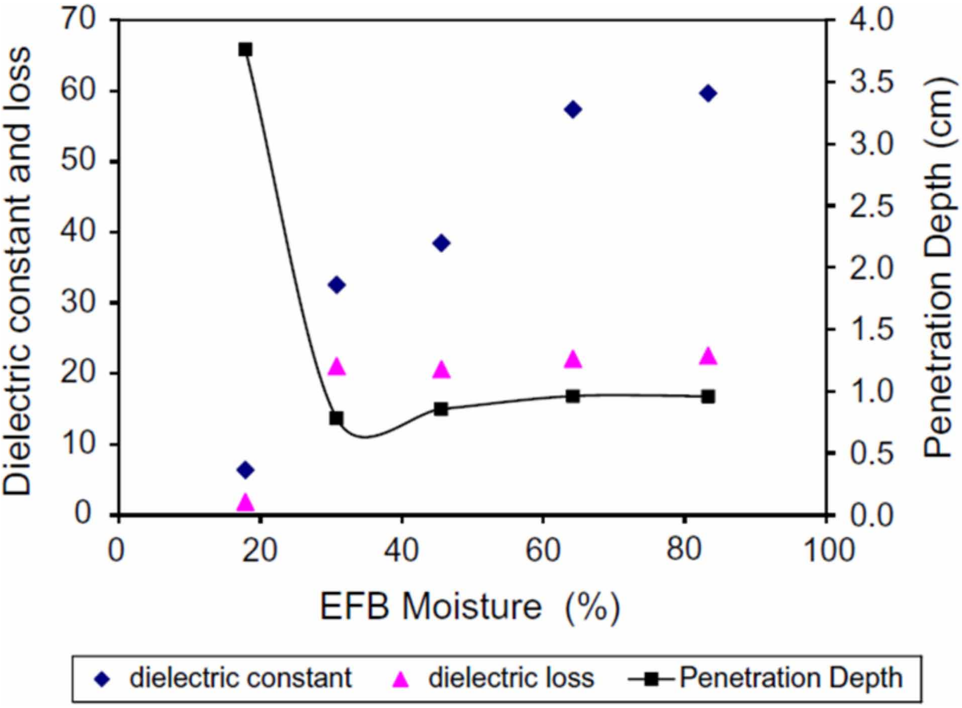
As shown in Equations (11) to (17), penetration depth is highly affected by the dielectric properties of the heated material and is directly proportional with $\varepsilon^{/}$ and inversely proportional with $\varepsilon^{//}_{\mathrm{eff}}$. This means when the heated material has a high ability to absorb electromagnetic waves, the applied electric field will be dramatically reduced within a short distance measured from the material's outer surface. On the other hand, heating a material that has a poor ability to absorb microwaves allows the applied waves to travel through with a slight decrease in field strength. For instance, the $\varepsilon^{/}$ and $\varepsilon^{//}$ of of distilled water, at 25 ^{o}C & 2.45 GHz, is equal to 78 and 12, respectively, which gives $D_p=1.44$ cm. In contrast, for fused quarts, at 20 ^{o}C & 2.45 GHz, $\varepsilon/=4$, $\varepsilon//=0.001$, and $D_p=3895$ cm, which means D_p of quartz is about 3000 times more than that of distilled water. Moreover, the microwaves' frequency also affects the penetration depth by an inverse relationship, for example, in the case of distilled water, at 25 ^{o}C & 915 MHz, $\varepsilon/=77.5$, $\varepsilon//=1.2$, and $D_p=38.26$ cm. This means, when the frequency of the exposure radiation drops from 2.45 GHz to 915 MHz, the calculated value of D_p increases up to 26 times more than the value calculated at 2.45 GHz. To sum up, the increase of $\varepsilon^{//}$, decrease of $\varepsilon^{/}$, and/or decrease of frequency results in a shorter D_p, which subsequently leads to creating non-uniform heating inside the volume of the heated material. Eventually, it presents non-uniform temperature distribution within the target workload.

Since water is a good microwave receptor, increase of the moisture content in the target dramatically enhances the dielectric properties of the material. In that regard, Omar et al. (Omar, Idris, Yunus, Khalid, & Aida Isma, 2011) examined the effect of the moisture content level on the values of $\varepsilon^{/}$, $\varepsilon^{//}$, and D_p of empty fruit bunches. As depicted in Figure 5, the value of $\varepsilon^{/}$ and $\varepsilon^{//}$ increases with increasing the moisture level. However, this significant role of water in absorbing microwave is limited to 60% and 30% of moisture content for $\varepsilon^{/}$ and $\varepsilon^{//}$, respectively. The authors interpreted the main reason of that based on the limited microwave penetration at high moisture content level, which is obvious in the calculated value of D_p.

Heating Rate of the Exposed Material

Increasing the rate of temperature of a heated material is affected by several factors, most importantly, the presence of heat lost from the target to the surrounding area and the uniform distribution of electromagnetic waves inside the oven cavity. In general, without considering the impacts of these two factors, applying energy balance on the heated material can present a mathematical formula that can calculate the target's heating rate. As expressed in Equation (18), the balance is based on the generated heat energy within the heated material and the amount of heat stored inside the material, and Equation (19) calculates the final form of the exposed material heating rate (in the case of non-magnetic materials):

Figure 5. Dielectric constant, dielectric loss, and penetration depth of empty fruit bunches (EFB) at various levels of moisture content at 2.45 GHz (© 2011 Elsevier Ltd. Used with permission) (Omar et al., 2011)



$$m\, c_p\, \Delta T/\Delta t = \omega\, \varepsilon_o\, \varepsilon^{//}_{\text{eff}} E^2_{rms} V \tag{18}$$

$$\Delta T/\Delta t = \omega\, \varepsilon_o\, \varepsilon^{//}_{\text{eff}} E^2_{rms} V/m\, c_p \tag{19}$$

where m is the mass of the heated material, c_p is the target's specific heat, ΔT is the temperature difference, and Δt is the time interval. In case of heating a wet material, Equation (18) should include a term that represents heat absorbed by the water.

BACKGROUND

Microwave Heating vs. Conventional Heating

MWH has been established in a number of applications to benefit from the advantages of electromagnetic radiation, which is an alternative to conventional heating

(CH). Basically, the dominant mechanism of MWH relies on direct conversion of electromagnetic energy within the heated material, which is fundamentally different from the superficial heat transfer of classical heating (Farag, Kouisni, & Chaouki, 2014; Motasemi & Afzal, 2013). This difference can avoid many issues and limitations associated with CH, the most important being the temperature gradient inside and outside the target material. In addition, electromagnetic waves only interact with particular types of materials; thus, they can heat selectively, especially where with CH it is not possible. This aspect is so significant that it can dramatically reduce the amount of heat energy needed to achieve a particular end, which consequently results in decreasing the operating costs as well as the potential of thermal hazards. Moreover, in the case of exposing multiple components, heating can be concentrated at a specific component, which might lead to producing material with a novel microstructure, initiating reactions that cannot be initiated when CH is applied, and/or achieving the existing reactions under conditions that are different from those of traditional processing. However, it should be noted that this mainly depends on the dielectric properties of each component.

In addition, since MWH is easily and rapidly initiated and terminated, the process can be completed in a fraction of the time that is needed in the conventional process. This could enhance the production rate in a number of industrial sectors as well as reduce the undesirable intermediate thermal steps. MWH is a highly precise and safe heating mode, which allows for a higher level of control and more compact equipment. Furthermore, it is an environmentally friendly process, as it reduces hazardous emissions, particularly if clean electricity is used. Last but not least, numerous investigations have documented that MWH can save more in energy consumption and enhance product quantity and quality compared to the conventional processed materials (Budarin et al., 2009; Chandra Shekara, Jai Prakash, & Bhat, 2012; Karthikeyan, Balasubramanian, & See, 2006; Lucchesi, Chemat, & Smadja, 2004; Paixão et al., 2011; Pan, Wu, Wang, & Hong, 2009; Zhang & Zhao, 2010).

In the field of thermal-decomposition of materials (pyrolysis), electromagnetic radiation can be employed to avert most of the problems associated with conventional heating pyrolysis (CP), most importantly, char layer formation during CP. This aspect can enhance product selectivity as a result of reducing undesirable secondary reactions. Moreover, since MWH is a volumetric heating mechanism, variously sized and non-homogeneous feedstock is acceptable. In addition, while penetration limits are respected, the dimension and low thermal conductivity of the workload is not an issue as it is in CP. This aspect might decrease local thermal stresses inside the target, which results from poor heat transfer within the heated material. Furthermore, microwaves can be transmitted through gasses, vacuum, and air without significant loss, which makes the process highly flexible, as the waves can be generated and guided anywhere.

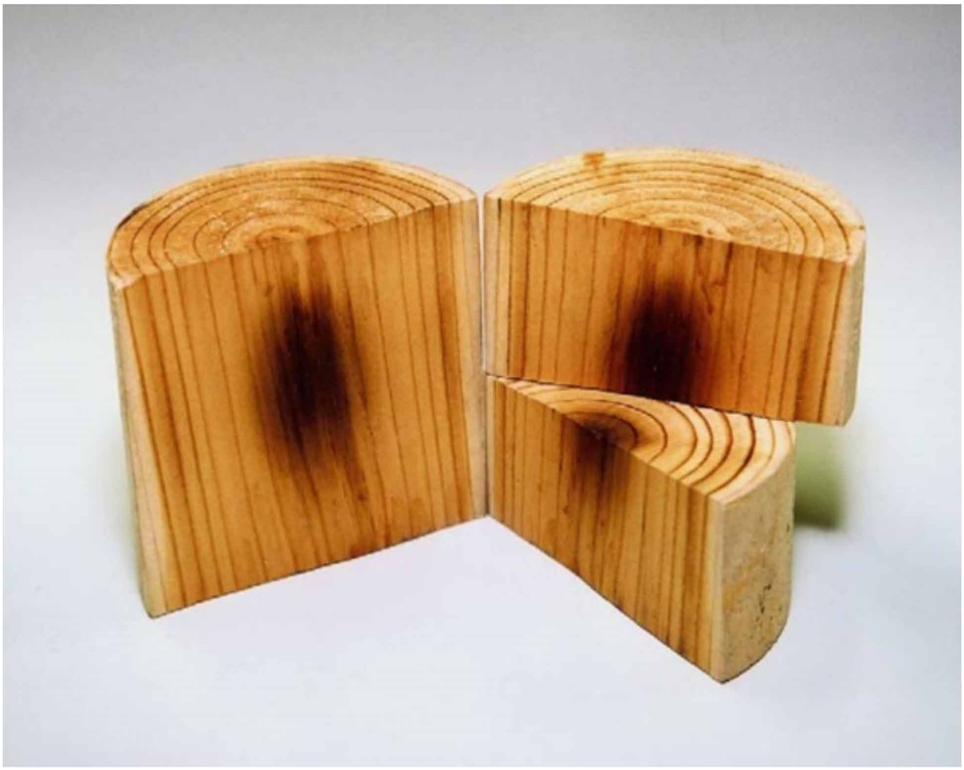
As a result, recently, MWH has attracted a staggering amount of attention in scientific research, manifest in the increasing number of publications and patent applications over the last few years. Research has focused on several parameters, such as reaction rate, reaction temperature, energy consumption, and catalyst loading, among other parameters (Farag, 2013). Although MWH has been proven to be a powerful heating mechanism for the biorefinery of biomass, it has not been industrialized yet in that field. Even so, it has been established in a number of other applications, such as drying, extraction, separation, and reactivation.

In contrast to the above advantages, MWH has some barriers. Most importantly, electromagnetic radiation brings an additional hazard to the thermal one. Since electromagnetic waves are absorbed by body, the exposure to high energy microwaves can be harmful and might cause some biological effects on human. This would cause thermal effect, related to heating the tissues, in addition to the non-thermal effects. Therefore, it is highly recommended to regularly check the leakage waves around the microwave heating systems. When heating a material that is not a good microwave-to-heat convertor, the use of a microwave-receptor is essential, which means low microwave absorbers need to be mixed with a good microwave-heat-convertor in order to enhance the heating process. Such cases are called “hybrid heating”. In addition, the rapid heating process could present hot spots within the heated material; therefore, care must be taken to eliminate this issue. The uniformity of electromagnetic waves inside the microwave oven cavity affects the temperature gradient within the payload. This makes using a metal plate stirrer inside the cavity necessary, which might improve distribution in the electromagnetic field. The more sophisticated electromagnetic large-scale apparatuses require an increase in the initial cost of the total system. In such situations using multiple small units instead of a one big unit is recommended.

Temperature Profiles within a Target Material

Since MWH is a volumetric energy conversion mechanism, theoretically it should lead to a uniform temperature gradient within the exposed material. However, in practice, it is likely to produce a non-uniform temperature distribution. To show that experimentally, Figure 6 shows a wood block, 80 *mm* in diameter, and exposed to electromagnetic irradiation for 3 *min*. Subsequently, it was cut as depicted in the figure. As it is obvious, no noticeable effect is spotted on the outer surface compared to the core, which indicates that the block’s core was at a temperature that was completely different than that at the surface. The presence of such thermal gradient within the exposed material makes an investigation of the temperature distribution

Figure 6. Wood block, 80 mm in diameter, heated by electromagnetic waves for 3 min (© 2004, Elsevier B.V. Used with permission)(Miura, Kaga, Sakurai, Kakuchi, & Takahashi, 2004)



within a material heated by microwaves imperative. To achieve this objective, two approaches could be performed: (1) temperature measurements at multiple points, and/or (2) temperature prediction using a theoretical modelling.

Experimental Approach

Measuring a transient temperature during an electromagnetic exposure is certainly an intricate issue for the interaction between the microwaves and the employed thermometer's probe. Moreover, the popular thermometer limitations present another barrier.

As recognized, thermocouple, infrared, and fibre optics are the popular thermometers employed in such applications. However, the use of a thermocouple thermometer inside a microwave oven is dangerous with low accuracy, which is a consequence of its metallic probe and electromagnetic field interaction. In the scientific literature, few publications used a thermocouple thermometer after switching off the oven-power. In such methodologies, heat lost after switching off the oven-power must be considered. Some effort has been made to use a shielded thermocouple thermometer inside the oven cavity during heating; however, it still needs further examination.

An infrared thermometer measures temperature while it is far away from the oven-cavity, i.e., there is no need for direct contact between the thermometer probe and the heated material. Nonetheless, it only measures surface temperature, which leads to presenting a value that does not represent the bulk material's temperature. It should take into consideration the temperature gradient between the surface and the core. Kindly refer to Figure 6. Furthermore, when a crucible is needed to carry the heated material in, it must be made from a material that is microwave transparent. Otherwise, the thermometer will measure the outer surface temperature of the crucible instead of the heated material. In addition, in applications where a dark vapour product covers the target during heating, as in pyrolysis and gasification, this thermometer cannot even measure the surface temperature of the material. Besides, it is highly affected by the ambient conditions, which makes frequent recalibration essential. Therefore, an infrared-thermometer is suitable only for thin materials, because there is no high temperature gradient between the outer surface and the core.

In contrast to the previous two thermometers, the fibre optics thermometer shows many advantages, most importantly, the independency of the target material carriers and no need for frequent recalibration. Also, it can reach any level inside the heated material. However, this thermometer measures only a point temperature and special attention must be paid to avoid damaging the probe.

In the literature, a modest effort has been made to discover a technique that can be performed for measuring transient temperature inside a microwave oven. Unfortunately, a technique still has not been found yet, which opens the door for further efforts to find the essential technique to achieve this objective experimentally.

Modeling Approach

Over the past two decades, various investigations have been documented to predict temperature gradient within a material heated by microwaves using a mathematical approach (Campañone & Zaritzky, 2005; Farag, Sobhy, Akyel, Doucet, & Chaouki, 2012; Klinbun & Rattanadecho; Zhou, Puri, Anantheswaran, & Yeh, 1995). The commonly reported key conclusions include that MWH leads to non-uniform distribution of temperature and hot and/or cold spots inside the heated material. In 2012, Farag et al. (Farag et al., 2012) published a scientific paper that presents a mathematical model to predict temperature profiles within a wood cube, 86 mm in a side length, subjected to electromagnetic irradiation under various conditions. As expressed in Equation (20), the presented model takes into consideration the effects due to the conversion of electromagnetic energy to heat, heat transfer by conduction inside the heated material, and heat transfer by convection from the outer surface. Furthermore, it considers power dissipation due to penetration limits:

$$k\nabla^2 T + \frac{P_o}{3}\sum\nolimits_i \left(e^{\frac{-i}{D_p}} + e^{\frac{i-l}{D_p}} \right) = \rho c \frac{\partial T}{\partial t} \tag{20}$$

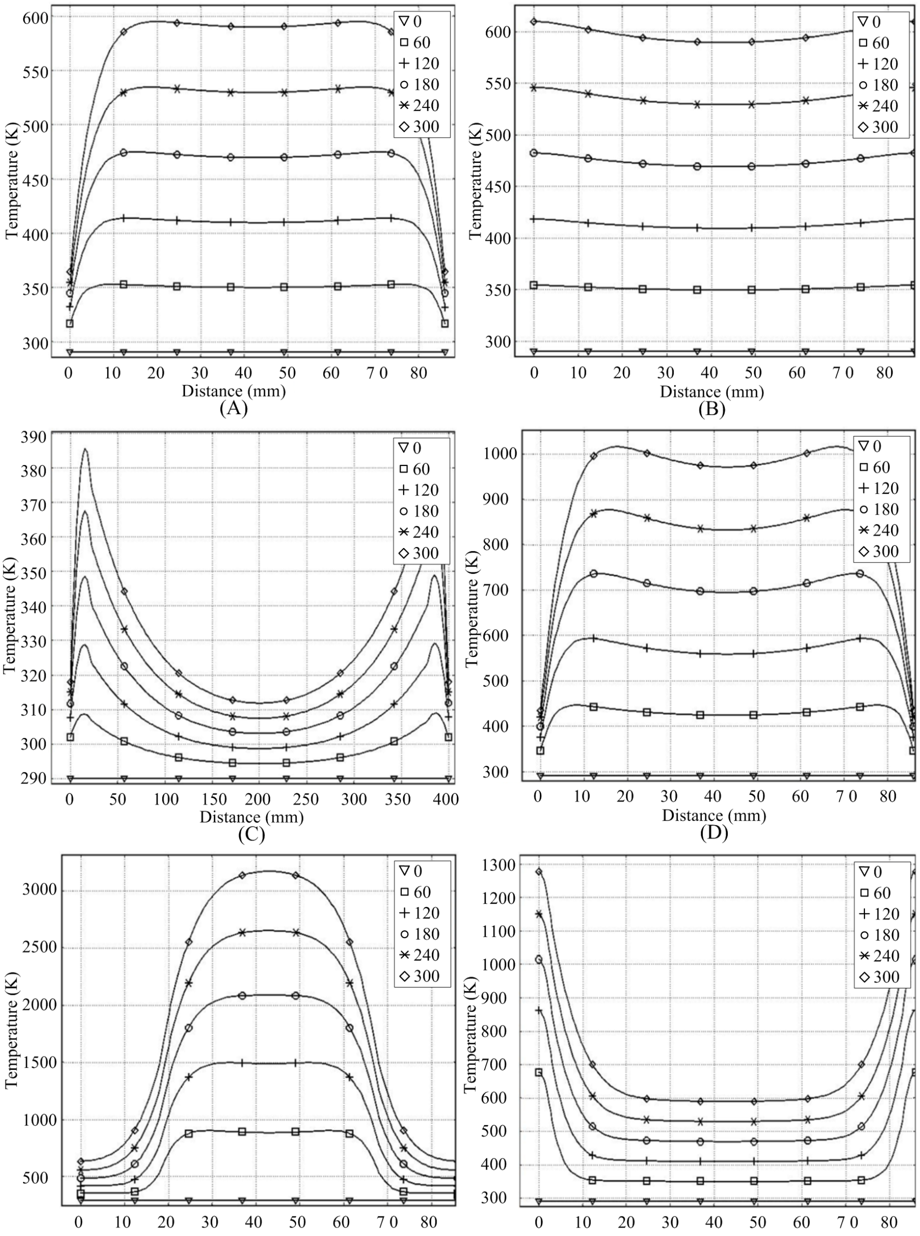
where k is the thermal conductivity of the heated material, T, the transient temperature, c, the specific heat, and $P_{o,}$ the power value at the outer surface of the exposed material, as it was defined in Equation (9). D_p is the power penetration depth, ρ is the density of the heated material, l is the cube length, and i refers to the x, y, and z directions. Kindly refer to paper of Farag et al. for further details.

Figure 7. shows the predicted temperature profiles along a line passing through the center of the wood cube, and parallel to the x axis. Two different conditions at the outer surface of the block were applied: (1) free convection and (2) perfect insulation. Even though the outer surface of the block has the highest electric field strength compared to the rest of the block, refer to Figure 3A, it has a low temperature compared to that at the core, as shown in Figure 7A. One of the reasons behind this gradient is the heat transfer on the outer surface. Thus, when a perfect thermal insulator covered the outer surface of the block, the temperature profiles tended to be more uniform, as illustrated in Figure 7B. This means that eliminating heat loss from the outer surface of the heated material is one of the approaches that can be applied to achieve a uniform temperature gradient. It should be noted that the use of an insulator for such purposes must be a microwave transparent. Otherwise, it can interact with the applied electromagnetic waves, resulting in temperature profiles similar to that in the traditional heating, which is a surface hotter than the core. Also, and most importantly, respecting the penetration limits of the applied electromagnetic waves is a critical issue, because if it is not considered, the temperature profiles are reversed, which results in a core that is colder than the surface as depicted in Figure 7C.

In short, to achieve a more uniform temperature gradient inside a material heated by microwaves, two factors must be respected: (1) surface heat loss needs to be eliminated, and (2) penetration limits must be considered when a target's dimensions are chosen. Also, if the payload can be shaken in the mean time of exposure, it would be useful to avoid any effects caused from the non-uniform distribution for the electromagnetic waves inside the cavity.

As explained earlier, the advantage of MWH as a selected heating mechanism sometimes becomes a problem, particularly when the heated material is not a good

Figure 7. Temperature profiles inside a wood block heated for 5 min (A) with free convection and (B) with perfect insulation, (C) wood block, 400 mm of side length with free convection, (D) block of 50 wt% wood + 50 wt% carbon, (E) 125 cm^3 carbon in the core, and (F) 125 cm^3carbon on the outer surface (reprinted from Farag et al., 2012).



microwave-to-heat convertor. In such cases, use of a good microwave-receptor is an option to enhance conversion of microwaves to heat. In Farag's paper (Farag et al., 2012), carbon was employed to accomplish this scenario, as it is one of the strong microwave absorbers. Thus, it offers a better and efficient microwave to heat conversion compared to wood itself. Figure 7D presents the temperature profiles inside the same block, when the heated material comprised of 50 wt% wood and 50 wt% carbon. Comparing Figure 7A and Figure 7D can elucidate that homogenous mixing of the heated material with a strong microwave-to-heat convertor leads to a significant increase in temperature compared to the basic material heated at the same power and heating time. Actually, this approach can present a positive impact on energy consumption, product yield and quality, heating period, and other aspects. As well, the employed microwave receptor in such applications should be chosen carefully, because it might have a positive/negative chemical effect on the heated material. This aspect should, therefore, be examined separately.

The choice of location of a strong microwave-to-heat receptor can be employed to create desired hot zones inside the target, which is needed in some applications in order to achieve specific temperature profiles. Figure 7E shows the temperature gradient when a 125 cm^3 cube of wood was replaced by the same volume of carbon, while Figure 7F depicts the profiles when the same carbon volume replaced the outer layer of the basic wood cube. Remarkably, there is a significant difference in the core heating rate between the case of Figure 7E and the basic case, Figure 7B: 600 K/min and 60 K/min, i.e., tenfold that of the basic case.

These investigations aim at improving the understanding of temperature gradient within material/composite materials exposed to microwave irradiation. Furthermore, they could provide useful insights in applications where creating a hot spot is needed to enhance product yield, such as in drying, pyrolysis, and gasification. For example, carbon and metals are pre-mixed with sewage sludge, crude oil, etc., in order to enhance thermal/catalytic processes (El harfi, Mokhlisse, Chanâa, & Outzourhit, 2000; Li, Zhang, Quan, & Zhao, 2009; Menéndez, Domínguez, Inguanzo, & Pis, 2004; Menéndez, Inguanzo, & Pis, 2002; Monsef-Mirzai, Ravindran, McWhinnie, & Burchill, 1995).

MAIN FOCUS OF THE CHAPTER

Over the past two decades, the impacts of electromagnetic radiation on a chemical reaction have been extensively investigated using various implementations. The prevalent examined parameters include reaction rate, product quantity and quality, reaction temperature, energy consumption, and catalyst loading. This great effort led to the documentation of a number of phenomena that are related to microwave processing. The common key conclusions include that MWH may have a faster reaction rate, lower energy consumption, a higher product quality, etc., compared to that of conventional heating processing. In contrast, few studies include an opposing standpoint; MWH does not have significant effects on some of these parameters. The main reason behind the conflicts between the obtained results as well as the claimed conclusions could be related to the differences in the process monitoring technique. As it is known, most of the parameters mentioned above rely heavily on temperature, and since in MWH temperature measurement is a challenge and heat distribution might be non-uniform, the reported conclusions from inaccurate investigations could be questionable. However, among the literature's publications, investigations that consider these issues, such as temperature measurement and gradient, could inspire more confidence and be more acceptable.

For the time being, the noticeable effects have been realized and might be a consequence of implementing microwaves in chemical reactions, known as "microwave heating effects" or "non-thermal effects" (Gupta & Eugene, 2007). Recently, a few research groups have made efforts to find a scientific exegesis for these effects by performing a kinetic investigation. Some of them believe that when electromagnetic radiation is applied, reaction activation energy decreases (Adnađević, Gigov, Sindjic, & Jovanović, 2008; Adnadjevic & Jovanovic, 2012; Adnadjević & Jovanović, 2012; Chen et al., 2013; Fukushima et al., 2013; Sun et al., 2012; Yan et al., 2012). However, others researchers have claimed the opposite. Reaction activation energy does not change whether MWH or CH is applied (Mazo, Estenoz, Sponton, & Rios, 2012; Yadav & Borkar, 2006). In our opinion, the effect of an electromagnetic exposure on a reaction activation energy is doubtful, because the wavelength of electromagnetic waves (for example, at 2.45 *GHz* the wavelength is 2.24 *cm*) is greater than the intermolecular distance of the exposed material. This makes direct hacking by microwaves of the chemical bonds of the heated material questionable. Therefore, there is still no strong evidence on the impact of electromagnetic waves on reaction activation energy.

Other research groups have claimed an impact for microwaves on the reaction pre-exponential factor. Some groups reported a positive impact, where the reaction pre-exponential factor increases under electromagnetic radiation, (Adnadjević & Jovanović, 2012; Temur Ergan & Bayramoğlu, 2011; Yadav & Borkar, 2006), while others believe the opposite; the pre-exponential factor decreases under MWH, (Adnađević et al., 2008; Adnadjevic & Jovanovic, 2012; Mazo et al., 2012). The influence of microwaves on the reaction pre-exponential factor is more believable than the effect that was reported on the reaction activation energy. As explained in the introduction, the mechanism of MWH mainly depends on the agitation of the molecules of the exposed material, which results in more collisions between them. As it is known, the reaction pre-exponential factor is commonly represented by collision frequency. Therefore, when molecular collisions are enhanced, the reaction pre-exponential factor should increase as well. Accordingly, the effect of MWH on molecular mobility is more obvious, which supports the claimed conclusion regarding the increase of the reaction pre-exponential factor.

In summary, the inconsistency in the documented conclusions still raises several questions regarding how much these influences belong to non-thermal effects or microwave challenges. As a result, further investigations include solutions for the microwave issues that are really needed, as it would lead to more positive evidence on the effects of electromagnetic waves.

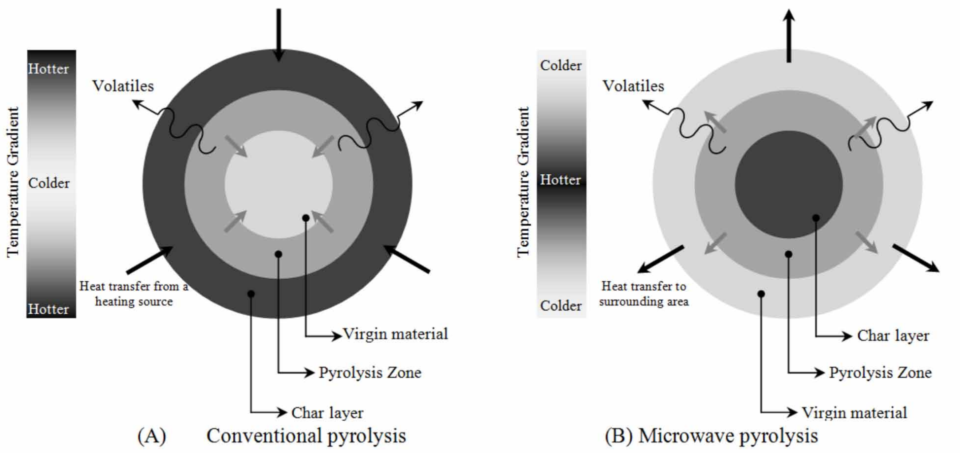
Microwave Heating Assisted Pyrolysis of Biomass

In the field of thermal decomposition of biomass, the dominant mechanism of MWH, which is an energy conversion rather than a superficial heat transfer, has been employed to avoid most of the issues and limitations associated with CH. Most importantly, the char layer formation begins in CP and is one of the critical problems in that field.

In CH, heat is transferred from a heating source, such as an electrical heating element or combustion, to the outer surface of the heated material via conduction, convection, and/or radiation. Subsequently, heat transfer into the core by a heating rate depends on the difference in temperature between the outer surface and the core of the heated material. In addition, heat capacity, thermal conductivity, and dimension of the workload, among other factors, also affect the heating rate. The material's temperature merely reaches the level that is needed to decompose the chemical bonds of the payload and the chemical bonds begin to decompose, following the same direction as that of the heat transfer. This mechanism leads to the creation of a temperature gradient that represents a surface hotter than a core. Consequently, a layer of char is created on the outer surface and moves toward the core. This phenomenon is called "char layer formation", which presents many issues in applications where CH is used. Most importantly, the reduction of heat transfer within the processed material, as char has low thermal conductivity, results in a temperature difference on the two sides of the formatted char layer, as illustrated in Figure 8A. In addition, while the produced volatiles from the thermal decomposition of the target flow through this thermal barrier, further degradations might take place, which could negatively affect the quantity and/or quality of the final product.

On the other hand, in the microwave processing of thermal decomposition, electromagnetic waves penetrate the entire heated material or part of it at almost the same time, limited only by the penetration limits. Therefore, theoretically, there should be uniform temperature distribution within the workload. However, as ex-

Figure 8. Schematic diagram of conventional pyrolysis and microwave pyrolysis (Adapted from Miura et al., 2004)



plained in the background section, MWH produces just the opposite in CH, where the core is hotter than the surface without overheating the surface. Accordingly, a char layer is created in the core and grows in the surface direction, as shown in Figure 8B. This means, while the produced vapour product is pushing out the workload, it flows through an un-reacted material, which has a temperature less than that of the decomposed zone (the material that produced the vapour product). Furthermore, it might present a kind of filtration for the vapour product, as a result of deposition through the porous area of the un-reacted material. Depending on the dielectric properties, this temperature gradient could be helpful to remove moisture and gases from the interior of the heated material without undesirable thermal cracking. Besides, the presence of this temperature gradient leads to creating a pressure difference between the outer surface and the core of the heated material, which might enhance the flow rate of the produced vapour and, consequently, lead to preserving the chemical structure of the product.

A considerable number of investigations have employed electromagnetic radiation in different reactions, especially in the field of biorefinery of biomass in order to benefit from the advantage of a thermal gradient inside the heated material. Actually, this is clear in the number of publications related to microwave processing of biomass. Table 2 demonstrates the product distribution and the major chemicals in the liquid and gas products obtained from microwave pyrolysis of biomass at various conditions. For further details, kindly refer to the cited references in this table. Table 3 summarizes the literature of various investigations employing MWH in contrast to CH.

Table 2. Product distribution from microwave-assisted biorefinery of biomass

Feedstock	Power [*kW*] / Temp. [^{o}C]	Product distribution (wt-%)			Gas major components	Identified chemicals in the liquid product	Ref.
		Solid	Liquid	Gas			
Kraft lignin[1]	1.5 / 625	42	26	32	na	Benzenes Phenols Guaiacols Catechols Others	(Farag, Fu, Jessop, & Chaouki, 2014)
	2.7 / 700	38	27	35			
	2.1 / 790	40	24	36			
	1.5 / 875	41	23	36			
	2.7 / 965	39	21	40			
Wheat straw pellets	1 / 130	29	57	14	na	Levoglucosan 2-Methoxy-4-vinylphenol/ benzofuran, 2,3-dihydro Phenol, 2,6-dimethoxy- Phenol, 2,6-dimethoxy-4-(2-propenyl) Phenol, 2-methoxy-	(Budarin et al., 2009)
Wheat straw pellets + H_2SO_4	1.2 / 140	45	40	15	na	Levoglucosan Levoglucosenone 1,4:3,6-Dianhydro-a-D-glucopyranose Phenol, 2-methoxy- Desaspidinol	
Wheat straw pellets + HC	1.2 / 140	32	49	19	na	Levoglucosan Phenol, 2,6-dimethoxy- 2-Methoxy-4- 1,4:3,6-Dianhydro-a-D-glucopyranose vinylphenol/benzofuran, 2,3-dihydro- Desaspidinol	
Wheat straw pellets + NH_3	1.2 / 165	41	39	20	na	Levoglucosan 2-Methoxy-4-vinylphenol/ benzofuran, 2,3-dihydro- Phenol, 2,6-dimethoxy- Desaspidinol Levoglucosan	
Wood sawdust	0.6 / 200	48	43	8	na	Furfuraldehyde phenol, methylphenol methoxyphenol dimethylphenol	(Wu et al., 2014)
	0.9 / 200	45	46	9			
	1.2 / 200	43	47	10			
Waste wood[2]	1 / na	20	66	13	CO = 48- 53 CO_2 = 46-34 CH_4 = 0.5-0.6 C_7H_8 = 0.6-1.2	na	(Lupa et al., 2012)

continued on following page

Table 2. Continued

Feedstock	Power [*kW*] / Temp. [^{o}C]	Product distribution (wt-%)			Gas major components	Identified chemicals in the liquid product	Ref.
		Solid	Liquid	Gas			
Coffee hulls	na/500	30	8	62	CO=26 CO_2=29 CH_4=7 H_2= 36	na	(Domínguez et al., 2007)
	na/800	26	9	65	CO=29 CO_2=23 CH_4=7 H_2= 38	na	
	na/1000	23	9	67	CO=33 CO_2=18 CH_4=7 H_2= 40	na	
Wood sawdust[3]	0.75 / 450-550	50-15	65-45	5-25	na	Acetic acid 2-Methoxy-4-vinylphenol 1,2-Benzenedio Furfural 2-Propanone, 1-hydroxy-	(Borges et al., 2014)
Corn stover[3]	0.75 / 450-500	25-12	63-48	12-38	na	Benzofuran, 2,3-dihydro- 2-Methoxy-4-vinylphenol Phenol, 3-ethyl- Furfural Phenol	
[4]Oil palm shells 1:0.25	0.45 / na	10	70	20	na	Ketones, aldehydes, carboxylic acids, nitrogenous compounds, alcohols, esters, ethers, and aromatic	(Salema & Ani, 2011)
[4]Oil palm shells 1:0.5		25	45	30			
[4]Oil palm shells 1:1		20	50	30			
[4]Oil palm fiber 1:0.25	0.45 / na	80	9	11			
[4]Oil palm fiber 1:0.5		50	23	27			
[4]Oil palm fiber 1:1		70	6	24			

continued on following page

Table 2. Continued

Feedstock	Power [*kW*] / Temp. [*°C*]	Product distribution (wt-%)			Gas major components	Identified chemicals in the liquid product	Ref.
		Solid	Liquid	Gas			
Oil palm empty fruit bunch pellets	1 / 280	79	5	15	na	2-methoxy-phenol	(Salema & Ani, 2012)
	1 / 300	69	8	25		2,6-dimethoxy-phenol 2-methoxy-phenol 1,2-benzenedicarboxylic acid 4-methyl phenol (p-cresol) 1-(2,6-dihydroxy-4-methoxyphenyl)-ethanone	
	1 / 450	51	20	29		2-methoxy-phenol 2,6-dimethoxy-phenol 4-methyl phenol (p-cresol) 2-methyl-phenol (o-cresol) 3-methoxy-1,2-benezenediol	
	1 / 550	48	21	31		2-methoxy-phenol 2,6-dimethoxy-phenol 4-ethyl-2-methoxy-phenol 2-methyl-phenol (o-cresol) 4-methyl phenol (p-cresol)	
Rice straw	50 –500 / 105-563	na	na	na	$CO = 11$ $CO_2 = 23$ $CH_4 = 7$ $H_2 = 51$	na	(Huang, Kuan, Lo, & Lin, 2010)

[1] the solid product was mixed with lignin at concentrations of 20, 20, 30, 40, and 40 wt%, respectively.
[2] three samples were used in that work; thus, the results were presented in a range format. The unit of the gas concentration is wt%.
[3] 11 experiments were done in that work; therefore, the results were presented in a range format.
[4] the feedstock was mixed with a microwave absorber, using the presented ratios.

As shown in Table 3, employing electromagnetic radiation in the conversion of biomass shows several significant effects, such as an increase in reaction rate, a decrease in reaction temperature, decreased consumption of catalyst, enhanced product yield and quality, and decreased energy consumption among other effects. The effects that electromagnetic radiation shows on the reaction rate and reaction temperature might be the result of increasing the molecular mobility of the heated material, because the MWH mechanism mainly depends on agitating the molecules of the heated material. This means that the increase in molecular mobility (in other words, molecular kinetic) leads to achieving a higher reaction rate at the same temperature as that of CH or achieving the same reaction rate at a lower temperature than that of CH. This aspect could also be the main reason behind reducing the catalyst loading as a consequence of increases in molecular activity. Furthermore, since the same reaction can be achieved at a lower temperature, reaction control

Table 3. Summary of scientific literature regarding the use of microwave heating compared to conventional heating in the biorefinery of biomass

Authors	Impact of MWH
Chandra Shekara et al (Chandra Shekara et al., 2012)	MWH achieves more conversion in contrast to CH.
Paixão, Monteiro et al (Paixão et al., 2011)	MWH modifies the porosity of samples and has a faster reaction rate with less energy consumption compared to CH.
Patil, Gude et al (Patil, Gude, Pinappu, & Deng, 2011)	MWH has a higher reaction rate than CH.
Zhang and Zhao (Zhang & Zhao, 2010)	MWH achieves more product yield in less reaction time.
Budarin, Clark et al (Budarin et al., 2009)	The obtained oil contains few impurities and is rich in aromatics compared to conventional processes.
Guiotoku, Rambo et al (Guiotoku, Rambo, Hansel, Magalhães, & Hotza, 2009)	MWH increases the carbonization yield.
Krzan and Zagar (Krzan & Zagar, 2009)	MWH decreases liquefaction time with less loading of catalyst.
Dogan and Hilmioglu (Dogan & Hilmioglu, 2009)	MWH has a shorter reaction time compared to the traditional methods.
Sithambaram, Nyutu et al (Sithambaram, Nyutu, & Suib, 2008)	MWH increases the conversion compared to CH.
Orozco, Ahmad et al (Orozco, Ahmad, Rooney, & Walker, 2007)	MWH has higher product yields in a short time and higher reaction rate at moderate temperature.
Karthikeyan, Balasubramanian et al (Karthikeyan et al., 2006)	MWH has a faster extraction rate with differences in the obtained chemical components.
Zhu, Wu et al (Zhu, Wu, Yu, Liao, & Zhang, 2005)	MWH enhances the obtained product quality.
Lucchesi, Chemat et al (Lucchesi et al., 2004)	MWH has a faster reaction rate and less energy consumption.
Menéndez, Domínguez et al. 2004 (Menéndez et al., 2004)	MWH has a faster reaction rate.
Adapted from Farag & Chaouki (2014)	

should increase, which results in a decrease of unwanted secondary reactions. In addition, temperature profiles in MWH, kindly refer to the background section, might be attributed to the exclusion of undesirable reactions, which is highly attributed to preserving product structure.

In general, the nature of microwaves, which is completely different from that of CH, should make an imprint on the conversion processing as well as the obtained product characteristics. However, it cannot be generalized, because the dielectric properties of the heated material as well as the obtained product are critical to describe the response to electromagnetic radiation. This means the reported effects in such reactions might take place with some reactants and might not exist with others. Accordingly, while a non-thermal effect is documented, the microwaves challenges and the performed measuring technique must be kept in mind. In addition, any microwave effect should be linked with the characteristics of the heated material and not considered as an absolute impact that can be expected to be found in other materials.

SOLUTIONS AND RECOMMENDATIONS

In spite of the extended attention that is given to MWH to be established in broad, large-scale applications, several challenges still need further research and innovations to be completely addressed. Most of these challenges are associated with scaling up a microwave system (i.e., moving from a laboratory scale to a production scale), which could cause the loss of some of the electromagnetic radiation advantages. The enlarged size of the heated material leads to a decrease in the penetration depth, relative to the dimensions of the material itself. This would call the problems regarding this aspect; kindly refer to Figure 6C, which creates an overheated zone that lays within a short distance from the outer surface of the material, whereas the rest of the target is at low temperature. Moreover, as discussed in the introduction, dielectric properties highly rely on temperature, i.e., as the heated material heats up, the dielectric properties of the heated material increase, which might enlarge the impact of overheating. This aspect causes serious negative effects on the obtained product among other factors. This issue can be reduced by shaking the payload well, which increases the chance of obtaining equal radiation for each of the heated material particles. In addition, the use of “a mode stirrer,” which is a multiple-blade fan that rotates inside the cavity close to the wave guide input, is recommended as it boosts the uniformity of the electromagnetic wave.

The advantage of magnetrons being available in a wide range of power outputs makes the process highly scalable and at the same time becomes a problem as it dramatically increases the capital cost of the designed microwave system. Subsequently, indirect capital and running costs might be increased as well and, eventually, the selling price of the produced product from the process will be affected. To overcome this challenge, using multiple small-scale units instead of one large-scale unit could help reduce the initial capital cost, because for this equipment the initial cost does not have a linear relationship with the unit’s size. Moreover, this approach will enhance uniform-distribution of electromagnetic waves inside the heating zone as it introduces the microwaves via a multiple wave guide.

FUTURE RESEARCH DIRECTIONS

More innovation is still essential to decrease the initial cost of a microwave system and improve the uniformity of electromagnetic waves inside the oven cavity, which will facilitate the establishment of MWH in a broader range of applications. In addition, monitoring and measuring techniques that are employed in small-scale MWH applications might not be suitable when the process is scaled-up. This aspect truly requires new innovating techniques that can be used in these large systems.

CONCLUSION

The key conclusions of this chapter include:

- Microwaves are in the electromagnetic spectrum, from 300 *MHz* to 300 *GHz* of frequency and from 1 m to 1 mm of corresponding wavelength;
- The rapid development of electromagnetic wave technology has established microwaves in a number of applications, such as communications, power transmission, microwave heating, etc;
- Depending on the interaction with microwaves, materials can be classified into absorbing, transparent, and impermeable materials;
- For non-magnetic materials, complex permittivity and loss tangent are the crucial parameters that describe the level of heat generation inside a heated material;
- Applied waves' frequency and heated material's temperature have a high impact on the dielectric properties of the exposed material;
- Electric field/dissipated power penetration depth can be expressed as a function of the dielectric properties of the heated material and the characteristics of the applied radiation;
- The dominant mechanism of microwave heating relies on electromagnetic energy conversion directly within the heated material rather than the superficial heat transfer of conventional heating;
- The nature of the microwave heating mechanism can be employed to avoid several issues and limitations associated with conventional heating;
- MWH leads to non-uniform distribution of temperature and hot and/or cold spots inside the heated material;
- To achieve a more uniform distribution of temperature inside a workload, two factors must be respected: (1) surface heat loss needs to be eliminated, and (2) penetration limits must be considered when a target's dimensions are chosen;

- Homogenous mixing of a strong microwave receptor with the payload leads to the exhibition of a dramatic increase in temperature compared to the basic material heated under the same conditions;
- Microwave heating shows a noticeable effect on chemical reactions, e.g., faster reaction rate, less in energy consumption, higher product quality, etc., in contrast to conventional heating; however, this aspect still needs to be confirmed for the inconsistency in the reported conclusions.
- Conventional pyrolysis leads to the presentation of a temperature gradient that creates a layer of char on the outer surface and moves toward the core, which negatively affects the quantity and/or quality of the final product;
- Temperature profiles in microwave pyrolysis (core hotter than surface) leads to the creation of a char layer in the core and grows toward the surface direction, which might enhance preserving the structure of the obtained product among other positive impacts;
- Scaling-up the microwave system still faces several challenges, most importantly, a relative decrease in the penetration depth, a dramatic increase in the system's capital cost, and the suitability of the monitoring and measuring techniques; and
- Further efforts still need to be made to (1) innovate a technique for measuring transient temperature during microwave exposure, (2) decrease the initial cost of a microwave system, and (2) enhance the uniformity of electromagnetic waves inside the oven cavity.

REFERENCES

Adnađević, B., Gigov, M., Sindjic, M., & Jovanović, J. (2008). Comparative study on isothermal kinetics of fullerol formation under conventional and microwave heating. *Chemical Engineering Journal*, *140*(1–3), 570–577. doi:10.1016/j.cej.2007.12.011

Adnadjevic, B. K., & Jovanovic, J. D. (2012). A comparative kinetics study on the isothermal heterogeneous acid-catalyzed hydrolysis of sucrose under conventional and microwave heating. *Journal of Molecular Catalysis A Chemical*, *356*(0), 70–77. doi:10.1016/j.molcata.2011.12.027

Adnadjević, B. K., & Jovanović, J. D. (2012). Kinetics of Isothermal Ethanol Adsorption onto a Carbon Molecular Sieve under Conventional and Microwave Heating. *Chemical Engineering & Technology*, *35*(4), 761–768. doi:10.1002/ceat.201100153

Borges, F. C., Du, Z., Xie, Q., Trierweiler, J. O., Cheng, Y., Wan, Y., & Ruan, R. (2014). Fast microwave assisted pyrolysis of biomass using microwave absorbent. *Bioresource Technology*, *156*(0), 267–274. doi:10.1016/j.biortech.2014.01.038 PMID:24518438

Budarin, V. L., Clark, J. H., Lanigan, B. A., Shuttleworth, P., Breeden, S. W., Wilson, A. J., & Ross, A. (2009). The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw. *Bioresource Technology*, *100*(23), 6064–6068. doi:10.1016/j.biortech.2009.06.068 PMID:19615895

Campañone, L. A., & Zaritzky, N. E. (2005). Mathematical analysis of microwave heating process. *Journal of Food Engineering*, *69*(3), 359–368. doi:10.1016/j.jfoodeng.2004.08.027

Chandra Shekara, B. M., Jai Prakash, B. S., & Bhat, Y. S. (2012). Microwave-induced deactivation-free catalytic activity of BEA zeolite in acylation reactions. *Journal of Catalysis*, *290*(0), 101–107. doi:10.1016/j.jcat.2012.03.005

Chen, F., Wang, G., Shi, C., Zhang, Y., Zhang, L., Li, W., & Yang, F. (2013). Kinetics of glycolysis of poly(ethylene terephthalate) under microwave irradiation. *Journal of Applied Polymer Science*, *127*(4), 2809–2815. doi:10.1002/app.37608

Dogan, H., & Hilmioglu, N. D. (2009). Dissolution of cellulose with NMMO by microwave heating. *Carbohydrate Polymers*, *75*(1), 90–94. doi:10.1016/j.carbpol.2008.06.014

Domínguez, A., Menéndez, J. A., Fernández, Y., Pis, J. J., Nabais, J. M. V., Carrott, P. J. M., & Carrott, M. M. L. R. (2007). Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *Journal of Analytical and Applied Pyrolysis*, *79*(1–2), 128–135. doi:10.1016/j.jaap.2006.08.003

Durka, T., Van Gerven, T., & Stankiewicz, A. (2009). Microwaves in Heterogeneous Gas-Phase Catalysis: Experimental and Numerical Approaches. *Chemical Engineering & Technology*, *32*(9), 1301–1312. doi:10.1002/ceat.200900207

El harfi, K., Mokhlisse, A., Chanâa, M. B., & Outzourhit, A. (2000). Pyrolysis of the Moroccan (Tarfaya) oil shales under microwave irradiation. *Fuel, 79*(7), 733-742. doi: 10.1016/s0016-2361(99)00209-4

Farag, S. (2013). *Production of chemicals by microwave thermal treatment of lignin* (Philosophiae Doctor), Montreal University, École Polytechnique de Montréal

Farag, S., & Chaouki, J. (2014). A Modified Microwave Thermogravimetric-Analyzer for Kinetic Purposes. *Applied Thermal Engineering*.

Farag, S., Fu, D., Jessop, P. G., & Chaouki, J. (2014). Detailed Compositional Analysis and Structural Investigation of a Bio-oil from Microwave Pyrolysis of Kraft Lignin. *Journal of Analytical and Applied Pyrolysis*, (0). doi:10.1016/j.jaap.2014.06.005

Farag, S., Kouisni, L., & Chaouki, J. (2014). Lumped Approach in Kinetic Modeling of Microwave Pyrolysis of Kraft Lignin. *Energy & Fuels*, *28*(2), 1406–1417. doi:10.1021/ef4023493

Farag, S., Sobhy, A., Akyel, C., Doucet, J., & Chaouki, J. (2012). Temperature profile prediction within selected materials heated by microwaves at 2.45GHz. *Applied Thermal Engineering*, *36*(0), 360–369. doi:10.1016/j.applthermaleng.2011.10.049

Fukushima, J., Kashimura, K., Takayama, S., Sato, M., Sano, S., Hayashi, Y., & Takizawa, H. (2013). In-situ kinetic study on non-thermal reduction reaction of CuO during microwave heating. *Materials Letters*, *91*(0), 252–254. doi:10.1016/j.matlet.2012.09.114

Guiotoku, M., Rambo, C. R., Hansel, F. A., Magalhães, W. L. E., & Hotza, D. (2009). Microwave-assisted hydrothermal carbonization of lignocellulosic materials. *Materials Letters*, *63*(30), 2707–2709. doi:10.1016/j.matlet.2009.09.049

Gupta, M., & Eugene, W. W. L. (2007). Microwaves and metals. Singapore: John Wiley & sons (Asia) Pte Ltd doi:10.1002/9780470822746

Huang, Y. F., Kuan, W. H., Lo, S. L., & Lin, C. F. (2010). Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. *Bioresource Technology*, *101*(6), 1968–1973. doi:10.1016/j.biortech.2009.09.073 PMID:19836946

Karthikeyan, S., Balasubramanian, R., & See, S. W. (2006). Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter. *Talanta*, *69*(1), 79–86. doi:10.1016/j.talanta.2005.08.060 PMID:18970535

Klinbun, W., & Rattanadecho, P. Analysis of microwave induced natural convection in a single mode cavity (Influence of sample volume, placement, and microwave power level). *Applied Mathematical Modelling*(0). doi: 10.1016/j.apm.2011.07.003

Krzan, A., & Zagar, E. (2009). Microwave driven wood liquefaction with glycols. *Bioresource Technology*, *100*(12), 3143–3146. doi:10.1016/j.biortech.2009.01.057 PMID:19261468

Li, D., Zhang, Y., Quan, X., & Zhao, Y. (2009). Microwave thermal remediation of crude oil contaminated soil enhanced by carbon fiber. *Journal of Environmental Sciences (China)*, *21*(9), 1290–1295. doi:10.1016/S1001-0742(08)62417-1 PMID:19999979

Lucchesi, M. E., Chemat, F., & Smadja, J. (2004). Solvent-free microwave extraction of essential oil from aromatic herbs: Comparison with conventional hydro-distillation. *Journal of Chromatography. A*, *1043*(2), 323–327. doi:10.1016/j.chroma.2004.05.083 PMID:15330107

Lupa, C. J. R., Wylie, S., Shaw, A., Al-Shamma'a, A. J., Sweetman, A., & Herbert, B. M. J. (2012). Experimental analysis of biomass pyrolysis using microwave-induced plasma. *Fuel Processing Technology*, *97*(0), 79–84. doi:10.1016/j.fuproc.2012.01.015

Mazo, P., Estenoz, D., Sponton, M., & Rios, L. (2012). Kinetics of the Transesterification of Castor Oil with Maleic Anhydride Using Conventional and Microwave Heating. *Journal of the American Oil Chemists' Society*, *89*(7), 1355–1361. doi:10.1007/s11746-012-2020-3

Menéndez, J. A., Domínguez, A., Inguanzo, M., & Pis, J. J. (2004). Microwave pyrolysis of sewage sludge: Analysis of the gas fraction. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 657–667. doi:10.1016/j.jaap.2003.09.003

Menéndez, J. A., Inguanzo, M., & Pis, J. J. (2002). Microwave-induced pyrolysis of sewage sludge. *Water Research*, *36*(13), 3261–3264. doi:10.1016/S0043-1354(02)00017-9 PMID:12188123

Metaxas, A. C., & Meredith, R. J. (2008). *Industrial Microwave Heating*. London, United Kingdom: The Institution of Engineering and Technology.

Miura, M., Kaga, H., Sakurai, A., Kakuchi, T., & Takahashi, K. (2004). Rapid pyrolysis of wood block by microwave heating. *Journal of Analytical and Applied Pyrolysis*, *71*(1), 187–199. doi:10.1016/S0165-2370(03)00087-1

Monsef-Mirzai, P., Ravindran, M., McWhinnie, W. R., & Burchill, P. (1995). Rapid microwave pyrolysis of coal: Methodology and examination of the residual and volatile phases. *Fuel*, *74*(1), 20–27. doi:10.1016/0016-2361(94)P4325-V

Motasemi, F., & Afzal, M. T. (2013). A review on the microwave-assisted pyrolysis technique. *Renewable & Sustainable Energy Reviews*, *28*(0), 317–330. doi:10.1016/j.rser.2013.08.008

Motasemi, F., Afzal, M. T., Salema, A. A., Mouris, J., & Hutcheon, R. M. (2014). Microwave dielectric characterization of switchgrass for bioenergy and biofuel. *Fuel*, *124*(0), 151–157. doi:10.1016/j.fuel.2014.01.085

Omar, R., Idris, A., Yunus, R., Khalid, K., & Aida Isma, M. I. (2011). Characterization of empty fruit bunch for microwave-assisted pyrolysis. *Fuel*, *90*(4), 1536–1544. doi:10.1016/j.fuel.2011.01.023

Orozco, A., Ahmad, M., Rooney, D., & Walker, G. (2007). Dilute Acid Hydrolysis of Cellulose and Cellulosic Bio-Waste Using a Microwave Reactor System. *Process Safety and Environmental Protection*, *85*(5), 446–449. doi:10.1205/psep07003

Paixão, V., Monteiro, R., Andrade, M., Fernandes, A., Rocha, J., Carvalho, A. P., & Martins, A. (2011). Desilication of MOR zeolite: Conventional versus microwave assisted heating. *Applied Catalysis A, General*, *402*(1–2), 59–68. doi:10.1016/j.apcata.2011.05.025

Pan, R., Wu, Y., Wang, Q., & Hong, Y. (2009). Preparation and catalytic properties of platinum dioxide nanoparticles: A comparison between conventional heating and microwave-assisted method. *Chemical Engineering Journal*, *153*(1–3), 206–210. doi:10.1016/j.cej.2009.06.009

Patil, P., Gude, V. G., Pinappu, S., & Deng, S. (2011). Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions. *Chemical Engineering Journal*, *168*(3), 1296–1300. doi:10.1016/j.cej.2011.02.030

Salema, A. A., & Ani, F. N. (2011). Microwave induced pyrolysis of oil palm biomass. *Bioresource Technology*, *102*(3), 3388–3395. doi:10.1016/j.biortech.2010.09.115 PMID:20970995

Salema, A. A., & Ani, F. N. (2012). Pyrolysis of oil palm empty fruit bunch biomass pellets using multimode microwave irradiation. *Bioresource Technology*, *125*(0), 102–107. doi:10.1016/j.biortech.2012.08.002 PMID:23026320

Salema, A. A., Yeow, Y. K., Ishaque, K., Ani, F. N., Afzal, M. T., & Hassan, A. (2013). Dielectric properties and microwave heating of oil palm biomass and biochar. *Industrial Crops and Products*, *50*(0), 366–374. doi:10.1016/j.indcrop.2013.08.007

Sithambaram, S., Nyutu, E. K., & Suib, S. L. (2008). OMS-2 catalyzed oxidation of tetralin: A comparative study of microwave and conventional heating under open vessel conditions. *Applied Catalysis A, General*, *348*(2), 214–220. doi:10.1016/j.apcata.2008.06.046

Sun, J., Wang, W., Liu, Z., Ma, Q., Zhao, C., & Ma, C. (2012). Kinetic Study of the Pyrolysis of Waste Printed Circuit Boards Subject to Conventional and Microwave Heating. *Energies*, *5*(9), 3295–3306. doi:10.3390/en5093295

Temur Ergan, B., & Bayramoğlu, M. (2011). Kinetic Approach for Investigating the "Microwave Effect": Decomposition of Aqueous Potassium Persulfate. *Industrial & Engineering Chemistry Research*, *50*(11), 6629–6637. doi:10.1021/ie200095y

Wu, C., Budarin, V. L., Gronnow, M. J., De Bruyn, M., Onwudili, J. A., Clark, J. H., & Williams, P. T. (2014). Conventional and microwave-assisted pyrolysis of biomass under different heating rates. *Journal of Analytical and Applied Pyrolysis*, *107*(0), 276–283. doi:10.1016/j.jaap.2014.03.012

Yadav, G. D., & Borkar, I. V. (2006). Kinetic modeling of microwave-assisted chemoenzymatic epoxidation of styrene. *AIChE Journal. American Institute of Chemical Engineers*, *52*(3), 1235–1247. doi:10.1002/aic.10700

Yan, W., Hu, X., Zhang, G., Deng, M., Yi, C., & Xu, Z. (2012). Microwave assisted preparation of monodisperse polymeric microspheres and its morphologies and kinetics. *Journal of Wuhan University of Technology-Mater. Science Editor*, *27*(6), 1100–1104. doi:10.1007/s11595-012-0609-x

Zhang, Z., & Zhao, Z. K. (2010). Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. *Bioresource Technology*, *101*(3), 1111–1114. doi:10.1016/j.biortech.2009.09.010 PMID:19800219

Zhou, L., Puri, V. M., Anantheswaran, R. C., & Yeh, G. (1995). Finite element modeling of heat and mass transfer in food materials during microwave heating - Model development and validation. *Journal of Food Engineering*, *25*(4), 509–529. doi:10.1016/0260-8774(94)00032-5

Zhu, S., Wu, Y., Yu, Z., Liao, J., & Zhang, Y. (2005). Pretreatment by microwave/alkali of rice straw and its enzymic hydrolysis. *Process Biochemistry*, *40*(9), 3082–3086. doi:10.1016/j.procbio.2005.03.016

ADDITIONAL READING

Abubakar, Z., Salema, A. A., & Ani, F. N. (2013). A new technique to pyrolyse biomass in a microwave system: Effect of stirrer speed. *Bioresource Technology*, *128*(0), 578–585. doi:10.1016/j.biortech.2012.10.084 PMID:23211483

Chandrasekaran, S., Ramanathan, S., & Basak, T. (2013). Microwave food processing—A review. *Food Research International*, *52*(1), 243–261. doi:10.1016/j.foodres.2013.02.033

Ciacci, T., Galgano, A., & Di Blasi, C. (2010). Numerical simulation of the electromagnetic field and the heat and mass transfer processes during microwave-induced pyrolysis of a wood block. *Chemical Engineering Science*, *65*(14), 4117–4133. doi:10.1016/j.ces.2010.04.039

Clark, D. E., Folz, D. C., & West, J. K. (2000). Processing materials with microwave energy. *Materials Science and Engineering A*, *287*(2), 153–158. doi:10.1016/S0921-5093(00)00768-1

Doucet, J., Laviolette, J.-P., Farag, S., & Chaouki, J. (2014). Distributed Microwave Pyrolysis of Domestic Waste. *Waste and Biomass Valorization*, *5*(1), 1–10. doi:10.1007/s12649-013-9216-0

Durka, T., Van Gerven, T., & Stankiewicz, A. (2009). Microwaves in Heterogeneous Gas-Phase Catalysis: Experimental and Numerical Approaches. *Chemical Engineering & Technology*, *32*(9), 1301–1312. doi:10.1002/ceat.200900207

Farag, S. (2013). *Production of chemicals by microwave thermal treatment of lignin* (Philosophiae Doctor), Montreal University, École Polytechnique de Montréal

Farag, S., Fu, D., Jessop, P. G., & Chaouki, J. Detailed Compositional Analysis and Structural Investigation of a Bio-oil from Microwave Pyrolysis of Kraft Lignin. Journal of Analytical and Applied Pyrolysis(0). doi: .10.1016/j.jaap.2014.06.005

Farag, S., Kouisni, L., & Chaouki, J. (2014). Lumped Approach in Kinetic Modeling of Microwave Pyrolysis of Kraft Lignin. *Energy & Fuels*, *28*(2), 1406–1417. doi:10.1021/ef4023493

Farag, S., Sobhy, A., Akyel, C., Doucet, J., & Chaouki, J. (2012). Temperature profile prediction within selected materials heated by microwaves at 2.45GHz. *Applied Thermal Engineering*, *36*(0), 360–369. doi:10.1016/j.applthermaleng.2011.10.049

Gabriel, C., Gabriel, S. H., Grant, E. H., Grant, E. S. J., Halstead, B., Michael, P., & Mingos, D. (1998). Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews*, *27*(3), 213–224. doi:10.1039/a827213z

Guo, W., Wang, S., Tiwari, G., Johnson, J. A., & Tang, J. (2010). Temperature and moisture dependent dielectric properties of legume flour associated with dielectric heating. LWT -. *Food Science and Technology (Campinas.)*, *43*(2), 193–201. doi:10.1016/j.lwt.2009.07.008

Hill, J. M., & Marchant, T. R. (1996). Modelling microwave heating. *Applied Mathematical Modelling*, *20*(1), 3–15. doi:10.1016/0307-904X(95)00107-U

Klinbun, W., & Rattanadecho, P. (2012). Analysis of microwave induced natural convection in a single mode cavity (Influence of sample volume, placement, and microwave power level). *Applied Mathematical Modelling*, *36*(2), 813–828. doi:10.1016/j.apm.2011.07.003

Miura, M., Kaga, H., Sakurai, A., Kakuchi, T., & Takahashi, K. (2004). Rapid pyrolysis of wood block by microwave heating. *Journal of Analytical and Applied Pyrolysis*, *71*(1), 187–199. doi:10.1016/S0165-2370(03)00087-1

Motasemi, F., & Afzal, M. T. (2013). A review on the microwave-assisted pyrolysis technique. *Renewable & Sustainable Energy Reviews*, *28*(0), 317–330. doi:10.1016/j.rser.2013.08.008

Ramasamy, S., & Moghtaderi, B. (2010). Dielectric Properties of Typical Australian Wood-Based Biomass Materials at Microwave Frequency. *Energy & Fuels*, *24*(8), 4534–4548. doi:10.1021/ef100623e

Rattanadecho, P. (2006). The simulation of microwave heating of wood using a rectangular wave guide: Influence of frequency and sample size. *Chemical Engineering Science*, *61*(14), 4798–4811. doi:10.1016/j.ces.2006.03.001

Thostenson, E. T., & Chou, T. W. (1999). Microwave processing: Fundamentals and applications. *Composites. Part A, Applied Science and Manufacturing*, *30*(9), 1055–1071. doi:10.1016/S1359-835X(99)00020-2

Yin, C. (2012). Microwave-assisted pyrolysis of biomass for liquid biofuels production. *Bioresource Technology*, *120*(0), 273–284. doi:10.1016/j.biortech.2012.06.016 PMID:22771019

KEY TERMS AND DEFINITIONS

Char Layer Formation: A layer of char that is created as a result of difference in temperature between the outer surface and the core of the heated material.

Complex Permittivity: A parameter that measures the ability of the material to absorb and store electric potential energy.

Dielectric Loss Factor: A parameter that indicates the ability of the material to dissipate microwave energy.

Loss Tangent: A parameter that represents the ability of the heated material to convert the absorbed microwave energy into heat energy.

Microwave Heating: A direct conversion mechanism of electromagnetic energy to heat within the heated material.

Non-Thermal Effects: The effects that are related to the nature of microwave heating.

Power Penetration Depth: The depth at which the magnitude of the power density drops by a factor of $1/e$ with respect to the surface's value.

Pyrolysis: Thermal decomposition of a material by adding heat in an inert environment.

Chapter 6

Liquid Products Characterization from Pyrolysis and Gasification:

How Can It Be Classified?

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ABSTRACT

In this chapter there is described a tentative of obtain and characterize pyrolysis liquids from cashew nut shell, using a suggested classification of tars. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture "tars" with a clear definition. And so, in order to facilitate the study of the evolution of liquid fraction composition, the compounds have been grouped according to their chemical nature, but differently from other works, it was extended the range of compounds in order to

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evaluate the influence of the reactor parameters in liquid fraction compositions. It is described, as well, the pyrolysis and gasification of cashew nut shell, that has been studied in a laboratory scale reactor. It was quantified and classified the production of liquids (tar) and evaluated the final temperature influence (800, 900 and 1000 °C) and the use of N_2 *in pyrolysis case, and a mixture of* N_2 *and steam or air in the gasification case. Finally, it is described the identification and quantification of tar compositions, by CG-MS and CG-FID analyzes. Around 50 different compounds have been detected in the liquid fraction obtained, most of them being present at very low concentrations and it is observed that in the pyrolysis and gasification processes, phenol and benzene were the major chemical groups, and this fact agree with others works, presented here in a bibliographic revision.*

INTRODUCTION

The liquids collection and classifying has long been a major difficulty for researchers. The capture of the pyrolysis vapors by almost all collection devices is very difficult and inefficient. The product vapors can be a combination of gas, micron sized droplets and polar molecules bonded with water vapor. The aerosols after cooling need to be impinged onto a surface to be collected and the most effective collectors are the electrostatic precipitator (Bridgewater, 1999).

Different sampling and analysis methods have been used by manufacturers and other workers to determine the level of particulates and organic contaminants in producer gas generated by biomass gasifier installations. This diversity of methods makes the comparison of operational data difficult and represents a barrier to the further development and commercialization of the technology. This problem was discussed by the members of the Gasification Task of the IEA Bioenergy Agreement in Zurich in October 1997 and divulgated by Knoef and Koele (2000).

Tar comprises a wide spectrum of organic components, generally consisting of several aromatic rings. Reported tar concentrations are strongly dependent on the tar definition used and the measurement method applied. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture “tars” with a clear definition. According to the ECN (Energy Research Centre of the Netherlands) definition, tar comprises all organic components having a higher molecular weight than to benzene (Bergman, van Paasen & Boerrigter, 2002).

Taking into account the issues raised in the preceding paragraphs, an attempt was made in this work, to obtain and characterize the pyrolysis liquids from cashew nut shell, using a suggested classification of tars. By this, a pyrolysis of cashew nut shell has been studied in a laboratory scale reactor.

BACKGROUND

Knowledge of various properties of biomass pyrolysis products is relevant for energy conversion, essential to identifying the utilization of each product. The experimental heating value of the pyrolysis products was determined by Raveendran and Ganesh (1996), and compared each other based on the elemental composition of its. The main conclusions include that heating values of biomass pyrolysis products are functions of the initial composition of the biomass feed, this has been explained through the correlations developed by then, and heating values of biomass pyrolysis liquid are comparable with those of ethanol.

In the study reported by Alén, Kuoppala and Oesh (1996), softwood and its main structural components (cellulose, hemicelluloses, and lignin) were treated separately under the same conditions. In each case, volatile GC-amenable thermal degradation products were identified by mass-selective detection (MSD) and were divided into several characteristic compound groups in weight %, i.e., w/w %, like could be seen in Figure 1.

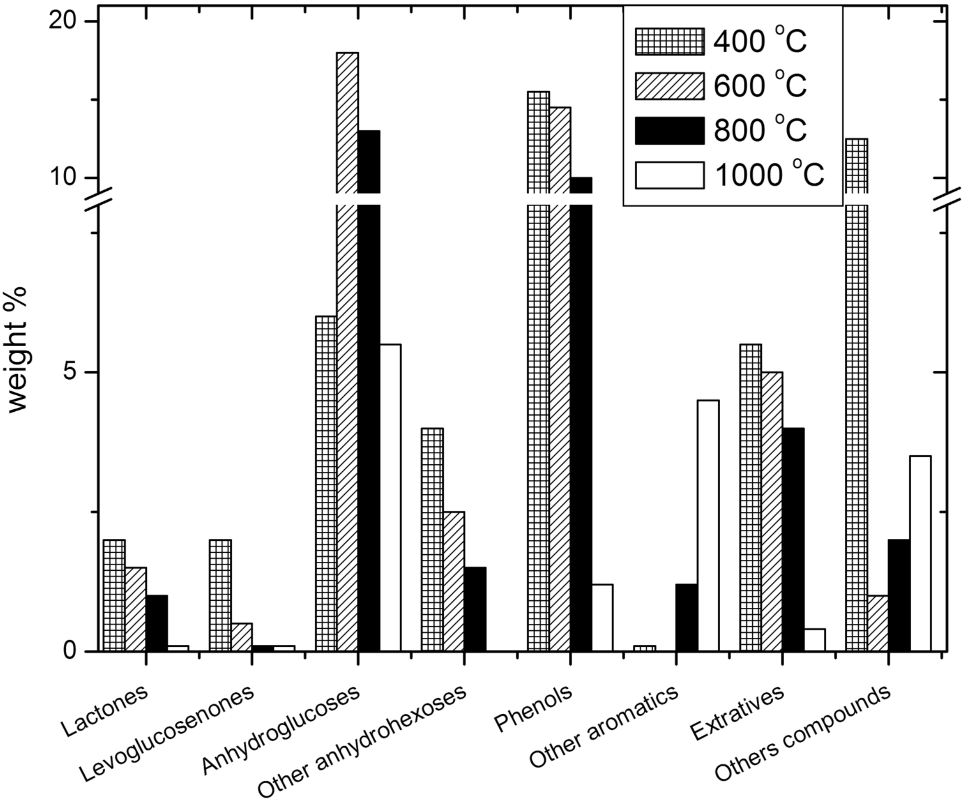
The chemical composition of biomass-based pyrolysis oils is complicated, comprising mainly water, carboxylic acids, carbohydrates and lignin-derived substances. The oils are acidic, viscous, reactive and thermally unstable. The composition and properties of the oils differ considerably from those of petroleum-based fuel oils. Due to the special properties of pyrolysis oils many problems arise in their handling and utilization. In their study, Sipila, Kuoppala, Fagernas, and Oasmaa, (1998) developed a characterization scheme for pyrolysis oils. The aim was to find a relatively simple and fast method that would give sufficient information with respect to chemical and physical properties. The characterization procedure chosen was based on the fractionation of the oils with water and on the analysis of the fractions separately. In addition to the analyses included in the basic scheme, additional analyses can be carried out if necessary. In table 1 is presented the amounts of water soluble compounds analyzed by them.

The complex interaction of time and temperature on liquid product quality has not been explored, because there is no ‘standard’ pyrolysis liquid (Bridgewater, 1999).

Di Bari, Barisano, Cardinale, Matera, Nanna, and Viggiano (2000), made a comparative study of the inorganic and organic products distribution in tar obtained from gasification of biomass, and tar samples were analyzed in a HP 6890 GC-MS. Mean percentage compositions of the identified tar constituents in weight %, i.e., w/w %, showed in figure 2.

Sricharoenchaikul, Frederick Jr and Agrawal (2002), realized the gasification of black Liquor (residue from cellulose production) and grouped the tar compounds detected into two categories, semi volatiles and nonvolatiles, based on their mo-

Figure 1. Relative composition of the main pyrolysis oils products from pine wood sawdust. Results from Alén et al. (1996)



lecular weights and boiling points. Some of the major Black Liquor tar identified was: benzene; toluene; o-,m-,p-xylene; methylstyrene; indene; phenol; naphthalene; 2,6-dimethoxy-phenol; trimethoxy-benzene; hydroxyl-methoxy-benzoic acid; acenaphthene; biphenylene; anthracene; phenanthrene;phenalene; fluoranthene; perylene and pyrene.

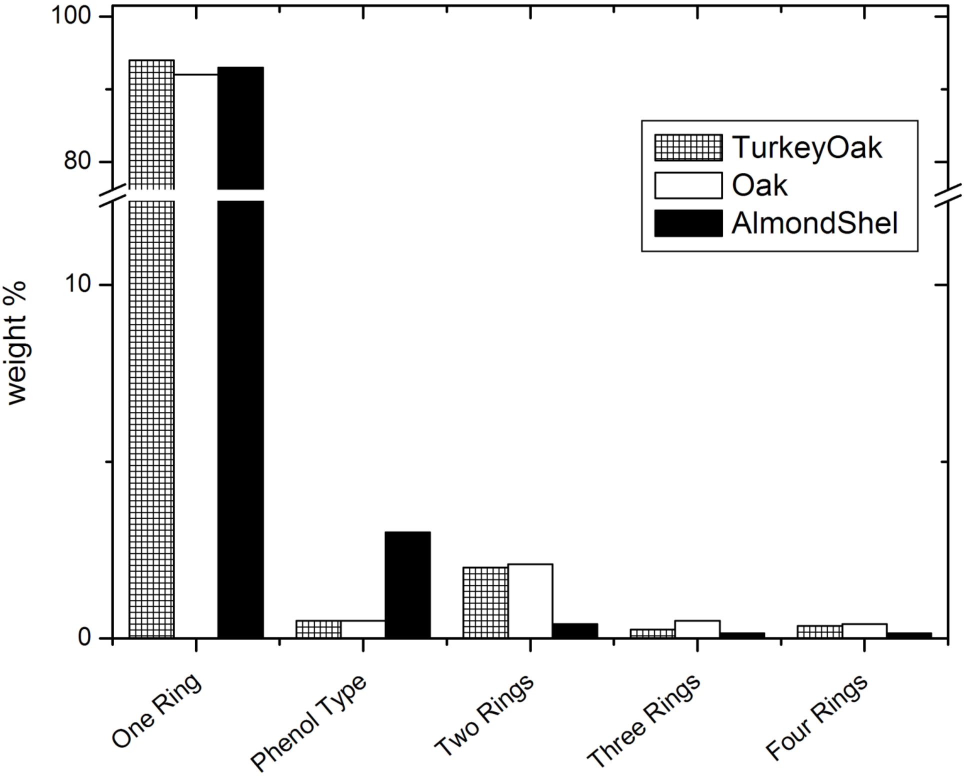
Generally, the results of chemical characterization were not very consistent. It is highly recommended to prepare standard solutions with known amounts of compounds for quantitative analyses. It seems that each laboratory uses its own technique and a lot of work and adaptation will be necessary to harmonize the methods. The complete range of organic acids should be analyzed after derivatization of the acids into their benzylic esters. However, derivatization is not necessary for the determination of the main acidic compound, acetic acid. For chemical characterization, it might be necessary to calibrate the gas and liquid chromatographic systems by preparing standard solutions with known amounts of compounds (Oasmaa & Meier, 2005).

Table 1. The amounts (weight % of pyrolysis oil) of water-soluble compounds analyzed quantitatively in pyrolysis oils (Results from Sipila et al., 1998)

Compound		Straw oil	Pine oil	Ensyn oil (hardwood)
Water content of oil	w/w %	19.9	11.1	23.2
pH of oil		3.7	2.6	2.8
Methanol	w/w %	4.0	1.5	0.4
Acids	w/w %	10.8	7.3	6.2
Methanoic (formic)	w/w %	1.85	2.47	1.10
Ethanoic (acetic)	w/w %	7.41	3.45	4.59
Propanoic (propionic)	w/w %	0.50	0.26	0.24
2-Methylpropanoic (isobutyric)	w/w %	0.07	0.04	0.03
Hydroxyethanoic (glycolic)	w/w %	0.58	0.78	0.11
Butanoic (butyric)	w/w %	0.11	0.06	0.09
2-Hydroxypropanoic (lactic)	w/w %	0.09	0.09	0.03
Allyl acetic	w/w %	0.08	0.07	0.03
Pentanoic acid (valeric acid)	w/w %	0.07	0.03	0.02
Hexanoic (caproic)	w/w %	0.05	0.06	-

The characterization of the initial devolatilisation products could provide important information for understanding synergistic effects and subsequently the formation routes leading to toxic organic compounds and soot during co-combustion. Initial devolatilisation characteristics of the fuels have been characterized, following co-pyrolysis experiments, by Jones and his team (Jones, Kubacki, Kubica, Ross & Williams, 2005). This team investigates the devolatilisation behavior during copyrolysis of pinewood together with one of three coals of different rank, lignite or high volatile bituminous of different origin. A range of pyrolysis experiments has been performed over a temperature range from 400 to 900 °C using pyrolysis–GC–MS (py–GC–MS) and thermogravimetric analysis (TGA). Larger scale batch pyrolysis experiments of the bituminous coal–pine mixture have been performed enabling collection of the evolved liquid fractions. These liquid fractions have then been characterized by GC–MS and size exclusion chromatography (SEC). For these batch pyrolysis tests, synergy (non-additive behavior) was observed and the blend pyrolysis oil contained a decrease in aromatics and an increase in phenols than would be expected for additive behavior. The molecular weight distributions of the evolved liquid fractions

Figure 2. Relative distribution of tar compounds grouped into four principal classes: one ring type (toluene, ethylbenzene, xylenes, and styrene), phenol type (phenol and cresols), two rings type (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and indene), three rings type (phenanthrene, anthracene, acenaphthylene, acenaphthene, and fluorene), and four rings type (fluoranthene and pyrene).The insert magnifies the phenol compounds region of the histogram (Adapted from Di Bari et al., 2000)



also show nonadditive behavior. For TGA experiments, additive behavior was seen for all the coal–pine blends studied. Similarly, no obvious synergy was observed by py–GC–MS for the bituminous coal–pine blends, or for model compound–coal and coal–biomass component blends. Non additive combustion behavior is not easily explained by devolatilisation studies because of the difficulty in replicating the conditions of temperature profile and residence time experienced by the volatiles. Thus, conflicting behavior is exhibited depending upon pyrolysis technique.

Tsai, Lee and Chang (2006) used fast pyrolysis for producing valuable products from the biomasses rice straw, sugar cane bagasse and coconut shell. These products were characterized by gas chromatography/mass spectrometry and chemical characterization (CHNO). In view of the results presented, it can be seen that, as expected, the chemical compositions of pyrolysis bio-oils are very similar with aromatics and oxygenated compounds such as carboxylic acids, phenols, ketones, etc. It was noted that the pyrolysis liquid product contains a significant amount of water and fewer contents of complex compounds (aromatic and carbonyl structures), resulting in low pH and low heating values. The results therefore indicate that a large quantity of water evolves within a short time due to the water content of biomass feedstock and dehydration reaction in the fast pyrolysis process. GC–MS analyses have shown that carboxylic acids, phenols, alcohols and branched oxygenated hydrocarbons are the main compounds of the bio-oil. It is necessary that the resultant liquid product would need further processing to remove the condensed water for chemical feedstock and/or biofuel production. They characterized liquid yield from various biomass wastes. The chemical characterization by elemental (CHNO), calorific, Fourier transform infrared (FT-IR) spectroscopy and gas chromatography/mass spectrometry (GC–MS) showed that the pyrolysis liquid products contain large amounts of water (>65 wt%), and fewer contents of oxygenated hydrocarbons composing of carbonyl groups. Table 2 shows the compounds obtained.

Ayllón, Aznar, Sánchez, Gea, and Arauzo, (2006), study meat and bone meal pyrolysis in a fixed bed reactor, analyzing the influence of the final pyrolysis temperature and heating rate on the product (char, liquid fraction and gas) distribution and composition and the char characterization. Two sets of experiments have been performed at different final pyrolysis temperatures between 300 and 900 °C and heating rates from 2 to 14 °C/min. From the results obtained it is observed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate. The liquid fraction obtained is mainly composed of more than 60% nitrogenated aliphatic compounds (such as nitriles, amides and cyclic compounds), 15% aliphatic hydrocarbons (such as alkanes and alkenes), 10% oxygenated aliphatic compounds (mostly carboxylic acids) and about 8% oxygenated aromatic compounds (mainly phenolics). Around 120 compounds have been detected in the liquid fraction obtained, most of them being present in very low percentages. The large amount of tar definitions and measurement methods, as well as the wide spectrum of organic compounds, makes it almost impossible to capture "tars" with a clear definition, than it was proposed, in order to facilitate the study of the evolution of the liquid fraction composition with the temperature, that the compounds detected have been grouped according to their chemical nature.

The tar content of the product gases from gasification of biomass is one of the major factors affecting the subsequent process stages. Brage, Yu, Chen and Sjostrom (1997) reported the evolution profiles of the main tar constituents, i.e. benzene, toluene, indene, naphthalene and phenol were obtained during about 1 h gasification runs of biomass and coal in a pressurized Fluidised-bed at 700 and 900

Table 2. Compounds obtained in a tentative GC-MS characterization of pyrolysis liquid products from biomass wastes[a] *. Adapted from Tsai et al. (2006)*

Peak no.	t_R (min)	Component	Molecular weight
1	14.4	Acetic acid ($C_2H_4O_2$)	60
2	21.8	Furan, 2,5-dimethyl- (C_6H_8O)	96
3	23.1	2-Furanmethanol ($C_5H_6O_2$)	98
4	24.5	2H-pyran, 3,4-dihydro (C_5H_8O)	84
5	25.7	2(3H)-furanone, 5-methyl- ($C_5H_6O_2$)	98
6	27.8	Phenol (C_6H_6O)	94
7	29.7	1,2-Cyclopentanedione-3-methyl- ($C_6H_8O_2$)	112
8	32.1	Phenol, 2-methoxy- ($C_7H_8O_2$)	124
9	32.7	Maltol ($C_6H_6O_3$)	126
10	33.0	2-Cyclopentan-1-one,3-ethyl-2-hydroxy-(C_7H_{10}O2)	126
11	34.3	Phenol, 4-ethyl- ($C_8H_{10}O$)	122
12	35.2	,2-Benzenediol ($C_6H_6O_2$)	110
13	35.9	Benzofuran, 2,3-dihydro- (C_8H_8O)	120
14	37.2	1,2-Benzenediol, 3-methyl- ($C_7H_8O_2$)	124
15	37.7	1,2-Benzenediol, 3-methoxy- ($C_7H_8O_3$)	140
16	38.2	Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	152
17	39.2	4-Hydroxy-3-methylacetophenone ($C_9H_{10}O_2$)	150
18	40.0	Phenol, 2,6-dimethoxy ($C_8H_{10}O_3$)	154
19	41.7	Benzaldehyde, 3-hydroxy-4-methoxy ($C_8H_8O_3$)	152
20	44.0	Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	164
21	44.9	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_9H_{10}O_3$)	166
22	46.1	2-Propanone, 1-(4-hydroxy-3-methoxypheny)- ($C_{10}H_{12}O_3$)	180
23	49.1	Benzeneacetic acid, 4-hydroxy-3-methoxy- ($C_9H_{10}O_4$)	182
24	51.1	Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)	194

[a] Obtained at heating rate of 400 °C/min, pyrolysis temperature of 500 °C, holding time of 1 min, particle size of <0.50 mm, nitrogen flow rate of 1000 cm^3/min STP (Standard Temperature and Pressure), and condensation temperature of -10 °C

C, 0.4 MPa. Sampling and analysis was achieved, using the solid-phase adsorption (SPA) method that combine sampling and subsequent liquid chromatographic (LC) sample preparation on the same sorbent tube, previously developed in their laboratory. Accurate tar sampling and analysis represent primary monitoring objectives for gas quality control and for benchmarking gasifier's performance. Accordingly, development of suitable analytical methods constitutes a vital part of their research program. Tar profiles of light compounds (ranging in molecular weight between 78 and 202) were obtained using the SPA method (Brage, Yu, Chen & Sjostrom, 2000). Thus, it may be possible to indirectly estimate the level of asphaltenes by measuring light compounds using SPA instead of time consuming cold trapping techniques currently used. It may then be possible to get a rough estimate of total tar, i.e. the sum of light and heavy tars. Asphaltenes are non-volatile high-molecular weight (about 1000±50,000) constituents of tar with essentially unknown structures. Although such compounds are readily cracked at elevated temperature, they can be of practical significance since their coke formation tendency can cause rapid catalyst deactivation.

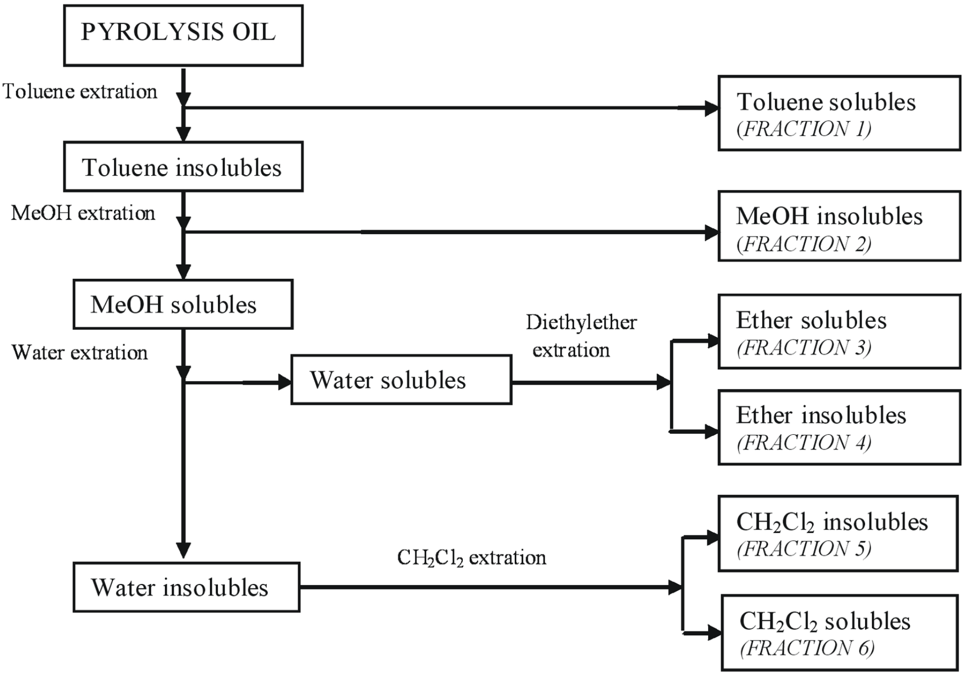
Brage, Yu, Chen and Sjostrom (2007) also developed a method for the analysis of heavy tar compounds in producer gas from biomass gasifiers. Heavy tars are mixtures of oxygenated "non-volatile" compound that cannot pass through a gas chromatographic (GC) column. A sampler prototype was made from two commercially available filter holders and in-house made parts. Results from various off-line tests with the sampler using tar extracts and mixtures of PAH applied to filters showed the overall precision was within 3% and accuracy about 95% for a 50 mg sample. Samples were analysed for total light tar using Chrompack CP 2002 gas chromatograph (GC) fitted with a flame ionization detector (FID) and a split-splitless injector using helium as carrier gas. The KTH heavy tar method can be used in combination with the SPA (solid phase adsorption) method for determination of total tar concentration.

Dufour, Girods, Massonc, Normanda, Rogaumeb, and Zoulalian, (2007), compare two methods for the sampling and analysis of tar produced from wood pyrolysis in nitrogen atmosphere. The first method used a conventional cold trapping technique in solvent-filled impingers followed by liquid injection. The second one is a new application of multi bed solid-phase adsorbent (SPA) tubes followed by thermal desorption (TD). Both methods are based on gas chromatography (GC) coupled with mass spectrometry (MS). Quantification was performed with a well reproducible GC–MS method with three internal deuterated standards. Fourteen compounds were analyzed: benzene, toluene, *m*-xylene, *o*-xylene, styrene, phenol, indene, *o*-cresol, naphthalene, 2-methylnaphtalene, 1-methylnaphtalene, acenaphtylene, phenanthrene, and anthracene. SPA/TD is a more accurate method than impingers especially for light PAHs. Tar sampling time is considerably shortened and limits of detection are increased. Moreover, because no solvent is used, SPA/TD is more convenient regarding operators' health, sample preparation, storage and sample sending for further analysis.

The distribution of fuel-nitrogen in gases, tar and char from gasification of biomass in a pressurised fluidised bed gasifier was investigated by Yu, Brage, Chen, and Sjostrom, (2007). An effective method for extracting NHCs from the acidic absorption of the product gas was introduced in this work. The method makes use of solid phase extraction (SPE) by a silica-based C_{18} tube to extract the NHCs which subsequently were analysed by gas chromatography (GC) with flame ionisation detection (FID). Four species of biomass: birch, Salix, Miscanthus and Reed canary grass were gasified at 0.4 MPa and 900 °C. Oxygen-enriched nitrogen was used as fluidising agent. As a reference, gasification of Daw Mill coal was also carried out under the same experimental conditions. The experimental results illustrate that both the nature of the original fuels and the chemical structure of the nitrogen in the fuel have influence on the distribution of fuel-nitrogen in gases (NH_3, HCN, NO), tar and char under the employed experimental conditions. They show that the types of nitrogen heterocyclic compounds (NHCs) in the tar from different kinds of biomass are the same and the major compound is pyridine.

Garcia-Perez, Chaala, Pakdel, Kretschmer, and Roy, (2007), describes an analytical approach to determine the chemical composition of bio-oils in terms of macro-chemical families. The scheme is showed in Figure 3. Bio-oils from the vacuum pyrolysis of softwood bark and hardwood were first fractionated using solvent extraction. Fractions obtained were then characterized using GC-MS, thermogravimetric techniques (TG) and Gel Permeation Chromatography (GPC).

Figure 3. Fractionation scheme for bio oil chemical characterization proposed by Garcia-Perez et al. (2007)



In July 2005 was published a document with guidelines for the collection and analysis of tar and particles in the gas generated from biomass. The document was prepared by a committee attended by several European groups, CEN BT/TF 143. This is an Technical Specification with the title *Biomass Gasification – Tar and Particles in Product Gases – Sampling and Analysis* and is complemented by a technical note with several relevant definitions, *Sampling and analysis of tar and particles in biomass producer gases – Technical Report - "Organic contaminants ("tar") in biomass producer gases"*. These documents are important because they are the first to detail all the steps of condensation of tar and also the methodologies for the analysis of liquid products generated in the processes of gasification. In this work various settings are made, for example, biomass is defined as any material of biological origin, excluding material in geological formations transformed into fossil. The pyrolysis is defined as thermal decomposition in the absence of any source of oxygen, such as air, O_2, H_2O or CO_2. The tar is considered a generic term and not specific to describe any and all organic compound present in the products of gasification, excluding hydrocarbon gases from one to six carbons. They recommend that the individual concentrations of tar are obtained by Chromatography. The compounds can be identified and quantified by using GC-MS or GC-FID. The major compounds identified in the literature, and cited by the protocols are shown with their structures in Table 3.

Therefore, the researchers still have not defined a specific protocol for sampling and analyzing tar from gasification and pyrolysis processes.

Table 3. Major compounds identified in the tar cited by CEN BT/TF 143

Compound	Molecular weight
Pyridine	79
Toluene	92
Phenol	94
Indene	116
Fluorene	166
Guaiacol	124
Naphtalene	128
Acenaphthylene	152
4-methylguaiacol	102
Anthracene	178
Phenanthrene	178
Fluoranthene	202
Pyrene	202
Benz(a)pyrene	252

By this analysis, it had been clear that we can not use a unique type of classification for all biomass tar product. In this work, in order to facilitate the study of the evolution of the liquid fraction composition, the compounds have been grouped according to their chemical nature (see Table 4), but differently from other works, it was extended the range of compounds in order to compare the influence of the parameters in liquid fraction compositions, in order to facilitate the use of more simple libraries in the analyzers (GC-MS or FT-IT) and quantitatively determine the compounds. It is hoped that in this way may be easier to identify the intended use of the liquid fraction.

In order to theoretically clarify the formation mechanism of main gaseous products (CO, CO_2 and CH_4) in lignin pyrolysis processes and in in cellulose pyrolysis processes, some authors (Liu, Huang, Huang,Liand zang, 2011 and Huang Liu, Tong Li and Wu, 2014) investigated the decarbonylation, decarboxylation and demethylation reactions of various lignin model compounds containing phenyl. These authors investigated too the thermodynamic and kinetic parameters of decarbonylation of butyraldehyde and decarboxylation of butyricacid as model compound of pyrolysis of cellulose. The main results of these investigations were: the formation of CO in lignin pyrolysis occurs more easily through decarbonylation reaction of phenyl and the release of CO_2 in lignin pyrolysis is related to the internal dehydration of cellulose and can take place more easily with increasing temperature. The

Table 4. Liquid fraction compound classification proposed by this work

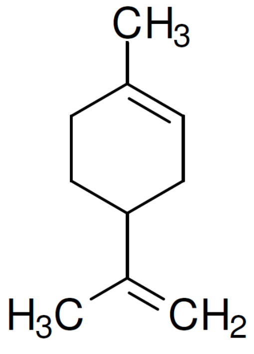
Class		Type	Examples	Principal Structure
Aliphatic hydro carbons		Alkanes	Tridecane Eicosane Docosane Tricosane	> 10 C C_nH_{2n+2} n>20
		Alkenes	Pentadecene	$CH_3(CH_2)_{11}CH_2CH=CH_2$
		Cyclic		

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Table 4. Continued

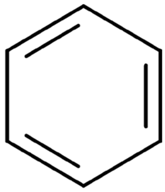
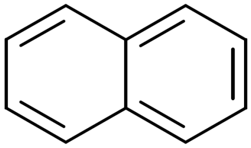
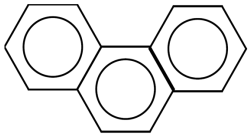
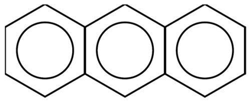
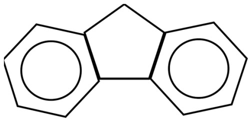
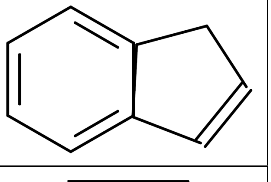
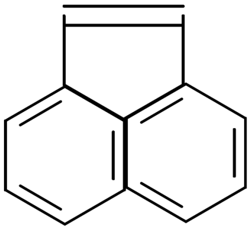
Class		Type	Examples	Principal Structure
Aromatic hydro carbons	1 ring	Benzene Methyl benzenes	Benzene	
	Polycyclics (2 rings)	Naphthalene Methyl naphthalenes	Naphthalene	
	Polycyclics (3 rings)	Phenanthrene	Phenanthrene	
		Anthracene	Anthracene	
	Polycyclic (other rings)	Fluorene	Fluorene	
		Indene	Indene	
		Acenaphthylenes	Acenaphthylene	
Oxygenated compounds	Oxygenated aliphatic	Carboxylic acids	Hexadecanoic acid	$CH_3(CH_2)_{14}COOH$
			Octadecanoic acid, Octadecanoic acid, methyl ester	$CH_3(CH_2)_{16}COOH$

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Table 4. Continued

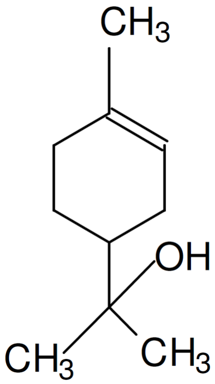
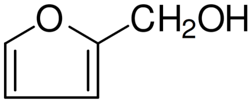
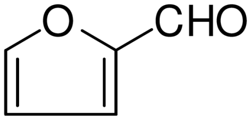
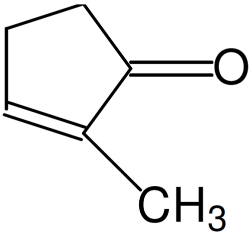
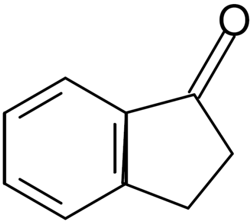
Class		Type	Examples	Principal Structure
	Oxygenated heterocycles	Alcohols	α-Terpineol	
	Oxygenated aromatics	Alcohols	Furfuril alcohol	
		Aldehydes	Furfural	
		Ketones	2-Methyl-2-cyclopenten-1-one	
			1-Indanone	

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Table 4. Continued

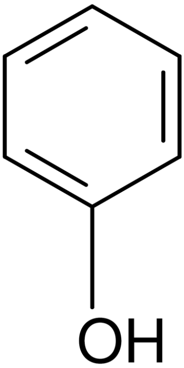
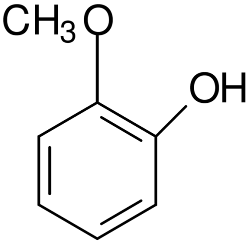
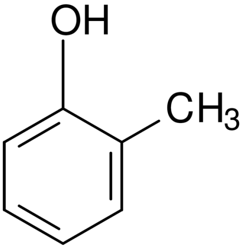
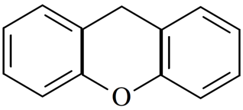
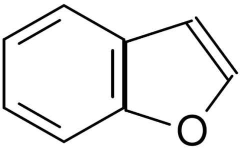
Class		Type	Examples	Principal Structure
		Phenols	Phenol	
		Guaiacol	2-methoxyphenol	
		Cresols	**o** m, p -cresol	
		Xanthenes	Xanthenoxanthene	
		Benzofuran	Benzofuran	

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Table 4. Continued

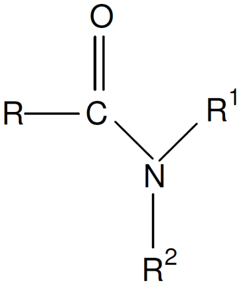
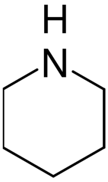
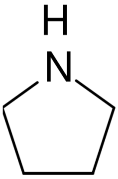
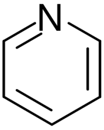
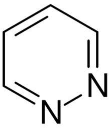
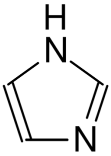
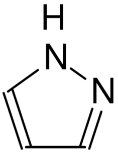
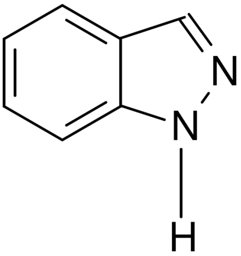
Class		Type	Examples	Principal Structure
Nitrogenated compounds	Nitrogenated aliphatic	Nitriles	Hexadecanitrile	$RC \equiv N$
		Amides	Hexadecamide	
		Amines cyclics	Piperidine Pyrrolidine	 
	Nitrogenated aromatics	Pyridines	Pyridine Pyridazine	 
		Nitrogen heterocyclic series	Imidazole Pyrazole	 
			Indazole	

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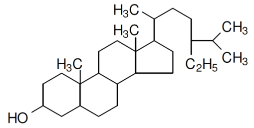
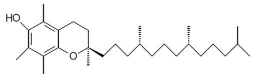
Table 4. Continued

Class		Type	Examples	Principal Structure
Others	Steroid alcohols	Cholesterol	Stigmast	
		Tocopherol	Tocopherol	

formation of CH_4, from lignin, can occurs at 550 K or above. The experimental results of the cellulose pyrolysis showed that the output of CO increases obviously with the increase of temperature, while the output of CO_2 which forms mainly in the low temperature region changes differently with the change of temperature. During cellulose pyrolysis, the outputs of CO and CO_2 mainly depend on the amount of carbonyl- and carboxyl-containing groups that are formed during pyrolysis, and are more a function of the kinetics than the thermodynamics.

These models are very complex. In order to simplify the explanation for the different fields of CO and CO_2 with the temperature variation, we used the elementary model of heterogeneous and homogeneous chemical reactions of carbon (Lipska-Quinn, Zeronian, & Mc Gee, 1985), as presented in the item *Results and Discussion.*

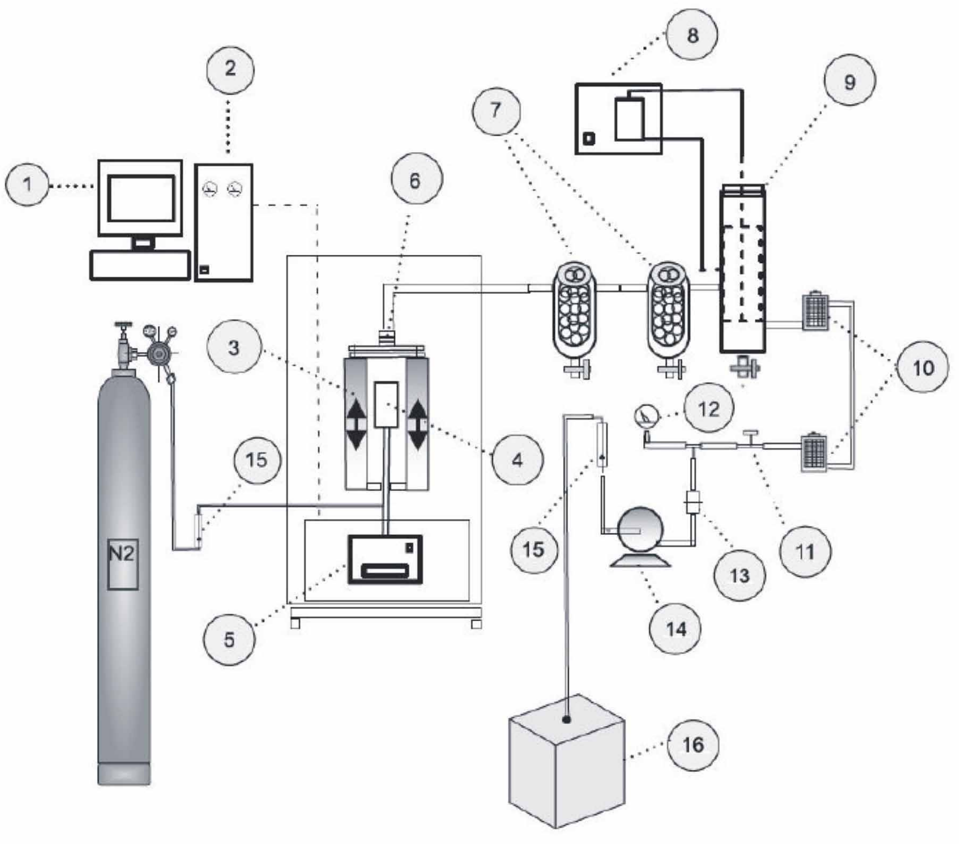
EXPERIMENTS PERFORMED IN PYROLYSIS AND GASIFICATION OF CASHEW NUT SHELL: A CASE STUDY

Experimental Setup

The material used in the experiments was cashew nut shell in powder format with a particle size smaller than 0.8 mm, appropriate particle size for minimizing the effects of heat transfer on the particle. In order to facilitate the transport phenomena and empowers the pyrolysis or gasification processes. The initial sample mass was 15 g in all the experiments performed.

The pyrolysis and the gasification runs were performed in a bench scale plant, shown in Figure 4, consisting of a fixed bed reactor of 90 mm diameter and 320 mm length, discontinuous for the solid feed. The reactor is inside a tubular electric furnace of 325 mm length, 355 mm external diameter and 120 mm internal diameter, connected to a temperature and heating control system. Computer software provides

Figure 4. Experimental setup used. 1) Computer; 2) Temperature control module; 3) Reactor furnace; 4)Basket with sample; 5) Eletronic balance; 6) Gas outlet; 7) Condensers; 8) High voltage source; 9) Electrostatic precipitator; 10)Filters; 11) Needle valve; 12) Manometer; 13) Filter; 14)Vacuum pump; 15) Mass flowmeter; 16) Sample bag or sample point



a continuous record of carrier gas flow rate, time, temperature of the furnace and temperature up to six thermocouples placed in the sample. In order to obtain additional and compatible information with previous work (Ayllón et al, 2006), we choose the maximum temperatures reaching the reactor (800, 900 and 1000 ºC). Chosen gasification atmospheres are typical found in these processes.

A steel basket with a radius of 28.3 mm and height of 41 mm containing a sample weight of 15 g was placed in the reactor prior to the experiment at a depth between 201 and 245 mm from the top. This basket has two mesh screens, the external one having a diameter of 1000 µm and the internal one of 40 µm. Once the reactor is closed, a nitrogen flow of 13 cm^3 NTP/s (NTP: normal temperature and pressure, 0 ºC and 1 atm) is set by means of a mass flow controller. After 30 min under nitrogen flow, when the air is purged from the reactor, the furnace is heated up to the temperature required and picked up to start the reactor heating. The temperature of the reactor is then kept constant for approximately 130 min to make sure that the pyrolysis process is complete. The exit gas passes through a tar condensation system, which consists of two glass condenser vessels cooled with a mixture of ice and water and an electrostatic precipitator. After the precipitator filters are used to confirm that the collection was complete (they must be clean). The method for collecting the gas, consists of taking gas samples every 3.5 min and analyzing them. The clean gas is analyzed by GC-TCD, in a system equipped with a Porapak N column and a molecular sieve. The compounds analyzed were H_2, CO, and CO_2. Heavier compounds were not detected in the experimental conditions used in this study. Once the experiment is finished and the system is cooled down to room temperature, the char is removed from the basket and weighed. Through biomass thermal conversion, in the pyrolysis processes, it was quantified the production of solids (char), liquids (tar) and gases. For pyrolysis, it was evaluated the influence of the temperature (800 and 1000 ºC). For gasification, it was evaluated the temperature (800, 900 and 1000 ºC) and the use of N_2, air, and mixtures of N_2 and steam, in the amounts of char, tar and gas. The liquid fraction collected by the tar condenser system is also weighed and subsequently extracted with 2-propanol. The liquid fraction diluted sample is analyzed through GC–MS and GC-FID in order to identify and quantify the compounds present. The interpretation of the mass spectra obtained by gas chromatography + mass spectrometry was based on automatic library search and by manual interpretation comparing on data from previous studies. The water amount was determined by Karl Fischer Reagent Titration Method (Crison-Micro KF2025).

Results and Discussion

Analysis of Cashew Nut Shell

A type of biomass used now for the production of energy is the cashew nut shell, originated from the Northeast area of Brazil. This area has beneficiating industries of the cashew nut that use your principal reject (shell) as fuel, avoiding with that your deposit in sanitary embankment, that due to the great volume of shells can saturate the embankment in a short space of time.

Table 5. shows the ultimate and proximate analysis (dry basis), moisture (wet basis) and higher heating value of the sample used in the pyrolysis.

We note that the values found for ultimate analysis are similar to those found for other biomasses, but proximate analysis, unlike other biomass, presents a very large

Table 5. Ultimate analysis, Proximate analysis and Heating Value of cashew nut shell

Element		
C	% (w/w) dry basis	52.91 ± 1.69
H	% (w/w) dry basis	6.87 ± 0.08
N	% (w/w) dry basis	0.78 ± 0.16
O	% (w/w) dry basis	39.44 ± 1.79
	% (w/w) dry basis	
Component		
Ash	% (w/w) dry basis	1.16 ± 0.37
Volatile matter	% (w/w) dry basis	78.12 ± 0.14
Fixed carbon	% (w/w) dry basis	20,71 ± 0.38
	% (w/w) dry basis	
Moisture	% (w/w) Wet basis	9.31 ± 0.14
Higher heating value (HHV)	MJ/kg	22.45 ± 0.34

amount of volatiles. Some of these are volatiles from an oily liquid that is impregnated into the bark. The oil probably increases the heat value that appears higher than for most biomasses.

Pyrolysis with 100% of N_2

Although our focus is centered in the liquid fraction, a brief and simplified explanation of the gaseous fraction is given.

The experiments results, average from 3 replicates each one, are shown in table 6, with the fed gas (N_2) flow rate, the temperature of process and your products, char, tar and gas.

It was observed that the increase of temperature increase gas production, decrease tar yield and decrease char yield. The yield of char did not change significantly

Table 6. Runs and respectives product yields from pyrolysis of cashew nut shell. Initial total Biomass fed: 15 g

Fed			**Product Yields**					
Run	**Temp**	**Q N_2**	**Char**	**Tar**	**Gas**	**Char**	**Tar**	**Gas**
	(°C)*	**(g/min)**	**(g)****	**(g)****	**(g)****	**w/w %**	**w/w %**	**w/w %**
1	1000	6,25	3,07	4,65	5,38	20.5	31.0	35.9*
2	800	6,25	4,04	6,58	2,51	26.9	43.9	16.7

Three repetitions average. Uncertainty: *±5 °C; **±0,01 g because the temperature was increased very little, not enough to increase hardly the degradation of biomass, ie, the degradation reactions of the components cellulose, hemicellulose and lignin have already happened and now, after a sufficient residence time, temperature only changes the field of gas due to homogeneous and heterogeneous reactions. In other words, the heterogeneous reaction (1 and 2) occur at the same rate (Lipska-Quinn, et al., 1985). We must bear in mind that the oxygen comes from the biomass itself.

$C_{(S)} + 1/2O_{2\,(G)} \Leftrightarrow CO$ reaction 1
$C_{(S)} + O_{2\,(G)} \Leftrightarrow CO_2$ reaction 2

In the experiments up to 800 ºC occurs the increase of the formation ratio of gases through the Boudouard reaction (3). It is well known that the equilibrium of the Boudouard reaction tends to increase the formation of CO with increasing temperature.

$C\ (s) + CO_2\ (g) \Leftrightarrow 2\ CO$ reaction 3

The tar formation occurred between the temperatures 350 ºC to 450 ºC. Up this temperature it has the conversion of tar in gases. Table 7 shows that the increases of temperature, since 800 ºC to 1000 ºC decrease the tar formation.

Table 7. Result of the gasification experiments with 15g initial mass of cashew nut shell

Run	**T**	**Process Identification**	**N_2 Flow**	**Steam Flow**	**Air Flow**	**Obtained Char**	**Obtained Tar**	**Obtained Gas**	**Obtained water**
	(°C)		**(g/ min)**	**(g/min)**	**(g/ min)**	**(g)***	**(g)***	**(g)***	**(g)***
1	800	100% Air	-	-	6.25	0.33	5.79	7.97	0.54
2	900	100% Air	-	-	6.25	0.33	6.43	7.36	0.46
3	1000	100% Air	-	-	6.25	0.33	5.59	9.23	0.39
4	800	20% N_2 80% Steam	1.25	3.21	-	2.42	12.83	8.53	5.51
5	900	20% N_2 80% Steam	1.25	3.21	-	1.14	4.1	15.26	8.01
6	1000	20% N_2 80% Steam	1.25	3.21	-	1.54	2.72	22.54	7.52
7	800	70% N_2 30% Steam	4.38	1.21	-	2.87	11.16	6.35	11.57
8	1000	70% N_2 30% Steam	4.38	1.21	-	2.01	1.57	14.83	3.34

* Uncertainty ± 0.01

The obtained gas concentration can be justified by the analysis of reactions displacement. In the experiments with 100% of N_2, it is verified that the reaction (4) has its displacement in accordance with the partial pressure intensity.

$CO + \frac{1}{2} O_2 \Leftrightarrow CO_2$ reaction 4

Figure 5. shows experiments at 800 ºC. The displacement reaction (4) leads to CO_2 formation, because the partial pressure displacement of the equilibrium leads to CO_2 formation. Figure 6 shows the experiment at 1000 ºC, where the equilibrium displacement lead to increase the CO formation, because reaction (3) leads to CO formation. Figures 5 and 6 are only examples of the release of the pyrolysis gases. The main objective of this study will be the analysis and classification of liquid fraction generated.

Figure 5. Concentration of CO_2 and CO, at temperature of 800 ^{0}C and 100% of N_2

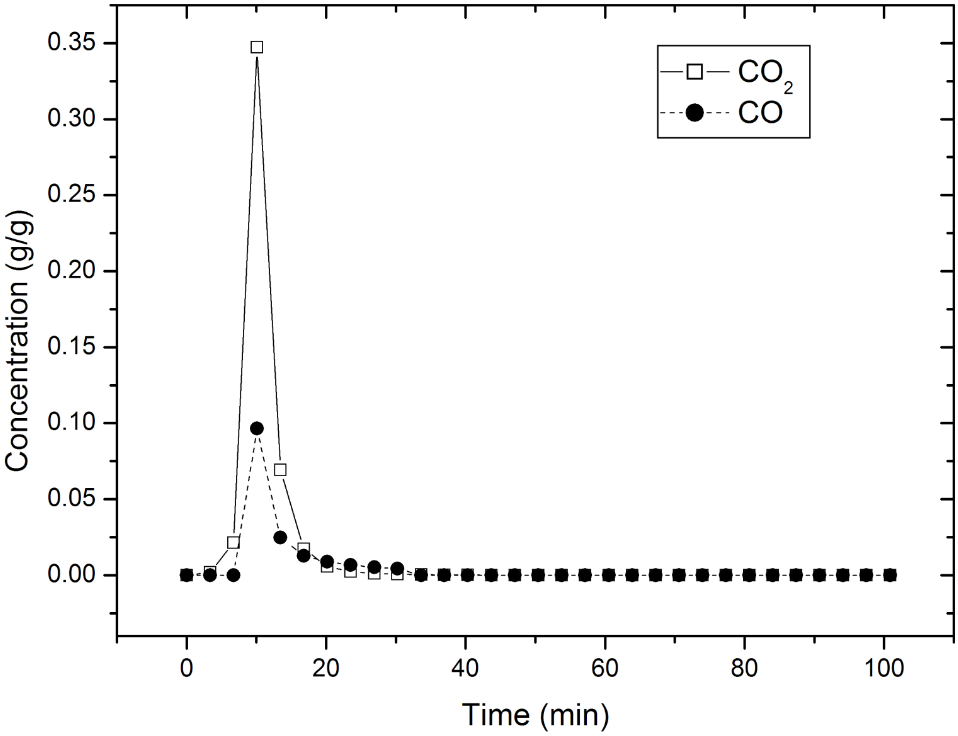
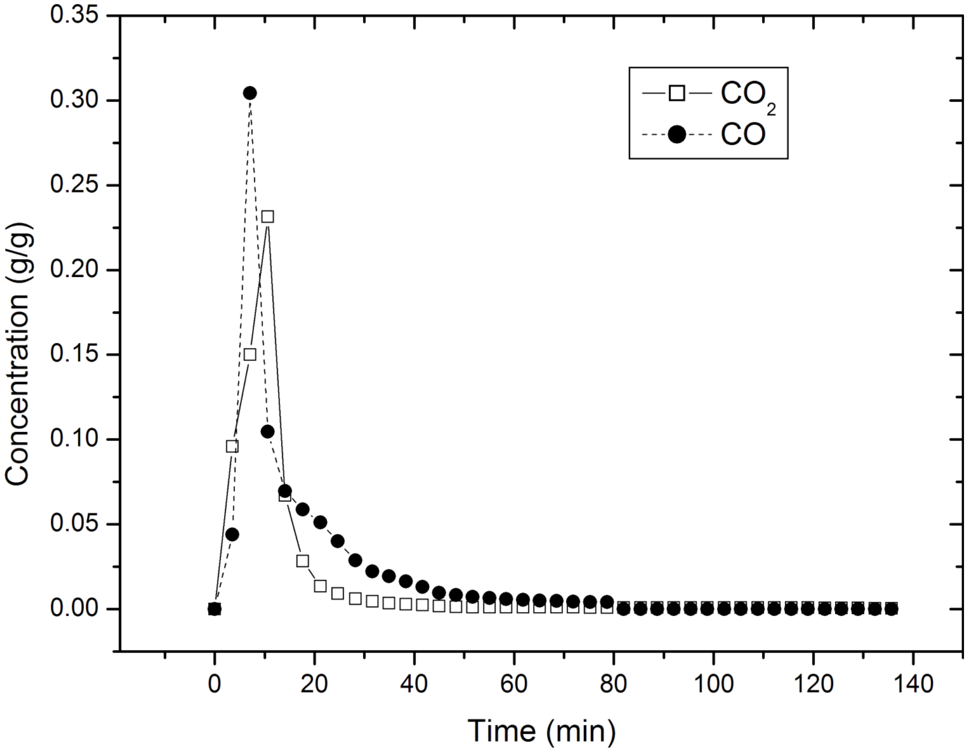


Figure 6. CO_2 *and CO concentration, at temperature of 1000* ^0C *and 100% of* N_2



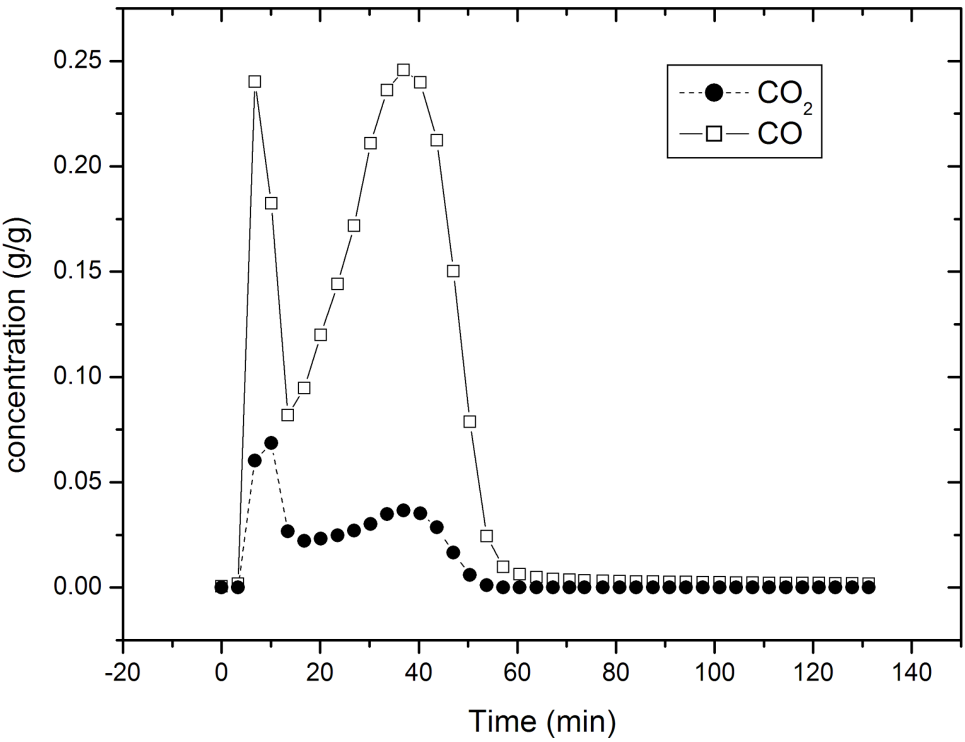
Gasification with Air, N_2 and Steam

Experiments at 800 ºC, 900 ºC and 1000 ºC, with mixtures of N_2 and steam had not change in the trend of formation of CO_2, where shift reaction (5) occurred. The shift reaction (5) remains towards the formation of CO_2. The Figure 7 shows the experiments at 1000 ºC, with steam.

$CO + H_2O \Leftrightarrow CO_2 + H_2$ reaction (5)
$C (s) + H_2O (g) \Leftrightarrow CO + H_2$ reaction (6)
$C (s) + 2 H_2O (g) \Leftrightarrow CO_2 + 2 H_2$ reaction (7)

Experiment at 1000 ºC shows the displacement of the reaction (4) leading to formation of CO_2. The inverse occurs with experiments without steam, where the reaction (4) equilibrium leads to CO formation. This inversion is justified by shift reaction (5), where the CO reacts with dissociated steam making CO_2 and H_2. The

Figure 7. Concentration of gases, at 1000 ^{0}C with 1.25 g/min of N_2 and 3.21 g/min of steam



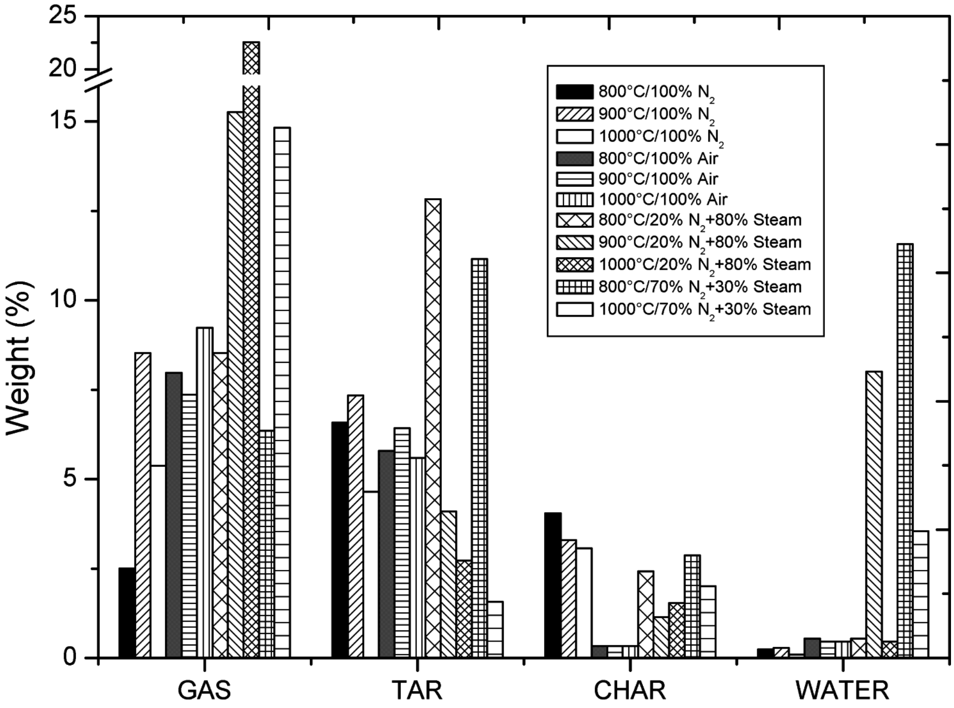
CO can also be made from reaction (6). Then, the shift reaction (5) increases the CO_2 formation. Thus we have an increase in the yield of gas generated when were introduced steam.

Process Products Distribution

The products obtained from gasification were gas, a liquid fraction (tar, water-solubles and water) and char. The experiments results are shown on Table 7, with the mix fed gas. The results of char, tar and gas, were obtained from the sample with 15g initial mass. Figure 8, shows well the main products, in weight %, i.e. w/w %, in pyrolysis and gasification process, at any temperature.

With the increase of temperature and steam flow ratio it was observed the increase in gas product (Table 7). With temperatures higher than 700 ℃, occurs the degradation of tar with increase on gas formation. In the experiments with steam up to 800 ℃ occur the increase of of gases formation through the Boudouard reaction (3) and carbon reaction with steam (6 and 7).

Figure 8. Product distribution obtained from pyrolysis and gasification



It was observed that, in most of experiments, the increase of temperature increase gas production, decrease yield of liquid fraction and did not have significant change in the amount of char.

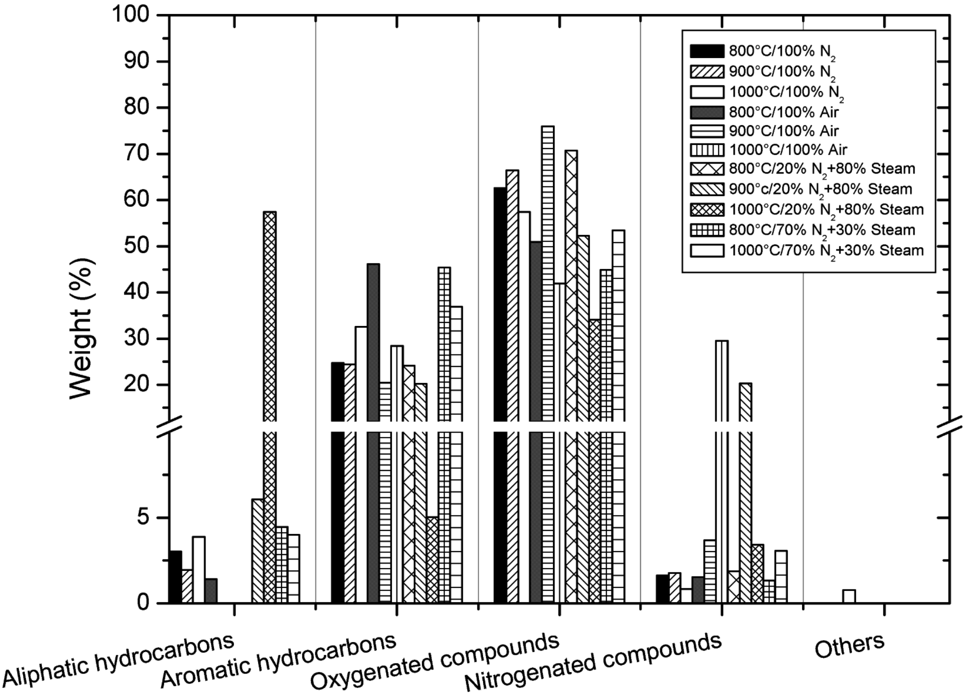
The utilization of steam increases the degradation of biomass, reducing the carbonaceous residue and increasing the generation of gases.

The water amount was determined by Karl Fischer Method. This test method is based essentially upon the reduction of iodine by sulfur dioxide in the presence of water.

Liquid Fraction Composition

Around 50 compounds have been detected in the tar obtained, most of them being present in very low percentages. In order to facilitate the evolution study of the tar composition with temperature, the compounds detected have been grouped according to their chemical nature, in the form proposed above (Table 3), and could be seen at each temperature and different flow ratio mixture in Figure 9, in weight %, i.e., w/w %. The liquid fraction composition and principal compounds obtained at each temperature and different flow ratio mixture is shown in Figure 10.

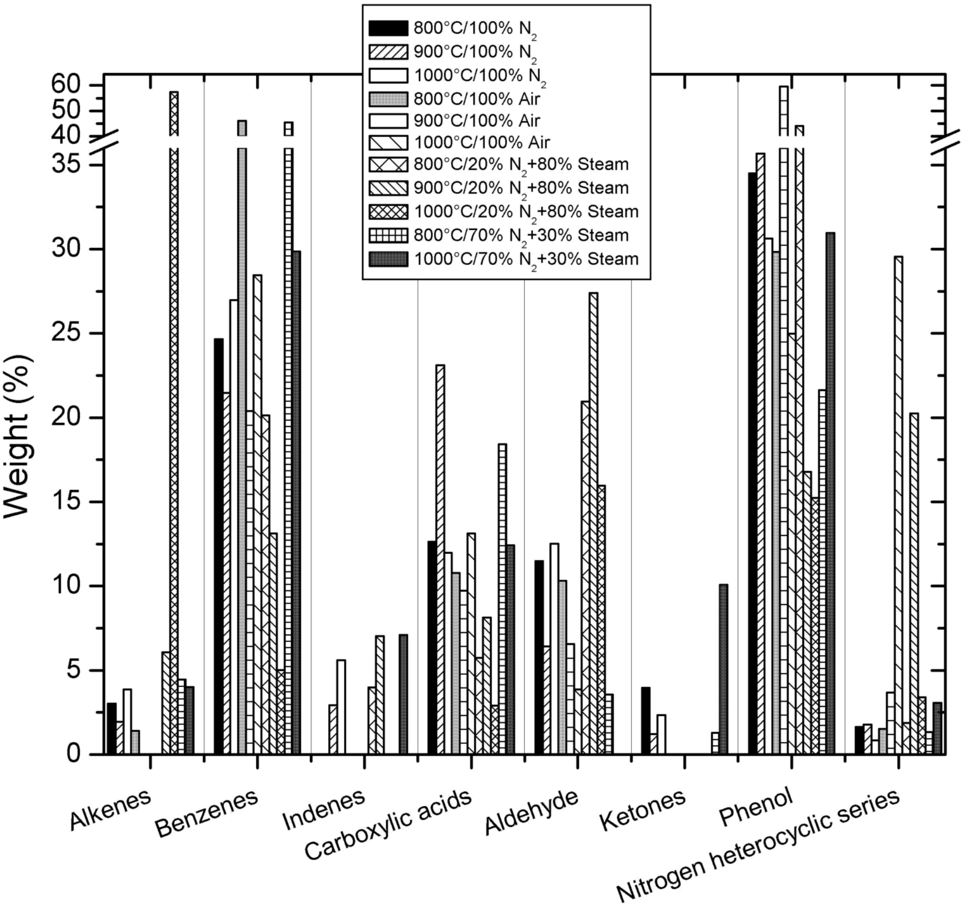
Figure 9. Proposed classification of Liquid fraction composition obtained



It can be observed that oxygenated compounds are the most significant group in all temperatures ranges, reaching 80% of the liquid fraction produced in the 900 °C/100% N_2, 900 °C/100% Air and 800 °C/20% N_2+80% Steam. It can be noted that with the temperature increase, the oxygenated compounds weight decreased in the experiments using only N_2 or air and in the experiments using steam, with the temperature increase, the oxygenated compounds weight increase. It can also be noted, that the aromatic hydrocarbons compounds are the second significant group in all the temperatures ranges. Phenols are the most significant compounds, reaching 60% in weight at 900 °C/100% Air and 40% in weight on other temperatures ranges, followed by benzenes and carboxylic acids compounds. The phenolic compounds feature the tar as input for various applications, including: use in the manufacture of chemical products, disinfectants (phenols and cresols), preparation of resins and polymers.

When compared, the results of each different author, would be seen that it differs by the different methods of tar collectors and by the different classifications applied. Despite of different materials and different pyrolysis conditions, the results

Figure 10. Principal compounds obtained



agree in order to the temperature. We obtain phenol and benzene like the mayor chemical groups in all cases at 700-900 °C, that agree with the works of Ayllón et al. (2006), Di Bari et al. (2000), Alén et al. (1996) and Dufour et al. (2007). At 1000 °C, the mayor chemical group had the influence of the reactive atmosphere gas, like air and steam. Phenol concentrations are reflected by lignin percentages in the biomass feedstocks (Di Bari et al., 2000), then the high concentrations of phenolic compounds in the tar are probably due to the high concentration of lignin in the cashew nut shell, like wood biomass. In Figure 10 we note that there was cracking of benzene by steam (1000 °C and 80% steam) leading to a significant increase of alkenes. In Figure 9 we can see the same effect among aromatic hydrocarbons and aliphatic hydrocarbons.

FUTURE RESEARCH DIRECTIONS

- Pyrolysis of cashew nuts shell in a pilot plant (large scale) to produce enough effluent to develop utilization processes of that;
- Study of physicochemical characteristics with respect to tar stability during storage;
- Economic feasibility study of cashew nuts shell pyrolysis process.
- Increase the field of temperatures tested; working at higher temperatures by checking the influence of the vapor, which probably favored the reactions of gas water and the reaction of Shift, generating more gas rich in hydrogen.
- Conducting trials in thermogravimetric balance because the kinetic of decomposition of biomass has its behavior strongly influenced by kinetics of CO formation.
- Verifying possible applications of the liquid fraction collected (tar).

CONCLUSION

In order to check the temperature influence on the product distributions, products from the pyrolysis of cashew nut shells - char, liquid fraction and gas - were obtained in a laboratory experimental plant. The temperature effects on the product yield distributions were observed. The increasing temperature effect leads to a decrease on char production, as well as on the tar production and leads to an increase on gas production. On the other hand, the increase on steam ratio leads to a decrease on char yield, an increase on tar and on gas yields.

The liquid fraction is the product of greatest interest from the pyrolysis of cashew nut shell. On the other hand, since pyrolysis are endothermic processes, the gas fraction can also be important for sustaining the process from an energy point of view.

The gas production follows a clear tendency, as the higher temperature should promote the gasification reactions and enhance the production of gas.

We tried, with this brief assessment of the results of pyrolysis and gasification of cashew nuts shell, show that beyond differences due process conditions, also collecting and presentation of the results differ. The presentation of results in compounds grouped according to their chemical nature may allow a better comparison of results from different authors, when compared with the classification proposed by protocols CEN BT/TF 143.

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REFERENCES

Alén, R., Kuoppala, E., & Oesch, P. (1996). Formation of the main degradation compound groups from wood and its components during pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *36*(2), 137–1148. doi:10.1016/0165-2370(96)00932-1

Ayllón, M., Aznar, M., Sánchez, J. L., Gea, G., & Arauzo, J. (2006). Influence of temperature and heating rate on the fixed bed pyrolysis of meat and bone meal. *Chemical Engineering Journal*, *121*(2-3), 85–96. doi:10.1016/j.cej.2006.04.013

Bergman, P. C. A., van Paasen, S. V. B., & Boerrigter, H. (2002). The novel OLGA technology for complete tar removal from biomass producer gas. In *Proceedings of Pyrolysis and Gasification of biomass and waste*, Expert Meeting, Strasbourg, France.

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (1997). Use of amino phase adsorbent for biomass tar sampling and separation. *Fuel*, *76*(2), 137–142. doi:10.1016/S0016-2361(96)00199-8

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (2000). Tar evolution profiles obtained from gasification of biomass and coal. *Biomass and Bioenergy*, *18*(1), 87–91. doi:10.1016/S0961-9534(99)00069-0

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (2007). A new method for the analysis of heavy tar in raw producer gases from biomass gasifiers. In *Proceedings of 15th European Biomass Conference & Exhibition*, p. 1221-1223. Berlin.

Bridgwater, A. V. (1999). Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of Analytical and Applied Pyrolysis*, *51*(1-2), 3–22. doi:10.1016/S0165-2370(99)00005-4

CEN (Ed.). (2005). Biomass Gasification — Tar and Particles in Product Gases — Sampling and Analysis CEN BT/TF 143 TC 143 WI CSC 03002.

Di Bari, I., Barisano, D., Cardinale, M., Matera, D., Nanna, F., & Viggiano, D. (2000). Air Gasification of Biomass in a Downdraft Fixed Bed: A Comparative Study of the Inorganic and Organic Products Distribution. *Energy & Fuels*, *14*(4), 889–898. doi:10.1021/ef990243g

Dufour, A., Girods, P., Massonc, E., Normanda, S., Rogaumeb, Y., & Zoulalian, A. (2007). Comparison of two methods of measuring wood pyrolysis tar. *Journal of Chromatography. A*, *1164*(1-2), 240–247. doi:10.1016/j.chroma.2007.06.049 PMID:17628580

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., & Roy, C. (2007). Characterization of bio-oils in chemical families. *Biomass and Bioenergy*, *31*(4), 222–242. doi:10.1016/j.biombioe.2006.02.006

Huang, J., Liu, C., Tong, H., Li, W., & Wu, D. (2014). A density functional theory study on formation mechanism of CO, CO_2 and CH_4 in pyrolysis of lignin. *Computational and Theoretical Chemistry*, *1045*, 1–9. doi:10.1016/j.comptc.2014.06.009

Jones, J. M., Kubacki, M., Kubica, K., Ross, A. B., & Williams, A. (2005). Devolatilisation characteristics of coal and biomass blends. *Journal of Analytical and Applied Pyrolysis*, *74*(1-2), 502–511. doi:10.1016/j.jaap.2004.11.018

Knoef, H. A. M., & Koele, H. J. (2000). Survey of tar measurement protocols. *Biomass and Bioenergy*, *18*(1), 55–59. doi:10.1016/S0961-9534(99)00067-7

Lipska-Quinn, A. E., Zeronian, S. H., & Mc Gee, K. M. (1985). Thermal degradation of rice straw and its components. In R. P. Overend, T. A. Milne, & L. K. Mudge (Eds.), *Fundamentals of Thermochemical Biomass Conversion* (pp. 453–471). London: Elsevier App. Sc. Pub. doi:10.1007/978-94-009-4932-4_26

Liu, C., Huang, J., Huang, X., Li, H., & Zhang, Z. (2011). Theoretical studies on formation mechanisms of CO and CO_2 in cellulose pyrolysis. *Computational and Theoretical Chemistry*, *964*(1-3), 207–212. doi:10.1016/j.comptc.2010.12.027

Mayerhofer, M., Fendt, S., Spliethoff, H., & Gaderer, M. (2014). Fluidized bed gasification of biomass - In bed investigation of gas and tar formation. *Fuel*, *117*, 1248–1255. doi:10.1016/j.fuel.2013.06.025

Oasmaa, A., & Meier, D. (2005). Norms and standards for fast pyrolysis liquids:1. Round robin test. *Journal of Analytical and Applied Pyrolysis*, *73*(2), 323–334. doi:10.1016/j.jaap.2005.03.003

Olivares-Gómez, E. (2002). Study Of The Elephant Grass Fast Pyrolysis In A Bubbling Fluidized Bed Reactor Throught The Fine Charcoal Characterization (Doctoral Thesis) Retrieved from Acervus Unicamp dissertations and Thesis database. (T/UNICAMP OL4e).

Raveendran, K., & Ganesh, A. (1996). Heating value of biomass and biomass pyrolysis products. *Fuel*, *75*(15), 1715–1720. doi:10.1016/S0016-2361(96)00158-5

Sipila, K., Kuoppala, E., Fagernas, L., & Oasmaa, A. (1998). Characterization Of Biomass-Based Flash Pyrolysis Oils. *Biomass and Bioenergy*, *14*(2), 103–113. doi:10.1016/S0961-9534(97)10024-1

Sricharoenchaikul, V., Frederick, Wm. J. Jr, & Agrawal, P. (2002). Black Liquor Gasification Characteristics. 2. Measurement of Condensable Organic Matter (Tar) at Rapid Heating Conditions. *Industrial & Engineering Chemistry Research*, *41*(23), 5650–5658. doi:10.1021/ie020208o

Tsai, W. T., Lee, M. K., & Chang, Y. M. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*, *76*(1-2), 230–237. doi:10.1016/j.jaap.2005.11.007

Yu, Q., Brage, C., Chen, G., & Sjostrom, K. (2007). The fate of fuel-nitrogen during gasification of biomass in a pressurised fluidised bed gasifier. *Fuel*, *86*(4), 611–618. doi:10.1016/j.fuel.2006.08.007

ADDITIONAL READING

Boateng, A. A., Daugaard, D. E., Goldberg, N. M., & Hicks, K. B. (2002). Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-Oil Production. *Industrial & Engineering Chemistry Research*, *46*(7), 1891–1897. doi:10.1021/ie0614529

Sanchez, C. G. (Ed.). (2010). *Tecnologia da gaseificação de biomassa*. Campinas: Editora Atomo.

Schröder, E. (2004). Experiments on pyrolysis of large beechwood particles in fixed beds. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 669–694. doi:10.1016/j.jaap.2003.09.004

KEY TERMS AND DEFINITIONS

Cashew Nut Shell: A type of biomass used now for production of energy. It is the peel of the cashew nut, originated from the Northeast area of Brazil.

Electrostatic Precipitator: Is a highly efficient filtration device that removes fine particles, like dust and smoke, from a flowing gas using the force of an induced electrostatic charge minimally impeding the flow of gases through the unit.

Flame Ionization Detector: (FID) is a scientific instrument that measures the concentration of organic species in a gas stream. It is frequently used as a detector in gas chromatography.

Fourier Transform Infrared Spectroscopy: (FT-IR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas.

Gas Chromatography–Mass Spectrometry: (GC-MS) is an analytical method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances within a test sample.

Gel Permeation Chromatography: (GPC) is a type of size exclusion chromatography (SEC) that separates components on the basis of size.

Polycyclic Aromatic Hydrocarbons: (PAHs) (also polyaromatic hydrocarbons) are hydrocarbons—organic compounds containing only carbon and hydrogen—that are composed of multiple aromatic rings.

Multi Bed Solid-Phase Adsorbent: (SPA) is a adsorbent method that use a stainless steel tube that has packed inside Carbotrap 300, a mix of Carbotrap C (graphitised carbon black), Carbotrap B (graphitized carbon black), and Carbosieve SIII (carbon molecular sieve), manufactured by Supelco (Bellefonte, PA, USA).

Tar: A part of the liquid fraccion of pyrolysis products. Tar comprises a wide spectrum of organic components, generally consisting of several aromatic rings.

Thermal Desorption: (TD) is the process of heating a material to release adsorbed compounds from it.

Chapter 7

Energy and Exergy Analysis on Gasification Processes:

A Preliminary Approach

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ABSTRACT

In recent years, attention has focused on exergy analysis, a type of thermodynamic analysis which is an important tool for the efficiency assessment and the processes optimization when dealing with energy conversion and, particularly, thermochemical processes such as gasification. Thus, this chapter aims to introduce the fundamental concepts of energy and exergy and describe the energy and exergy evaluation tools, elucidating its importance for calculations applied to gasification processes. A case study was performed to show the proposal of energy and exergy analysis. Therefore, a single global gasification chemical reaction was used to represent the gasification process. This analysis can provide a tool to assess and develop models, simulations, calculations, and to optimize real gasification processes. Information and experiences covered in this chapter help to be put into perspective the technology, research and overcoming of challenges.

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INTRODUCTION

Gasification technology has been given a lot of attention in these recent years through the analyses of the first and second laws of thermodynamics as an alternative for biomass and waste processing, a way for obtaining global thermodynamic efficiencies, and even for many purposes, such as biological, chemical, thermal and mechanical processes.

Efficiency estimates from the First and the Second Law of Thermodynamic and also from thermodynamic global analyses of thermal schemes using coal, firewood and biomass residue in gasification and combustion processes, are reported in the literature (Abuadala et al., 2010; Cortez & Gómez, 1998; McKendry, 2002; Park et al., 2014; Rodrigues & Gaggioli, 1980; Singh, Weil, & Babu, 1980; Tiangco, Jenkins, & Goss, 1990).

Generally these thermodynamic analyses are directed to the identification of major points of low thermodynamic efficiencies; in other words, identify the points of great energy waste and/or with larger exergy destruction. The balances and analyses reports of First and Second Law of Thermodynamic as well as exergy efficiency analyses, allows the improvement of thermodynamic processes and cycles. However, a detailed evaluation through thermodynamic specific tools for gasification processes, considering the process in its thermochemical nature, has not yet been verified.

This chapter is divided in two sections. The first section begins with a review about concepts of First and Second Law of Thermodynamics. This section is particularly important to introduce the main concepts to understand the energy and exergy methodology proposed to evaluate the gasification process. In the second section will be presented the thermodynamic study based on combined analyses of First and Second Law of Thermodynamic for a continuous biomass gasification process, considering that the process occurs under only one specific global thermochemical reaction. Two equilibrium models are then proposed for the global equilibrium reaction, both based on the chemical reactions stoichiometry, a first model based in the theoretical gasification reaction, and a second one based in the actual gasification reaction. Estimations are made for the energy and exergy stream flow, the First Law Efficiency (cold and hot), the associated irreversibilities with the theoretical and actual process and the exergy or the Second Law Efficiency. The calculation methodology used it is based on an algorithm that considers balances of mass, energy and exergy on the gasification thermochemical reaction.

Before modelling the single reaction of biomass gasification proposed in this study, it is needed to start a discussion on the different methodologies based on kinetic, thermodynamic and stoichiometric models of chemical reactions involving the development of physical-chemical processes. Through to kinetic models, which are highly rigorous, it is possible to known what occur during the chemical reaction; investigate a nature of the reaction systems and phenomena; understand as the chemical links are formed and broken and estimate the involved energy, among others. On the other hand, the equilibrium models based in the thermodynamic are less rigorous, but no less simple. On a chemical reaction systems it is possible to get the molar concentrations reached at equilibrium, without consider the reaction mechanisms established by the kinetic. Finally, from the equilibrium models based in the chemical reactions stoichiometry, although considered very simple, it is possible to get rapid and practical data in relation to evolution of the chemical transformations, such as equilibrium displacement, molar and mass quantities of reactants and products, and to calculate the absorbed and released energy from the establishment of the chemicals reaction balance.

On the other hand, it is necessary to establish the concept of the theoretical model (ideal model) adopted in this study, as well as to represent the global phenomenon of gasification reactions regarding this study. With this purpose, in this study is defined as a theoretical model of chemical reaction that one based on the theory that explains the mass conservation principle in a reagent system. The theoretical term concerns the mass conservation in a reagent system where as the ideal term concerns the formation of new species via a chemical route, along with an ideal or complete conversion of reactants to products.

Thus, the stoichiometric model chosen as one single and global gasification chemical reaction lies in the fact that there is still not sure of the main reactions mechanisms in gasification process. Nevertheless many authors propose possible stoichiometric partial chemical reactions, where can establish the equilibrium conditions, plus that the kinetics routes are unknown and, thus, creating a limitation of thermodynamic and kinetic approaches. Thus, the importance of the proposed model chosen is supported by its simplicity and thermodynamic robustness.

Given this scenario, it is sufficient to analysis a gasification process using a simpler approach, but also very practical and useful, to achieve the proper conditions and compounds that are favorable for exergy analysis in a gasification process.

BACKGROUND OF FIRST LAW OF THERMODYNAMICS

Energy

One of the most important concepts of thermodynamic is energy. The idea of energy is that energy can be stored within systems in various forms such as kinetic energy and internal energy. Thus, energy can be converted from one form to another and transferred between systems mainly by work and heat. For every process, the total amount of energy is conserved in all conversions and transfers (Jordan, 1992; Moran & Shapiro, 2006).

Heat and Work

As stated by Moran and Shapiro (2006), work is done by a system on its surroundings if the sole effect on everything external to the system could have been the raising of a weight. The work can be written as:

$$W = \int_{L_1}^{L_2} \vec{F}.d\vec{L} \tag{1}$$

where W is the work done where $W > 0$ is the work done by the system [J] whereas $W < 0$ is the work done on the system [J], F is the force [N], L is the displacement [m], L_1 is the initial state [m] and L_2 is the final state [m].

According to the same authors, heat means an amount of energy transferred across the boundary of a system in a heat interaction with the system's surroundings. Furthermore, heat transfer into a system is considered positive whereas heat transfer from a system is considered negative as follow:

$Q > 0$ is the heat transferred to the system [J];
$Q < 0$ is the heat transferred from the system [J].

The amount of energy transfer by heat Q is given by the following equation:

$$Q = \int_{L_1}^{L_2} dQ \tag{2}$$

where the limits mean from state L_1 to state L_2 and do not refer to the value of heat at those states.

As for work W, the notion of heat at a state function has no meaning, thus the integral should never be evaluated as $Q_2 - Q_1$ (Dincer & Rosen, 2013).

First Law of Thermodynamics

As stated by Dincer and Rosen (2013), the First Law of Thermodynamics is the law of the conservation of energy, in which, although energy can change form, it cannot be neither created nor destroyed. Therefore, the First Law of Thermodynamics provides no information about the direction in which processes can spontaneously occur, i.e., the reversibility aspects of thermodynamic processes. Such information is provided in the Second Law of Thermodynamics that will be explained later in this chapter.

Energy and the First Law of Thermodynamics

The First Law of Thermodynamics for a control mass can be written by the following expression (Dincer & Rosen, 2013):

$$dQ = dE + dW \tag{3}$$

where dQ is the amount of heat, dE is the total internal energy and dQ is the amount of work.

Unlike the change in total internal energy dE, the quantities dQ and dW are not independent of the manner of transformation, so it not possible specify dQ and dW simply by knowing the initial and final states.

Integrating equation (3) from an initial state 1 to a final state 2, the following equation is obtained:

$$Q_{1-2} = E_2 - E_1 + W_{1-2} \tag{4}$$

where E_1 and E_2 are the initial and final value of the energy E of the mass control, $Q_{1\text{-}2}$ is the heat transferred to the control mass from state 1 to state 2 and $W_{1\text{-}2}$ is the work done by the control mass from state 1 to state 2.

Internal energy U, kinetic energy E_k and potential energy E_p are terms that can be included in the energy E:

$$E = U + E_k + E_p \tag{5}$$

With a constant gravitational acceleration g, for a change of state 1 to state 2, the equation (5) can be written as:

$$E_2 - E_1 = U_2 - U_1 + (m(v_2^2 - v_1^2))/2 + mg(Z_2 - Z_1) \quad (6)$$

where m is the fixed amount of mass contained in the system, v is the velocity, g is the local gravity and Z is the elevation of system.

The quantities dQ and dW can be specified in terms of the rate for heat transfer and work. For a control volume an additional terms appears from the fluid flowing across the control surface (entering at state i and exiting at state e). The First Law of Thermodynamics for a control volume (cv) can be written as follow:

$$\dot{Q}_{cv} = \dot{E}_{cv} + \dot{W}_{cv} + \sum \dot{m}_{out}\hat{e}_{out} - \sum \dot{m}_{in}\hat{e}_{in} \quad (7)$$

where $\dot{Q}_{cv}$ is the heat transferred in a control volume, $\dot{E}_{cv}$ is the total internal energy transferred in a control volume, $\dot{W}_{cv}$ is the transferred for a control volume, $\dot{m}$ is the mass flow rate and $\hat{e}$ is the total specific energy, which is equal to the sum of specific enthalpy, kinetic energy and potential energy as follow:

$$\hat{e} = h + v^2/2 + gZ \quad (8)$$

where h is the specific enthalpy.

Conversion Energy and Energy balance

The balance for a general quantity in a system may be written as (Dincer & Rosen, 2013):

$$Input - Output + Generated - Consumed = Accumulated \quad (9)$$

Since energy cannot be created or destroyed (First Law of Thermodynamics), the energy balance is written as:

$$Energy\ input + Energy\ output = Energy\ accumulated \quad (10)$$

For a closed system, there are no mass interactions between the system and the surroundings, thus the total energy change of the system is equal to the heat added to the system minus the work done by the system:

$$\Delta E = \Delta U + \Delta E_k + \Delta E_p = Q - W \quad (11)$$

When there are no changes in kinetic and potential energy, the balance may be written as:

$$\Delta E = \Delta U = Q - W \tag{12}$$

In an open system with *j* streams flowing in and out, the energy balance may be written as:

$$\sum\nolimits_{in} \dot{m}_j (h_j + ek_j + ep_j) - \sum\nolimits_{out} \dot{m}_j (h_j + ek_j + ep_j) + \dot{Q} - \dot{W}_s = dE / dT \tag{13}$$

where $\dot{m}_j$ is the mass flow rate of *j* stream, h_j is the specific enthalpy of *j* stream, ek_j is the specific kinetic energy of *j* stream, ep_j is the specific potential energy of *j* stream, $\dot{Q}$ is the heat flow rate, $\dot{W}_s$ is the shaft work done by the system and *t* is the time.

Energy Analysis Applied to Gasification Process: Energy Efficiency

In this section, it is presented the theoretical approach for mass and energy balance calculation in the gasification process (Gómez, 1996; Sánchez, 1994), considering the control volume presented in the Figure 1. The heat loss associated with the product gas, solid product and to environment are calculated based on gasifier stream outlet temperature.

A mass balance of gasifier is presented in equation (14).

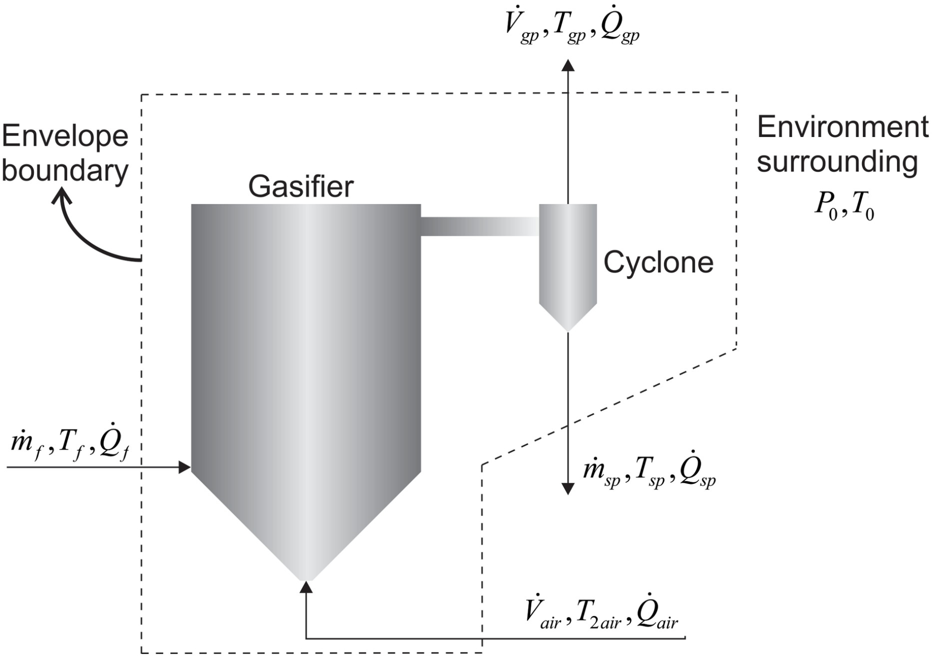
$$((\dot{V}_{pg}\rho_{pg} + \dot{m}_{sp}) / (\dot{V}_{air}\rho_{air} + \dot{m}_f))100 = MBC \tag{14}$$

where $\dot{V}_{pg}$ is the volumetric flow of product gas (product gas) [$Nm^3.s^{-1}$], ρ_{pg} is the density of gas product [$kg.m^{-3}$], $\dot{m}_{sp}$ is the mass flow of the solid product [$kg.s^{-1}$], $\dot{V}_{air}$ is the volumetric flow of air [$Nm^3.s^{-1}$], ρ_{air} is the density of air [$kg.m^{-3}$], $\dot{m}_f$ is the mass flow of the biomass fuel [$kg.s^{-1}$] and *MBC* is the mass balance closure (100% when ideal).

The gasifier energy balance is represented as the following equations:

$$Q_f + Q_{air} = Q_u + Q_{pg} + Q_{sp} + Q_{es} + Q_{others} \tag{15}$$

Figure 1. Flow diagram of the gasifier energy balance



$$Q_f = LHV_f \tag{16}$$

$$Q_{air} = ER(h_{2air} - h_{1air}) = ER(AVcp_{a2}t_{a2} - AVcp_{a1}t_{a1}) = ERAV(cp_{a2}t_{a2} - cp_{a1}t_{a1}) \tag{17}$$

$$ER = (\dot{V}_{air} / \dot{m}_f) / AV \tag{18}$$

$$AV = 0.0889C^w + 0.265H^w + 0.0330^w \tag{19}$$

$$Q_u = (\dot{V}_{pg} / \dot{m}_f)LHV_{pg} \tag{20}$$

$$Q_{pg} = LHV_{pg} - ERh_{1air} = (C_{CO}LHV_{CO} + C_{CH_4}LHV_{CH_4} + C_{H_2}LHV_{H_2})(\dot{V}_{pg} / \dot{m}_f) - ERh_{1air} \tag{21}$$

$$Q_{sp} = Q_{carb} + Q_{ash} = (\dot{m}_{sp} / \dot{m}_f)100C_{carb}LHV_{carb} + (\dot{m}_{sp} / \dot{m}_f)100c_{ash}(t_c - t_f) = (\dot{m}_{sp} / \dot{m}_f)100(C_{carb}LHV_{carb} + c_{ash}(t_c - t_f)) \tag{22}$$

$$Q_{es} = \sum_{i=1}^{n}(u_i A_i / \dot{m}_f)(t_{et} - t_{amb}) \tag{23}$$

$$\dot{V}_{dpg} = r\dot{m}_f \tag{24}$$

$$r = R_{air/f} / R_{air/dpg} \tag{25}$$

$$R_{air/dpg} = 28.84N_{dpg} / 22.4N_{air} \tag{26}$$

$$R_{air/f} = 1.293\dot{V}_{air} / \dot{m}_f \tag{27}$$

where A_i is the cross-sectional area i of the reactor [m^2], AV is the stoichiometric air volume [$Nm^3.kg_f^{-1}$], C_i is the concentration of i element is product gas [%], C^w, H^w and O^w are carbon, hydrogen and oxygen mass content on biomass (% wet basis), cp_{a2} is the specific heat of air in compressor outlet [$MJ.(Nm^3\,{}^oC)^{-1}$], cp_{a1} is the specific heat of air in compressor inlet [$MJ.(Nm^3\,{}^oC)^{-1}$], c_{ash} is the specific heat of ash in solid product [$MJ.(kg_{sp}\,{}^oC)^{-1}$], C_{carb} is the concentration of carbon in solid product [%], ER is the equivalent ratio (related to air), h_{1air} is the specific enthalpy of air in compressor inlet [$MJ.kg_f^{-1}$], h_{2air} is the specific enthalpy of air in compressor outlet [$MJ.kg_f^{-1}$], LHV_{carb} is the lower heating value of carbon [$MJ.kg_f^{-1}$]; LHV_f is the lower heating value of the biomass fuel [$MJ.kg_f^{-1}$], LHV_i is the lower heating value of *i* element [$MJ.kg_f^{-1}$], LHV_{pg} is the lower heating value of gas product [$MJ.Nm^{-3}$], $\dot{m}_f$ is the mass flow of the biomass fuel [$kg_f.s^{-1}$], $\dot{m}_{sp}$ is the mass flow rate of solid product [$kg_{sp}.s^{-1}$], N_{air} is the nitrogen content in air [%], N_{dpg} is the nitrogen content in dry product gas [%], Q_{air} is the heat of inlet air [$MJ.kg_f^{-1}$], Q_{ash} is the heat loss by ash in solid product [$MJ.kg_f^{-1}$], Q_{carb} is the heat loss by unburned carbon in solid product [$MJ.kg_f^{-1}$], Q_{es} is the heat loss by environment surrounding [$MJ.kg_f^{-1}$], Q_f is the heat available in the biomass fuel [$MJ.kg_f^{-1}$], Q_{pg} is the heat loss by product gas [$MJ.kg_f^{-1}$], Q_{sp} is the heat loss by solid product [$MJ.kg_f^{-1}$], Q_u is the useful heat [$MJ.kg_f^{-1}$], *r* is the air-fuel to air-dry volumetric flow rate of product gas ratio [$Nm_{dpg}^{3}.kg_f^{-1}$], where *dpg* means dry product gas, $R_{air/dpg}$ is the air to dry volumetric flow rate of product gas ratio [$kg_{air}.Nm_{dpg}^{-3}$], where *dpg* means dry product gas, $R_{air/f}$ is the air to fuel ratio [$kg_{air}.kg_f^{-1}$], t_{a1} is the temperature of air in compressor inlet [°*C*], t_{a2} is the temperature of air in compressor outlet [°*C*], t_{amb} is the environmental temperature [°*C*], t_c is the cyclone inlet temperature [°*C*], t_{et} is the external temperature in a section *i* of the reactor [°C], t_f is the fuel inlet temperature in the gasification reactor [°C], u_i is the heat transfer coefficient in a section *i* [$MJ.m^{-2}$], $\dot{V}_{air}$ is the volumetric flow of air [$Nm^3.s^{-1}$], $\dot{V}_{dpg}$ is the dry volumetric flow of product gas, [$Nm^3.s^{-1}$] and, finally, $\dot{V}_{pg}$ is the volumetric flow of gas product [$Nm^3.s^{-1}$].

Particularly, two main concepts on the gasification process are used: the cold gasification efficiency and the hot gasification efficiency. The first concept it considers only the chemical enthalpy (combustion enthalpy) of the gas. The second concept considers the gas chemical enthalpy and its sensible enthalpy (due to its temperature). In both the cases, the equations are the following:

$$\eta_c = \dot{V}_{pg} LHV_{pg} \,/\, (\dot{m}_f LHV_f + h_{2air}) \tag{28}$$

$$\eta_h = (\dot{V}_{pg} LHV_{pg} + Q_{pg}) \,/\, (\dot{m}_f LHV_f + h_{2air}) \tag{29}$$

where η_c is the cold gasification efficiency [%] and η_h is the hot gasification efficiency [%].

Energy Flux and Sankey Diagram

"No portion of a steam plant is perfect, and each is the seat of losses more or less serious", with this sentence, Sankey (1898) describes the importance of considering the energy flux in a steam system. Since then, the use of thermodynamic diagrams to represent processes has long been a standard practice in science and engineering (Schmidt, 2008a). Indeed, there are some ways to represent the energy flux graphically, which one deserves more attention (Schmidt, 2008b): the Sankey diagram.

The Sankey diagram is commonly used to represent the energy balance putting a visual emphasis on the major transfers within a system where the width of the band is associated to the energy rate or energy flow rate of a given energy conversion process (Oliveira Júnior, 2013), in other words, the Sankey diagrams present the energy outputs defined in the system boundaries (Schmidt, 2008b).

BACKGROUND OF SECOND LAW OF THERMODYNAMICS

The energy balance given by the First Law of Thermodynamics is essential for the thermodynamic analysis of any chemical process. However, it does not impose restrictions on the process direction or differences between the forms of energy. Joule’s experiment, for instance, shows that work is easily transformed into heat by a dissipative process, while heat is never completely converted into work.

The Second Law of Thermodynamics completes the basis of thermodynamics by making statements that describe these restrictions. Clausius and Kelvin–Planck statements are the most common statements used in engineering thermodynamics (Moran & Shapiro, 2006):

Clausius statement: *It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.*

Kelvin-Planck statement: *It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.*

The Clausius statement declares that it is not possible to construct a refrigeration cycle that operates without any input of work while the Kelvin-Planck statement enunciates that it is not possible to construct an engine that has the sole effect of extracting heat and converting it all into work. These two statements are equivalent and it can be proved by demonstration that the violation of one statement implies the violation of the other.

The Second Law of Thermodynamics can be also represented by the entropy postulate (Kotas, 1995):

There is an extensive property of a system called entropy S*. The entropy of an isolated system can never decrease:*

$$\Delta S_{isolated} \geq 0$$

The restriction imposed by the increase in entropy indicates what processes, chemical reactions or directions of heat transfer can occur, besides limiting the energy conversion among forms of energy.

Reversible Work and Irreversibility

A logical question derived from the second law statements should be: *if it is impossible to achieve an efficiency of 100% in a heat transfer process, what is the maximum possible?* In order to answer this question we should first define reversible and irreversible processes.

Reversible processes are idealized processes that can never be fully realized, but are good parameters to judge a real process. In a reversible process, the system and the surroundings can return to their initial state, while in an irreversible process there is an unavoidable increase in entropy in the combined system. This means that there has been a change from a more organized form of energy to one consisting of more randomness. From Clausius statement, it is clear that a process of spontaneous transfer of heat from a hot body to a cold body is an irreversible process; otherwise it would be possible to return the energy from the cold body without any other effect in the system or the surroundings (Smith & Van Ness, 1987).

As a consequence of the second law, regarding the concept of irreversibility, it is possible to state that all energy transfers or conversions are irreversible.

The maximum work achieved by a process is an important parameter that can be evaluated by the study of reversibility.

Suppose an initial i and final f states of a cycle and consider all the process as reversible and irreversible, between initial and final stages. In addition, suppose that the system can exchange heat and work. In this case, it is valued the first law of thermodynamics where the maximum work W_{max} is equal to $Q - \Delta U$, where Q is the heat flowing into the system through a quasi-static isothermal process at the temperature T, i.e. $Q = T\Delta S$. It means that the maximum amount of work is achieved when a thermodynamic cycle is reversible, i.e. $\Delta U = 0$ and, thus, $W_{max} = T\Delta S$ (Nussenzveig, 2002).

Finally, part of the energy is lost as heat instead of being converted to work in an irreversible process and the maximum amount of work that can be obtained from a process occurs under reversible conditions.

Exergy as Work Potential of Energy: Environmental, Reservoirs and Dead State

Energy is conserved in every process. However, the energy conservation is inadequate for depicting some important aspects of resource utilization. Thus, for considering the quality of this energy, it must be introduced the state function to describe the quality of this energy called exergy, which is also called the availability or available energy (Çengel & Boles, 2006; Moran & Shapiro, 2006).

The quality of an energy form is associated with the ability to make changes. Any difference in the conditions of the system towards the surroundings, that means, any lack of mutual equilibrium between the two, can be used to produce work. Exergy can then be defined as the maximum useful work that can be obtained when the system reaches complete equilibrium (thermodynamic equilibrium) with the surroundings conditions. The work output is maximized when the process between two specified states is executed in a reversible manner (for example, the Carnot thermal engine). These surroundings, in exergy analysis, are referred to as the reference environment or environment, an infinite system in state of perfect equilibrium (no gradients of pressure, temperature, chemical potential, kinetic or potential energy). The environment may be conceived as the union of three huge reservoirs, one of volume, one of energy and one of mass, acting then as a zero reference level for pressure, temperature and chemical potential.

On the other hand Çengel and Boles (2006) realize a distinction between the surroundings, immediate surroundings and the environment. Surroundings are everything outside the system boundaries. The immediate surroundings refer to the portion of the surroundings that is affected by the process, and environment refers to the region beyond the immediate surroundings whose properties are not affected by the process at any point. Therefore, any irreversibilities during a process occur within the system and its immediate surroundings, and the environment is free of any irreversibilities.

Exergy is an extensive property like enthalpy and entropy, whose values depend on the quantity of material, but, unlike enthalpy, that is conserved, and entropy, that can only be created, exergy is always destroyed when there are irreversible processes occurring. Processes at high temperature as combustion and gasification have great loss of exergy, since the reactions occurring are irreversible (Azevedo, 2013).

The environment is usually described with the conditions of the atmosphere, the seas and oceans and the earth's crust (Kotas, 1995). A common specification for the environment is the atmospheric conditions of $T_0 = 298.15\ K, P_0 = 101\ kPa,\ y_{N_2} = 0.7567,\ y_{O_2} = 0.2035,\ y_{Ar_2} = 0.0091,\ y_{H_2O} = 0.0303,\ y_{CO_2} = 0.0003,\ y_{H_2} = 0.0001$, being T the temperature, P the pressure and y_i is the mole fraction of the i component (Dincer & Rosen, 2013). When the system is under conditions of complete thermodynamic equilibrium (same temperature, pressure and chemical potential for each component and it has not kinetic or potential energy relative to the environment – zero velocity and zero elevation above a reference level) with the environment, also, there are no unbalanced magnetic, electrical and surface tension effects between the system and its surroundings, it is said to be in the dead state. It is clear that exergy is not a property of a system alone, but of a system combined with the environment. Finally, a system will deliver the maximum possible work output as it undergoes a reversible process from the specified initial state to the state of its environment, that is, the dead state. A system has zero useful work potential, exergy or availability at the dead state.

Physical and Chemical Exergy, Exergy Balance and Exergy Efficiency

When performing an exergy analysis of a process, the first step is to calculate the exergy of each of the flows of mass or energy present. Kotas (1995) defines the exergy of a steady stream of matter as *the maximum work obtainable when the stream is brought from its initial state to the dead state by processes during which the stream may interact only with the environment.* A flow of pure mechanical energy (work) is, therefore, a pure exergy flow, while the same is not true for a flow of heat. Lozano and Valero (1988) use other words to define the exergy of a system as *the minimum technical work required to make up this system from the reference environment.*

In process such as gasification, fuels are converted into fuel and/or heat. Particularly, the gasification involves converting fossil and renewable fuels into chemical energy contained in the gaseous products and sensible energy in produced gas. Whereas the first law means that the energy can never be lost, the second law addresses that this energy from gasification process is accompanied by an irreversible increase in entropy, which leads to the decrease in available energy, i.e. exergy (Prins, 2005).

Therefore, the energy is conserved, nevertheless, the quality of energy decreases because part of it is converted into a non useful sort of energy, which means less work will be obtained.

Neglecting nuclear, magnetic, electric and surface tension effects, the exergy flow of a stream, $\dot{B}$, is usually divided into four components, the kinetic $\dot{B}_k$, potential $\dot{B}_p$, physical $\dot{B}_{ph}$ and chemical exergy $\dot{B}_{ch}$ (Oliveira Júnior, 2013):

$$\dot{B} = \dot{B}_k + \dot{B}_p + \dot{B}_{ph} + \dot{B}_{ch} \tag{30}$$

The equation (30) may also be written in the specific form *b*, as follow:

$$b = \dot{B} / \dot{n} \tag{31}$$

where $\dot{n}$ is the mol flow rate $[mol.s^{-1}]$.

Thus, the specific exergy flow b of a stream takes the following form:

$$b = b_k + b_p + b_{ph} + b_{ch} \tag{32}$$

The kinetic and potential constituents of exergy are equal to the kinetic and potential constituents of energy, since these can be fully convertible to work (equations (33) and (34) respectively). Usually these values are not taken into account since they tend to be rather low when compared to physical and chemical exergy.

$$b_k = v^2 / 2 \tag{33}$$

$$b_p = gZ \tag{34}$$

Where v is the stream velocity [$m.s^{-1}$], g is the local gravity [$m.s^{-2}$] and Z is the elevation [m].

The physical exergy of a flow, $\dot{B}_{ph}$, is equal to the maximum work obtainable when a stream is taken from its thermodynamic initial state to the state of temperature and pressure equal to those of the environment (environmental state*)*, i.e., where it is in thermal and mechanical equilibrium with environment, through processes of heat transfer with the environment (equation 35).

$$\dot{B}_{ph} = \dot{n}((h_1 - h_0) - T_0(s_1 - s_0)) \tag{35}$$

Where h is the specific enthalpy, T is temperature, s is the specific entropy and the subscript 1 refers to the initial state and the subscript 0 refers to a restricted reference state which it is in thermal and mechanical equilibrium with the environmental state. The demonstration of equation (35) as well as other demonstrations can be found in Kotas (1995).

The physical constituent of exergy specific flow for a perfect gas with constant pressure specific heat (c_p) and for solids and liquids (when the behavior of incompressible substance can be assumed, it is supposed constant specific heat c and v_m is the average specific volume between P and P_0) can be written by equation (36) and equation (37), respectively (Oliveira Júnior, 2013):

$$b_{ph} = c_p(T - T_0 - T_0 \ln(T / T_0)) + RT_0 \ln(P / P_0) \tag{36}$$

Where R is the ideal gases universal constant.

$$b_{ph} = c(T - T_0 - T_0 \ln(T / T_0)) + v_m(P - P_0) \tag{37}$$

When the system is in the environmental state, there is still capacity for doing work in case the chemical composition of the system differs from that of the environment. Work can be done in this case if the concentrations of the species are different from those of the environment and if there are chemical reactions taking place. The chemical exergy is thus defined as the maximum work obtained when the present species are taken from the environmental state (T_0, P_0, μ_i) to the dead state (T_0, P_0, μ_i^0), through processes of heat and mass transfer with the environment, in which there is a complete thermodynamic equilibrium (mechanical, thermal and chemical equilibrium) where μ is the chemical potential. The chemical exergy means the maximum work that is possible to be performed when a given system (or mass flow rate) is taken from the restricted reference state up to the dead state in which there is a thermodynamic equilibrium (mechanical, thermal and chemical equilibrium). In that situation, the system is submitted to reversible processes interacting only with the environment (Oliveira Júnior, 2013). Kotas (1995) gives the alternative definition of chemical exergy as the *minimum amount of work necessary to synthesize, and to deliver in the environmental state, the substance under consideration from environmental substances, by processes involving heat transfer and exchange of substances only with the environment.*

The chemical exergy determination requires a model of the standard environment, as proposed by Szargut, Morris, and Stewart (1988), which is composed of the following gaseous components of the atmosphere O_2, N_2, CO_2, H_2O, Ar, He, Ne, Kr, and Xe, given an environment at $T_0 = 298.15$ *K* and $P_0 = 101.325$ *kPa*. Also, the model of the standard environment considers solid, ionic and molecular reference substances (Oliveira Júnior, 2013).

The chemical exergy of a mole flow rate can be written as equation (38):

$$\dot{B}_{ch} = \dot{n}(h_0 - T_0 s_0 - \sum_{i=1}^{n} \mu_i^0 y_i) \tag{38}$$

where μ_i^0 is the chemical potential of substance i in the environment calculated by equation (39) and $\mu_i^{f,0}$ refers to the pure ideal gas formed at $T_0 = 298.15$ *K* and P_0 = 101.325 *kPa* (Prins, Ptasinski, & Janssen, 2003).

$$\mu_i^0 = \mu_i^{f,0} + RT_0 \ln y_i^0 \tag{39}$$

Some works consider equation (38) for the calculation of the chemical constituent of exergy, based on values of standard chemical exergy that are tabulated in literature. The standard chemical exergy of a pure chemical compound 0 is equal to the maximum amount of work obtainable when a compound is brought from the environmental state, characterized by the environmental temperature T_0 and environmental pressure P_0, to the dead state, characterized by the same environmental conditions of temperature and pressure, but also by the concentration of reference substances in standard environment (Prins et al., 2003).

Some works consider equation (38) for the calculation of the chemical constituent of exergy of mixtures $\dot{B}_{ch,mixt}$, based on values of standard chemical exergy that are tabulated in literature (Szargut et al., 1988). The symbol ψ_i in equation (40) represents the standard chemical exergy of substance *i*:

$$\dot{B}_{ch,mixt} = \dot{n}\left(\sum_{i=1}^{n} y_i\psi_i + RT_0\sum_{i=1}^{n} y_i \ln(\gamma_i y_i)\right) \tag{40}$$

Where y_i is the mole fraction of component *i*, *R* is the universal gas constant and γ_i is the activity coefficient, where for ideal mixtures, the activity coefficient is equal to 1.

Based on equation (35) and equation (38), the total exergy of a mole flow rate can then be written as equation (41):

$$\dot{B} = \dot{n}\left(h_1 - T_0 s_1 - \sum_{i=1}^{n} y_i \mu_i^0\right) \tag{41}$$

For a thermodynamic transformation in open system in stationary state, the difference between the inlet and outlet flows is the maximum work obtained by equation (42) which presents the general exergy balance for a stationary state.

$$\dot{B}_{out} - \dot{B}_{in} = \dot{B}^H - \dot{B}^W - \dot{B}^M - \dot{B}_{dest} \tag{42}$$

where the exergy rate associated with the heat reservoir ($\dot{B}^H$) is determined from the work of a Carnot engine operating between *T* e T_0 and receiving $\dot{Q}$ at *T* while rejecting heat at T_0 as equation (43). The second term $\dot{B}^W$ on the right side of equation (43) is the effective work performed or received by the control volume as equation (44). The third term $\dot{B}^M$ is exergy rate transferred by mass (mass flow is a mechanism to transport exergy, entropy and energy into or out of a system). When mass in the amount of m enters or leaves a system, exergy in the amount of $(m\varepsilon)$ accompanies it, as equation (45) (Çengel & Boles, 2006). The last term $\dot{B}_{dest}$, that also can be represented with the letter *I*, accounts for the exergy that is destroyed throughout the process due to irreversibilities, as equation (47).

$$\dot{B}^{H} = \dot{Q}(1 - T_0 / T) \tag{43}$$

$$\dot{B}^{W} = \dot{W} + \dot{W}_v = \dot{W} + P_0 \Delta V = \dot{W} + P_0(V_2 - V_1) \tag{44}$$

Where V is the volume and the subscripts 1 means initial state and 2 means final state of the control volume.

$$\dot{B}^{M} = \sum m_{in}\varepsilon_{in} - \sum m_{out}\varepsilon_{out} \tag{45}$$

where ε is the stream specific exergy, as equation (46):

$$\varepsilon = (h - h_0) - T_0(s - s_0) + v^2 gZ / 2 \tag{46}$$

$$\dot{B}_{dest} = T_0 \dot{S}_g \tag{47}$$

where $\dot{S}_g$ is the entropy generation rate.

Finally, the general exergy balance for a steady flow can be writing as equation (48):

$$\dot{B}_{out} - \dot{B}_{in} = \sum \dot{Q}(1 - T_0 / T) - \dot{W} - P_0(V_2 - V_1) + \sum m_{in}\varepsilon_{in} - \sum m_{out}\varepsilon_{out} - \dot{B}_{dest} \tag{48}$$

The exergy balance equation above can be defined as the rate of exergy change within the control volume during a process is equal to the rate of net exergy transfer through the control volume boundary by heat, work and mass flow minus the rate of exergy destruction within the boundaries of the control volume.

From the balance of exergy, the exergy efficiency φ, also called efficiency of the second law, can be written as:

$$\varphi = \dot{B}_{out} / \dot{B}_{in} = \dot{B}_{dest} / \dot{B}_{in} \tag{49}$$

The equation (46), called degree of perfection by Szargut et al. (1988) is useful to evaluate chemical processes:

$$\varphi = \textit{Exergy of useful products / Feeding exergy} \tag{50}$$

The equation (51) is indicated to the analysis of thermal processes (Oliveira Júnior, 2013):

$$\varphi = \textit{Useful exergy effect / Driving exergy} \tag{51}$$

To pure dissipative processes, that is those where the only considered effect is the exergy destruction, such as the flow of steam through an expansion valve, heat rejection in a condenser of a thermal power plant or a refrigerating system, among others, the equation (48) is used to quantify the exergy efficiency (Oliveira Júnior, 2013):

$$\varphi = \Sigma(\textit{Exit exergy}) / \Sigma(\textit{Inlet exergy}) \tag{52}$$

Exergy Flux and Grassmann Diagram

There are some ways to graphically represent the exergy fluxes. Among these graphics, the Grassmann diagram is the most common. Whereas the well-known Sankey diagram is used to represent the energy balance, the Grassmann diagram represents the exergy balance.

Generally, Grassmann diagram is a graphical representation where the width of the bands is associated to the exergy rate or exergy flow rate of a given energy conversion process (Oliveira Júnior, 2013).

In both the Sankey and Grassmann diagrams, the width of the arrows represents the magnitude of the flux, but the main difference between the two is that in the Grassmann diagram there is a loss of exergy that is not associated to any of the flows. This loss is, instead, associated to the destruction of exergy due to an irreversible process.

Renewability Analysis

Nowadays, the use of renewable processes for real life applications has been increasing due to the growing concern about the clean, efficient and sustainable development in the world (Gräbner & Meyer, 2014; Hepbasli, 2008; Park, Pandey, & Tyagi, 2014;). According to Koroneos, Spachos and Moussiopoulos (2003), renewable energy sources should provide a solution regarding this development, as they cause less environmental impacts than fossil fuels.

With exergy analysis it is possible to assess the energy conversion processes based on renewability analysis. The renewability analysis is associated to the process instead of to the product or the particular energy source (Oliveira Júnior, 2013). The use of renewable energy offers a wide range of benefits that are also linked with exergy analysis, which has been widely used in the design, simulation and performance process assessment (Hepbasli, 2008). Park et al. (2014) stated that for every renewable energy process, the exergy efficiency is smaller than the energy efficiency.

According to Oliveira Júnior (2013), the concept of renewability has been associated only with mass and energy analyses, i.e., not making use of the exergy analysis. In fact, some definitions about renewability can be found in literature. The renewability parameter λ given by Arredondo, Colorado, and Oliveira Júnior (2009) is defined in equation (53).

$$\lambda = \sum B_{product} \,/\, (B_{fossil} + B_{destroyed} + B_{de-activation} + \sum B_{emission}) \tag{53}$$

where $B_{product}$ represents the net exergy associated with the products; B_{fossil} is the non-renewable exergy consumed in the production process chain. For biofuels productions, this considers growing, transport and the processing plant; $B_{destroyed}$ is the exergy destroyed inside the system, punishing the process for its inefficiencies; $B_{de\text{-}activation}$ is the deactivation exergy for treating wastes, when they are carried to equilibrium conditions with the environment. It accounts for exergy required for passing the stream leaving the system, considered as wastes, to no harmful environmental conditions; $B_{emission}$ is the exergy of wastes that are not treated or deactivated.

The parameter λ means:

$0 < \lambda < 1$, the processes are considered non-renewable and it is impossible to return the environment to its initial conditions;
$\lambda = 1$, for internally and externally reversible processes with non-renewable inputs;
$\lambda > 1$, the process is considered renewable and the exergy in the products can be used to restore the environment to its initial conditions;

$\lambda \rightarrow \infty$, for an internally and externally reversible process with only renewable inputs.

Exergy Analysis Applied to Gasification Processes

Oliveira Júnior (2013) begins his work with the following sentence “Our main challenge is to live better, more and using less exergy”. The author used these words because exergy explains better the real processes than only regarding the First Law energy analysis. Nowadays, some studies deal with exergy analysis focusing on thermochemical processes such as gasification (Abuadala, Dincer, & Naterer, 2010; Cruz, 2010; Gräbner & Meyer, 2014; Iribarren, Susmozas, & Petrakopoulou, 2014; Jason & Ibrahim, 2014; Pellegrini, 2007; Sues, Jurascík, & Ptasinski, 2010).

Gasification is a promising way to convert products into energy products more useful for applications (Campoy, Gómez-Barea, & Villanueva, 2008). Gasification can be defined as a thermochemical conversion of biomass into a gaseous fuel in a gasification medium such as air, oxygen and/or steam (McKendry, 2002), with temperatures between 750 and 900 ^{o}C, producing around 5% of liquid, 10% of solid and 85% of gas (Bridgwater, 2012). In addition to this, the gas produced from gasification, called syngas, is important for many biofuel products (Balan, Chiaramonti, & Kumar, 2013; Haro, Ollero, & Perales, 2013; Liew, Hassim, & NG, 2014; Nigam & Singh, 2011; Swain, Das, & Naik, 2011): methane, ethane, propane, methanol, ethanol, dimethyl ether, ammonia, butanol, gasoline C_5-C_{12}, diesel C_{13}-C_{15}, paraffin and wax C_{20}-C_{33}, kerosene of aviation C_{12}-C_{14}, among others.

According to Iribarren et al. (2014), exergy analysis is an appropriate method for assessing the effectiveness of energy conversion processes. When dealing with gasification processes, one of the main parameters of exergy analysis that needs to be evaluated is the exergy efficiency. Although many methodologies can be found in literature for performing exergy analyses, the different paths do not affect the final remarks (Iribarren et al., 2014).

Palma and Martin (2013) showed that the exergy efficiency in a poultry litter gasification process varies between 46.8% and 65.7%, while the cold gasification efficiency for the same process varies between 58.4% and 79.5%.

Gräbner and Meyer (2014) studied the performance of a coal gasification process and explained why the gas cooling techniques are responsible for the highest exergy losses in the overall system. They obtained a high value for cold gas efficiency (88.4%) and a high exergy efficiency (79.2%).

According to Iribarren et al. (2014), the calculated exergy efficiency in a plant for hydrogen production via lignocellulosic biomass gasification was 48%. They reported that the total exergy losses are mostly related to the flue gas stream (4.6% of the fuel exergy), while 47% of the fuel exergy is destroyed in the process.

Finally, a general discussion about exergy analysis is focused on exergy global balances assessing each exergy stream, exergy efficiency of the process, loss exergy in the system related to gas product and solid product streams, destroyed exergy in relation to fuel exergy and irreversibilities.

A METHOD TO CONDUCT ON ENERGY AND EXERGY ANALYSIS APPLIED TO GASIFICATION PROCESS – CASE STUDY

Reactions

Basically, the biomass gasification process can be represented as three serial processes: pyrolysis or volatilization process, which produces volatile matter and charcoal; gas-gas reactions or volatile matter reactions; and charcoal gasification. The main chemical reactions involved in charcoal gasification are (Bacon, Downie, Hsu, & Peters, 1985):

$$C + CO_2 + heat \rightarrow 2CO \tag{54}$$

$$C + H_2O + heat \rightarrow H_2 + CO \tag{55}$$

$$CO_2 + H_2 + heat \rightarrow CO + H_2O \tag{56}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O + heat \tag{57}$$

The reactions (54) and (55) are the Boudouard reaction and water-gas reaction respectively. The reaction (56) is the water-gas shift reaction, which govern the interaction of the gaseous species formed during pyrolysis and gasification process. Although quite low, usually something of methane is formed in biomass gasification at low pressure through to reaction (57), a well-known reaction of formation of methane or methanation reaction, which proceeds very slowly at low temperature in the absence of catalysts. This reaction is too quite exothermic, providing heat to the system. The first three reactions above are endothermic and very slow at temperature below 800 °*C*. However, basically the heat required to the charcoal gasification reactions is provided by the following exothermic reactions (Barrio, 2002):

Volatile matter combustion:

$$(C_xH_y + CO + H_2 + CH_4) + O_2 \rightarrow CO_2 + H_2O + heat \tag{58}$$

Partial combustion of charcoal (quite exothermic):

$$C + O_2 \rightarrow CO_2 + heat \tag{59}$$

$$C + 1/2O_2 \rightarrow CO + heat \tag{60}$$

The reactions in equation (54), equation (55) and the partial combustion of charcoal (equation (59) and (60)) are well known as gas-solid heterogeneous reactions. Other chemical reactions in the gaseous phase well-known as gas-gas homogeneous reactions are the following (Bacon et al, 1985):

$$CO + H_2O \rightarrow CO_2 + H_2 + heat \tag{61}$$

$$CH_4 + H_2O + heat \rightarrow CO + 3H_2 \tag{62}$$

The tar decomposition can be represented in a simple way for the following reaction well-known as tar decomposition reaction (Bacon et al, 1985):

$$Tar+(gas+vapor)+heat \rightarrow gases(CO+CO_2+CH_4+\ldots) \tag{63}$$

Such as presented by some authors (Barrio, 2002; Makray, 1984), biomass gasification could be expressed through a single gasification global reaction. In Barrio (2002), it can be seen that the wood biomass (fuel basis), represented by the chemical formula $CH_{1.4}O_{0.6}$, will react with the minimum amount of oxygen required in order to obtain a mixture of CO and H_2 according to the following theoretical single gasification global reaction, neglecting the ashes and water in the fuel (dry ash free basis-daf basis):

$$CH_{1.4}O_{0.6} + 0.2O_2 \rightarrow CO + 0.7H_2 \tag{64}$$

When a certain extra-oxygen amount is necessary, the real single gasification global reaction, neglecting the ashes and water in the fuel (dry ash free basis) is:

$$CH_{1.4}O_{0.6} + 0.4O_2 \rightarrow 0.7CO + 0.3CO_2 + 0.6H_2 + 0.1H_2O \tag{65}$$

In Makray (1984), the wood continuous gasification process is represented by the following single global reaction:

$$\begin{aligned}&(\dot{m}_f / M_f)(CH_{1.45}O_{0.65}N_{0.0017} + wH_2O(l))_f + (aO_2 + bN_2 + cH_2O(g))_{air} \rightarrow \\ &sC + dH_2 + eCO + fCH_4 + gCO_2 + hN_2 + iC_nH_m + jH_2O(g)\end{aligned} \tag{66}$$

where $\dot{m}_f$ is the mass flow rate of biomass fuel [kg.s^{-1}], M_f is the molecular mass of biomass fuel [kg.mol^{-1}] and *(l)* and (*g)* mean liquid and gas (vapor) phase, respectively.

Energy and Exergy Analysis Methodology of the Gasification Process

The evaluation methodology adopted in presented study was originally proposal by Jordan (1992) for Texas lignite fired boilers. After, Cortez and Gómez (1998) adapted this methodology to sugarcane bagasse fired boilers. For the thermodynamic analysis of biomass gasification process, two global chemical reaction models based on the stoichiometry are studied to characterize the chemical reactions that take place during the gasification process: the first model characterize the theoretical (or ideal) gasification reaction, which was considered as having only CO, H_2, CH_4, N_2, Ar, and *ash* as the reaction product (tar and solid carbon it was not considered to be present in the reaction products); and the second model characterize the actual gasification reaction, in which CO, H_2, CH_4, CO_2, H_2O, N_2, O_2, Ar, C, and *ash* are present in the reaction products. In the actual gasification reaction tars was assumed to be assimilated in the solid carbon fraction due to lack of experimental data.

The Cousins Simplified Model was considered to estimate the gaseous fuels components presented as a result of the gasification process (Bacon et al, 1985; Lora, Andrade, & Sanchez, 2008). This gasification model assumes that the fundamental chemical reactions in the oxidation zone are the following:

$$CO + CO_2 \rightarrow 2CO + 172.6\ kJ.(kmol)^{-1} \tag{67}$$

$$C + H_2O \rightarrow CO + H_2 + 131.4\ kJ.(kmol)^{-1} \tag{68}$$

$$C + 2H_2 \rightarrow CH_4 - 74.93\ kJ.(kmol)^{-1} \tag{69}$$

The model establishes the following simplifying hypothesis: a) the biomass is composed only by C, H, O and N; b) the sulfur and its reactions are neglected; c) all nitrogen entering the reduction zone leaves in the form of nitrogen; d) all carbon and hydrogen become CO_2 and H_2O in the reaction reduction zone.

The theoretical model that characterizes the gasification chemical reaction was development considering the no-kinetic chemical model proposed by Cousins and represented through a global chemical reaction. Then, the mass balance of this reaction, considering equilibrium, was made in order to determine the stoichiometric coefficients of the model. Already, the actual model characterizing the gasification chemical reactions was development considering data collected from a biomass fixed-bed gasifier of 20 *kW* of thermal power (Gaggioli, 1980; Tiango et al., 1990). Energy and exergy flow was then calculated for stream crossing the control volume. Through the exergy balance, the irreversibility flow rate was calculated. Finally, the theoretical reaction model is compared with the actual reaction model.

In this first attempt to develop the proposed method, it was not to make the mass balance for each model considering the CH_4 component. In reality, the CH_4 content in the gasification gaseous products, in relation to H_2 and CO, is very small (Gaggioli, 1980; Tiango et al., 1986;).

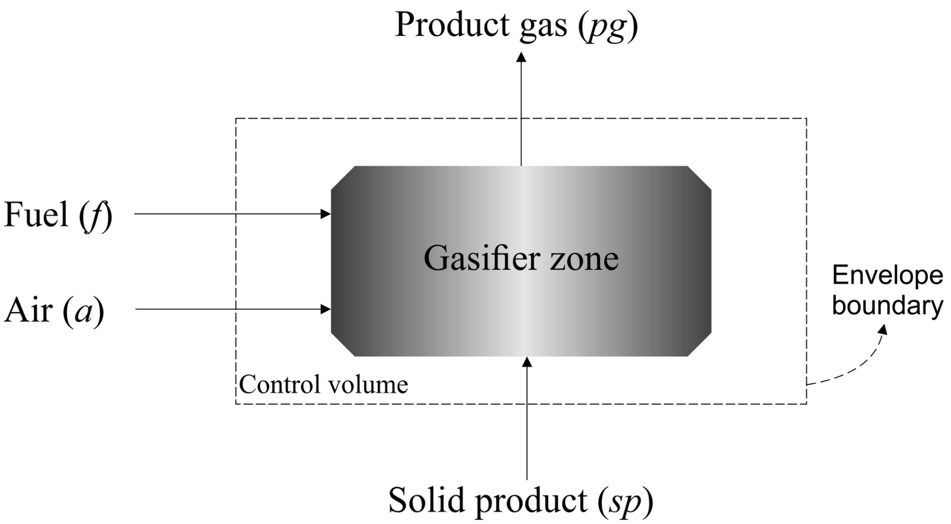
This method allows a thermodynamic analysis of the gasifier (chemical reactions zones of the reactor) considering the whole gasifier as a thermodynamic system, and taking into account only the main flow rates crossing the control volume.

Also, in order to simplify the thermodynamic analysis it is assumed thermodynamic equilibrium in the global reaction. A simplified view of the thermodynamic system is presented in Figure 2.

Energy Balance

The energy conservation principle or the First Law of Thermodynamic for steady-state-flow is given by:

Figure 2. A simplified view of the thermodynamic system in the gasifier zone of the biomass gasifier



$$dE/dT + \sum_{i=1}^{n} (\dot{m}h)_{out} = \sum_{i=1}^{n} \dot{W} + \sum_{i=1}^{n} \dot{Q} + \sum_{i=1}^{n} (\dot{m}h)_{in} \tag{70}$$

Applying this principle to the gasification process and considering negligible variation of kinetic energy and an adiabatic thermodynamic process. Then:

$$\dot{m}_f h_f + \dot{m}_{air} h_{air} = \dot{m}_{pg} h_{pg} + \dot{m}_{sp} h_{sp} \tag{71}$$

In this case, $\sum_{i=1}^{n} \dot{W} = 0$.

For chemical reactions, it is convenient to work in mole flow rate $\dot{n}$ and specific mole enthalpy $\overline{h}$. Then:

$$\dot{n}_f \overline{h}_f + \dot{n}_{air} \overline{h}_{air} = \dot{n}_{pg} \overline{h}_{pg} + \dot{n}_{sp} \overline{h}_{sp} \tag{72}$$

The Exergy Balance: Irreversibility Calculation

In any system, the exergy balance may then be defined when the irreversibility due to the entropy increase are calculated. It can also be calculated the exergy efficiency. Therefore, considering the gasification process under stationary conditions of flow, where mass, energy and exergy flow continuously through any point of the control volume, the total irreversibility flow rate or destroyed exergy is given by:

$$\dot{I} = \dot{n}_f \bar{b}_f + \sum_{i=1}^{n} \dot{n}_{air,i} \bar{b}_{air,i} - \sum_{i=1}^{n} \dot{n}_{pg,i} \bar{b}_{pg,i} - \dot{n}_{sp} \bar{b}_{sp} \tag{73}$$

where $\dot{I}$ is the total irreversibility flow rate and $\bar{b}$ is the mole specific exergy.

The equations below carried out by Gaggioli and Petit (1977) for ideal gas mixtures can be used to calculate the exergy of air and gas product from gasification.

$$\bar{b}(T,P) = \bar{h}(T,P) - T_0 \bar{s}(T,P) - \sum y_i \mu_i^0 \tag{74}$$

$$\bar{h}(T,P) = \sum y_i \bar{h}_i(T_0) + \sum y_i \int c_p dT \tag{75}$$

$$\bar{s}(T,P) = \sum y_i \bar{s}_i(T_0, P_0) + \sum y_i \int c_p (dT / T) - R \ln(P / P_0) - R \sum y_i \ln y_i \tag{76}$$

The chemical potential for a given substance in the dead state is determined by the equation (77) for stable substances in the reference state. It is the Gibbs function:

$$\mu_i^0 = \bar{h}_i(T_0) - T_0 \bar{s}_i(T_0, P_0) + RT_0 \ln y_i^0 \tag{77}$$

where y_i^0 is the mole fraction of the *i* substance at dead state.

For example, in the case of the *CO* (carbon monoxide), the Gibbs function is given by:

$$\mu_{CO}^0 = \bar{h}_{CO_2}(T_0) - (1/2)\bar{h}_{O_2}(T_0) - T_0((\bar{s}_{CO_2}(T_0, y_{CO_2}^0, P_0) - (1/2)\bar{s}_{O_2}(T_0, y_{O_2}^0, P_0) \tag{78}$$

Now, for the solid products (non-gasified carbon and ash in the fuel), the exergy is calculated by:

$$\bar{b}_{sp} = \bar{h} - \bar{h}_0 - T_0(\bar{s} - \bar{s}_0) + \bar{b}_{sp}^0 \tag{79}$$

$$\bar{h}-\bar{h}_0=((\dot{m}_{ash}/\dot{m}_{daf})(\dot{m}_{daf}/\dot{n}_{daf})c_{ash}+(\dot{m}_c/\dot{n}_c)(\dot{n}_c/\dot{n}_{daf})c_c)(T_{sp}-T_{sp,0}) \tag{80}$$

$$\bar{s}-\bar{s}_0=((\dot{m}_{ash}/\dot{m}_{daf})(\dot{m}_{daf}/\dot{n}_{daf})c_{ash}+(\dot{m}_c/\dot{n}_c)(\dot{n}_c/\dot{n}_{daf})c_c)\ln(T_{sp}/T_{sp,0}) \tag{81}$$

Where c is the specific heat of carbon and $\bar{b}_{sp}^{0}$ is the solid product exergy referred to the reference state given by the following equation:

$$\bar{b}_{sp}^{0}=\bar{G}_0-((\bar{h}_0-\bar{h}_{ref})+T_0(\bar{s}_0-\bar{s}_{ref})) \tag{82}$$

where in the equations above $\dot{m}_{ash}/\dot{m}_{daf}$ is the ash mass fraction in daf basis [$kg_{ash}.kg_{daf}^{-1}$]], $\dot{m}_{daf}/\dot{n}_{daf}$ is the fuel mole mass in *daf* basis [$kg_{daf}.(kmol)_{daf}^{-1}$], $\dot{m}_c/\dot{n}_c$ is the solid carbon mole mass [$kg_c.(kmol)_c^{-1}$], $\dot{n}_c/\dot{n}_{daf}$ is the solid carbon mole fraction in daf basis [$kmol_c.(kmol)_{daf}^{-1}$], $\bar{G}_0$ is the mole Gibbs free energy at T_0 [$kJ.(kmol)_{daf}^{-1}$], $\bar{h}_0$ is the mole enthalpy of the element at ambient temperature T_0 [$kJ.(kmol)^{-1}$] and $\bar{s}_0$ is the absolute mole entropy of the element at ambient temperature T_0 [$kJ.(kmol)^{-1}$].

For the reference state (T_0 and P_0), the ash exergy $\bar{b}_{sp,ash}^{0}$ is considered zero for being this substance considered stable in the reference conditions (environment conditions), and the non-gasified solid carbon exergy $\bar{b}_{sp,c}^{0}$ is given considering the carbon chemical reaction $C+O_2\rightarrow CO_2$, thus:

$$\bar{b}_{sp,c}^{0}=\bar{G}_0=\bar{h}_{F,0}C+\bar{h}_{F,0}O_2-\bar{h}_{F,0}CO_2-T_0(\bar{s}_0C+\bar{s}_0O_2+\bar{s}_0CO_2) \tag{83}$$

where $\bar{h}_{F,0}i$ is the mole enthalpy of formation of chemical specie i at temperature T_0 [$kJ.(kmol)^{-1}$], being this element considered non-stable substances in the reference conditions (environment).

The fuel chemical exergy $\bar{b}_f$ is calculated according to the correlation equations proposals by Szargut and Styrylska cited by Woudstra (2012):

$$\bar{b}_f=(LHV+2442w)\beta+\bar{b}_w w \tag{84}$$

where β is the coefficient to be determined as a function of the mass fraction ratio $X_{O/C}$, being *O* and *C* the oxygen and carbon mass fraction in the dried fuel, respectively. If $X_{O/C} > 0.6666$, then:

$$\beta = (1.0438 + 0.0013X_{H/C} - 0.4453X_{O/C}(1 + 0.0051X_{H/C}) + 0.0521X_{N/C}) / (1 - 0.5385X_{O/C}) \tag{85}$$

where $X_{H/C}$, $X_{O/C}$ and $X_{N/C}$ are hydrogen carbon mass fraction ratio, oxygen carbon mass fraction ratio and nitrogen carbon mass fraction ratio, *LHV* is the lower heating value of wet fuel in wet basis (wet basis) [$kJ.kg_f^{-1}$], 2442 is the latent heat of water vaporization at 25 ^oC, [$kJ.kg_w^{-1}$] and *w* is the fuel moisture content in wet basis in mass fraction. The sulfur content in the fuel is negligible.

The chemical exergy of the water in the fuel is determined in agreement with Szargut et al. (1988):

$$\bar{b}_w = RT_0 \ln(1/\varphi_0) \tag{86}$$

where $\bar{b}_w$ is the chemical exergy of the water [$kJ.kg_f^{-1}$] and φ_0 is the air relative humidity [%].

The exergy balance of the gasification process (gasification reactor), then becomes:

$$\dot{n}_f\bar{b}_f + \dot{n}_{air}\bar{b}_{air} = \dot{n}_{gp}\bar{b}_{gp} + \dot{n}_{sp}\bar{b}_{sp} \tag{87}$$

Finally, the exergy efficiency is given by:

$$\Phi = \sum \bar{b}_{out} / \sum \bar{b}_{in} = (\bar{b}_{pg} + \bar{b}_{sp}) / (\bar{b}_f + \bar{b}_{air}) \tag{88}$$

Energy and Exergy Modelling

In order to conduct the First and Second Law of Thermodynamic analysis considering the two stoichiometric models to represent a gasification global chemical reaction, it was necessary to obtain information about: the physical-chemical properties of fuel to be used (rice hull) and outlet gas and solid products conditions. Therefore, Table (1) shows the inlet variables for the gasification process whereas the Table (2) shows the outlet variables from gasification process. All these data was published by Tiango et al. (1990).

Table 1. Inlet variables for gasification process

Biomass	Rice hulls
Ultimate analysis [%]	
C	40.96
H	4.30
O	35.86
N	0.40
S	0.02
Ash	15.46
Moisture content [%]	16.0
Higher Heating Value [$MJ.kg^{-1}$, dry basis]	16.14
Feedstock condition	
T_0 [K]	298.15
P_0 [kPa]	101.1
Air conditions	
T_0 [K]	298.15
P_0 [kPa]	101.1
φ [%]	60.0

Theoretical Gasification Reaction Model

It was adopted a stoichiometric approach and the main assumptions about the model are:

1. Complete gasification of dry fuel, with only the gaseous species CO, H_2, N_2 and Ar, except CH_4 and nitrogen compounds such as NO_x, N_2O and NH_3 appearing on the products, according to the Cousins Simplified Model, and considered in equilibrium;
2. The produced gas was modeled as a mixture of ideal gases;
3. Dry air is used as the gasifying agent;
4. Water formation is not considered;
5. Chemically, the fuel is constituted only of: C, H, O, N and A (ash). The sulfur is neglected.

Table 2. Outlet variables from gasification process

Product gas and solid products conditions	
T [K]	500
P [kPa]	101.1
Product gas composition [%]	
CO	15.642
CO_2	11.575
H_2	10.521
O_2	2.173
Environment conditions	
T_0 [K]	298.15
P_0 [K]	101.1
φ [%]	60.0

From the data compiled of fuel and atmospheric air it was possible to set the theoretical gasification reaction model defined based on the above assumptions. The chemical reaction model is the following:

$$(0.5107C + 0.3192H_2 + 0.1678O_2 + 0.002136N_2 + A) + \\ a(O_2 + 3.7279N_2 + 0.0446Ar + 0.00148CO_2) \rightarrow bCO + cH_2 + dN_2 + eAr + A \tag{89}$$

The calculation of the five stoichiometric coefficients was done by balancing the number of atoms on each side for each of the five elements. Then, with five equations and five unknown stoichiometric coefficients was possible to solve the equation system. The standard chemical reaction balanced is the following:

$$(0.5107C + 0.3192H_2 + 0.1678O_2 + 0.002136N_2 + A) + \\ (0.0874O_2 + 0.3261N_2 + 0.0039Ar + 0.000129CO_2) \rightarrow \\ 0.5108CO + 0.3192H_2 + 0.3282N_2 + 0.0039Ar + A \tag{90}$$

From the data and equations above, it was possible to calculate the energy and exergy balance and determine, finally, the irreversibilities associated to gasification process.

For irreversibilities calculation the following assumptions were made: as residual solid product in the exit gaseous products only A is presented; the ash exergy in relation to the dead state is negligible; the fuel sulfur content is negligible.

Actual Gasification Reaction Model

It was adopted a stoichiometric approach and the main assumptions about the model are:

1. No complete wet fuel gasification;
2. The gaseous species CO, H_2, CO_2, O_2, N_2, H_2O and Ar, except CH_4 and nitrogen compounds such as NO_x, N_2O and NH_3 appearing on the products, according to the Cousins Simplified Model, and considered in equilibrium;
3. The gasifying agent is humid air;
4. There is water formation;
5. Chemically, the fuel is constituted only of: C, H, O, N and A. The sulfur is neglected.

From the data compiled of fuel, atmospheric air and the gasification product gas composition measured using gas chromatography, it was possible to set the actual gasification reaction model defined based on the above assumptions. The chemical reaction model is the following:

$$\begin{gathered}(0.5107C + 0.3192H_2 + 0.1678O_2 + 0.002136N_2 + 0.1584H_2O + A) + \\ a(O_2 + 3.7279N_2 + 0.0446Ar + 0.00148CO_2 + 0.0925H_2O) \rightarrow \\ bC + cCO_2 + dCO + eH_2 + fO_2 + gH_2O + hN_2 + iAr + A\end{gathered} \tag{91}$$

In this case, non-gasified carbon (NGC) appears as solid product in the gasification process (gas smoke or mixed with the ash). Therefore, from a mass balance for each element, we have 5 equations and 9 unknown coefficients. On other hand, knowing from flue gas composition analysis (measured averages readings), a system of 4 equations is obtained. Thus, the numerical solution of this linear equations system parts from the solution of the following general matrix system:

$$Ax = b \tag{92}$$

where A is the matrix of coefficient, x is the matrix of variable and b is the independent vector.

Numerically, the equation (92) can be written as:

$$\begin{bmatrix} 0.00148 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.09252 & 0 & 0 & 0 & -1 & 0 & -1 & 0 & 0 & 0 \\ 2.09548 & 0 & -2 & -1 & 0 & -2 & -1 & 0 & 0 & 0 \\ 0.0446 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 3.7279 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -0.11575 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -0.15642 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -0.10521 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -0.02173 \\ 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & -0.39911 \end{bmatrix} \begin{bmatrix} a \\ b \\ c \\ d \\ e \\ f \\ g \\ h \\ i \\ j \end{bmatrix} = \begin{bmatrix} -0.5107 \\ -0.4776 \\ -0.4940 \\ 0 \\ -0.0021 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{93}$$

where the last row (row 10) in matrix A is the sum of rows 6, 7, 8, and 9 represented by coefficient j. It was a mathematical procedure done in order to add more one equation and, thus, become a square matrix.

The matrix above can be solved using Gauss elimination giving the value of stoichiometric coefficient of the actual model as follow:

$$\begin{aligned} &(0.5107C + 0.3192H_2 + 0.1678O_2 + 0.002136N_2 + 0.1584H_2O + A) + \\ &(0.3405O_2 + 1.2693N_2 + 0.0152Ar + 0.0005CO_2 + 0.0315H_2O) \rightarrow \\ &0.0716C + 0.2479CO_2 + 0.3349CO + 0.2253H_2 + 0.04650O_2 + \\ &0.2838H_2O + 1.2715N_2 + 0.015Ar + A \end{aligned} \tag{94}$$

This result for the chemical actual reaction shows a bigger error for closure carbon balance than that report in the literature (7.4%). The possible cause of this error is the uncertainty regarding rice husk chemical composition employed in relation to the dry gaseous products composition also employed CO_2, CO, H_2, and O_2.

From the data and equations above, it was possible to calculate the energy and exergy balance as well as the irreversibilities associated to gasification process.

For irreversibilities calculation the following assumptions were made: non-gasified carbon (NGS) and A constitute the solid products leaving the system; the ash exergy in relation to the dead state is negligible; the fuel sulfur content is negligible.

Results and Discussion

The Table (3) shows the main operational parameters of gasification process and energy and exergy performance indicators. The thermodynamic analysis was made under mass and energy flow stationary conditions of the gasification reactor.

Table 3. Obtained results of the analysis of First and Second Law of Thermodynamic Balance

Variables	Theoretical model	Actual model
Stoichiometric Air Volume VA [$Nm^3.kg_f^{-1}$]	3.02	3.02
Air/fuel mass ratio $R_{air/f}$ [$kg_{air}.kg_f^{-1}$]	0.6738	2.6733
Air flow rate $\dot{V}_{air}$ [$Nm^3.h^{-1}$]	1.82[a]	6.24[b]
Equivalent ratio ER	0.17	0.59
Lower heating value of gas LHV_g [$MJ.Nm^{-3}$]	8.50[c]	3.11[c]
Air mass per dry gas volume ratio $R_{air/dpg}$ [$kg_{air}.Nm^{-3}$]	0.4784	1.0056
Dry gas volume per biomass mass ratio r [$Nm_{dpg}^3.kg_f^{-1}$]	1.41	2.66
Dry gas volumetric flow $\dot{V}_{dpg}$ [$Nm^3.h^{-1}$]	4.93	9.30
Cold thermal efficiency of gasification process η_{cold} [%]	93	64
Hot thermal efficiency of gasification process η_{hot} [%]	96	67
Irreversibility flow rate I [kW]	4.29	5.30
Exergetic efficiency Φ [%]	72	66
Exergy losses (destroyed exergy) B_{dest} [%]	28	34
(a) Dry air (b) Wet air (c) From equation (21)		

The results obtained indicated gasification efficiencies of First Law of Thermodynamic, both in cold and hot conditions, of 93% and 96% respectively for the theoretical model of reaction, and of 64% and 67% respectively for the actual reaction model. For both the studied models, the Second Law of Thermodynamic Efficiency (exergy efficiency) reached values of 72% and 66% with irreversibility ratios of 4.29 *kW* and 5.30 *kW* respectively, demonstrating that around 28% for the theoretical model and 34% for the actual model from the exergy that enters into gasifier is destroyed during the gasification process.

The considerable destroyed and lost exergy during the gasification process are due to the irreversibilities associated with the thermochemical reaction of gasification that occurs during the transformation of the reactants to products. The differences in the destroyed exergy considering both models of reaction, 28% for the theoretical model and 34% for the actual model, are due to the fact that the actual model considers not only the irreversibilities of the thermochemical reaction, but also the vaporization of the water content in the biomass entering in the gasifier and in the gasifying agent (air, in this case), and the loss exergy considers the presence of solid carbon particles that were not gasified completely in the gas produced of the process (neglecting the exergy rate losses associated with the heat and work transferred).

The weaknesses of the approaches are in the simplicity of the hypotheses. The strengths of the approaches are in results that may be used to design and simulate gasifiers.

The results of the lower heating value of produced gas obtained was 8.50 $MJ.Nm^{-3}$ for the theoretical model of reaction and 3.11 $MJ.Nm^{-3}$ for the actual model of reaction, respectively. This difference indicates how the theoretical model represents the ideal situation of gasification reaction, whereas the actual model represents the inefficiencies intrinsically related to the gasification process. The same analysis can be performed for others variables that represent each model, such as air/fuel mass ratio $R_{air/f}$ and equivalent ratio ER.

Finally, it is very important to show how the theoretical model is that which should be followed, because it represents the model which lesser exergy is destroyed during the gasification process. The exergy balance of gasification process show how far we are in relation to the theoretical model.

FUTURE RESEARCH DIRECTIONS

We expect that our proposal of energy and exergy analysis may be improved involving some more detailed methods such as equilibrium model.

There is need of experimental data with more accuracy to validate the streams, biomass characterization, gasification parameters and others.

In the near future, we expect that all energy analysis be coupled with exergy analysis simultaneously. This assessment may be performed to improve design and operation data on integrated gasification process in first and second generation plants.

CONCLUSION

The applied combination of mass, energy and exergy balances for evaluation of global reaction models of biomass gasification, theoretical and actual, showed very efficiently on the study of thermodynamic phenomena.

The proposed method showed coherent values for the thermodynamic variables that were studied. The methodology used allows the study of parametric sensibility focusing on the evaluation of the effect of nominal variables, such as water content and physic-chemical characteristics of the feed and the gasification agent (air, in this case), and also of variables of associated effect, like properties based on the effect of the mixture quality inside the bed, temperature profiles, and constructive and operational aspects (pressure, air factor, among others).

The proposal presented for the thermodynamic analyses of the gasification processes indicates a necessity of elevated severity in the consistence of the experimental data used in thermodynamic analyses, specially, over balances of actual reaction models. Little deviations in the analyses data, specially the gas analyses data, are enough for causing great uncertainties in the atom balances of the chemical equations and, consequently, in the matrix solution of the linear equations system.

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REFERENCES

Abuadala, a., Dincer, I., & Naterer, G. F. (2010). Exergy analysis of hydrogen production from biomass gasification. *International Journal of Hydrogen Energy, 35*(10), 4981–4990. doi:10.1016/j.ijhydene.2009.08.025

Arredondo, V., Junior, O., & Medellin, S. (2009). Ethanol production from banana fruit and its lignocellulosic residues: Exergy and renewability analysis*. *International Journal of Thermodynamics*, *12*(3), 155–162.

Bacon, D. W., Downie, J., Hsu, J. C., & Peters, J. (1985). Modelling of fluidized bed wood gasifiers. In R. P. Overend, T. A. Milne, & L. K. Mudge (Eds.), *Fundamentals of thermochemical biomass conversion* (pp. 717–732). London, New York: Elsevier Applied Science Publishers. doi:10.1007/978-94-009-4932-4_37

Balan, V., Chiaramonti, D., & Kumar, S. (2013). Review of US and EU initiatives toward development, demonstration, and commercialization of lignocellulosic biofuels. *Biofuels. Bioproducts and Biorefining*, *7*(6), 760–760. doi:10.1002/bbb.1452

Barrio, M. (2002). *Experimental investigations of small-scale gasification of woody biomass*. (Doctoral dissertation). The Norwegian University of Science and technology.

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, *38*, 68–94. doi:10.1016/j.biombioe.2011.01.048

Campoy, M., Go, A., Villanueva, A. L., & Ollero, P. (2008). Air - Steam Gasification of Biomass in a Fluidized Bed under Simulated Autothermal and Adiabatic Conditions. *Industrial & Engineering Chemistry Research*, *47*(16), 5957–5965. doi:10.1021/ie800220t

Çengel, Y. A., & Boles, M. A. (2006). *Thermodynamics: an engineering approach*. Boston: McGraw Hill College.

Cortez, L. A. B., & Gómez, E. O. (1998). A method for exergy analysis of sugarcane bagasse boilers. *Brazilian Journal of Chemical Engineering*, *15*(1). doi:10.1590/S0104-66321998000100006

Cruz, F. E. (2010). *Produção de hidrogênio em refinarias de petróleo: avaliaçao exergética e custo de produção*. (Master dissertation). Universidade de São Paulo. Retrieved from http://www.teses.usp.br/teses/disponiveis/3/3150/tde-17082010-123008/pt-br.php

de Azevedo, A. L. (2013). *Análise exergética da produção de NH_3 via oxigaseificação de bagaço de cana*. (Master dissertation). Universidade Federal do Rio de Janeiro.

Dincer, I., & Rosen, M. A. (2013). *Exergy: energy, environment and sustainable development (Second.)*. San Diego: Elsevier Science.

Gaggioli, R. A. (1980). Thermodynamics: second law analysis. In American chemical Society, Symposium Series (p. 52). Whashington, ACS Symposium Series. Retrieved from http://pubs.acs.org/isbn/9780841205413

Gaggioli, R. A., & Petit, P. J. (1977). Use the second law first. *Chemtech*, *7*, 496–506.

Gómez, E. (1996). *Projeto, construção e avaliação preliminar de um reator de leito fluidizado para gaseificação de bagaço de cana-de-açúcar.* (Master dissertation). Universidade Estadual de Campinas. Retrieved from Acervus Unicamp Dissertations and Theses Database. (D/UNICAMP OL4p)

Gräbner, M., & Meyer, B. (2014). Performance and exergy analysis of the current developments in coal gasification technology. *Fuel*, *116*, 910–920. doi:10.1016/j.fuel.2013.02.045

Haro, P., Ollero, P., Perales, Á. L. V., & Vidal-barrero, F. (2013). Potential routes for thermochemical biorefineries, 551–572. doi:10.1002/bbb

Hepbasli, A. (2008). A key review on exergetic analysis and assessment of renewable energy resources for a sustainable future. *Renewable & Sustainable Energy Reviews*, *12*(3), 593–661. doi:10.1016/j.rser.2006.10.001

Huang, J., & Dincer, I. (2014). Parametric analysis and assessment of a coal gasification plant for hydrogen production. *International Journal of Hydrogen Energy*, *39*(7), 3294–3303. doi:10.1016/j.ijhydene.2013.12.054

Iribarren, D., Susmozas, A., Petrakopoulou, F., & Dufour, J. (2014). Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification. *Journal of Cleaner Production*, *69*, 165–175. doi:10.1016/j.jclepro.2014.01.068

Jordan, P. D. (1992). *Class Notes of Macroscopic Thermodynamic, Draft 1, Part B. Department of Mechanical Engineering, Class Handbook.* Lubbock, Texas, USA: Texas Tech University.

Koroneos, C., Spachos, T., & Moussiopoulos, N. (2003). Exergy analysis of renewable energy sources. *Renewable Energy*, *28*(2), 295–310. doi:10.1016/S0960-1481(01)00125-2

Kotas, T. J. (1995). *The exergy method of thermal plant analysis*. Malabar: Krieger Publishing Company.

Liew, W. H., Hassim, M. H., & Ng, D. K. S. (2014). Review of evolution, technology and sustainability assessments of biofuel production. *Journal of Cleaner Production*, *71*, 11–29. doi:10.1016/j.jclepro.2014.01.006

Lora, E. E. S., Andrade, R. V., Sanchez, C. G., Gómez, E. O., & Sales, C. A. V. B. (2008). Gaseificação. In L. A. B. Cortez, E. E. S. Lora, & E. O. Gómez (Eds.), *Biomassa para energia*. Campinas: Editora Unicamp.

Lozano, M. A., & Valero, A. (1988). Methodology for calculating exergy in chemical process. In W. Wepfer, G. Tsatsaronis, & R. A. Bajura (Eds.), *Thermodynamic analysis of chemically systems*. Zaragoza: ASME Book.

Makray, Z. T. (1984). *Gaseificação de biomassa em gaseificador co-corrente para a produção de gás de médio poder calorífico e gás de síntese* (Doctoral dissertation). Faculdade de Engenharia de Alimento, Universidade Estadual de Campinas, Campinas, SP.

McKendry, P. (2002). Energy production from biomass (Part 3): Gasification technologies. *Bioresource Technology*, *83*(1), 55–63. http://www.ncbi.nlm.nih.gov/pubmed/12058831 doi:10.1016/S0960-8524(01)00120-1 PMID:12058831

Moran, M. J., & Shapiro, H. N. (2006). *Fundamentals of engineering thermodynamics* (5th ed.). England: John Wiley & Sons Ltd.

Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science*, *37*(1), 52–68. doi:10.1016/j.pecs.2010.01.003

Nussenzveig, H. M. (2002). *Curso de física básica: fluidos oscilações e ondas de calor. Volume number two* (4th ed.). Rio de Janeiro: Editora Blucher.

Oliveiras Júnior, S. (2013). *Exergy – production, cost and renewability*. London: Springer-Verlag.

Palma, C. F., & Martin, A. D. (2013). Model based evaluation of six energy integration schemes applied to a small-scale gasification process for power generation. *Biomass and Bioenergy*, *54*(0), 201–210. doi:10.1016/j.biombioe.2013.03.024

Park, S. R., Pandey, K., Tyagi, V. V., & Tyagi, S. K. (2014). Energy and exergy analysis of typical renewable energy systems. *Renewable & Sustainable Energy Reviews*, *30*, 105–123. doi:10.1016/j.rser.2013.09.011

Pellegrini, L., & Oliveira Júnior, S. (2007). Exergy analysis of sugarcane bagasse gasification. *Energy*, *32*(4), 314–327. doi:10.1016/j.energy.2006.07.028

Prins, M., J., Ptasinski, K., & J. J. G. Janssen, F. (. (2003). Thermodynamics of gas-char reactions: First and second law analysis. *Chemical Engineering Science*, *58*(3-6), 1003–1011. doi:10.1016/S0009-2509(02)00641-3

Prins, M. J. (2005). *Thermodynamic analysis of biomass gasification and torrefaction* (Doctoral dissertation). Technische Universiteit Eindhoven, Netherlands.

Rodrigues, S. J., & Gaggioli, A. R. (1980). Second-law efficiency analysis of a coal gasification process. *Canadian Journal of Chemical Engineering*, *58*(3), 376–381. doi:10.1002/cjce.5450580314

Sánchez, C. G. (1994). *Estudo da volatilização e da gaseificação de biomassa em leito fluidizado* (Doctoral dissertation). Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica, Campinas.

Sánchez, C. G., Silva, E. L., & Olivares-Gómez, E. (1997). Gaseificação. In: L. A. B. Cortez, & E. L. Silva (Ed.), Tecnologias de Conversão Energética da Biomassa (pp. 255-347).Universidade de Manaus-EFEI, Manaus, Série Sistemas Energéticos II.

Sankey, H. R. (1898). Introductory note on the thermal efficiency of steam-engines. *The Engineer*, *86*, 236–237.

Schmidt, M. (2008a). The Sankey Diagram in Energy and Material Flow Management. *Journal of Industrial Ecology*, *12*(1), 82–94. doi:10.1111/j.1530-9290.2008.00004.x

Schmidt, M. (2008b). The Sankey Diagram in Energy and Material Flow Management. *Journal of Industrial Ecology*, *12*(2), 173–185. doi:10.1111/j.1530-9290.2008.00015.x

Singh, P. S., Weil, A. S., & Babu, P. S. (1980). Thermodynamic Analysis of Coal Gasification Processes. *Energy*, *5*(8-9), 905–914. doi:10.1016/0360-5442(80)90106-1

Smith, J. M., & Van Ness, H. C. (1987). *Introduction to chemical engineering thermodynamics*. New York: McGraw-Hill Book Company.

Sues, A., Juraščík, M., & Ptasinski, K. (2010). Exergetic evaluation of 5 biowastes-to-biofuels routes via gasification. *Energy*, *35*(2), 996–1007. doi:10.1016/j.energy.2009.06.027

Swain, P. K., Das, L. M., & Naik, S. N. (2011). Biomass to liquid: A prospective challenge to research and development in 21st century. *Renewable & Sustainable Energy Reviews*, *15*(9), 4917–4933. doi:10.1016/j.rser.2011.07.061

Szargut, J., Morris, R. D., & Steward, R. F. (1988). *Exergy analysis of thermal chemical and metallurgical processes*. Berlin: Springer – Verlag.

Tiangco, M. V., Jenkins, M. B., Goss, R. J., Chancellor, J. W., & Camacho, R. I. (1990). Variation of engine performance with reactor size for rice hull fueled gasification system. *American Society of Agricultural Engineers*, paper (6076) presented at 1990 International Summer Meeting.

Tiango, M. V., Jenkins, M. B., Goss, R. J., & Chancellor, W. J. (1986). Design and development of a continuous small-scale rice hull gas producer. *American Society of Agricultural Engineers*, paper (3070) presented at ASAE Summer Meeting.

Woudstra, N. (2012). *Sustainable energy systems: limitations and challenges based on exergy analysis.* (Doctoral dissertation). Delft University of Technology, Delft, Netherlands.

ADDITIONAL READING

Cortez, L. A. B. *S.* (2010). *Sugarcane bioethanol: R&D for productivity and sustainability*. São Paulo, Edgard Blücher Ltda.

Cortez, L. A. B., Lora, E. E. S., & Gómez, E. O. (2008). *Biomass para energia*. Campinas: Editora Unicamp.

Gómez, E. O. (2002). *Estudo da pirólise rápida de capim elefante em leito fluidizado borbulhante mediante caracterização dos finos de carvão* (Doctoral dissertation). Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica, Campinas, SP. Retrieved from Acervus Unicamp Dissertations and Theses database. (T/UNICAMP OL4e).

Neves, R. C. (2013). *Reforma de gás de gaseificação por meio de tocha de plasma: ensaios preliminares* (Master dissertation). Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica, Campinas, SP. Retrieved from Acervus Unicamp Dissertation and Theses Database. (D/UNICAMP N414r).

Sánchez, C. G. (2010). *Tecnologia da gaseificação de biomassa*. Campinas, Editora átomo.

Souza-Santos, M. L. (2010). *Solid fuels combustion and gasification: modeling, simulation and equipment operations.* Boca Raton, CRC press Taylor & Francis Group.

KEY TERMS AND DEFINITIONS

Chemical Reaction: A phenomenon of transformation of a substance into another substance.

Energy: Term related to molecules movement of a matter portion.

Energy Forms: Chemical, electrical, heat, radiant, mechanical and nuclear.

Exergy: Maximum useful work that can be obtained from or at a system.

Exergy Forms: Chemical, physical, kinetic and potential.

Gasification: A thermochemical process which carbonaceous materials are transformed in a combustible gas.

Irreversibility of a System: A system that cannot back to initial point/state.

Mass: Term related to matter quantity.

Product Gas: A gas produced from gasification process which has impurities and contaminants (e.g. tar, particulate matter, water, others).

Syngas: A gas produced from gasification process which has the mole ratio H_2/CO of approximately 2 and is free of impurities and contaminants.

Chapter 8

Biomass Processing Routes for Production of Raw Materials with High Added Value:

Prospects and Challenges for the Developing Routes

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ABSTRACT

In this chapter sugarcane bagasse may be submitted to a biological route in which the technologies used to obtain lignocellulosic ethanol (2nd generation ethanol) from lignocellulosic materials involve pre-treatment and the hydrolysis of the polysaccharides in the biomass into fermentable sugars for subsequent fermentation. Taking into consideration the use of sugarcane bagasse as a raw material for 2nd generation ethanol, the acid hydrolysis / pretreatment of sugarcane bagasse could be more

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feasible that others, and must be evaluated in this context. On the other hand, from biomass is possible to obtain products with high added value and energy, mainly by the use of thermochemical processes (e.g. pyrolysis and gasification) and biochemical processes (e.g., fermentation and anaerobic digestion). However, the products obtained from the thermochemical processes can be used as raw material for biochemical processes which multiplies the quantity of products to be obtained from biomass.

INTRODUCTION

One of the alternatives that could be implemented for the agro-industries to continue increasing their production of biofuels as well as to provide feedstock for chemicals is to use the byproducts formed as a source of energy. Amongst these by-products, sugarcane bagasse occupies a prominent position in Brazilian agricultural activities. The interest in sugarcane bagasse in Brazil is justified by the fact that it is available in the ethanol and sugar production units, without the problems and costs associated with the logistics and transport of lignocellulosic materials. A glance in this material brings huge possibilities for use, amongst which in the production of animal feed, in the chemical industry, in the production of microbial biomass and in the production of 2nd generation ethanol via sugarcane bagasse and straw to generate electricity.

The biological technologies used to obtain ethanol from lignocellulosic materials (2nd generation ethanol) involve pre-treatment and the hydrolysis of the polysaccharides in the biomass into fermentable sugars for subsequent fermentation. Pre-treatment is necessary due to the strong bonds existing between the cellulose, hemicelluloses and lignin. Thus, the lignocellulosic biomass requires selective separation of the components; this implies in rupturing the cellulose-hemicelluloses-lignin complex and the removal of each fraction by pre-treatment techniques for subsequent enzymatic degradation, if that is the route chosen for the hydrolysis step. Various pre-treatment methods have been proposed and developed. These methods can be classified in different methods: physical, chemical and biological pre-treatments or a combination of these, aiming at reducing the recalcitrance of this lignocellulosic biomass (sugarcane bagasse). Among all these methods the chemical and combined pre-treatments have drawn more attention, since they remove the lignin without degrading the cellulose chain (Sun & Cheng, 2002), and more recently physical methods (Boussarsar, Rogé, & Mathlouthi, 2009) and combined methods (Rocha, Martín, da Silva, Gómez, & Gonçalves, 2012) have been more extensively considered.

Nowadays, liquid hot water (LHW) pretreatment associated with high pressure carbon dioxide (HP-CO_2) from depicted sugarcane bagasse coupled to enzymatic hydrolysis reported a glucose yield of 30.43 g/L and a cellulose conversion of 41.17% (Gurgel, Pimenta, & Curvelo, 2014). On the other hand, Phan and Tan (2014) proposed a pretreatment of sugarcane bagasse using sequential combination of supercritical CO_2 ($scCO_2$) and alkaline hydrogen peroxide (H_2O_2) and results showed that the glucose recovery reach 97.8% when compared to individual H_2O_2, ultrasound and $scCO_2$ pretreatment methods (22.9%, 20.2% and 61.3%, respectively).

The hydrolysis process involves breaking the glycosidic bonds of the polysaccharides, which are the pre-treated raw material, into fermentable sugars, monosaccharides (either hexoses or pentoses, depending on the polysaccharide) and the conversion of the sugars of the components of the sugarcane bagasse (cellulose and hemicelluloses). For the feasible production of 2nd generation ethanol, two strategies have been conceived, each with a different stage of development: acid hydrolysis and enzymatic hydrolysis.

On the other hand, the sugarcane bagasse can be used as raw material in the thermochemical route, which is based on pyrolysis and gasification processes to produce Syngas (hydrogen and carbon monoxide mainly) and tar (Jordan & Akay, 2012), that are further processed by either chemical transformation (as for instance by Fischer-Tropsch) or biochemically, trough fermentation. Therefore, the thermochemical route coupled to biochemical route allows full biomass utilization (cellulose, hemicelluloses and lignin), which offers potentially a great advantage over the 2G technology, which it will name as hybrid thermochemical-biochemical route (Liu et al., 2014).

The biochemical route ferments syngas using anaerobic microorganisms, but is a little explored area, when this is connected to the gasification process (Liu et al., 2014; D. Xu, Tree, & Lewis, 2011). Therefore, it is necessary to investigated as well as to evaluate the potential of integration thermochemical to biochemical route, when is used the sugarcane bagasse.

BACKGROUND

Brazilian sugar factories can be classified into three types of installation: sugar factories exclusively producing sugar, those with distilleries annexed producing both sugar and ethanol, and installations producing only ethanol or autonomous distilleries (BNDES & CGEE, 2008). However in addition to sugar and alcohol, the sugar-alcohol industry also colligated electrical energy (co-generation) to its basic production mix (Dias, Junqueira, Cavalett, et al., 2012; Macedo, Seabra, & Silva, 2008). This last alternative is, in fact, a very flexible and attractive approach to deal with possible market prices fluctuations that are usually common when the feedstock is based on agriculture activities and the products prices are in some how affected by government economical policies.

One of the alternatives that could be implemented for the agro-industries to continue increasing their production of this fuel (i.e. ethanol) is to use the byproducts formed as a source of energy. Amongst these by-products, sugarcane bagasse occupies a prominent position in Brazilian agricultural activities. Nowadays, sugarcane bagasse (lignocellulosic material) is a target of various studies aimed at using its energy potential with respect to the production of bio-fuel to substitute gasoline and attend the future demand for energy in the transport sector in Brazil for between 20 – 25% (Tavares et al., 2011) and in the United States for between approximately 20 – 30% (Krishnan et al., 2010). At this point is worthwhile mentioning that its use is not restricted to this purpose, since many chemicals may be produced by the fractions of sugar cane bagasse.

Due to the increased consciousness of the environmental problems, there is a need for the recognition of new energy sources and new technologies to expand the production of biofuels (de Andrade, Maugeri Filho, Maciel Filho, & da Costa, 2013). For large-scale biological production of fuel ethanol, it is desirable to use cheaper and more abundant substrates (Cardona, Quintero, & Paz, 2010). Ethanol, for fuel use, has been produced on a large scale basis in Brazil for over three decades using sugarcane as feedstock (Balat & Balat, 2009; Dias et al., 2013). This is considered the most efficient and important biofuel technology (Dias, Junqueira, Jesus, et al., 2012; Gauder, Graeff-Hönninger, & Claupein, 2011; Rocha et al., 2011), inclusive being recognized as advanced biofuel by EPA (Environmental Protection Agency of USA). Dias, Junqueira, Cavalett, et al. (2012) analyzed the integrated 1st and 2nd generation ethanol (with 2015 expected hydrolysis technology) and pentoses biodigestion and the main results for the process simulation and economic analysis showed a anhydrous ethanol and surplus electricity production equals to 107 $L/ton_{dry\ sugarcane}$ and 77 $kWh/ton_{dry\ sugarcane}$, respectively, and 133 $kg/\ ton_{dry\ sugarcane}$ of lignocellulosic material hydrolyzed (LMH) corresponding to 181 $L/ton_{dry\ LMH}$ or 24 $L/ton_{dry\ sugarcane}$ in reference to second generation ethanol production.

Sugarcane bagasse is chemically composed by hard fibrous structures, polysaccharides (cellulose and hemicelluloses), lignin and nonstructural components. Its mean composition is between: 50 - 60% moisture, 1.8±0.67 - 8.9±1.2% soluble extractives, 33.8 - 51.1±1.3% (on % dry weight basis) cellulose, 16.9±0.2 - 31.0±2.5% (on % dry weight basis) hemicelluloses, 5.2±0.5 -24.7±1.6% (on % dry weight basis) lignin, and 0.34±0.03 - 20.9±4.3% (on % dry weight basis) ash (Table 1). Hence, cellulose is an unbranched homopolysaccharide consisting of *D*-glucopyranosyl units. On the other hand hemicellulose is a branched heteropolysaccharides consisting of both hexose and pentose sugar residues, which may also carry acetyl groups.

Table 1. Sugarcane bagasse characterization (on % dry weight basis) reported in the published literature

Reference	Cellulose / %	Hemicellulose / %	Lignin / %	Extractives / %	Acetyl / %	Others / %	Ash / %
Tovar, dos Santos, Maciel, and Filho (2013)	41.81±3.31	31.00±2.54	17.08±2.19	8.93±1.16	-	-	2.53±0.13
Bian et al. (2014)	43.6	33.5	18.1	-	-	-	2.3
Biswas, Uellendahl, and Ahring (2014)	33.8	27	23.9	-	-	-	6.3
Prado et al. (2014)	51.1±1.3	30.3±2.1	5.2±0.5	-	-	-	2.6±0.1
Khuong et al. (2014)	40.7±0.2	16.9±0.2	23.4±0.4	-	-	2.9±0.3	-
Gao et al. (2013)	41.95	21.7	23.61	-	-	-	-
Rocha et al. (2013)	42.8±0.3	25.9±0.3	22.1±0.2	6.1±0.1	-	-	1.4±0.1
Arsène, Bilba, Savastano Junior, and Ghavami (2013)	43.1±1.8	29.5±1.8	24.7±1.6	4.7±0.5	-	-	-
Chen, Ye, and Sheen (2012)	48.45	29.92	17.12	-	-	4.51	-
Gurgel, Marabezi, Zanbom, and Curvelo (2011)	49.49±0.31	24.34±0.78	22.69±0.08	1.80±0.67	-	-	0.34±0.03
Rocha et al. (2012)	42.3±0.5	25.1±0.3	24.7±0.1	-	3.7±0.0	-	3.5±0.0
Abril, Medina, and Abril (2012)	46.4±0.2	25.9±0.4	23.60	2.4±0.1	-	-	3.7±0.3
Rocha et al. (2011)	45.5±1.1	27.0±0.8	21.1±0.9	4.6±0.3	-	-	2.2±0.1
Rezende et al. (2011)	35.2±0.9	24.5±0.6	22.2±0.1	-	-	-	20.9±4.3
Silva, Arruda, Felipe, Gonçalves, and Rocha (2011)	42.8±0.3	25.9±0.3	22.1±0.2	6.1±0.1	-	-	1.4±0.1
Mesa et al. (2011)	44.94	28.24	18.93	-	-	7.89	-

At last, lignin, consists of phenylpropane units linked together by different types of interunit linkages of which ether bonds are the most common (Jönsson, Alriksson, & Nilvebrant, 2013).

ACID HYDROLYSIS / PRETREATMENT OF SUGARCANE BAGASSE STRATEGIES OVER HIGH SOLIDS LOADING

Several approaches are being explored in order to obtain polymeric components of the lignocellulosic materials in maximum yield and purity (Chandel, Singh, Chandrasekhar, Rao, & Narasu, 2010). Acids breakdown the cellulose and hemicellulose polymers in lignocellulosic biomass form individual sugar molecules, which can be fermented into biofuels (Lenihan et al., 2010; Wyman, 1994). The advantages of acid hydrolysis / pretreatment are that the acid can penetrate lignin without pretreatment, the rate of acid hydrolysis is faster than enzyme hydrolysis, but glucose also degrades rapidly under acidic conditions (Cheung & Anderson, 1996), so that operational conditions and strategies should be found to minimize this last undesired reaction. Further, acid hydrolysis / pretreatment of lignocellulosic feedstocks is a simple and inexpensive approach for pretreatment that efficiently improves the susceptibility to cellulolytic enzymes, even for more recalcitrant types of lignocellulose (Jönsson et al., 2013).

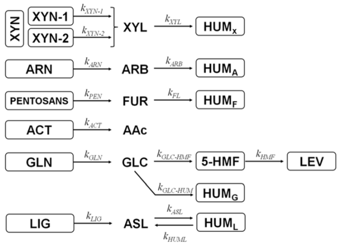
With the development of the kinetic study (Table 2), evaluations of pre-treatments for sugarcane bagasse considered to be of greater potential for implementation was carried out, released sugar, formation of inhibitors and the process conditions for the production of 2nd generation ethanol. With the data obtained, mathematical models were developed and validated for the dilute acid hydrolysis / pre-treatment process. The reaction conditions studied were solids loadings (10 - 25%), acid solution concentration (1.0 - 3.0% w/v) and reaction time (0 - 150 min).

The rate constants of the dilute acid hydrolysis / pretreatment scheme published in the literature (Table 2) were estimated using an optimization routine. The rate constants were combined with the mass balance equations to model the dependence of the reducing sugar concentration on time, based on the experimental data (Tovar et al., 2013; Tovar, Maciel, & Filho, 2014b).

First Strategy: Acid Hydrolysis / Pretreatment of Sugarcane Bagasse Coupled to Enzymatic Hydrolysis

In the process line of the 2G alcohol, one strategy for a sustainable and a consolidated process for processing sugarcane bagasse consisted of a dilute acid hydrolysis / pretreatment at temperatures 121±1 °C at 1.0% w/v using high solids loading (20 and

Table 2. Reaction mechanisms occurring during the acid hydrolysis / pretreatment published in the literature

Reaction scheme	Reference
	Lavarack, Griffin, and Rodman (2002)
	Lavarack et al. (2002)
	Lavarack et al. (2002)
	Gámez, González-Cabriales, Ramírez, Garrote, and Vázquez (2006)
	Chang, Ma, and Cen (2006)
	Lavarack et al. (2002)

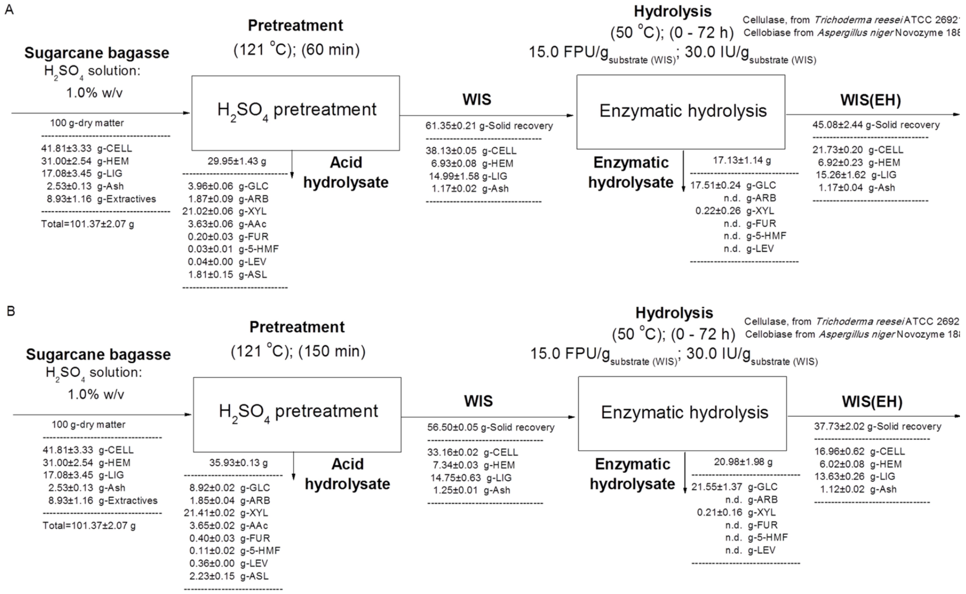
[*XYN-1*], [*XYN-2*] are the substrate (easy-to-hydrolyze xylan and hard-to-hydrolyze xylan, respectively) concentrations; [*XYL*] is the xylose concentration; k_{XYN-1} is the rate of conversion of *XYN-1* to *XYL*; k_{XYN-2} is the rate of conversion of *XYN-2* to *XYL*; k_{XYL} is the rate of decomposition of *XYL* into decomposition products (HUM_x); [*ARN*] is the substrate (arabinan) concentration; [*ARB*] is the arabinose concentration; k_{ARN} is the rate of conversion of *ARN* to *ARB*; k_{ARB} is the rate of decomposition of *ARB* into decomposition products (HUM_A); [*Pentosans*] is the substrate (xylan plus arabinan) concentration; [*FUR*] is the furfural concentration; k_{PEN} is the rate of conversion of pentosans to *FUR*; k_{FL} is the rate of decomposition of *FUR* into decomposition products (HUM_P); [*ACT*] is the acetyl groups concentration; [*AAc*] is the acetic acid concentration; k_{ACT} is the rate of conversion of the *ACT* linked to sugars to *AAc*; [*GLN*] is the substrate (glucan) concentration; [*GLC*] is the glucose concentration; k_{GLN} is the rate of conversion of *GLN* to *GLC*; $k_{GLC-HMF}$ is the rate of decomposition of *GLC* into *5-HMF*; $k_{GLC-HUM}$ is the rate of decomposition of *GLC* into decomposition products (HUM_G); k_{HMF} is the rate of decomposition of *5-HMF* into levulinic acid (*LEV*); [*LIG*] is the substrate (total lignin) concentration; [*ASL*] is the acid soluble lignin concentration; k_{LIG} is the rate of conversion of *LIG* into *ASL*; k_{ASL} is the rate of decomposition of *ASL* into decomposition products (HUM_L) and k_{HUML} is the rate of formation of *ASL* with precursor decomposition products (HUM_L)

25%) at 60 and 150 min followed by 72 h of enzymatic hydrolysis (Figures 1 - 2). This experimental study is based on detailed kinetic data of the pretreatment based on sequences for a single-stage of dilute H_2SO_4-acid hydrolysis / pretreatments using arrangement of comparatively acid solution concentration and high solids loading, at relatively low temperature (121±1 °C) considering a batch reaction system.

Figures 1 – 2 show the sugars and inhibitors released during the dilute acid hydrolysis / pretreatment, as products of the cellulosic and hemicellulosic fractions. It is clear that glucose and 5-HMF is more resistant to acid attack than xylose, arabinose and furfural (Aguilar, Ramírez, Garrote, & Vázquez, 2002). Their concentrations at an acid concentration of 1.0% w/v were about two times lower than xylose and twenty times lower than furfural, respectively (Tovar et al., 2013).

With respect to cellulose dissolution, it increases rapidly with time, exhibiting a partially dissolved fraction which depends on the acid concentration, reaching a conversion of about 20.75±0.04% with an acid concentration equal to 1.0% w/v, 20% of solids loading at 150 min. However, this result is probably not an appropriate scenery in 2nd generation ethanol, since it is required the minimum dissolution of the cellulose fraction. In this sense, the highest hemicellulose conversion with the minimal cellulose dissolution were obtained under 1.0% w/v of acid concentra-

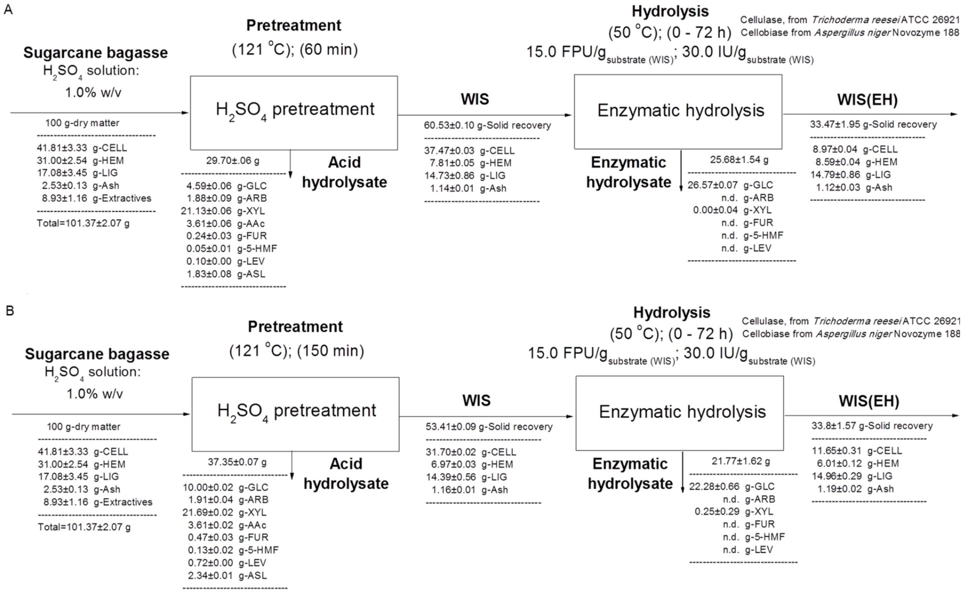
Figure 1. Sugarcane bagasse processing by H2SO4 hydrolysis / pretreatment at: (A) 20% of solids loading, 1.0% w/v and 60 min and (B) 20% of solids loading, 1.0% w/v and 150 min coupled to enzymatic hydrolysis at 3.0% w/v WIS loading (CELL: Cellulose, HEM: Hemicellulose and LIG: Total Lignin)



tion at 121 ± 1°C between 60 and 90 min and results ranged from 8.77±0.10% to 13.03±0.21% at 20% of solids loading and from 10.36±0.15% to 15.10±0.20% at 25% of solids loading. Hence, using solids loading of 20%, about 74.35 ± 0.29% (at 60 min) and 76.20 ± 0.05% (at 90 min) of the hemicellulose was hydrolyzed with a direct relationship observed for the dissolution and hydrolysis of cellulose. Similar results were obtained at solid loading equals 25% (Tovar et al., 2014b). According to the total lignin content in sugarcane bagasse (17.08 ± 2.19% on a dry weight basis), the highest percentage of lignin removal was lower than 13.70±0.07% under 1.0% w/v of acid concentration, at solids loading of 25% at 121 ± 1°C on 150 min.

Y. Chen et al. (2012) studied the biomass acid loading (grams of acid/grams of biomass) and found that this was the more dominant factor in determining biomass digestibility. The digestibility of the WIS fraction obtained with a solids loading of 20%, acid concentration of 1.0% w/v and acid hydrolysis / pretreatment time of 150 min at 121 ± 1°C was investigated. It was found that the increases in grams of acid per gram of sugarcane bagasse (0.05 and 0.15) associated with the acid concentration used in the pretreatment (1.0 and 3.0% w/v, respectively) significantly affected the cellulose content of the WIS, reporting losses of 20.68 ± 0.06% and 49.74 ± 2.68%, respectively.

Figure 2. Sugarcane bagasse processing by H2SO4 hydrolysis / pretreatment at: (A) 25% of solids loading, 1.0% w/v and 60 min and (B) 25% of solids loading, 1.0% w/v and 150 min coupled to enzymatic hydrolysis at 3.0% w/v WIS loading (CELL: Cellulose, HEM: Hemicellulose and LIG: Total Lignin)



The digestibility of the WIS fraction from sugarcane bagasse pretreated at 121 ± 1°C with a solids loading of 20% and 0.15 grams of acid per gram of sugarcane bagasse (69.55 ± 0.59%), was higher than those pretreated with 0.05 grams of acid per gram of sugarcane bagasse (58.75 ± 0.78%, respectively). Figures 3 - 4 show the glucose concentration over different WIS materials (at different hydrolysis / pretreatment conditions) submitted to enzymatic hydrolysis, the glucan digestibility calculated based on the Equation 1 and the total glucose yield after enzymatic hydrolysis calculated based on the Equation 2.

$$Digestibility = \left(Total\ glu\cos e\ in\ enzymatic\ hydrolysis \times 0.9 \middle/ Total\ glucan\ in\ WIS \right) \times 100 \tag{1}$$

$$Y^{EH}{}_{GLC} = \left(Total\ glu\cos e\ in\ enzymatic\ hydrolysis \times 0.9 \middle/ Total\ glucan\ in\ SCB \right) \times 100 \tag{2}$$

Figure 3. (A) Glucose concentration (GLC), (B) glucan digestibility and (C) total glucose yield (Y^{EH}_{GLC}) after enzymatic hydrolysis (superscript EH) from WIS fraction obtained by acid hydrolysis / pretreatment (HPAC) at 20% of solids loading on 30, 60 and 150 min and 1.0% w/v acid concentration. Error bars represent the standard error of the duplicate samples

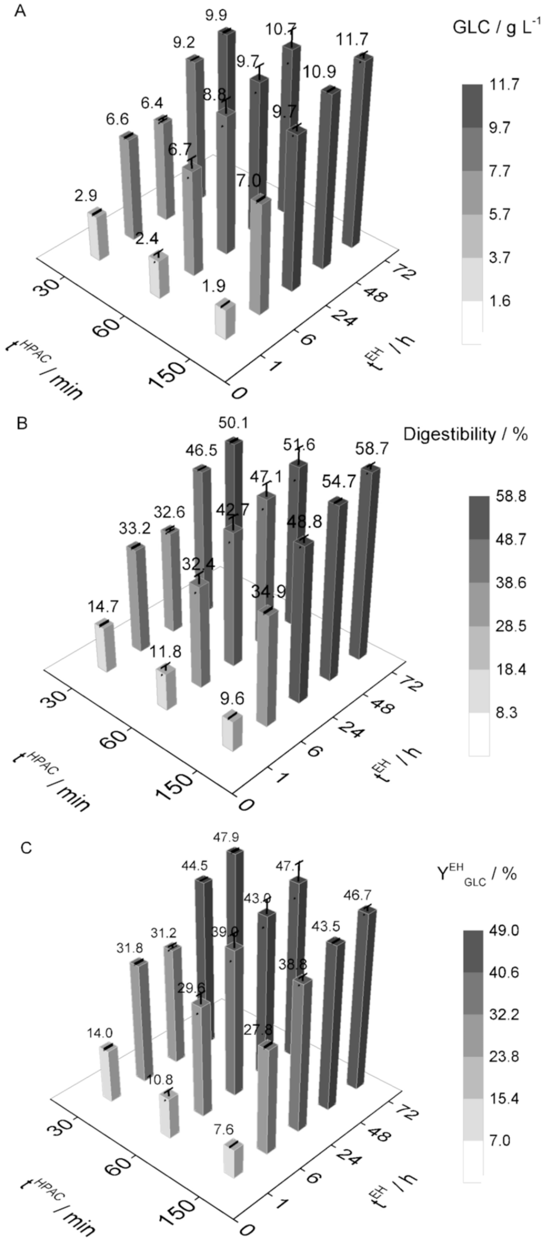
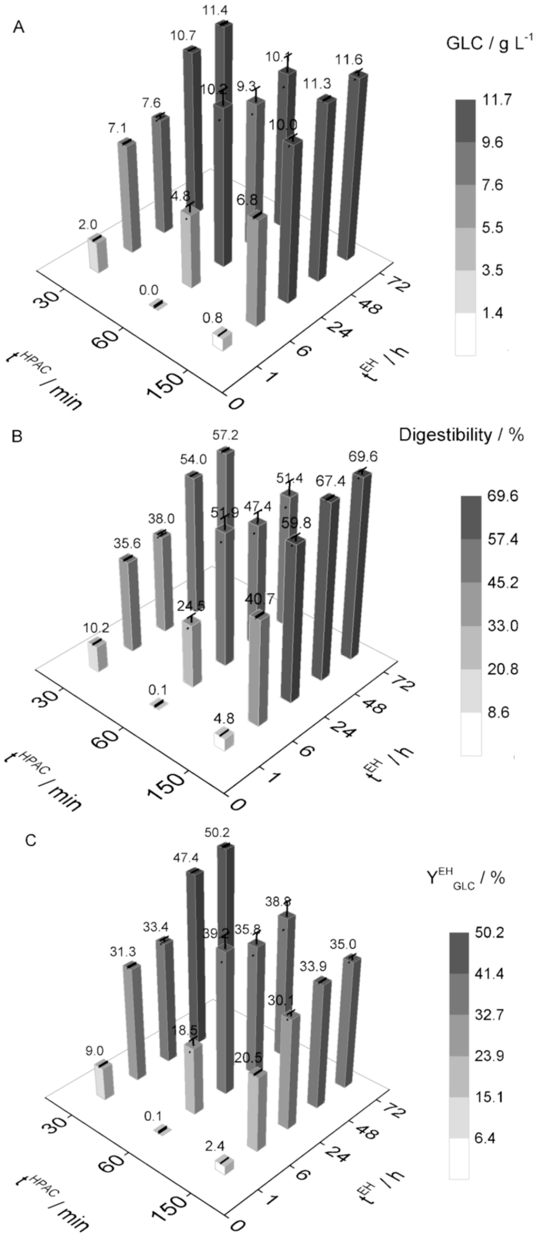


Figure 4. (A) Glucose concentration (GLC), (B) glucan digestibility and (C) total glucose yield (Y^{EH}_{GLC}*) after enzymatic hydrolysis (superscript EH) from WIS fraction obtained by acid hydrolysis / pretreatment (HPAC) at 20% of solids loading on 30, 60 and 150 min and 3.0% w/v acid concentration. Error bars represent the standard error of the duplicate samples*



Second Strategy: Acid Hydrolysis / Pretreatment of Sugarcane Bagasse over Optimum Conditions Coupled to Enzymatic Hydrolysis

Detailed and optimized process models incorporating H_2SO_4-acid hydrolysis / pretreatment and enzymatic hydrolysis were developed to enhance pentose sugars recovery and enzymatic digestibility. In the published literature, the acid hydrolysis / pretreatment has allowed to use up to 15% solids loading to process lignocellulosic biomass, whereas only 10% solids in lignocellulose conversion has been using at pilot-scale reactor. Hence, optimizing the H_2SO_4-hydrolysis / pretreatment of sugarcane bagasse at 121±1 °C in a single-stage batch hydrolysis reactor and investigate the effects of the acidic solution concentration (0.159 – 1.841% w/v), reaction time (10 – 110 min) and solid loading (4.89 – 30.11%) on the hemicellulose removal and consequently on the production of sugars (xylose, glucose and arabinose) as well as on the formation of by-products (furfural, 5-hydroxymethylfurfural, levulinic acid and acetic acid) was possible to define the optimum conditions (Tovar, Maciel, & Filho, 2014a).

The optimal working conditions during the acid hydrolysis were defined under the following criteria: low cellulose dissolution, high hemicellulose conversion in released sugar, and high levels of catalytic efficiency. Therefore, the working conditions satisfying the above criteria and in being in the studied ranges were defined as: 1.0% w/v of acid concentration, 20% of solids loading and 80 min at 121 °C. Under these conditions, 76.31±3.77% of the total hemicellulose was removed and the hydrolysate contained ($g/100_{gsugarcane\_bagasse}$) 21.89±1.09 xylose, 1.81±0.09 arabinose, 5.42±0.11 glucose, 3.51±0.17 acetic acid, 0.20±0.01 furfural, 0.05±0.01 5-hydroxymethylfurfural and 0.09±0.00 levulinic acid (Tovar et al., 2014a).

After enzymatic hydrolysis, the raw material (untreated sugarcane bagasse) was 9.83 $g/100g_{SCB\ DRM}$ (at 72 h). The highest glucose yield of WIS fraction (under optimum conditions) was 62.27 ± 0.28% using 8.0% w/v of solids loading (S^{EH}) and an enzyme loading of 15.0 FPU $cellulase/g_{substrate\ (WIS)}$ and 33.0 IU β-glucosidase/$g_{substrate\ (WIS)}$. Digestibility of the WIS fraction revealed that at optimum conditions investigated was reasonably effective for preparing the sugarcane bagasse for enzymatic digestibility since more than 75% of the hemicellulose was removed and 12.12 ± 0.25% of cellulose was affected during pretreatment and digestibility about 62.27 ± 0.28% were attained (Tovar et al., 2014a).

THERMOBIOCHEMICAL HYBRID ROUTE FROM BIOMASS TRANSFORMATION

Thermochemical Route

There are several types thermochemical processes, but in order to obtain products with high added value, here are exposed only the processes of pyrolysis and gasification since they appear to be the most attractive for the quality of the products obtained. These two processes transform a solid material, such as biomass, into three main products: a gas of high added-value- for interest as raw material in the chemical industry (consisting primarily of H_2, CO, CO_2 and CH_4), a liquid fraction known as tar and a solid residual fraction. Both pyrolysis and gasification are carried out at relatively high temperatures; pyrolysis operates generally at 400 °C to 600 °C in the absence of an oxidizing agent. The gasification works between 600 °C to 1200 °C performing a partial oxidation using a gassing agent. The two processes are quite complex, but understanding the pyrolysis leads to a better knowledge of the gasification process since for all gasification, the pyrolysis step takes place implicitly.

The efficiency of thermochemical processes depends on several factors, mainly the type of reactor used, reaction temperature and amount of oxidizing agent used (in case of gasification). it is possible to direct the process in order to produce what is required. Because of this there is a great effort by the scientific community to investigate the behavior of pyrolysis and gasification when using biomass as feedstock, among which is the sugarcane bagasse.

Raw Material Characterization for Thermochemical Processes

For most biochemical processes, the characterization of biomass that determines the amount of cellulose, hemicellulose, lignin and extractives is the most common and is always used, is well established and is in fact as a standard characterization of this type (Rabelo, Maciel Filho, & Costa, 2013). But, when thermochemical processes is considered, the approach for biomass characterization can be carried out done in several ways, but basically either it can use the biochemical characterization of all components involved (Ardila, Figueroa, Lunelli, Maciel Filho, & Wolf Maciel, 2014), or otherwise can make an elementary approach (percentages of carbon, nitrogen, hydrogen, chlorine, sulfur, and oxygen), for which no matter what type of compound was formed, only the elemental composition (Figueroa, Ardila, Filho, & Maciel, 2014). Each type of characterization has its advantages, but if a further study is required, the biochemical approach is the most recommended. There is another type of characterization, the ultimate analysis (percentages of moisture, fixed carbon, volatile material and ash) that is more superficial and provides a quick indication of the biomass potential to the thermochemical route, a parameter which is displayed with the volatile material percentage in the sample.

Pyrolysis

Figueroa, Ardila, Lunelli, Maciel Filho, and Wolf Maciel (2013a) conducted a study of biomass pyrolysis in a fixed bed; varying the temperature from 500 °C to 900 °C using argon as the carrier gas. Finding the distribution of products was strongly influenced by temperature: the gas mass percentage shows an increase when the temperature increases; at a temperature of 500 °C the amount of gas is 32.5 wt% and when the temperature was increased to 900 °C, the mass percentage increased to 53.1 wt%. The amount of tar was found no to be very temperature dependent, with an average value of 22.1 wt% in the temperature range studied. The gas with a higher percentage of CO_2 was produced at 500 °C (70 mol%), obtaining at the same temperature 8 mol% CO and 22 mol% CH_4.

R. Xu, Ferrante, Briens, and Berruti (2011) carried out fast pyrolysis of biomass in a fluidized bed, ranging the temperature from 300 °C to 600 °C and 2 seconds of vapor residence time. It was found, that, like the fixed bed, the mass percentage of gas is increased with temperature rising from 10 mol% to 300 °C up to 40 wt% at 600 °C. The tar decreased from 50 wt% to 40 wt% with a maximum of 58 wt% when the reaction temperature was 400 °C. The char presented the greatest variation, with 37 wt% at 300 °C and decreasing to 18 wt% at 600 °C.

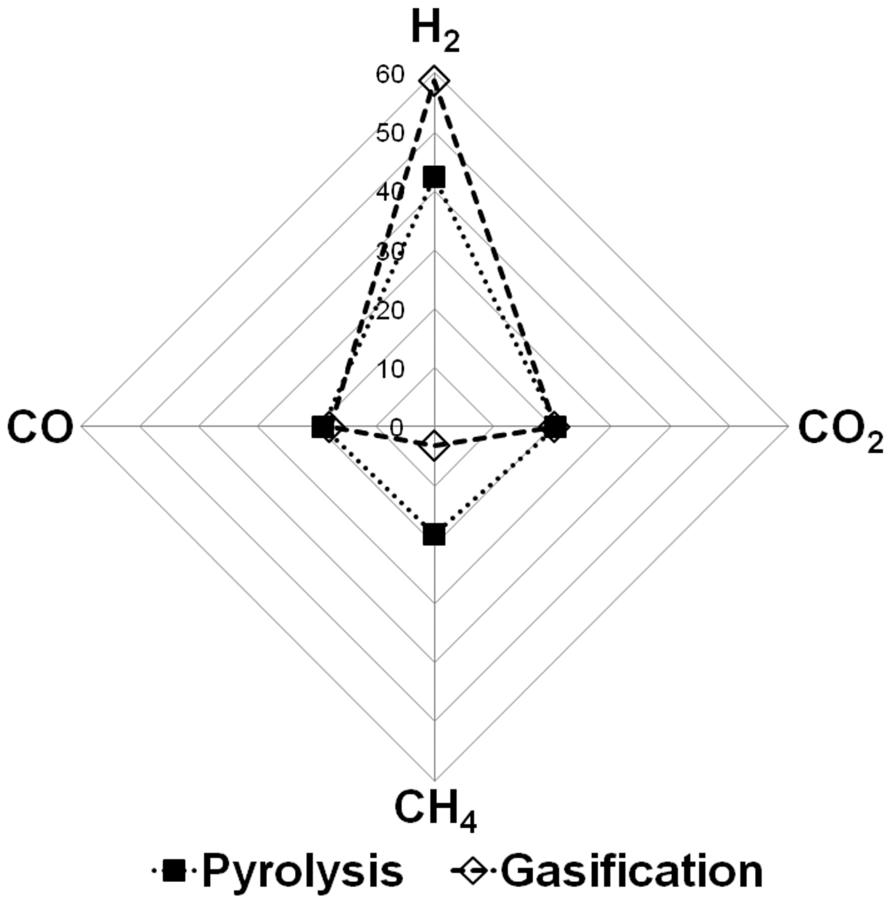
Comparing the results obtained by Figueroa et al. (2013a) and R. Xu et al. (2011), it can be concluded that the type of reactor (fixed or fluidized bed) influences the product distribution. The fluidized bed using lower temperatures provided had higher percentages of gas. Moreover, it was shown that the fluidized bed led an increase in the gas production. Based on mention before, choosing a type of reactor (i.e. fixed or fluidized bed) comprises an important operational strategy in the thermochemical route depending upon the product is desired. The evaluation of the whole process allows to observe that the pyrolysis in a fluidized bed could decrease the yields of char and increasing the tar and gas product being more attractive economically.

Gasification

Figueroa et al. (2013a) showed the distribution of products obtained when biomass is processed in a fixed bed gasifier using steam as agent (SB ratio = 2.0) at 900 °C. The gasified biomass is converted into 66 wt% gas, 27 wt% of tar and 7 wt% of char. In fact, it has been seen that the gasification produces greater percentages of gases, which makes the amount of char produced to be minimal. The difference in the composition of the gas produced at 900 °C using a fixed bed reactor for the pyrolysis and gasification processes is shown in Figure 5 (Figueroa et al., 2013a).

Figueroa et al. (2014) designed and built an experimental gasification plant level bench with of a fluidized bed reactor that makes use of biomass as a raw material, air as gasification agent and silica as part of the inert bed. The results demonstrated that the fluidized bed gasification becomes an attractive process for the production of gas. The authors varied the equivalence ratio (ER), using 0.23 and 0.28 which was reflected in the reaction temperature of 741 °C and 802 °C, respectively. In the upper and lower temperature were obtained around 93 wt% (gas), 4 wt% (tar), 3 wt% (char) and 95 wt% (gas), 3 wt% (tar), 2 wt% (char), respectively.

Figure 5. Gas composition by fixed-bed pyrolysis and gasification (mol%)



The gases produced in these two conditions of ER exhibited almost the same composition, such as: 43 mol% of CO_2, 8.0 mol% of CH_4, 31.0 mol% of CO and 14.0 mol% H_2 (normalized values).

Analyzing the previous thermochemical processes, it is concluded that the increase in temperature and the addition of an agent aerator (air or steam) process lead to an increase in gas fraction obtained at the expense of a strong decrease in the amount of char. At this point is important to mention that the amount of tar produced depends on the type of process, and its production is seen most favored in pyrolysis than in gasification.

In the case of gasification, after defined the equivalent ratio (ER), automatically the reaction temperature is defined. The highest ratio ER leads to higher reaction temperature. The increase in ER leads to an increase in the percentage of gas, but there is a point at which the gas is no longer attractive, because it has large amounts of CO_2. The challenge in fact is to find the operational strategy and the suitable reaction conditions to produce the largest amount of gas, but with attractive composition, that is, higher percentages of CO and H_2 (syngas). In order to do that computational simulation is a valuable tool and this is discussed in the next section.

SIMULATION OF SUGARCANE BAGASSE GASIFICATION USING ASPEN PLUS

Simulation of Pyrolysis (Thermal Decomposition) of Biomass

One of the most important steps in the simulation of gasification is to define the conditions or compositions of the pyrolysis step that occurs within the whole gasification process. Ardila, Figueroa, Lunelli, Maciel Filho, and Wolf Maciel (2012b) based on ultimate and proximate analysis and making use of the minimization of Gibbs free energy, assumed that in the sugarcane bagasse pyrolysis the products generated are H_2, CO, CO_2, CH_4, C_2H_2, carbon (char) e naphthalene (tar). Figueroa, Ardila, Lunelli, Maciel Filho, and Wolf Maciel (2013b) also based on the same type of characterization, showed a simulation of the pyrolysis using correlations. The correlations defined the yields of char, tar and gases (CO, CO_2, H_2, CH_4) according to the experimental data obtained by Figueroa et al. (2013a) in a fixed-bed reactor. Correlations were inserted in Aspen Plus using blocks of calculation in Fortran, in the same simulation platform. Ardila et al. (2014) suggest a methodology to define the simulation of the sugarcane bagasse pyrolysis, based on the biological characterization, considering the content of lignin, cellulose, hemicellulose and ash. The authors define the temperatures at which begins and ends the bagasse decomposition, known as primary and secondary pyrolysis as well as the maximum conversions for each of the pseudocomponents (lignin, hemicellulose and cellulose). Thus, it is considered that the gases generated in the decomposition of the three pseudocomponents are mainly CO, H_2, CO_2, CH_4, C_2H_6, C_2H_4 and formaldehyde, tar is composed of levoglucosan, acetic acid, hydroxyacetaldehyde, 1,3-dihydroisobenzofuran, propanedial, acetaldehyde, xylose, phenol, hydroxymethylfurfural, furfural, methanol and ethanol and finally the carbon as char.

Simulation of Gasification (Combustion-Reduction)

One possibility to address the simulation of biomass gasification with the gasifying agent is to predict the composition in thermodynamic equilibrium calculations by minimizing the Gibbs free energy for atoms C, H, O, N and S (Ardila, Figueroa, Lunelli, Maciel Filho, & Wolf Maciel, 2012a; Ardila et al., 2012b; Doherty, Reynolds, & Kennedy, 2009a, 2009b; Panopoulos, Fryda, Karl, Poulou, & Kakaras, 2006). Ardila et al. (2012b) used the minimization of Gibbs free energy method to predict the composition of the gas produced. A simulation of a circulating fluidized bed gasifier with sugarcane bagasse using the simulator Aspen Plus^{TM} was performed. The influence of operating conditions such as temperature, equivalence ratio (ER) and steam injection on the performance of the gasifier were investigated. In this study it was confirmed that the composition of CO_2 in gasification gas is increased when is increased the ratio ER, but the composition of H_2 and CO decreases. Higher temperatures increased the composition of CO in the gasification gas when it was used a mixture of air and steam, but the compositions of H_2 and CO_2 decreases. The formation of H_2 was shown to be sensitive to the variation of SB ratio.

Figueroa et al. (2013b) performed a fixed-bed gasifier simulation using steam water as gasification agent. The authors determined the composition of the gasification gas using the minimization of the Gibbs free energy for the reactions set of char in elemental form (C, H, O), tar and pyrolysis gas. The simulation provided good prediction of the composition of gases when compared with the experimental data reported by Figueroa et al. (2013a). Ardila et al. (2014) used the simulator to impersonate a fixed bed gasifier. Chemical kinetics and minimization of Gibbs free energy was used to define the composition of the gasification gas using steam and air as gasification agents. The compositions of the gasification gas showed a considerable error in the CH_4 composition for different simulations found in the literature when using the Gibbs energy minimization to represent the gasification of tar, char, gases from the pyrolysis (Ardila et al., 2014; Doherty et al., 2009b; Figueroa et al., 2013b).

Simulation of the Synthesis Gas Cleaning System

Eliminating traces of nitrogenous components, sulfur components and tar still present in the gas, is an important operation and various authors have used different catalysts (CaO, MgO, CaOMgO, Ni) in fixed bed reactors usually with steam reforming at the output of the gasifier (methods secondary cleaning), thus allowing to obtain the necessary conditions to be able to handle this synthesis gas for subsequent procedures (Corella, Aznar, Gil, & Caballero, 1999; Torres, Pansare, & Goodwin, 2007). Other authors use the catalyst in the gasification reactor itself (primary cleaning methods) to eliminate these undesirable components (Coll, Salvadó, Farriol, & Montané, 2001; Corella et al., 1999). Corella et al. (1999) focused their study to define the best position to use the catalyst (dolomite) as an additive for cleaning gases by primary or secondary methods. According to these studies and varying some operational variables regarding oxidizing agents such as air and a mixture of steam-oxygen, it was concluded that the efficacy of the catalyst in the secondary method is only slightly higher than compared to the primary method (dolomite in bed). This slight improvement was evidenced in the experiments with steam-oxygen mixture, but no significant differences were found in the two methods when air is used as oxidizing agent.

Figueroa et al. (2014) during the gasification of sugarcane bagasse in a bubbling fluidized bed reactor used two cyclones to remove the solids present and a condensing system to separate the tar and water. On the other hand Akay and Jordan (2011) for the gasification of sugarcane bagasse in a fixed bed reactor (downdraft), used two cyclone separators and a water scrubber to clean the synthesis gas. Erlich and Fransson (2011) for the same type of reactor used as a cleaning system a cyclone and two fixed-bed filters. Thus, char, tar and water were removed from the synthesis gas.

Ardila et al. (2012b); Ardila et al. (2014); Ardila et al. (2012a); Doherty et al. (2009b); Figueroa et al. (2013b) considered the cleaning of gasification gas in Aspen simulations Plus^{TM} simply as cyclones to separate the solids and condensation system for separation of liquids such as tar and water. Ardila et al. (2012a) discussed and simulated two rigorous gasification models of sugarcane bagasse to study the technologies of tar removal using the simulator Aspen Plus ^{TM}. It was considered the catalyst in the gasification reactor and also the output of the gasifier. For all of this is possible to concluded that high temperatures increase the conversion of tar, but more significantly in secondary method. The change on the catalyst placement may improve the quality of the product gas.

FERMENTATION OF SYNTHESIS GAS

The synthesis gas is an important element in the production of fuels and chemicals. Catalytic processes may be used to convert synthesis gas in a variety of fuels and / or chemicals such as methane, methanol, formaldehyde, acetic acid and ethanol (Spath & Dayton, 2003). The microorganisms can also be used to convert synthesis gas into fuels and chemicals components. Biological processes, although generally slower than chemical reactions, have several advantages over catalytic processes, such as greater specificity, greater productivity and lower energy costs and generally a greater resistance to poisoning (Klasson, Ackerson, Clausen, & Gaddy, 1993). Unlike the hydrolysis, the gasification technologies can convert all biomass (hemicellulose, cellulose, lignin and extractives) in synthesis gas that can be potentially fermented by bacteria (Rajagopalan, Datar, & Lewis, 2002). According to Munasinghe and Khanal (2010) the pathways thermochemical for transforming the biomass involved the biomass gasification into synthesis gas and then converts the synthesis gas to biofuels, using chemical catalysts or also using microbial catalysts, known as fermentation synthesis gas.

Anaerobic bacteria such as *Clostridium ljungdahli, Clostridium autoethanogenum* and *Clostridium carboxidivivorais* have been shown suitable to convert CO, CO_2 e H_2 into ethanol and acetic acid (Ahmed, Cateni, Huhnke, & Lewis, 2006; Henstra, Sipma, Rinzema, & Stams, 2007; Köpke et al., 2010; Mohammadi et al., 2011; Mohammadi, Younesi, Najafpour, & Mohamed, 2012; Phillips, Clausen, & Gaddy, 1994; Phillips, Klasson, Clausen, & Gaddy, 1993; Younesi, Najafpour, & Mohamed, 2005, 2006).

Anaerobic bacteria such as *Clostridium ljungdahlii* and *Clostridium autoethanogenum*, have been demonstrated to produce ethanol and acetic acid from CO, CO_2 e H_2 by acetogenic pathways (Rajagopalan et al., 2002). According to Henstra et al. (2007) the fermentation of ethanol from synthesis gas by *Clostridium ljungdahlii* was developed into a commercial process that combines biomass gasification, fermentation of synthesis gas and distillation of ethanol. The synthesis gas is cooled before being introduced into the bioreactor and is coupled to the heat recovery. Ardila et al. (2014) presented a simulation of the synthesis gas fermentation from gasification of sugarcane bagasse. It was confirmed that using air as the oxidizing agent (ER = 0:25) at a temperature of 800 °C to produce a synthesis gas (H_2: 25% /CO: 20% /CO_2: 15% /N_2: 40%) which was subsequently fermented can produce ethanol and acetic acid with concentrations of 2.5 g/L and 5.2 g/L, respectively. The authors compared the results with experimental data obtained by Gaddy (2000), finding that the simulation adequately represents the process of fermentation under the conditions studied. Table 3 presents some studies in the literature with different operational conditions and yields obtained in the fermentation of synthesis gas for the production of ethanol and acetic acid.

Table 3. Performances of syngas fermentation for ethanol and acetate production from the acetogenic bacterium Clostridium ljungdahlii

Reactor type	**Feed stock**	**pH**	**T (°C)**	**Cell**[a]	**X %**	**Maximun Production**	**Reference**
CSTR[b], 13.5 L, (560 h), 300-500 rpm	CO:55%/H_2:20%/ CO_2:10%/Ar:15%	4.5	36	0.4	-	1.5g Eth/L, 3.5 g Acac/L	Phillips et al. (1993)
CSTR[c], 13.5 L, (560 h) 300-500 rpm	CO:55%/H_2:20%/ CO_2:10%/Ar:15%	4.5	36	1.5	-	23 g Eth/L, 3.0 g Acac/L	Phillips et al. (1993)
CSTR[c], with recycle, 1 L, (560 h), 450 rpm	CO:55%/H_2:20%/ CO_2:10%/Ar:15% F_G=30 mL/min, F_M=12 mL/h	4.5	36	4.0	X_{CO}=90 X_{H2}=70	48 g Eth/L, 3 g Acac/L 21 mol Eth mol^{-1} Acac	Phillips et al. (1993)
CSTR[b], 2L, 720 h, 500 rpm	CO:55%/H_2:20%/ CO_2:10%/Ar:15%, F_G=14 mL/min, F_M=0.55 mL/min	4.0	37	2.34	X_{CO}=98 X_{H2}=100	6.5 g Eth/L, 5.43 g Acac/L 1.53 mol Eth mol^{-1} Acac	Mohammadi et al. (2012)
CSTR[b], 2L, 105 days, 400 rpm	CO:55%/H_2:20%/ CO_2:10%/Ar:15%, F_G= 14 mL/min, F_M=0.55 mL/min	4.5	37	1.1	X_{CO}=90	0.072 g Eth/ mmol CO 0.067 g Acac/ mmol CO	Younesi et al. (2006)
CSTR[b], 2L, 105 days, 500 rpm	CO:70%/H_2:15% / Ar:15%, F_G=14 mL/min, F_M=0.55 mL/min	4.5	37	2.1	X_{CO}=96	CEth=4.4, CAcac=4.5 1.26 (molEthOH/ molAc)	Younesi et al. (2006)
CSTR[b], 2L, 105 days, 400 rpm	CO pure, F_G= 14 mL/min, F_M=0.55 mL/min	4.5	37	1.92	X_{CO}=80	0.114 g Eth/ mmol CO 0.11 g Acac/ mmol CO	Younesi et al. (2006)
Batch, 130 rpm	CO:65%/H_2:24%/ CO_2:11%	4.5	37		X_{CO}=80 X_{H2}=80	0.113 mol [Eth+Acac]/g CO 0.533 mol [Eth+Acac]/g H_2	Phillips et al. (1994)
[a] Cell density (g L^{-1}), [b]ATCC 1754 PETC Medium, [c] Designed medium based on E. Coli $F_{M:}$ Medium flow, F_G: Syngas flow, Eth: Ethanol, Acac: Acetic acid, X: conversion							

Impurities and Conditions That Are Allowed in the Synthesis Gas for Fermentation

Most of the studies that are reported in the literature, made use of a synthetic synthesis gas for fermentation, being used mainly H_2, CO, CO_2, N_2, prepared as a mixture. However, typically additional components or contaminants that may generally be present in the synthesis gas are forgotten, such as methane, traces of NO, H_2, light hydrocarbons and tar. One of the work focused on the use of such toxic compounds in syngas has been reported by Ahmed and Lewis (2007). These authors have focused on studying the effects of NO on fermentation of synthesis gas, and showed that it inhibits the hydrogenase in *Clostridium carboxidivivorais*, but also leads to an increase in ethanol production and affects cell growth. It was estimated that the synthesis gas with NO < 40 ppm can be tolerated by cells in the fermentation without compromising the activity of hydrogenase, cell growth and product distribution. The presence of NO in the synthesis gas, is mainly from the combustion and is generated by the content of N_2 present in biomass that is generally low or by gasifying agent when air is used.

Ahmed et al. (2006) studied the effects of impurities such as tar and NO and concluded that the cell inactivity and redistribution of products were probably caused by tar (benzene, 327 μg/ml toluene, 117 μg/ml, ethylbenzene, 131 μg/ml and p-xylene-92μg/ml) dragged in the synthesis gas, however, it was adapted to tar after prolonged exposure. In the case of NO (150 ppm) it was observed that it inhibits the enzyme hydrogenase. It was demonstrated that the use of a filter of 0.025 mm in the stream inlet of the synthesis gas is desirable to remove particles larger than 0.025 μm, mitigating the effects of tar in the fermentation. D. Xu et al. (2011) studied the effects of impurities generated during the production of synthesis gas and its potential in the fermentation medium associated with cellular toxicity, cell inhibition and product distribution. In this study it was concluded that ammonia (NH_3) present in the synthesis gas as an impurity is most likely to accumulate in the growth medium, due to which ammonia is highly soluble in water and can form ion ($NH^+{}_4$) solution. Thus the potential impact of ammonia in the fermentation of synthesis gas may be large due to that ammonium ions may remain and accumulate over time to achieve solubility limits of ammonia.

Klasson et al. (1993) studied the effect of the presence of H_2S in the synthesis gas for cell growth and absorption of CO when using *Clostridium ljungdahlii*. It was observed that the presence of H_2S is not a threat for cell growth and for the absorption of CO at concentrations of 2.7% v/v. However, at concentrations of 5.2% v/v small reductions were found on cell growth and small delays in the absorption of CO, but they concluded that the impact is not significantly to affect the process for concentrations as high as 5.2% H_2S v/v.

This type of studies focusing on the influence of impurities in the synthesis gas fermentation, is necessary to identify the severity of the required cleanliness to guarantee a good process performance. Evidently, the impurity content is also associated with raw material used, the operating conditions, the type of gasifier and gasification agent. Bearing this in mind is important to account for the relationship among raw material, techniques of synthesis gas production and cleaning, microorganism and fermentation conditions.

FUTURE RESEARCH DIRECTIONS

Based on the fact that gasification and pyrolysis processes use biomass rich in C, H and O elements, different streams in the sugarcane mill could be processed in the hybrid biochemical - thermochemical route.

Therefore, as presented by Sun and Cheng (2002), the purpose of a pretreatment is to efficiently separate and provide easier access to the main biomass components (cellulose, hemicellulose and lignin), eventually removing lignin, preserving the hemicellulose, reducing the cellulose crystallinity and increasing the porosity of the material by different techniques for subsequent hydrolysis. In this sense, the present evaluation showed that the hemicellulose is well suited for biofuels production due to their enormous availability, low cost and environmental benign process. As reported in the literature, the major fraction in hemicelluloses is pentosans, these (primarily xylan) account for 16.9±0.2 - 31.0±2.5% (on % dry weight basis) (Table 1) of the overall mass. Thus, from an economic-viability point of view, it is critical to convert xylan/xylose to ethanol or other biofuels (Weber et al., 2010). Thereby, the conversion of hemicelluloses into fuels with maximum yields is the deciding factor for more cost-effective bioconversion processes more cost-effective (Chandel et al., 2010).

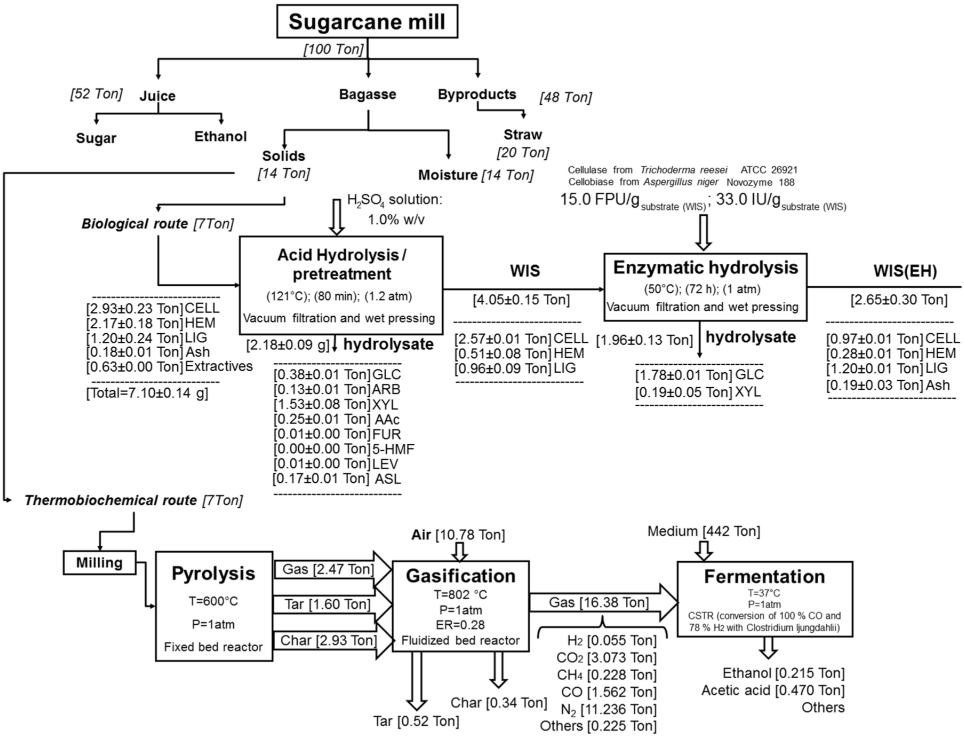
CONCLUSION

The sugarcane bagasse, already available in the production site, is a renewable and economical alternative for the sustainable production of biofuels using the biological route and the hybrid biochemical - thermochemical routes, so that the sugar cane based process may share some of the available infrastructure for the first generation ethanol production (Dantas, Legey, & Mazzone, 2013).

Aiming the comparison between 1st and 2nd generation ethanol and hybrid thermochemical-biochemical route it is showed a mass balance of a sugarcane mill which could uses these routes (Figure 6).

Furthermore, in general, 1 ton of sugarcane generates 280 kg of bagasse, and 5.4 x 10^8 dry tons of sugarcane are processed annually throughout the world (Cerqueira, Rodrigues Filho, & Meireles, 2007). Therefore, the sugarcane bagasse can be used as raw material in the biological route (dilute acid hydrolysis / pretreatment) coupled to enzymatic hydrolysis to produce fermentable sugars for subsequent fermentation of hexose and/or pentose sugars connected to hybrid thermochemical-biochemical route in which the pyrolysis and gasification processes produce Syngas and tar (Figure 6).

Figure 6. Sugarcane bagasse processing using the biological process (acid hydrolysis/pretreatment coupled to enzymatic hydrolysis) and the hybrid thermochemical-biochemical route



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REFERENCES

Abril, D., Medina, M., & Abril, A. (2012). Sugar cane bagasse prehydrolysis using hot water. *Brazilian Journal of Chemical Engineering*, *29*(1), 31–38. doi:10.1590/S0104-66322012000100004

Aguilar, R., Ramírez, J. A., Garrote, G., & Vázquez, M. (2002). Kinetic study of the acid hydrolysis of sugar cane bagasse. *Journal of Food Engineering*, *55*(4), 309–318. doi:10.1016/S0260-8774(02)00106-1

Ahmed, A., Cateni, B. G., Huhnke, R. L., & Lewis, R. S. (2006). Effects of biomass-generated producer gas constituents on cell growth, product distribution and hydrogenase activity of Clostridium carboxidivorans P7T. *Biomass and Bioenergy*, *30*(7), 665–672. doi:10.1016/j.biombioe.2006.01.007

Ahmed, A., & Lewis, R. S. (2007). Fermentation of biomass-generated synthesis gas: Effects of nitric oxide. *Biotechnology and Bioengineering*, *97*(5), 1080–1086. doi:10.1002/bit.21305 PMID:17171719

Akay, G., & Jordan, C. A. (2011). Gasification of fuel cane bagasse in a downdraft gasifier: Influence of lignocellulosic composition and fuel particle size on syngas composition and yield. *Energy & Fuels*, *25*(5), 2274–2283. doi:10.1021/ef101494w

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2012a). Simulation of the syngas production based on technologies removal of tar using Aspen PlusTM *International Symposium on Gasification and its Applications (ISGA-3)*. Vancouver.

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2012b). Syngas production from sugar cane bagasse in a circulating fluidized bed gasifier using Aspen PlusTM: Modelling and Simulation. In F. Ian David Lockhart Bogle and Michael (Ed.), Computer Aided Chemical Engineering (Vol. Volume 30, pp. 1093-1097): Elsevier.

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2014). Simulation of ethanol production via fermentation of the synthesis gas using Aspen PlusTM. *Chemical Engineering Transaction*, *37*, 637–642. doi:10.3303/CET1437107

Arsène, M.-A., Bilba, K., Savastano Junior, H., & Ghavami, K. (2013). Treatments of non-wood plant fibres used as reinforcement in composite materials. *Materials Research*, *16*(4), 903–923. doi:10.1590/S1516-14392013005000084

Balat, M., & Balat, H. (2009). Recent trends in global production and utilization of bio-ethanol fuel. *Applied Energy*, *86*(11), 2273–2282. doi:10.1016/j.apenergy.2009.03.015

Bian, J., Peng, P., Peng, F., Xiao, X., Xu, F., & Sun, R.-C. (2014). Microwave-assisted acid hydrolysis to produce xylooligosaccharides from sugarcane bagasse hemicelluloses. *Food Chemistry*, *156*(0), 7–13. doi:10.1016/j.foodchem.2014.01.112 PMID:24629931

Biswas, R., Uellendahl, H., & Ahring, B. K. (2014). Wet explosion pretreatment of sugarcane bagasse for enhanced enzymatic hydrolysis. *Biomass and Bioenergy*, *61*(0), 104–113. doi:10.1016/j.biombioe.2013.11.027

BNDES, B., & CGEE, C. (2008). *Sugarcane-Based Bioethanol: Energy for sustainable development*. Brazil, Rio de Janeiro-RJ: Coordination BNDES and CGEE.

Boussarsar, H., Rogé, B., & Mathlouthi, M. (2009). Optimization of sugarcane bagasse conversion by hydrothermal treatment for the recovery of xylose. *Bioresource Technology*, *100*(24), 6537–6542. doi:10.1016/j.biortech.2009.07.019 PMID:19664914

Cardona, C. A., Quintero, J. A., & Paz, I. C. (2010). Production of bioethanol from sugarcane bagasse: Status and perspectives. *Bioresource Technology*, *101*(13), 4754–4766. doi:10.1016/j.biortech.2009.10.097 PMID:19945863

Cerqueira, D. A., Rodrigues Filho, G., & Meireles, C. S. (2007). Optimization of sugarcane bagasse cellulose acetylation. *Carbohydrate Polymers*, *69*(3), 579–582. doi:10.1016/j.carbpol.2007.01.010

Chandel, A. K., Singh, O. V., Chandrasekhar, G., Rao, L. V., & Narasu, M. L. (2010). Key drivers influencing the commercialization of ethanol-based biorefineries. *Journal of Commercial Biotechnology*, *16*(3), 239–257. doi:10.1057/jcb.2010.5

Chang, C., Ma, X., & Cen, P. (2006). Kinetics of levulinic acid formation from glucose decomposition at high temperature. *Chinese Journal of Chemical Engineering*, *14*(5), 708–712. doi:10.1016/S1004-9541(06)60139-0

Chen, W.-H., Ye, S.-C., & Sheen, H.-K. (2012). Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment. *Applied Energy*, *93*(0), 237–244. doi:10.1016/j.apenergy.2011.12.014

Chen, Y., Stevens, M. A., Zhu, Y., Holmes, J., Moxley, G., & Xu, H. (2012). Reducing acid in dilute acid pretreatment and the impact on enzymatic saccharification. *Journal of Industrial Microbiology & Biotechnology*, *39*(5), 691–700. doi:10.1007/s10295-011-1068-7 PMID:22167347

Cheung, S. W., & Anderson, B. C. (1996). Ethanol production from wastewater solids. *Water Environment and Technology*, *8*(5), 55–60.

Coll, R., Salvadó, J., Farriol, X., & Montané, D. (2001). Steam reforming model compounds of biomass gasification tars: Conversion at different operating conditions and tendency towards coke formation. *Fuel Processing Technology*, *74*(1), 19–31. doi:10.1016/S0378-3820(01)00214-4

Corella, J., Aznar, M.-P., Gil, J., & Caballero, M. A. (1999). Biomass gasification in fluidized bed: Where to locate the dolomite to improve gasification? *Energy & Fuels*, *13*(6), 1122–1127. doi:10.1021/ef990019r

Dantas, G. A., Legey, L. F. L., & Mazzone, A. (2013). Energy from sugarcane bagasse in Brazil: An assessment of the productivity and cost of different technological routes. *Renewable & Sustainable Energy Reviews*, *21*(0), 356–364. doi:10.1016/j.rser.2012.11.080

de Andrade, R. R., Maugeri Filho, F., Maciel Filho, R., & da Costa, A. C. (2013). Kinetics of ethanol production from sugarcane bagasse enzymatic hydrolysate concentrated with molasses under cell recycle. *Bioresource Technology*, *130*(0), 351–359. doi:10.1016/j.biortech.2012.12.045 PMID:23313680

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Cunha, M. P., Jesus, C. D. F., Rossell, C. E. V., & Bonomi, A. et al. (2012). Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. *Bioresource Technology*, *103*(1), 152–161. doi:10.1016/j.biortech.2011.09.120 PMID:22019267

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Pavanello, L. G., Cunha, M. P., Jesus, C. D. F., & Bonomi, A. et al. (2013). Biorefineries for the production of first and second generation ethanol and electricity from sugarcane. *Applied Energy*, *109*(0), 72–78. doi:10.1016/j.apenergy.2013.03.081

Dias, M. O. S., Junqueira, T. L., Jesus, C. D. F., Rossell, C. E. V., Maciel Filho, R., & Bonomi, A. (2012). Improving bioethanol production – Comparison between extractive and low temperature fermentation. *Applied Energy*, *98*(0), 548–555. doi:10.1016/j.apenergy.2012.04.030

Doherty, W., Reynolds, A., & Kennedy, D. (2009a). Computer simulation of a biomass gasification-solid oxide fuel cell power system using Aspen Plus. *Energy*, *35*(12), 4545–4555. doi:10.1016/j.energy.2010.04.051

Doherty, W., Reynolds, A., & Kennedy, D. (2009b). The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation. *Biomass and Bioenergy*, *33*(9), 1158–1167. doi:10.1016/j.biombioe.2009.05.004

Erlich, C., & Fransson, T. H. (2011). Downdraft gasification of pellets made of wood, palm-oil residues respective bagasse: Experimental study. *Applied Energy*, *88*(3), 899–908. doi:10.1016/j.apenergy.2010.08.028

Figueroa, J. E. J., Ardila, Y. C., Filho, R. M., & Maciel, M. R. W. (2014). Fluidized bed reactor for gasification of sugarcane bagasse: Distribution of syngas, bio-tar and char. *Chemical Engineering Transactions*, *37*, 229–234. doi:10.3303/CET1437039

Figueroa, J. E. J., Ardila, Y. C., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2013a). Evaluation of pyrolysis and steam gasification processes of sugarcane bagasse in a fixed bed reactor. *Chemical Engineering Transactions*, *32*, 925–930. doi:10.3303/CET1332155

Figueroa, J. E. J., Ardila, Y. C., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2013b). Evaluation of pyrolysis and steam gasification processes of sugarcane bagasse in a fixed bed reactor *AIDIC Conference Series*.

Gaddy, J. L. (2000). US 6136577 United StatesMon Apr 09 07:57:11 EDT 2007CHO-English.

Gámez, S., González-Cabriales, J. J., Ramírez, J. A., Garrote, G., & Vázquez, M. (2006). Study of the hydrolysis of sugar cane bagasse using phosphoric acid. *Journal of Food Engineering*, *74*(1), 78–88. doi:10.1016/j.jfoodeng.2005.02.005

Gao, Y., Xu, J., Zhang, Y., Yu, Q., Yuan, Z., & Liu, Y. (2013). Effects of different pretreatment methods on chemical composition of sugarcane bagasse and enzymatic hydrolysis. *Bioresource Technology*, *144*(0), 396–400. doi:10.1016/j.biortech.2013.06.036 PMID:23891836

Gauder, M., Graeff-Hönninger, S., & Claupein, W. (2011). The impact of a growing bioethanol industry on food production in Brazil. *Applied Energy*, *88*(3), 672–679. doi:10.1016/j.apenergy.2010.08.020

Gurgel, L. V. A., Marabezi, K., Zanbom, M. D., & Curvelo, A. A. S. (2011). Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic Study of cellulose saccharification and glucose decomposition. Part I: Sulfuric acid as the catalyst. *Industrial & Engineering Chemistry Research*, *51*(3), 1173–1185. doi:10.1021/ie2025739

Gurgel, L. V. A., Pimenta, M. T. B., & Curvelo, A. A. S. (2014). Enhancing liquid hot water (LHW) pretreatment of sugarcane bagasse by high pressure carbon dioxide (HP-CO2). *Industrial Crops and Products*, *57*(0), 141–149. doi:10.1016/j.indcrop.2014.03.034

Henstra, A. M., Sipma, J., Rinzema, A., & Stams, A. J. M. (2007). Microbiology of synthesis gas fermentation for biofuel production. *Current Opinion in Biotechnology*, *18*(3), 200–206. doi:10.1016/j.copbio.2007.03.008 PMID:17399976

Jönsson, L. J., Alriksson, B., & Nilvebrant, N.-O. (2013). Bioconversion of lignocellulose: inhibitors and detoxification. *Biotechnology for Biofuels, 6*(1), 16-. doi:10.1186/1754-6834-6-16

Jordan, C. A., & Akay, G. (2012). Occurrence, composition and dew point of tars produced during gasification of fuel cane bagasse in a downdraft gasifier. *Biomass and Bioenergy*, *42*(0), 51–58. doi:10.1016/j.biombioe.2012.03.014

Khuong, L. D., Kondo, R., De Leon, R., Kim Anh, T., Shimizu, K., & Kamei, I. (2014). Bioethanol production from alkaline-pretreated sugarcane bagasse by consolidated bioprocessing using Phlebia sp. MG-60. *International Biodeterioration & Biodegradation*, *88*(0), 62–68. doi:10.1016/j.ibiod.2013.12.008

Klasson, K. T., Ackerson, M. D., Clausen, E. C., & Gaddy, J. L. (1993). Biological conversion of coal and coal-derived synthesis gas. *Fuel*, *72*(12), 1673–1678. doi:10.1016/0016-2361(93)90354-5

Köpke, M., Held, C., Hujer, S., Liesegang, H., Wiezer, A., Wollherr, A., & Dürre, P. et al. (2010). Clostridium ljungdahlii represents a microbial production platform based on syngas. *Proceedings of the National Academy of Sciences*. doi:10.1073/pnas.1004716107

Krishnan, C., Sousa, L. C., Jin, M., Chang, L., Dale, B. E., & Balan, V. (2010). Alkali-based AFEX pretreatment for the conversion of sugarcane bagasse and cane leaf residues to ethanol. *Biotechnology and Bioengineering*, *107*(3), 441–450. doi:10.1002/bit.22824 PMID:20521302

Lavarack, B. P., Griffin, G. J., & Rodman, D. (2002). The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. *Biomass and Bioenergy*, *23*(5), 367–380. doi:10.1016/S0961-9534(02)00066-1

Lenihan, P., Orozco, A., O'Neill, E., Ahmad, M. N. M., Rooney, D. W., & Walker, G. M. (2010). Dilute acid hydrolysis of lignocellulosic biomass. *Chemical Engineering Journal*, *156*(2), 395–403. doi:10.1016/j.cej.2009.10.061

Liu, K., Atiyeh, H. K., Stevenson, B. S., Tanner, R. S., Wilkins, M. R., & Huhnke, R. L. (2014). Continuous syngas fermentation for the production of ethanol, n-propanol and n-butanol. *Bioresource Technology*, *151*(0), 69–77. doi:10.1016/j.biortech.2013.10.059 PMID:24211485

Macedo, I. C., Seabra, J. E. A., & Silva, J. E. A. R. (2008). Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy*, *32*(7), 582–595. doi:10.1016/j.biombioe.2007.12.006

Mesa, L., González, E., Cara, C., González, M., Castro, E., & Mussatto, S. I. (2011). The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse. *Chemical Engineering Journal*, *168*(3), 1157–1162. doi:10.1016/j.cej.2011.02.003

Mohammadi, M., Najafpour, G. D., Younesi, H., Lahijani, P., Uzir, M. H., & Mohamed, A. R. (2011). Bioconversion of synthesis gas to second generation biofuels: A review. *Renewable & Sustainable Energy Reviews*, *15*(9), 4255–4273. doi:10.1016/j.rser.2011.07.124

Mohammadi, M., Younesi, H., Najafpour, G., & Mohamed, A. R. (2012). Sustainable ethanol fermentation from synthesis gas by Clostridium ljungdahlii in a continuous stirred tank bioreactor. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *87*(6), 837–843. doi:10.1002/jctb.3712

Munasinghe, P. C., & Khanal, S. K. (2010). Biomass-derived syngas fermentation into biofuels: Opportunities and challenges. *Bioresource Technology*, *101*(13), 5013–5022. doi:10.1016/j.biortech.2009.12.098 PMID:20096574

Panopoulos, K. D., Fryda, L. E., Karl, J., Poulou, S., & Kakaras, E. (2006). High temperature solid oxide fuel cell integrated with novel allothermal biomass gasification: Part I: Modelling and feasibility study. *Journal of Power Sources*, *159*(1), 570–585. doi:10.1016/j.jpowsour.2005.12.024

Phan, D. T., & Tan, C.-S. (2014). Innovative pretreatment of sugarcane bagasse using supercritical CO2 followed by alkaline hydrogen peroxide. *Bioresource Technology*, *167*(0), 192–197. doi:10.1016/j.biortech.2014.06.006 PMID:24983689

Phillips, J. R., Clausen, E. C., & Gaddy, E. (1994). Synthesis gas as substrate for the biological production of fuels and chemicals. *Applied Biochemistry and Biotechnology*, *45-46*(1), 145–157. doi:10.1007/BF02941794

Phillips, J. R., Klasson, K. T., Clausen, E. C., & Gaddy, E. (1993). Biological production of ethanol from coal synthesis gas. *Applied Biochemistry and Biotechnology*, *39-40*(1), 559–571. doi:10.1007/BF02919018

Prado, J. M., Follegatti-Romero, L. A., Forster-Carneiro, T., Rostagno, M. A., Maugeri Filho, F., & Meireles, M. A. A. (2014). Hydrolysis of sugarcane bagasse in subcritical water. *The Journal of Supercritical Fluids*, *86*(0), 15–22. doi:10.1016/j.supflu.2013.11.018

Rabelo, S. C., Maciel Filho, R., & Costa, A. C. (2013). Lime pretreatment and fermentation of enzymatically hydrolyzed sugarcane bagasse. *Applied Biochemistry and Biotechnology*, *169*(5), 1696–1712. doi:10.1007/s12010-013-0097-2 PMID:23334836

Rajagopalan, S., Datar, R. P., & Lewis, R. S. (2002). Formation of ethanol from carbon monoxide via a new microbial catalyst. *Biomass and Bioenergy*, *23*(6), 487–493. doi:10.1016/S0961-9534(02)00071-5

Rezende, C., de Lima, M., Maziero, P., deAzevedo, E., Garcia, W., & Polikarpov, I. (2011). Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for Biofuels*, *4*(1), 1–19. doi:10.1186/1754-6834-4-54 PMID:22122978

Rocha, G. J. M., Martín, C., da Silva, V. F. N., Gómez, E. O., & Gonçalves, A. R. (2012). Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification. *Bioresource Technology*, *111*(0), 447–452. doi:10.1016/j.biortech.2012.02.005 PMID:22391588

Rocha, G. J. M., Martin, C., Soares, I. B., Souto Maior, A. M., Baudel, H. M., & Moraes de Abreu, C. A. (2011). Dilute mixed-acid pretreatment of sugarcane bagasse for ethanol production. *Biomass and Bioenergy*, *35*(1), 663–670. doi:10.1016/j.biombioe.2010.10.018

Rocha, G. J. M., Silva, V. F. N., Martín, C., Gonçalves, A. R., Nascimento, V. M., & Souto-Maior, A. M. (2013). Effect of xylan and lignin removal by hydrothermal pretreatment on enzymatic conversion of sugarcane bagasse cellulose for second generation ethanol production. *Sugar Tech*, *15*(4), 390–398. doi:10.1007/s12355-013-0218-9

Silva, V. F. N., Arruda, P. V., Felipe, M. G. A., Gonçalves, A. R., & Rocha, G. J. M. (2011). Fermentation of cellulosic hydrolysates obtained by enzymatic saccharification of sugarcane bagasse pretreated by hydrothermal processing. *Journal of Industrial Microbiology & Biotechnology*, *38*(7), 809–817. doi:10.1007/s10295-010-0815-5 PMID:20740373

Spath, P. L., & Dayton, D. C. (2003). *Preliminary Screening—Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas* (p. 142). Golden: National Renewable Energy Laboratory. doi:10.2172/15006100

Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology*, *83*(1), 1–11. doi:10.1016/S0960-8524(01)00212-7 PMID:12058826

Tavares, J. R., Sthel, M. S., Campos, L. S., Rocha, M. V., Lima, G. R., da Silva, M. G., & Vargas, H. (2011). Evaluation of pollutant gases emitted by ethanol and gasoline powered vehicles. *Procedia Environmental Sciences*, *4*(0), 51–60. doi:10.1016/j.proenv.2011.03.007

Torres, W., Pansare, S. S., & Goodwin, J. G. Jr. (2007). Hot gas removal of tars, ammonia, and hydrogen sulfide from biomass gasification gas. *Catalysis Reviews*, *49*(4), 407–456. doi:10.1080/01614940701375134

Tovar, L. P., dos Santos, R. A., Maciel, M. R. W., & Filho, R. M. (2013). Experimental evaluation and kinetic modeling studies on the hydrothermal and H2SO4-catalyzed hydrothermal pretreatments of sugarcane bagasse: Focusing on pretreatment at low temperature and batch process for high-solids loading *35th Symposium on Biotechnology for Fuels and Chemicals* (pp. 196). Hilton Portland: Portland, OR.

Tovar, L. P., Maciel, M. R. W., & Filho, R. M. (2014a). Optimizing dilute H2SO4-hydrolysis/pretreatment in a batch reactor at high solids loading to enhance pentose sugars recovery and enzymatic digestibility: a critical step for 2G ethanol production from sugarcane bagasse *36th Symposium on Biotechnology for Fuels and Chemicals* (pp. 68). Hilton Clearwater Beach: Clearwater Beach, FL.

Tovar, L. P., Maciel, M. R. W., & Filho, R. M. (2014b). Plug flow reactor model to analyse operating conditions on the dilute H2SO4-acid hydrolysis of sugarcane bagasse at high-solids loading. *Chemical Engineering Transactions*, *37*, 325–330. doi:10.3303/CET1437055

Weber, C., Farwick, A., Benisch, F., Brat, D., Dietz, H., Subtil, T., & Boles, E. (2010). Trends and challenges in the microbial production of lignocellulosic bioalcohol fuels. *Applied Microbiology and Biotechnology*, *87*(4), 1303–1315. doi:10.1007/s00253-010-2707-z PMID:20535464

Wyman, C. E. (1994). Ethanol from lignocellulosic biomass: Technology, economics, and opportunities. *Bioresource Technology*, *50*(1), 3–15. doi:10.1016/0960-8524(94)90214-3

Xu, D., Tree, D. R., & Lewis, R. S. (2011). The effects of syngas impurities on syngas fermentation to liquid fuels. *Biomass and Bioenergy*, *35*(7), 2690–2696. doi:10.1016/j.biombioe.2011.03.005

Xu, R., Ferrante, L., Briens, C., & Berruti, F. (2011). Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 263–272. doi:10.1016/j.jaap.2011.03.001

Younesi, H., Najafpour, G., & Mohamed, A. R. (2005). Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, Clostridium ljungdahlii. *Biochemical Engineering Journal*, *27*(2), 110–119. doi:10.1016/j.bej.2005.08.015

Younesi, H., Najafpour, G., & Mohamed, A. R. (2006). Liquid Fuel Production from Synthesis Gas via Fermentation Process in a Continuous Tank Bioreactor (CSTBR) Using Clostridium ljungdahlii. *Iranian Journal of Biotechnology*, *4*(1), 45–53.

ADDITIONAL READING

Canilha, L., Chandel, A. K., Milessi, T. S. S., Antunes, F. A. F., Freitas, W. L. C., Felipe, M. G. A., & da Silva, S. S. (2012). Bioconversion of sugarcane biomass into ethanol: An overview about composition, pretreatment methods, detoxification of hydrolysates, enzymatic saccharification, and ethanol fermentation. *Journal of Biomedicine & Biotechnology*, *2012*, 1–15. doi:10.1155/2012/989572 PMID:23251086

Gómez-Barea, A., & Leckner, B. (2010). Modeling of biomass gasification in fluidized bed. *Progress in Energy and Combustion Science*, *36*(4), 444–509. doi:10.1016/j.pecs.2009.12.002

KEY TERMS AND DEFINITIONS

Biomass Acid Loading: The acid charge on the dilute acid hydrolysis/pretreatment per unit feedstock basis.

Equivalence Ratio (ER): The ratio between the flow rate of air introduced into the gasifier and the stoichiometric flow rate of air required for complete combustion of the sugarcane bagasse.

Gasification Agent: Compound which provides the oxygen for the combustion reaction occurs in part of the biomass as well as being the agent which fluidizes the reactor.

SCB: Sugarcane bagasse.

Solid Loading: The amount of dry material entering the process (dilute acid hydrolysis / pretreatment) divided by the total mass of acid solution.

Steam to Biomass Ratio (SB): Defined as the flow rate of steam fed to the reactor divided by the flow rate of sugarcane bagasse.

WIS Fraction: Solid stream after acid hydrolysis / pre-treatment constituted basically by cellulose and lignin.

Chapter 9

Technical and Marketing Criteria for the Development of Fast Pyrolysis Technologies

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ABSTRACT

The management of projects regarding the use of biomass requires human resources with specific technical knowledge and tools to assess the real potential of raw materials within one or several production chains. Storage and transportation logistics, conservation and handling of the biomass, available technologies of transformation, and consumer market for the products are critical stages in the management process. The following chapter will present the technical, financial, and market criteria for managing production chains that use biomass as raw material in processes of fast pyrolysis.

INTRODUCTION

The chapter scope is to show the main technical and market criteria for the development of fast pyrolysis. A major concern of the authors is to show the reader in which cases the application of fast pyrolysis is feasible, as well as what the most appropriate biomass is and under what conditions the process and the technology is commercially viable.

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BACKGROUND FOR FAST PYROLYSIS: COMPOSING ELEMENTS OF THE PRODUCTION CHAIN

Biomass Thermo-Conversion Processes

The thermo-conversion processes are aimed at transforming solid biomass into new solid, liquid, and gas products of greater aggregate value (Basu, 2013). The distribution of the new products from this transformation will occur according to the quantity of oxygen involved in the thermo-chemical reactions and the temperature of the process. For example: in the combustion process, thermo-chemical reaction occurs in stoichiometric conditions that correspond approximately to the band of (6-7) kg of air/kg of dry biomass. In this process, the intended product is the heat from the combustion reaction. As the quantity of air in relation to the stoichiometric value decreases, the main primary product changes, as indicated in Figure 1.

Fast pyrolysis of biomass is defined as the thermal degradation of organic material in the absence of oxygen for the production especially of bio-oil. Charcoal and gases are also produced during this process.

Production Chain of Biomass Transformation

Pyrolysis is only one element in a series of interconnected stages that compose what we have defined as the Production Chain of Biomass Transformation – PCBT. This can be divided into three primary elements (Figure 2):

Figure 1. Intended products in the thermo-conversion processes

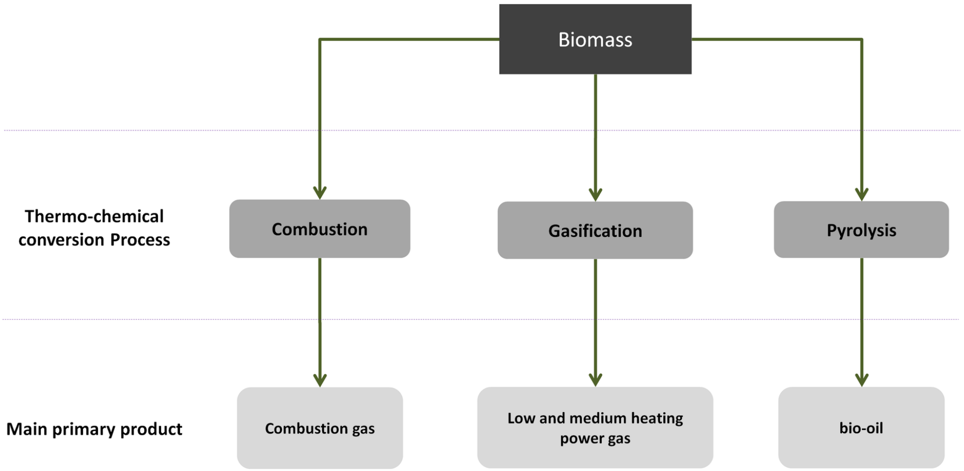
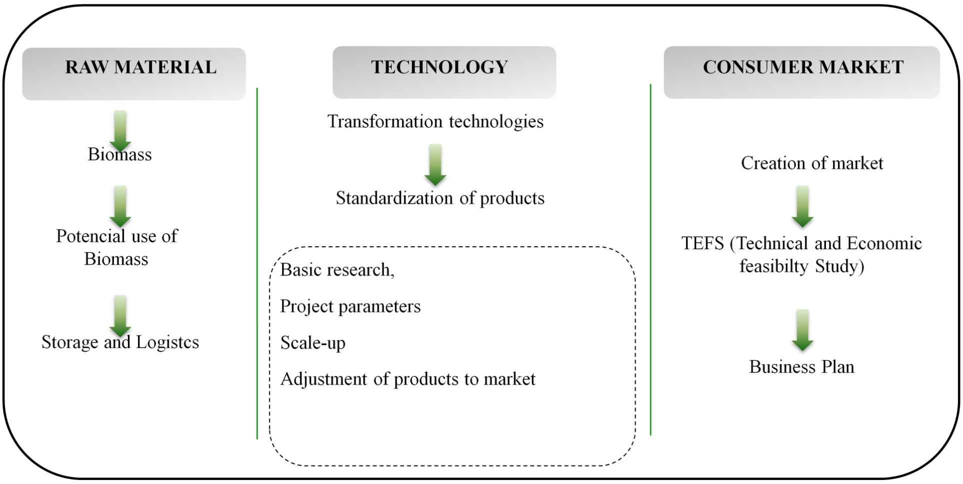


Figure 2. Composing elements of the Production Chain of Biomass Transformation – PCBT



1. Raw material;
2. Transformation Technology;
3. Consumer market.

Regardless of the PCBT used to elaborate a business plan, there are requirements that characterize the investment risks, which we list below according to the PCBT's primary elements (Nagano, Stefanovitz, & Vick, 2014).

Raw Material

"Good biomass is that which ensures":

- Large scale supply (from 100 ton/day);
- Standard quality (size, shape, and composition);
- Absence of environmental restriction;
- Competitive prices (defined by a sensitivity analysis).

Transformation Technology

The investment risks of innovative technology are directly related to the experience accumulated by the technical team involved in all the stages of the development, from the pilot to the demonstrative commercial scale. The rigorous definition and standardization of procedures and methodologies for obtaining the products, as well as the definition of project parameters and scale-up of minimize the risks by ensuring:

- The stable operation of the technology's composing equipment,
- Processed products which are made standard according to consumer market,

Consumer Market

The largest risk element in PCBT is when the consumer market is inexistent or under development.

The product that will be inserted in the consumer market, in most cases, intends to replace already existing fuels and/or inputs, which are generally derived from petroleum. Adjustment of pyrolysis products to the final consumer in the most effective way possible supposes the need to minimize the incompatibilities between biomass- derived products and petroleum-derived products. In other words, this adjustment must create standardized fuels. This requires the conduction of appropriateness and adjustment tests on pyrolysis products alongside the final consumer.

Regardless of the environmental gains that may come from the use of a green technology, the determining factor nowadays is the product's final price in relation to other existing products in the market. A good approach consists of ensuring that prices are 10% lower in comparison to equivalent petroleum-derived products.

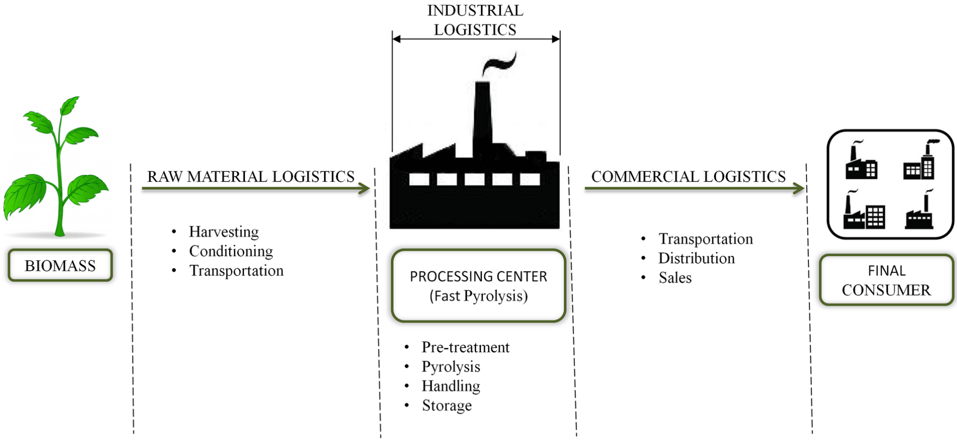
PCBT Logistics

A deeper analysis of the composing, ansformation of biomass is the logistics associated to each element of PCBT (Alonso-Pippo, Luengo, Felfli, Garzone, & Cornacchia, 2009). Figure 3 illustrates this logistics.

- Raw material logistics: involves harvesting, conservation, and transportation to the transformation center,
- Industrial logistics: involves the pre-treatment of biomass, pyrolysis, handling, and storage of pyrolysis products.
- Commercial logistics: involves transportation, distribution, and sale of pyrolysis products.

Pyrolysis is a process whose final goal is to solve the logistics problems associated to the "in natura" use of biomass. In the next topic we will discuss the criteria for the analysis and management of the composing elements of PCBT.

Figure 3. Logistics chain



BACKGROUND FOR CRITERIA FOR THE ANALYSIS OF RAW MATERIAL

Logistics vs. Origin

Since the beginning of mankind, human beings have used biomass (wood) as fuel for heating and cooking their food. With the development of modern society, the use of biomass as fuel was transformed and the use of forests for generating energy was discontinued in order to prioritize biomass sources that are not in conflict with the balance of nature, such as the so-called biomass residues. Biomass residues may be classified in several ways. Following the goals of this paper, we will classify them here according to their origin, as shown in Table 1.

The logistics of biomass may be divided in two phases:

1. Harvesting, transportation, and storage logistics;
2. Conservation for the use in the transformation center logistics.

The operations that must be considered in harvesting, transportation and storage logistics are defined by the origin of the biomass, as detailed in Table 1. In the sequence, a detailed analysis of the materials classified as non-forest is presented.

- **Energy-Generating Plantations:** In the handling of this kind of bio-fuel the logistics of planting, harvesting, transportation, handling, and storage of biomass to the processing center needs to be considered. The costs and the complexity of the logistics involved are extremely high and justified only in

Table 1. Biomass classification

Origin	Type of Residue	Definition
Forest	Forest residues	Biomass obtained from planted forests for energy-generating uses or not. They result in branches or logs inferior to 8 cm in diameter.
	Residues from wood processing	Wood chips, shavings, and sawdust resulting from the processing of wood for the production of furniture and other wood artifacts.
	Residues from recovered wood processing	Residues produced from wood recovered from social-economical activities that employ materials originated in forests. For example, construction wood and wood from packaging and pallets.
Non-Forest	Energy-generating plantations	Biomass obtained from energy-generating plantations, such as sugarcane, elephant grass, sorghum, and others.
	Agricultural Residues	Residue generated during the harvest of agricultural products such as the straw from sugarcane, rice, soy, corn, among others.
	Agro-industrial Residues	Residues generated during the agro-industrial processing of different crops, such as sugarcane bagasse, rice husks, peanut husks, soy husks, and others.

large-scale projects such as, for example, the production of ethanol, which has a national market and therefore justifies the investment. However, ethanol's case must be seen with caution because it involves historical and political factors that contribute positively to its success.

- **Agricultural Residue:** This kind of residue is usually found in the field. Therefore it is necessary to plan logistics that will take the harvesting, handling, and transportation of these residues from the field to the process center into consideration. Example: sugarcane straw.
- **Agro-Industrial Residues:** This kind of residue is generated in agro-industries and is concentrated in the transformation center. Example: sugarcane bagasse.

The comparisons indicated above make it possible to conclude that not all non-forest residues potentially available may be considered as a business opportunity because the costs with harvesting, transportation, storage, and conservation logistics may prove to be excessively expensive.

Environmental Restrictions for the Use of Biomass

Social-environmental aspects may also create restrictions for the use of non-forest residues and must be taken into consideration when analyzing their potential use.

In the case of agricultural, it is important to highlight that some of them must be maintained in the soil since they are necessary for the conservation and nutrition of the soil. For this reason, their indiscriminate removal may also present environmental restrictions.

It is important to observe that the energy-generating plantations compete directly against food-producing plantations creating a conflict with the concept of second generation bio-fuel. It is for this reason that not all energy-generating cultures may be considered as an available resource. On the other hand, agricultural residues also present some environmental restrictions because their indiscriminate use can create a substantial decrease of organic material and soil nutrients.

Concerning agro-industrial residues, social-environmental restrictions are related to the final disposal of residues and their impact on the environment.

Example 1: Residues whose availability is for the use in combustion processes. In this case, particulate and ash emissions are what constitute an environmental restriction.

Example 2: Rice Shell and sawdust, largely used as chicken beds, become contaminated with microorganisms, viruses, and other substances at the end of their use, constituting an environmental restriction.

Example 3: Processes in which biomass is used partially, creating liquid and solid contaminants. For example, bio-digestion and hydrolysis processes.

Standardized Quality of Biomass

Vegetable biomass is composed basically of celluloses, hemicelluloses, lignin, and extractives as well as inorganic matter (ashes).

When element analysis is conducted, it is possible to observe that the level of oxygen is around 35 to 50% in mass, carbon between 35 and 50%, and hydrogen between 5 and 7%. Therefore, biomass is an extremely oxygenated compound, a factor which contributes negatively to the product's energetic density. Due to these characteristics, the higher heating value (HHV) of biomasses is around 13,000.00 to 20,000.00 kJ/kg, practically half of any petroleum-derived fuel, which present very little or no oxygen in its element composition.

In addition to this, the apparent bulk density of biomasses (bagasse, straw, Grass, sawdust, rice shell, agro-industrial residues) stays around 80 to 600 kg/m^3 and the level of moisture between 30 and 50%. These physical-chemical characteristics make biomass a fuel of low energetic density, causing it to have low portability (low capacity for transportation) and requiring the use of high volumetric capacity equipment for its transformation. This makes its large scale use unfeasible compared to fossil fuels. These reasons justify the need to know the physical-chemical characteristics when assessing the potential of a biomass source. Below, we will analyze some of the physical-chemical characteristics and their influence in biomass potential (Mesa-Pérez, 2014).

Moisture: It is the level of water which is not linked to the biomass's chemical structure and is incorporated into the agro-industrial processes, such as in the case of bagasse, or in natural forms, as is the case of sugarcane straw. Moisture influences the biomass's energetic density and the effective level of available fuel energy (Lower Heating Value) negatively. For instance, the combustion processes that use moist biomass not only consume energy to evaporate the moisture, but also have an additional expenditure to overheat vapor to the operation temperature of the combustor. In the case of pyrolysis, an additional expenditure of energy is also generated not only in the pyrolysis reaction, but also in the later drying process of liquid fractions. Traditional drying eliminates biomass moisture through its evaporation at temperatures above 100^o C and consumes part of the biomass's primary energy.

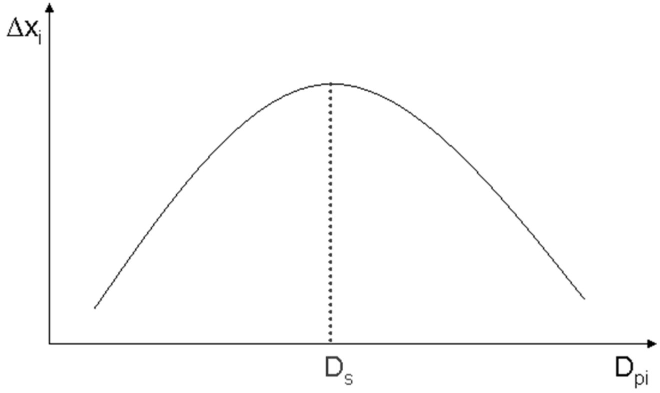
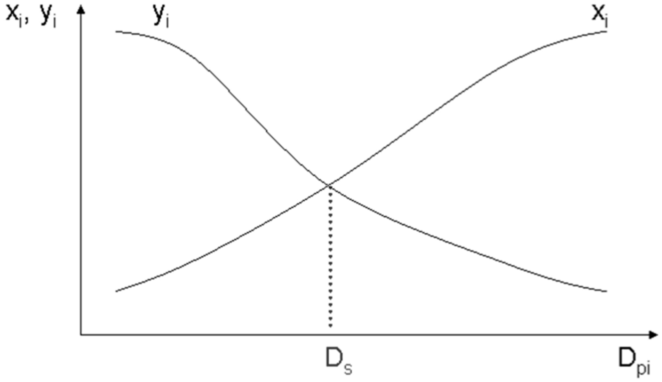
Therefore, moisture can be a determining factor when choosing the type of biomass to be transformed since the energetic cost to eliminate it may be a decisive factor in pre-treatment logistics.

Homogeneity: Biomass is naturally polymorphic and transformation processes such as fast pyrolysis require materials in a homogeneous state and therefore need grinding and milling processes as part of the unit operations of the pre-treatment. Segregation is a frequently observed phenomenon when biomass is ground and/or milled. A first fraction in the form of a powder precipitates in the inferior part of the packaging and in the superior part a second fraction in the form of a fiber can be identified. Statistically, when this happens, we can say that there are two populations, i.e., the sample is heterogeneous and any physical-chemical analysis must consider both populations independently. Determining the ashes content in heterogeneous biomass is a kind o analysis that experiences great dispersions. This happens because the frailty of the constituting parts of plants and grasses is variable. During the grinding in mills, the more fragile part of biomass presents itself in the form of a powder and the most resistant one in the form of fibers. The powder fraction in general concentrates the larger quantity of ashes. Biomass that presents high segregation may not be viable as raw material for pyrolysis.

Three methods used to determine the average diameter of particles when granulometric distribution follows a normal distribution, i.e., when the particles are distributed in a single population, are presented Figure 4 (Mesa-Pérez, 2014).

It is advisable that the differential curve be represented graphically in order to verify if the data is distributed in a normal way. In work with biomass, normally the curves are bimodal and in this case the result of the average diameter is different for each method applied. This happens because bimodal curves indicate the existence of more than one population within the analyzed samples and any method applied,

Figure 4. Methods for determining the particle size

Methods	
Mathematical equation	$$D_s = \frac{1}{\Sigma \Delta x_i / D_{pi}}$$
Differential Curve	 *Curve Δx_i versus D_{pi} (normal distribution)*
Cumulative curve	 Curve x_i, y_i versus D_{pi}.

be it graphic or using equations, is not rigorous. When the data is distributed in a normal way, the value obtained for the diameter of particles is approximately the same in any method described.

Ashes content: The ashes content represents the quantity of inorganic material incorporated to the biomass in a natural way or acquired during the harvesting, handling, and transportation logistics. The ashes may possess expressive quantities of potassium, calcium, and phosphorous, among other components. The calcium and potassium oxides, when mixed with inert material used in fluidized beds, reduce the melting point creating problems in sintering. On the other hand, excessive ashes content limits the organic fraction present in biomass, damaging the yield from liquid products of pyrolysis.

Bulk density: Biomass, depending on its origin, presents bulk densities at the (80-500) kg/m3 range. Low bulk densities generate high logistics costs both in the raw material and in the use of the installed capacity in the transformation center. An example of this comes from the high investments in supply systems in pyrolysis technology.

Chemical composition: The chemical composition is analyzed in terms of element composition and immediate analysis. Element composition measures the content in percentage of carbon mass (C), hydrogen (H), sulfur (S), oxygen (O), nitrogen (N), moisture (W), and ashes (A). This characterization constitutes the base of stoichiometry calculations and, consequently, it determines the limit volume of air that must be injected in the pyrolysis reactor. The immediate composition analyzes the level of fixed and volatile carbon in the biomass. The level of volatiles determines the yield of the liquid and gas products in pyrolysis (Mesa-Pérez, 2004).

BACKGROUND FOR CRITERIA FOR ANALYSIS AND INDUSTRIAL LOGISTICS MANAGEMENT OF PYROLYSIS

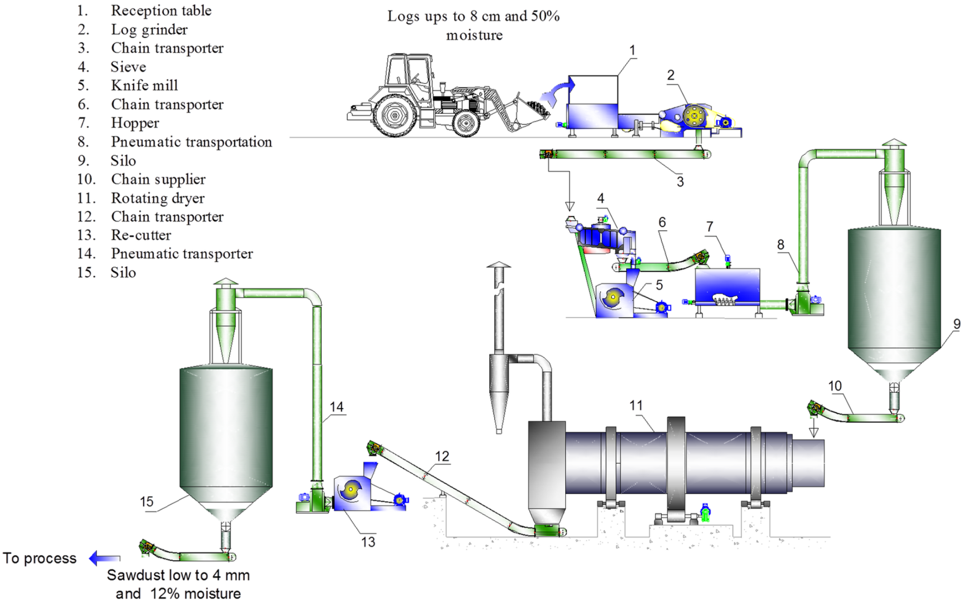
Pre-Treatment of Solid Biomass

Biomass needs to be pre-treated so that its characteristics are adjusted to the requirements of the fast pyrolysis process. Traditionally, pre-treatment concerns the adjustment of granulometric distribution and moisture in the biomass to the conditions of the process. The number of unit operations to be performed during pre-treatment depends on the physical-chemical characteristics of the biomass and the quality parameters required in the transformation process.

As an example, Figure 5 shows the flowchart of a pre-treatment process for forest residues with 8 cm average diameter and 50% moisture. The process of fast pyrolysis requires particles between 2 and 4 mm and moisture between 10 and 15%. In order to reach these conditions, the pre-treatment of this residue involves four unit operations and fifteen pieces of equipment:

1. Cutting of logs
2. Milling of humid residues
3. Drying of residues
4. Re-cutting of residues

Figure 5. Flow chart of pre-treatment process



Pre-treatment logistics for wood residues for the use in rapid pyrolysis processes may be seen with criticism due to the great number of unit operations and equipment involved, which reflects in high costs per ton of biomass.

The costs of pre-treatment may be expressed through the sum of individual costs for each unit operation as can be seen in equation 1.

$$C_{PT} = \sum_{i=1}^{n} C_i \qquad (1)$$

where:

C_{PT} – Cost of pre-treatment (R$/t)
C_i – Cost of each unit operation in pre-treatment (R$/t)

Unit costs include operational costs, variable costs, fixed costs, and depreciation of machinery.

Table 2 shows the relation between biomass origin, unit operations, and the costs involved in pre-treatment.

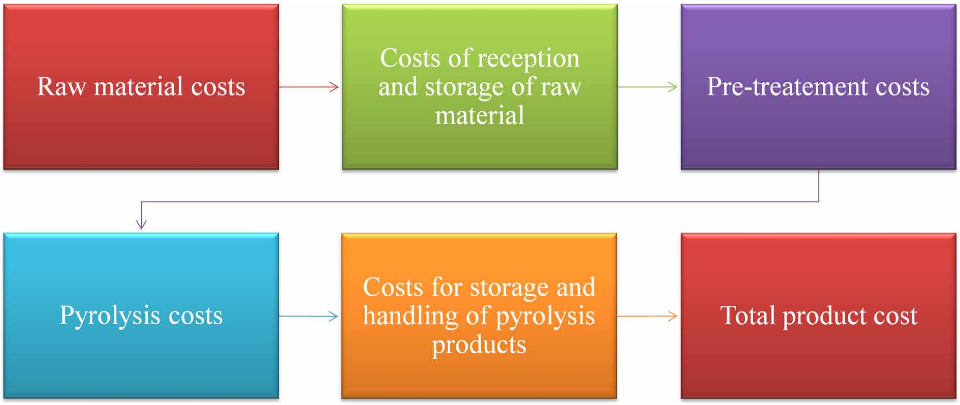
Figure 6. shows the main cost centers that are part of industrial logistics for the pre-treatment and pyrolysis of biomass.

Table 2. Unit operations and cost

Origin	Type of residue and physical-chemical characteristics	Number of single operations	Approximate pre-treatment cost(1)
Wood	Branches and logs under 8 cm in diameter, 50% moisture	Cutting of logs Milling of humid residues Drying of residues Re-cutting of dried residue	85 R$/t
	Sawdust with average granulometry of 5-6 mm 25% moisture	Drying Milling	50 R$/t
Agricultural	Sugarcane straw, 25% moisture	Cutting of straw Drying of saw Milling	70 R$/t
Agro-industrial	Rice husk	No unit operations	0 R$/t

(1) Exchange rate: 1 USD = 2,39 R$ (October 2014)

Figure 6. Cost centers



Pre-treatment costs may be higher than pyrolysis costs. Table 3 shows the detailing of the costs involved in the fast pyrolysis process of forest residue as an example.

Standardization of Solid Biomass

The traditional pre-treatment process promotes only physical transformations, therefore there are no changes in the biomass's chemical structure and even some physical properties like the visco-elastic properties are not substantially altered. For this reason, the use of different types of biomass in the same transformation unit is complex or even unfeasible (Stanislav, Vassileva, Baxterb, Andersenb, and Vassileva, 2010). Traditional pre-treatment does not ensure a physical or a chemi-

Table 3. Detailing cost of fast pyrolysis

Description of cost centers	**Value (R$/t)(1)**	**Percentage (%)**
Raw material: Forest residues (50% moisture)	25	10.6
Pre-treatment: Cutting of logs, milling, drying, re-cutting	85	36.2
Pyrolysis: Pyrolysis and separation of products	100	42.6
Storage of pyrolysis products (bio-oil and charcoal)	25	10.6
Total	235	100

(1)Exchange rate: 1 USD = 2,39 R$ (October 2014)

cal standardization for solid biomass. Table 4 illustrates the significant variation of physical-chemical properties of different biomasses (Cortez, Lora & Gomez, 2008).

The torrefaction process is a treatment that makes it possible to accomplish controlled physical-chemical transformations and is, therefore, an effective way to standardize biomass in its solid state (Stelt, Gerhauser, Kiel, and Ptasinski, 2011). Standardized solid biomass (SSB) is a new concept proposed here to be used in the characterization of biomass groups that present similar physical-chemical properties after their pre-treatment (Figure 7).

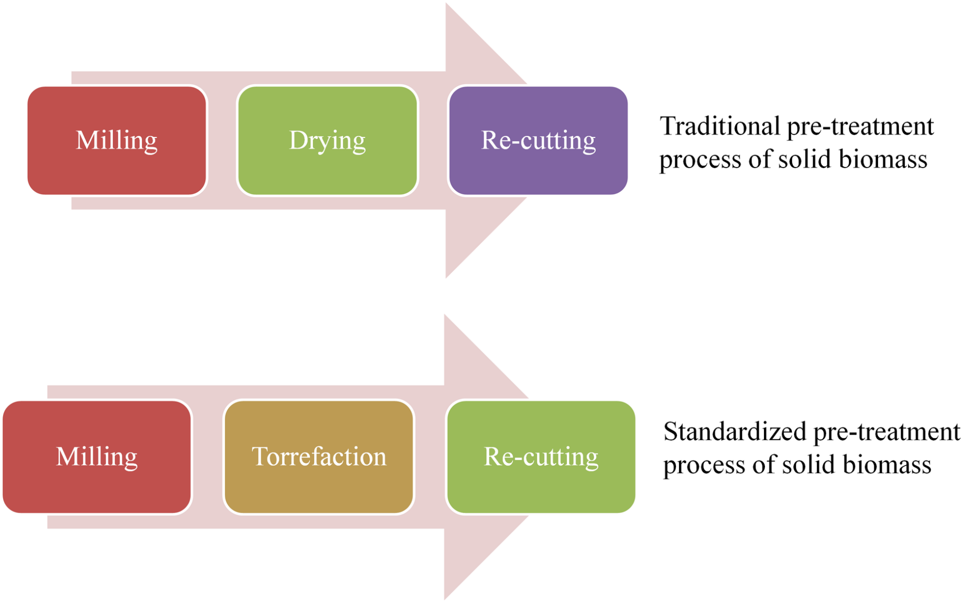
Torrefaction of biomass develops between 220 and 228° C (Schwob, 1985). Under these conditions, moisture is removed and hemicelluloses is degraded causing the release of acetic acid, fractions of phenol, and other low calorific power compounds. Lignin and celluloses suffer slight degradation. The conversion yielding varies between 60 and 80% due to the temperature conditions under which the process is done (Antal, De Almeida, Sinha, and Mok, 1991; Doat, 1985).

During torrefaction, two types of reactions, classified as thermo-condensation and carbonization reactions, can be identified .Carbonization is kinetically slow in the thermal domain of torrefaction, but can increase abruptly above 250° C with

Table 4. Physico-chemical characteristics of biomass (Jenkins, 1990)

Biomass	**Element Composition (%)**						**Moisture "in Natura" (%)**	**Bulk Density (kg/m^3)**	**Lignin level (%)**
	C	**H**	**O**	**N**	**S**	**Ash**			
Eucalyptus residues	49.00	5.87	43.97	0.30	0.01	0.72	35	250	24.68
Rice shell	40.96	4.30	35.86	0.40	0.02	18.34	12	110	14.30
Sugarcane bagasse	44.80	5.35	39.55	0.38	0.01	9.79	50	100	18.26
Cotton residues	47.05	5.35	40.77	0.65	0.21	5.89	35	80	0.00

Figure 7. Unit operations in the traditional and standardized pre-treatment process



strongly exothermal reactions, which may possibly lead to an uncontrolled increase in temperature and consequently to total carbonization of the material. Therefore, in order to ensure that the process will develop in the required thermal domain it is necessary to evacuate the heat generated during the parasite reactions of carbonization (Schwob, 1985).

The properties of torrefied biomass vary according to the time and temperature of the processing (Bourgois, 1984). Torrefied biomass presents the following properties:

1. **High Energetic Density:** Free and linked water is eliminated and high energy level volatiles are preserved in the solid increasing in up to 20% the biomass's calorific power;
2. **Hydrophobia:** Due to physical-chemical transformations, the re-absorption of moisture is practically non-existent during storage. Equilibrium moisture stabilizes at around 3%;
3. **Friability:** Torrefied biomass fibers lose their elastic properties and become friable material that can be ground or re-cut into very thin particles (in the form of powders) with low energy consumption and in a homogeneous form.

Table 5 shows the characteristics of torrefied eucalyptus wood under different conditions of temperature and time of residence (Felfli, 2003; Felfli, Luengo, Suarez, and Soler, 2005).

Table 5. Characterization of torrified eucalyptus wood (Felfli, 2003)

Temperature (°C)	Time (hr)	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	HHV (kJ/kg)
220	0.5	75.2	18.2	6.6	20426
	1.0	74.6	19.0	6.4	20989
	1.5	73.6	19.8	6.6	21065
250	0.5	65.2	27.0	7.8	21209
	1.0	65.0	27.2	7.8	22061
	1.5	60.0	32.1	7.9	22674
270	0.5	55.7	34.6	9.7	22772
	1.0	52.1	38.2	9.7	22981
	1.5	41.0	49.2	9.8	23066

Controlling torrefaction parameters allows for the production of fuel with a predefined physical-chemical standard regardless of the origin and initial composition of the biomass. It is important to highlight that the ash content is the only component that cannot be altered through the process.

The advantages of the standardization process via torrefaction are:

- **Homogeneous Physical-Chemical Properties:** Raw material fed into the pyrolysis reactor has a homogeneous standard that makes the supplying and controlling of operational parameters in the reactor easier.
- **More Efficient Use of Installed Capacity in the Reactors:** Due to the increase of the torrefied biomass's energetic density, pyrolysis units can use installed capacity more efficiently.
- **Improved Fluid Dynamics:** Due to the high level of friability of torrefied biomass, it is possible to decrease the size of the particle in a homogeneous way. This minimizes the appearance of undesirable phenomena such as sintering, segregation, inefficient mixture between the inert bed and biomass, and inadequate de-volatilization of biomass.
- **Higher Quality Bio-Oils:** Torrefaction process eliminates free and linked water from the biomass's structure as well as volatiles of lower energetic level, especially acids. It also concentrates the level of lignin. This makes it possible to obtain low-acidity, low-moisture, and low-viscosity bio-oils during pyrolysis since the improvement in fluid dynamics renders chemical degradation more efficient and makes the size of the chemical chains of components smaller.

The standardization process of biomass through torrefaction can contribute significantly to the improvement of industrial logistics in the process of fast pyrolysis, decreasing costs and increasing the efficiency of the process and the quality of pyrolysis.

Technological Bottlenecks for Fast Pyrolysis

A machine's availability and reliability are determining factors in terms of cost and efficiency in industrial logistics. Below, we will analyze the main technological bottlenecks that define availability and reliability in the technologies of fast pyrolysis.

1. Feeding of Non-Standardized Biomass

Non-standardized biomass creates a series of negative effects such as:

- Leakage of gas through the feeding system
- Fluctuation of feeding capacity
- Fluctuation in the yielding of pyrolysis products

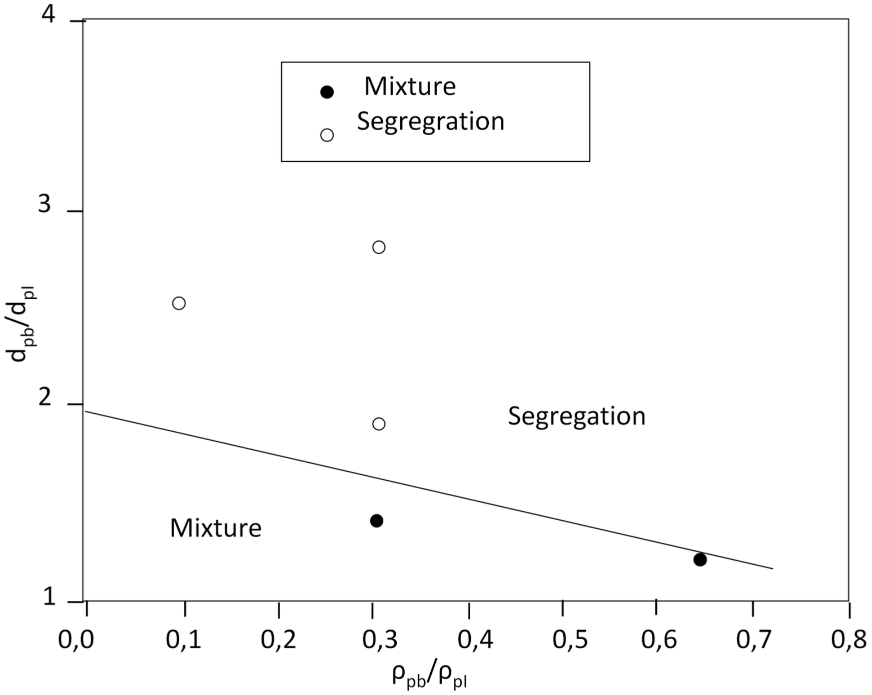
2. Biomass Mixture – Inert

An adequate mixture between inert material and biomass avoids the segregation phenomenon. Biomass may be segregated in the inferior part of the bed or on the surface. In both cases the bed's temperature increases rapidly in the area where the biomass layer is segregated. If the surface speed of gas is close to the speed of minimal fluidization, the biomass layer is formed in the superior part of the bed. For gas surface speeds that are greater than the speed of minimal fluidization, there is an inversion of layer, i.e., biomass is segregated in the inferior part of the bed. The mapping of the mixture regime (Figure 8) according to (Rasul & Rudolph, 2000) can be done from the study of the graphic behavior between d_{pb} / d_{pI} as a function of ρ_{pb} / ρ_{pI} (where d_{pb} is biomass particle diameter, d_{pI} is inert particle diameter, ρ_{pb} is biomass particle density and ρ_{pI} s inert material apparent density).

3. Residence Time of Vapors

Time of residence of vapors should be the least possible to avoid secondary reactions among the solid, liquid, and gas components. This situation causes the qualities and yielding of products to be different. The estimated time of residence must be counted from the moment de-volatization occurs until their separation at room

Figure 8. Mixture and segregation in fluidized bed (sand and bagasse). Adapted from Rasul and Rudolph, (2000).



temperature. Although part of pyrolysis vapors condensate at high temperatures (200-400° C), because they have micrometric particle sizes they do not sediment. The combination of cooling processes and mechanical separation of mists is used to decrease the time of residence in these liquids in the vapor phase.

4. Fractioned Separation of Products

De-volatization of biomass creates three phases: first a solid phase (charcoal); second a condensable vapor phase (mixture of organic products); and third a gassy phase. The pyrolysis process aims at optimizing the obtaining of liquids from the vapor condensation phase. In pyrolysis, vapors are collected fully in the liquid form and with a complex chemical composition where over 200 different compounds may be found (Kanaujia, Sharma, Garg, Tripathi, & Singh, 2014). The separation of specific chemical species from the condensed liquid through thermal fractioning is inefficient since approximately 35% of liquids turn solid (tar or coke) when heated at temperatures above 200 °C, making it impossible to separate the fractions of interest efficiently .

5. Clogging of Tubes and Equipment

Avoiding condensation of liquids in the tubes is advisable in order to prevent clogging and increase in pressure in the pyrolysis reactor. When this is not possible, the use of mechanical actuators to eliminate the build-up of material is indispensable to avoid halts in the process.

6. Scale-Up

Although fluidized bed reactors like combustion and catalytic cracking are being utilized frequently in commercial operations, engineers still face uncertainties when they develop new commercial projects. Typically, the development of processes takes place in discontinuous units in the laboratory, pilot plants, and large demonstrative unit levels.

Many of the operation's important characteristics may vary in units of different sizes. This is a critical problem for the broadening of the scale (*scale-up*). In other words, it is difficult to anticipate with precision a plant's performance when the size is changed so that a commercial plant can have a satisfactory performance.

These problems may be related to insufficient gas flow rate, inappropriate mixture of solids in the bed, and operational problems (Matsen, 1985).

If the degree of mixture and the efficiency of the gas-solid contact are maintained constant between beds of different dimensions, then the thermal characteristics and the speed of the chemical reaction must also be similar. However, in general, the bed's fluid dynamics might not remain the same.

Scale-up involves the understanding of changes in fluid dynamics and how these changes influence the thermal and chemical conditions through the variation in the gas-solid contact, time of residence, circulation of solids, and mixture and distribution of the gas. Until there is a better understanding of the phenomenon or a complete verification of the equations is done, numerical models cannot be used to describe the fluid dynamics of these systems. Therefore, the numerical models alone cannot be considered reliable tools for the scale-up of plants.

The use of experimental planning in small scale makes it possible to simulate the fluid dynamics of pilot or commercial reactors directly. Different diameter reactors, geometry, and conditions of operation can be simulates in the laboratory through these modeling techniques.

The empirical mathematical models derived from the experimental planning describe the main characteristics of a product's or process's quality in a limited experimental area. For each experimental condition, there is a group of non-dimensional numbers that define the system's behavior (for example, Reynolds, Froude, Archimedes, etc.). The relations of scales obtained after the parameters have been equaled in plants of different sizes allow the estimation of the effect of the change in scale (models corrected by the change in scale) if they are incorporated to the adjusted mathematical model. The difference between the values of the responses predicted by the adjusted mathematical model and the corrected one is called distortion. The use of experimental planning reduces incompatibilities between systems of different sizes (Mesa-Pérez et al., 2014).

BACKGROUND FOR CRITERIA FOR MARKET ANALYSIS

The Main Paradigms of PCBT

The introduction of pyrolysis products in the market requires the breaking of paradigms in different aspects of this PCBT. Some of these paradigms are:

1. Not very rigorous evaluation of energetic potential among fossil fuels and biomass derivates;
2. Extrapolation of technological and market knowledge logics of petroleum derivates to pyrolysis products;
3. Both petroleum and bio-oil are fuels. However, “bio-oil is not petroleum”;
4. Market and bio-oil regulation according to the same rules used for petroleum and derivates.

Strategies for Consumer Market Insertion of Pyrolysis Products

The insertion of new pyrolysis products in consumer markets is defined by the strategic alliance between the company detaining the pyrolysis technology and the final potential consumer or residue generator. Below we list the components of the action plan to create one or several success cases.

Management of Strategic Alliance

- Identification of partners among the potential clients.
- Negotiation of partnership to install and operate a demonstrative commercial scale unit.
- Follow-up and data collection for the assessment of results.

Market Tests with Consumer Companies

- Identification of consumer companies of products generated by the transformation technology and who are interested in participating in market tests.
- Adaptation of the products to the company's processes.
- Follow-up and assessment of test results.

Elaboration of an Economic Viability Study

- Gathering of information on technology and the market.
- Elaboration of an economic viability study for the promising production chains.

Definition of Marketing Strategy

- Publicizing of success cases.
- Market prospection using appropriate methodology for technological innovation products.
- Assessment of data resulting from prospection.
- Definition of marketing strategy to commercialize the technology.

FUTURE RESEARCH DIRECTIONS

Future work should be directed to the optimization of the separation of pyrolysis liquids. Seeking bio-oils high standardization. Another aspect that should be developed is the methodology for scaled-up of pyrolysis plants. The standardization of solid biomass must be another route to be studied and tested.

CONCLUSION

The knowledge of the production chain of pyrolysis makes it possible to establish the technical and market criteria necessary for the development and implementation of the technology.

PCBT logistics can be divided into three components: raw material logistics, industrial logistics, and commercial logistics of the pyrolysis products.

Raw material logistics is defined by the origin, the environmental restrictions, and the quality of biomass. The knowledge of these factors guarantees the establishment of technical-economical criteria to assess the potential of the raw material.

In industrial logistics, biomass pre-treatment is one of the operations of greatest importance from the technical and economic point of view. In this sense, the standardization process of biomass through torrefaction can contribute significantly to the improvement of the industrial logistics of fast pyrolysis processes by decreasing cost and increasing the process's efficiency and the quality of pyrolysis products. The new pre-treatment process proposed by the authors intends to create a new concept of biomass called Solid Standardized Biomass (SSB).

Industrial logistics also takes into consideration the pyrolysis process per se. a deep knowledge of the processes and of the technological bottlenecks makes it possible to establish strategies to increase the reliability of pyrolysis technology and therefore reduce logistics costs in the industrial process. This allows for the obtaining of standardized liquid fractions with the intention of introducing new products to the consumer market.

The authors have created the term Liquid Standardized Biomass (LSB) to define a fuel of vegetable origin with constant physical-chemical characteristics that can be offered to the consumer market with guarantees of quality.

Pyrolysis technology presents a Radical level of innovation because it promotes changes in the structure of the existing market and creates a potential for the appearance of new models that will eventually change traditional models. In a broader perspective, it concerns breaking the old paradigm in the concept of technology in the production of bio-fuels. The concept of technology is composed of three aspects: Machine, Knowledge, and Ability to apply knowledge. Therefore the strategy for market insertion must also deal with the implicit knowledge that aims at consolidating the application of pyrolysis products and the skill to put these products in the market. The most appropriate way to reach these goals is through the establishment of a strategic alliance between the players in the production chain (the holder of technology, the producer, and the final consumer). This kind of alliance intends to create a success case in which the risks associated to the market and the technology are reduced and to provide a learning period in which a larger scale consumer market can be consolidated.

REFERENCES

Alonso-Pippo, W., Luengo, C.A., Felfli, F. F., Garzone P., & Cornacchia, G. (2009). Energy recovery from sugarcane biomass residues: Challenges and opportunities of bio-oil production in the light of second generation biofuels. *Journal of Renewable and Sustainable Energy, 1,* 063-102. doi: 10.1063/1.3259170

Antal, M. J., De Almeida, C., Sinha, S., & Mok, W. S. L. (1991). A New Technology for Manufacturing Charcoal from Biomass. In *Proceedings of the Energy from Biomass &Wastes, XV Conference*, Washington, D.C., USA.

Basu, P. (2013). *Biomass gasification, pyrolysis and torrefaction - Practical design and theory* (2nd ed.). San Diego, California: Academic Press.

Bourgeois, J. P. (1984). Torrefied wood from temperate and tropical species, advantages and prospects. In: Egneus, & Ellegard (Eds.), Bioenergy 84, v.III, 153-159. London.

Cortez, L. A. B., Lora, E. S., & Gómez, E. O. (2008). Caracterização da biomassa. In L. A. B. Cortez, E. E. S. Lora, & E. O. Gómez (Eds.), *Biomassa para energia* (pp. 31-60). Campinas, SP, Brazil: Unicamp.

Doat, J. (1985). CTFT Research into wood pyrolysis. In: *Proceedings of Symposium Forest Products Research International Achievements and the Future*, 12-24.

Felfli, F. F. (2003). *Torrefação de Biomassa, Viabilidade Técnica e Potencial de Mercado*. (Doctoral Thesis). Retrieved from Acervus Unicamp dissertations and Theses database. (vtls000321223)

Felfli, F. F., Luengo, C. A., Beaton, P., & Suarez, A. (1999). Efficiency test for bench unit torrefaction and characterization of torrefied biomass. In *Proceedings of the 4th Biomass Conference of Americas*, *1*, 589-592. California, USA.

Felfli, F. F., Luengo, C. A., Suarez, J. A., & Soler, B. (2005). Wood briquette torrefaction. *Energy Sustainable Development*, *9*(3), 19–22. doi:10.1016/S0973-0826(08)60519-0

Glicksman, L. R. (1999). Fluidized bed scale-up. In W. C. Yang (Ed.), Fluidization solid handling and processing (1-42). Westwood, New Jersey, USA: Noyes Publications.

Jenkins, B. M. (1990). *Fuel properties for biomass materials*. Paper presented at the International Symposium on Application and Management of Energy in Agriculture: The Role of Biomass Fuels. Delhi.

Kanaujia, P. K., Sharma, Y. K., Garg, M. O., Tripathi, D., & Singh, R. (2014). Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. *Journal of Analytical and Applied Pyrolysis*, *105*, 55–74. doi:10.1016/j.jaap.2013.10.004

Mesa-Pérez, J. M., Cortez, L. A. B., Marín-Mesa, H. R., Rocha, J. D., Peláez-Samaniego, M. R., & Cascarosa, E. (2014). A statistical analysis of the auto thermal fast pyrolysis of elephant grass in fluidized bed reactor based on produced charcoal. *Applied Thermal Engineering, 65*(s 1–2), 322–329. doi: 10.1016/j.applthermaleng.2013.12.072

Mesa-Perez, J. M., Cortez, L. A. B., Rocha, J. D., Brossard-Perez, L. E., & Olivares-Gómez, E. (2005). Unidimensional heat transfer analysis of elephant grass and sugar cane bagasse slow pyrolysis in a fixed bed reactor. *Fuel Processing Technology*, *86*(5), 565–575. doi:10.1016/j.fuproc.2004.05.014

Nagano, M. S., Stefanovitz, J. P., & Vick, T. E. (2014). Innovation management processes, their internal organizational elements and contextual factors: An investigation in Brazil. *Journal of Engineering and Technology Management*, *33*(7-9), 63–92. doi:10.1016/j.jengtecman.2014.02.004

Painuly, J. P. (2001). Barriers to renewable energy penetration; a framework for analysis. *Renewable Energy*, *24*(1), 73–89. doi:10.1016/S0960-1481(00)00186-5

Rasul, M. G., & Rudolph, V. (2000). Fluidized bed combustion of Australian bagasse. *Fuel*, *79*(2), 123–130. doi:10.1016/S0016-2361(99)00144-1

Schwob, Y. (1985). Process for converting ligneous matter from vegetable origin by torrefaction, and product obtained thereby. US patent. 4553978.

Stanislav, V., Vassilev, B., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913–933. doi:10.1016/j.fuel.2009.10.022

Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., & Ptasinski, K. J. (2011). Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy*, *35*(9), 3748–3762. doi:10.1016/ j.biombioe.2011.06.023

ADDITIONAL READING

Luengo, C. A., Felfli, F. F., & Bezzon, G. (2008). Pirólise e Torrefação de Biomassa. In *Biomassa para energia* (pp. 334–352). Campinas: Editora Unicamp.

Yang, W. C. (1999). *Fluidization Solids Handling and Process*. Noyes Publications.

KEY TERMS AND DEFINITIONS

Biomass Pre-Treatment: Concerns the adjustment of granulometry and moisture in the biomass to the conditions of the process.

Fast Pyrolysis: Thermal degradation of organic material around 600 oC in the absence of oxygen for the production of bio-oil, charcoal and gases.

Liquid Standardized Biomass (LSB): A fuel of vegetable origin with constant physical-chemical characteristics that can be offered to the consumer market with guarantees of quality.

Production Chain of Biomass Transformation (PCBT): A series of interconnected stages to manager the production and harvest the raw biomass, the transformation of biomass into final product and the use or application.

Standardized Solid Biomass (SSB): A new concept proposed to be used in the characterization of biomass groups that present similar physical-chemical properties after their pre-treatment by torrefaction.

Torrefaction: Thermal degradation of organic material in the absence of oxygen between 220 and 330o C for the production of high energy density solid fuel.

Chapter 10

Sustainability, Business Models, and Techno-Economic Analysis of Biomass Pyrolysis Technologies

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ABSTRACT

The objective of this chapter is to review and discuss sustainability and techno-economic criteria to integrate pyrolysis, biochar activation, and bio-oil refining into sustainable business models. Several business models such as the production of biochar with heat recovery and bio-oil refining are discussed. Cost data needed by engineering practitioners to conduct enterprise-level financial analyses of different biomass pyrolysis economy models are presented. This chapter also reviews

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life cycle assessments of pyrolysis business models. If the feedstock used is produced sustainably and if the pyrolysis vapors are used for bio-oil or heat production, both, the production of biochar through slow pyrolysis and its use as a soil amendment to sequester carbon, and the production and refining of fast pyrolysis oils to produce transportation fuels could have a positive environmental impact.

INTRODUCTION

In 2002, in a speech at the Jorburg Summit, Kofi Annan pointed out the existence of two extreme schools of thought about economic development and the environment (Annan, 2002). The first school considers that it is not possible for any economic growth because of its effect on the environment. The second proclaims that economic growth at all cost is socially acceptable. Under these extreme schools of thought it will be difficult to spread the prosperous life style enjoyed by nearly one fifth of the population especially considering rapid population growth, high standards of living, and resource consumption rates. Current world population consumes more resources than the world can sustainably produce by 20% (World Fund for Nature, WFN). Regardless of environmental destruction, economic growth cannot be reduced dramatically because even greater damages that could be inflicted by market forces (AtKisson, 2001). Dr. Annan recommended to look beyond these two paradigms and to find ways to live in harmony with the environment. Anan calls for finding synergisms between economic growth and environmental protection rather than allowing social degradation by inhibiting economic growth or enduring the consequences industrial growth inflicts on the environment (Annan, 2002).

Attaining a more sustainable future increasingly includes the development and expansion of biomass-based fuels, chemicals and materials. Anex et al. (2007) underscored this when they stated:

> *Whether this is a positive impact or a negative impact will depend largely on how biomass feedstocks are produced and converted, and the extent to which these two activities are integrated. As in any managed ecosystem, nutrient management in industrial biomass … must address multiple criteria, including air and water quality, nutrient use efficiency, and … economics.*

Biomass pyrolysis is one of the thermochemical conversion technologies currently studied for the production of fuel and chemicals from lignocellulosic materials, which is carried out in the absence of air/oxygen at temperatures between 350 and 600 ^{o}C. This process can be controlled to maximize either the production of charcoal or liquid products. “Fast pyrolysis” is optimized to produce liquid products (bio-oil).

This is achieved by processing biomass with particle sizes < 2 mm at temperatures ~ 500 °C and with carrier gas flows reducing pyrolysis vapors residence time inside the reactor to < 2 seconds. The most common fast pyrolysis reactors are: bubbling fluidized bed, circulating bed and ablative reactors. Conversely, "slow pyrolysis" or "carbonization" maximizes the production of biochars. The biomass is processed in chip form.

This chapter focuses on biomass pyrolysis technologies, prospective business models to maximize growth and key financial considerations for sustainable recovery of energy, carbon, nutrients, and products from lignocellulosic and organic wastes.

A SUSTAINABLE BIOMASS ECONOMY

Laird (2008) argued that given that the half-life of carbon (C) in soil charcoal is more than 1000 years, the application of this material will have a lasting contribution to soil quality and to the removal of C from the atmosphere. The authors concluded that given that the United States can annually produce 1.1×10^9 Mg of biomass, the implementation of a pyrolysis based economy could displace 1.91 billion barrels of fossil oil every year (or about 25% of current US annual consumption) and could lead to the permanent sequestration of around the 10% of the 2008 annual U.S. emissions. Woolf, Amonette, Street-Perrott, Lehmann and Joseph (2010) estimated that the use of biochar to combat global warming could result in a maximum reduction of annual net emissions of carbon dioxide (CO_2), methane, and nitrous oxide of 1.8 Pg CO_2-C equivalent (CO_2-Ce) (approximately 12% of current anthropogenic CO_2-C_e emissions).

Triple bottom line analysis (i.e., economic profitability, environmental protection and social equity) is one example of the ways sustainability is being integrated into corporate practices. Corporations have adopted this model to improve environmental performance without compromising economic goals. As a result, social and environmental liabilities along with resource efficiency and waste management have become key components for sustainability (McDonough & Braungart, 2002). Implementing sustainable business practices offers many benefits; reduced risk and liability, operating efficiencies, cost savings, synergies with stakeholders, enhanced reputation and brand differentiation (MBDC, 2010).

The triple top line approach presented by McDonough and Braungart (2002), emphasize the beginning of a development. Implementation of the "top line" approach *"enhance(s) the wellbeing of nature and culture while generating economic value"*. Following both of these models, sustainable pyrolysis technology business models must provide advantageous environmental services and improved personal wellbeing, while supplying valuable economic products: heat, power, transportation fuels, and chemicals. Considering economic, social, and environmental impacts of current and future generations are conditions essential to a sustainable business model (US DOE, 2010).

Environmental Sustainability

The area of biochar sustainability is receiving great global attention (Flora, 2012). An outstanding discussion on biochar production and sustainability is presented by The International Biochar Initiative (IBI, 2014). Biochar sustainability principals prepared by the IBI can be found at (IBI, 2012). Biochar and bio-oil sustainability issues (feedstock and land use, personnel production safety, environmental applications and potential impacts, transportation, application, economics, soil and crop sustainability, carbon sequestration ability, stability of carbon in soil, and energy use and output) are challenging to completely analyze. Publications on this topic are accelerating in number. This section considers many of the latest and greatest publications.

Few methods exist for sequestering carbon, however biomass pyrolysis on an industrial scale could be surprisingly effective for building a sustainable future. Significantly, biomass carbonization partially reproduces the natural process of carbon fixation. Moreover, biomass carbonization produces heat (in turn electricity) and/or produces bio-oil, which could take place of fossil fuels. These are important considerations when determining the sustainability of this industry (Woolf et al., 2010).

Modern pyrolysis techniques have the ability to recover heat for combined heat and power (CHP), further refine oils, and provide with charcoal and heat for industrial applications. Unfortunately, there are currently no bio-oil refineries to provide these benefits. Speculatively, pyrolysis heat from commercially produced biochar will be used for CHP. Bio-oil refining may soon have the capability for condensable liquid fuel recovery. The combustion of pyrolysis vapors and their byproducts are arguably cleaner than fossil fuel combustion as more studies are demonstrating.

In CHP distributed systems half of the energy is available for heat and electricity while the other half is contained in the biochar. Small scale CHP's have some advantages over larger systems since they have shorter manufacturing time as well as lower capital and interest costs.

The ability to incorporate small systems into existing facilities is a huge advantage. Heat could be generated at lower prices as small units can use distributed local resources. Small scale systems have a smaller footprint and potential impacts than larger systems. Construction risks would also be reduced.

The production and advancement of small units could scale to demand and be responsive to innovative evolutions. Likewise, small systems could be built on a "pay-as-you-go" model.. Development and implementation of innovations is typically harder with large units. Inefficiencies or potential improvements observed during operation would more easily be implemented incrementally and without delay to next-generation units. The small units are also extremely versatile; adaptations could easily be made in response to variations in feedstock composition or local environmental regulations. Recyclability is much higher with small units when compared to larger ones, which also tend to carry high removal costs. Also small systems are more portable offering quicker sales and high salvage values (Lovins, 2002).

Today's 'waste' is rich in biomass resources such as recycled and reclaimed wood materials, sawdust, biomass from food harvesting/processing and agricultural residues (e.g. bagasse, palm oil, nut hulls,, coffee and cocoa, banana stalks, rice hulls, rice straw, wheat straw, corn stover, etc.). The availability and reliability of year-round waste materials is problematic in some areas. Waste biomass generated from rural and urban forest and agriculture processes could be combined with purpose-grown biomass to provide consistent supply solutions.

When considering a viable biomass business model, maintaining or enhancing soil quality and biological diversity while minimizing detrimental impacts to the land during feedstock production are vital factors. Small scale operations produce less impact. Other environmental factors that are central to a sustainable biomass economy include replenishing, maintaining and even improving soil organic matter. Upholding healthy soil cover with biomass protects the soil from variations of natural erosion (Flora, 2010a).

Biochar is attracting high international interest because of its unique abilities to: improve soils for crop production, retain soil moisture, remediate polluted sites, raise soil pH, adsorb contaminants (mine drainage, storm water, industrial sites) and to sequester carbon by storing atmospheric carbon dioxide (CO_2) in stable form in soil (Woolf et al., 2010).

The Millennium Ecosystem Assessment (2005) report defined fourteen categories of ecosystem services. The chart below summarizes these findings along with biochar services related to those features.: (1) food production, (2) fiber production, (3) genetic resources (4), fresh water, (5) air quality, (6) climate regulation, (7) water regulation, (8) erosion regulation, (9) water purification, (10) water treatment, (11) disease regulation, (12) pest regulation, (13) pollination, (14) natural hazard regulation/cultural services. Specially designed biochars can provide several environmental services: (1) Improve crop productivity, soil nutrients, microbial activity; (2) Improve biomass production; (3) Sorption of nutrients (nitrogen, phosphorus); (4) Air filtration, odor sorption (hydrogen sulphide);(5) Carbon sequestration reduced GHG emissions; (6) Moisture-holding capacity; (7) Promotes more vigorous root systems; (8) Water filtration; (9) Sorption of contaminants (zinc, copper, and lead); (10) Under study in plants and animals; (11) Improved health vs cooking over open fires.

Although biochar is not currently recognized as an official method of producing carbon credits in the future it could be an important component of this market (Baranick, McElwee, & Zazycki, 2011); Weisberg, Delaney, & Hawkes, 2010). The Climate Trust (Weisberg et al., 2010) conducted an assessment of biochar to determine its appropriateness as a terrestrial carbon sequestration offset and concluded that attractive projects must meet the following criteria: (1) Projects must use waste biomass, that in the absence of the project, will be left to decompose. (2) Projects must account carbon credits by producing 25,000 t (or more) of biochar in 20 years. This capacity is only related to minimum size for which the carbon credits will be counted and does not depend on the scale needed to ensure the economic viability of the business. (3) Projects must consistently monitor the biochar application.

Social Sustainability

A critical element of developing a business model is ensuring social sustainability (Baranick et al., 2011). Although it is highly desirable to build companies that provide jobs in economically depressed settings, supporting these communities with services such as brownfield remediation, access to clean water, or community-generated waste processing is even better. Some of the recommendations made by Flora (2010a) to build sustainable business models are: 1) ensuring that technology contributes to the creation of healthy and satisfying jobs in communities, 2) demonstrating a positive net energy balance compared to fossil fuels, 3) increasing access of isolated communities to affordable clean energy, and 4) improving energy densification and security.

Aesthetic and cultural aspects of using forests have to be carefully considered especially taking into account that wood was one of the first resources used by humans to sustain life. Cultural values have an impact on the way we relate to our forests. Important forest-based economic and social values range from employment in the forest products industry to unique cultural, spiritual and recreational experiences, both historic and current.

Biomass pyrolysis proponents need to understand and respond positively to potential detractors to gain and maintain social capital. According to Flora (2010a, b) the primary concerns regarding biomass use are the following: (1) Ethical and economic problems with converting food and animal feed to bioproducts (2) Conversion of native forests or prairie to biomass production (3) Converting Conservation Reserve Program lands to biomass production (4) Acceleration and expansion of forest thinning, including removal of mature, live trees for biomass (5) Building roads and developing wild lands to collect biomass (6) Shorting current biomass uses/users (7) Deleterious effects on soil nutrients, habitat, erosion, water and air quality by removal of too much biomass (8) Loss of up-cycling opportunity (9) Lack of recognition of the importance of biomass to ecosystem functions. These concerns are valid and need to be proactively addressed when the business model is developed (McDonough & Braungart, 2002).

Financial Sustainability

Financial sustainability (profitability) should be achieved without externalizing costs to the environment or to the people (McDonough & Braungart, 2002).

In a very interesting comparison with the Terra Preta Cultures, Schmidt (2012) argues that to make economic sense biochar should be considered a waste product that will eventually become a soil amendment. He stressed that biochar is much too valuable to be a soil amendment without performing more beneficial and high value purposes first (storage of volatile nutrients, adsorbent in functional clothing, insulation in the building industry, energy storage in batteries, filter in a sewage plant). Schmidt (2012) argues that biochar should be worked into the soil at the end of a well planned "cascade of uses." The author also presented a list of 55 possible uses for the biochar.

FRAMEWORKS FOR THE DEVELOPMENT OF BUSINESS MODELS

Current Status in Biochar Business Development

In 2011, worldwide biochar production reached 49.9 million tons (FAOSTAT, 2014). Currently most of the biochar for soil amendment is commercialized in US in two forms: 100% pure biochar ready to be mixed with fertilizers by the consumer (e.g., Aztec Wonder, Blue Sky, Hawaii Biochar Product, Phoenix Energy, Black Owl Biochar) and biochar compost/mixes, inoculated or other engineered blends formulated for specific soil amendment needs (e.g., biocharm, char crow, soil reef, vermichar, black earth products) (Baranick et al., 2011). However, the production of biochar for soil amendment still faces several challenges such as production technology, feedstock selection, post-processing steps, etc.

Table 1 shows a summary of feedstock, sustainability challenges, production technology, post-processing steps, potential co-products, biochar point of use, economic and social challenges, and advantages of several potential business models.

Table 1. Biochar business models (Retrieved from http://www.biochar-international.org/commercialization)

	Feedstock	Sustainability challenges	Production Technology	Potential co-products	Biochar point of use	Economic challenges	Social challenges	Advantages
Restoration Site (forest, wetland, etc)	Thinning slash, noxious weeds		Mobile pyrolysis, charring piles in situ	Biochar, bio-oil, heat for drying feedstock	Soil and watershed reclamation site	Labor intensive, need to value ecosystem restoration	Accepting the need to pay for restoring ecosystems services	Restored ecosystems store more carbon
Managed Forest	Thinning slash logging slash	Overcutting diminishes ecosystem services, transportation footprint	Mobile pyrolysis, hog fuel for co-gen. Feedstock for pellets or briquettes	Biochar, process heat, electricity, home heat	Commercial fertilizer, home garden	Forest thinning is labor intensive, low density slash is expensive to haul	Need to train workforce for ecological thinning	Can improve forest health, cheap fuel source, provides long term employment
Forest product processing waste	Sawdust, shavings, hog fuel	Overcutting diminishes ecosystem services	Co-gen pyrolysis or gasification, feedstock for pellet or briquettes	Biochar, process heat, electricity, home heat	Commercial home garden	Supply dependent on economic growth and housing starts, resource is already fully utilized	Competition for resource	Already in widespread use
4. Biomass Plantation	Trees, grass, hemp, kudzu	Could displace native ecosystems & people, water use, monoculture problems, GM species	Co-gen pyrolysis or gasification, feedstock for pellets or briquettes	Biochar, process heat, electricity, home heat	Plantation soils, commercial fertilizer, home garden	Large capital investment & pressure to adopt unsustainable practices	Need to strengthen land tenure rights of poor people	Could be used for afforestation of degraded land

continued on following page

Table 1. Continued

	Feedstock	Sustainability challenges	Production Technology	Potential co-products	Biochar point of use	Economic challenges	Social challenges	Advantages
Urban Forestry and landscaping	Thinning, slash, logging slash, weeds, grass, clippings	Co-gen pyrolysis or gasification, feedstock for pellets or briquettes	Biochar, process heat, electricity, home heat	Commercial fertilizer, home garden	New capital investment	Nee to train workforce force for ecological thinning	Avoids disposal cost	
Agricultural Waste – Industrial	Straw, cobs, orchard trimmings	Need to leave some decomposing organic matter in soil	Mobile pyrolysis, co-gen, pyrolysis or gasification	Biochar, process heat, electricity, home heat	Farm soils, commercial fertilizer, home garden	New capital investment	Avoids disposal cost	
Agricultural Waste Subsistence	Straw, cons, orchard, trimmingskernels, peels,	Need to leave some decomposing organic material in soil	Stoves, kilns feedstock for briquettes	Biochar, process heat, home heat and cooking	Farm soils	New capital investment	Avoids disposal cost	
Municipal Solid Waste (MSW)	Trash, paper	Pollution, losing resource that could be recycles	Co-gen pyrolysis or gasification	Biochar, process heat,, electricity	Suitable for use as carbon sink only	Supply depends on economic growth, consumption	Avoids disposal cost	

Biochar Market Limitations

Baranick et al. (2011) evaluated the environmental, social, and economic value of a biochar business converting slash piles from forest management activities in the Methow Valley of North Central Washington State (Okanogan National Forest). They concluded that the main challenges facing the soil amendment biochar industry are: higher startup costs than the competing composting sector, lack of consensus on biochar benefits, difficulty in educating potential consumers on the benefits of the product (limited production makes it very difficult to test biochar at commercial scale), over-competition for feedstock resources, high costs of distribution, and the lack of well-defined biochar specifications. These challenges are typical of an industry at the market introduction stage in which the costs are high and the volume sales are low, with poor competition and low demand. Under existing conditions, *"demand must be created, which requires educating the potential consumer"*.

A way to accelerate market acceptability is to develop regulations to identify and avoid pollutants in commercial biochar such as the characterization standards developed by the IBI (2012). The activation of a fraction of the biochar produced could contribute to the growth of the industry (PRWeb, 2014).

Clearly, slow pyrolysis is well-suited for producing biochar and heat/electricity from agricultural and forest wastes; however there are several major hurdles for the deployment of this technology. Environmentally friendly technologies to produce heat and biochar have to be developed. The potential use of boilers to produce cheap biochar is a major challenge to pyrolytic biochar producers. High value products from biochar are essential. Low consumer awareness and financing difficulties biochar also require attention. Biochar producers should also characterize and document the performance of their products. The lack of performance certification is hampering industry advancement.

Heat Recovery and Bio-Oil Combustion

A major weakness of most biochar production business models in some developing countries is that energy produced from pyrolysis vapors is disregarded (Pelaez-Samaniego et al., 2008). Revenue from commercialization of the heat and/or electricity derived from pyrolysis vapors could be critical for the success of biochar businesses, at least for units scaled to use/transform pyrolysis gases. Figure 1 presents a system in which the pyrolysis vapors are combusted to produce heat. However, very little information is found on business models to utilize pyrolysis vapors.

Pyrolysis vapors can be condensed to produce bio-oils. Some of the most important properties of bio-oils derived from the pyrolysis of woody biomass are shown in Table 2.

Figure 1. Pyrolysis system with combustion of pyrolysis vapors (Courtesy of Jerry Whitfield)

Table 2. Main properties of wood derived bio-oils (Bridgwater, 2002; Mohan, Pittman, & Steele, 2006)

Property	Characteristics
Appearance	From almost black or dark-brown to dark green
Miscibility	Water content from approximately 15 wt. % to 30-50 % before phase separation occurs. Miscible with polar solvents (methanol, acetone, etc) but almost totally immiscible with petroleum derived fuels.
Density	Approximately 1.2 kg/L
Viscosity	Viscosity varies from 25 cSt to 1000 cSt (measured at 40 °C)
Distillation	Cannot be completely vaporized. Above 100 oC, rapidly reacts and eventually produces a solid residue 50 wt. % of the original liquid.
Stability	Chemically unstable. Store liquid at or below room temperature.

Bio-oil properties and combustion performance has been researched for years. Many combustion tests at atmospheric pressure in flame tunnels and boilers have been reported in the literature (Salvi & Salvi, 1991; Freel & Huffman, 1998; Gust, 1997; Oasmaa, 2001). An advantages converting biomass into liquid fuels is the possibility of using these fuels for gas turbines (Andrews, Zukowski, & Patnaik, 1997) and diesel engines (Ormrod & Webster, 2000). Nevertheless, several limitations must be overcome prior to using crude bio-oils as fuels in gas turbines and diesel engines (Pelaez-Samaniego, Garcia-Perez, Cortez, Rosillo-Calle, & Mesa, 2008). Table 2 describes the properties of wood-derived bio-oil.

Diesel engines, boilers and gas turbines can be designed or modified to burn almost any organic liquid. However, if a system is operated with a fuel different than the one for which it was designed, the system may show important performance problems. The main hurdle for this business model alternative is the construction and commercialization of gas turbines and diesel engines able to operate with bio-oils. A legitimate fuel must fulfill a set of technical and environmental requirements related to its combustion, storage, handling and safety. The lack of fuel specifications for bio-oils is another major barrier for the use of these oils as fuels (Solantausta et al., 2012).

Typically bio-oils is received and stored in tanks. Each of these tanks must be heated so bio-oil viscosity is low enough (12-15 cSt, usually at 55 °C is enough) to allow pumping to a small tank to feed the combustion unit which is coupled to a solvent reservoir. Adding complexity, bio-oils' chemical and physical properties can change during storage due to "aging" caused by the loss of water and other volatile compounds. Prolonged heating contributes to aging.

The complex multiphase properties of bio-oils can create serious problems during storage and handling such as the formation of separated phases, waxes crystals and heavy compounds (Garcia-Perez et al., 2006). The layering or separation of bio-oil phases requires facilities to homogenize these liquids. The aqueous upper layer in bio-oils is attributed to the inability of water to disperse in the oily matrix. A separate waxy upper phase can also form due to wood extractives. Specifications must ensure that bio-oils are supplied as homogeneous liquids.

Odor caused by carboxylic acids and aldehydes is a potential bio-oil disadvantage. Bio-oils have a distinct acrid smoky smell, which can irritate the eyes with prolonged exposures. Bio-oil esterification with alcohols can improve its odor (Li et al., 2011).

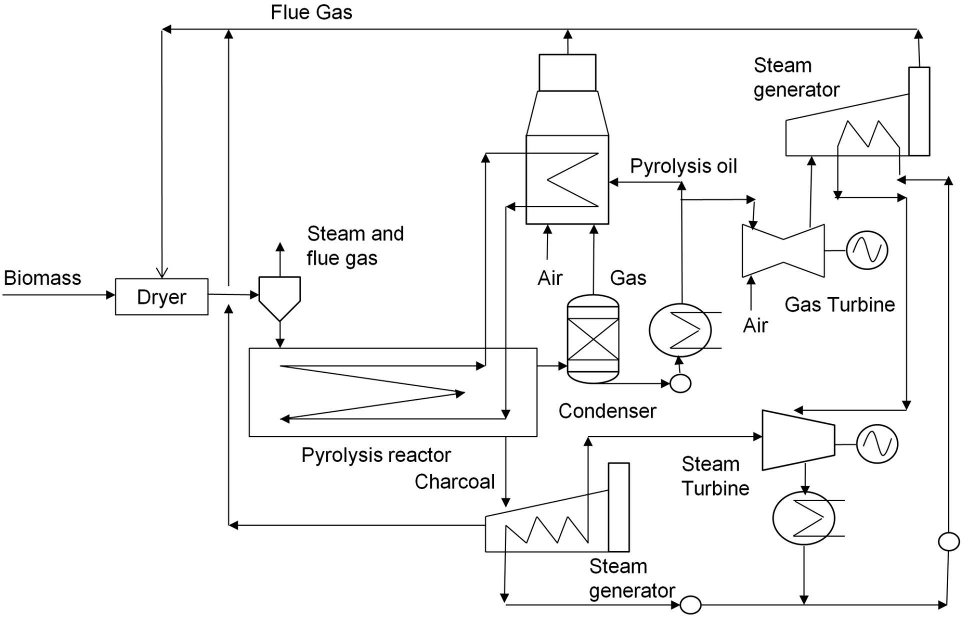
Bio-oils require storage in non-corroding tanks. Acetic and formic acids found in bio-oil lead to pH values around 2.2. Tanks, fuel lines, pumps, heaters and nozzles must be made of 316 SS, copper or various plastics like polyester resin and polyolefins. Upon contact with bio-oil, iron species present in the SS 316 surface leach and chromium species migrate from the metal bulk toward the surface forming a chromium oxide layer that prevents further oxidation.

The maximum allowable char content and it particle size should be limited by the bio-oil fuel specifications, however, n-line filters are highly recommended to avoid nozzle plugging and erosion by fine particles,

An excellent review of the primary challenges of using bio-oils as fuel for power generation was published by Chiaramonti, Oasmaa and Solantausta (2007). Among the main strategies so far studied for upgraded bio-oil are: (1) Production of micro-emulsions, (2) Extraction of fractions with bio-diesel, (3) Blending with solvents; (4) Acetilization and esterification, and (5) Calcium enriched bio-oil (CEB).

The current primary use of bio-oil is as a substitute for heavy fuels used for industrial applications. Figure 2 shows a pyrolysis combined cycle (IPCC) for the production of electricity from the pyrolysis vapors (Roy & Morin, 1999).

Figure 2. Integrated Pyrolysis Combined Cycle (Roy & Morin, 1999)



The integrated pyrolysis combined cycle scheme shown in Figure 2 was proposed by Roy and Morin in 1999. This system a vacuum pyrolysis reactor is coupled with a gas turbine, steam generators and steam turbines. It was estimated through energy balances that a 21% increase of energy output per ton of biomass was possible using IPCC schemes as compared to direct biomass combustion with a Rankine cycle.

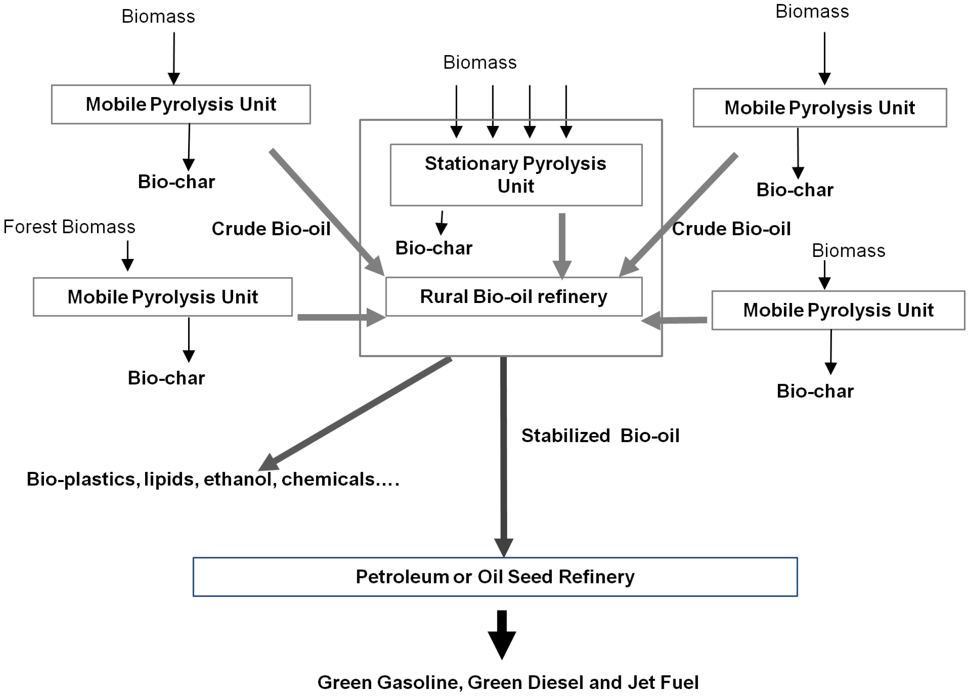
Bio-Oil Refining

Pyrolysis oils can also be an important source of chemicals. In fact the old wood distillation industry produced at large scale acetic acid, acetone and methanol from the liquid collected from slow pyrolysis reactors (Klar & Rule, 1925; Brown, 1917). In the last 20 years there has been a renewed effort to obtain chemicals from pyrolysis oils. Some of the products that have been obtained from these oils are: Acetic Acid (Patel et al., 2006; Adhesives (Czernik & Bridgwater 2004; Mohan et al., 2006); Aldehydes and Ketones (Vitasari et al., 2010); Alkyloaromatics (Resasco et al., 2010); Antioxidants (Garcia-Nunez, Cardenas, & Yanez-Angarita, 2010); Asphalt paving substitute (Mullaney, Farag, LaClaire, Batter, & Hall, 2002); Bio-carbon electrodes (Coutinho, Rocha, & Lungo, 2000); Coal dust suppression (Mullaney et al., 2002); Fertilizer (Radlein et al., 2005); Food additives (Czernik & Bridgwater, 2004; Mohan et al., 2006); Glucose (Lian et al., 2010; Patel et al., 2006); 5-hydroxymethyl furfural (Patel et al., 2006); Levoglucosan (Radlein, 1999); Methanol (Emrich, 1985); Pesticides (Booker et al., 2010); Impermiabilizer (Emrich, 1985); Road de-icer (Czernik & Bridgwater, 2004); Sufactants (Falcon & Carbonell, 2003); wood preservatives (Czernik & Birdgwater, 2004; Mohan et al., 2008); hydrogen (Galdamez, Garcia, & Bilbao, 2005; Medrano, Oliva, Ruiz, Garcia, & Arauzo, 2011); Synthesis gas (Mohan et al., 2006; Van Rossum, Kersten, &Van Swaaij, 2007); Ethanol (Lian et al., 2010, Olson & Freel, 2007; Patel et al., 2006); and Hydrotreatment to produce hydrocarbons (Adjaye, Sharma, & Bakhshi, 1996; Baker & Elliott, 1993; Elliott & Hart, 2009).

Figure 3. outlines a biomass economy formed by mobile and stationary pyrolysis units where the biomass is converted into a crude bio-oil that is then shipped to a rural refinery for the production of high-value products and a stabilized bio-oil that can then be refined in an existing petroleum or oil seed refinery for the production of transportation fuels. Deployment of this model of biomass economy depends on having the capable rural bio-oil refineries mentioned above.

Although several bio-oil refinery concepts are under study at the laboratory level (Garcia-Perez et al., 2011a) to produce fuel and chemicals from bio-oils, only the two-step bio-oil hydrotreatment and bio-oil gasification concepts are currently

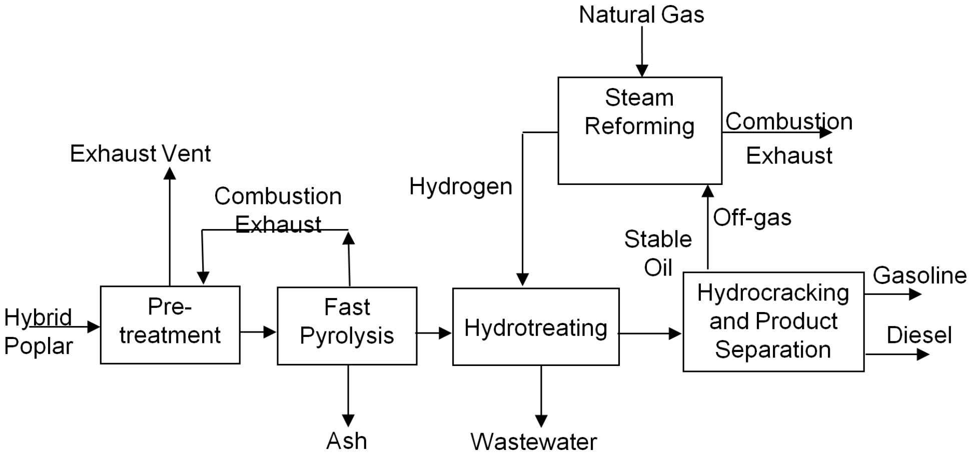
Figure 3. Scheme of Biomass economy based on pyrolysis units



being evaluated at pilot and demonstration scales (Yu & Wu, 2010; Pelaez-Samaniego et al., 2008). Figure 4 shows a scheme of a two step hydrotreatment unit for bio-oil refining (Jones et al., 2009). In this concept the feedstock is first dried to < 10% moisture content then ground to 2- 6 mm (Jones et al., 2009). Pyrolysis can then be conducted in one of the well known fast pyrolysis reactors (Ablative pyrolysis, Auger Pyrolysis, Rotating Cone, bubbling fluidized bed, circulating bed) at temperatures between 400 and 550 °C. The stabilization and hydrocracking steps consists of contacting the bio-oil with hydrogen under pressure and temperatures below 400 °C. The first stabilization step is typically conducted at 240 °C, a hydrogen pressure of 2500 psig and a LHSV 1 (v/h/v). The hydrocracking step is typically conducted at higher temperatures (370 °C), slightly lower pressure (2015 psig) and much lower LHSV (0.14 v/h/v) (Jones et al., 2009). Although this is the most promising concept for transportation fuels production, it has some drawbacks: high hydrogen consumption, no high value by-products to improve economic viability and fuels rich in aromatics. These will be needed to be addressed as the technology matures.

At this pre-commercial stage, business models based on bio-oil production will be successful if they develop one or two high-value products from bio-oil. For example, Ensyn, which started by producing food ingredients and specialty chemicals and is now working with Universal Oil Products (UOP) Honeywell to build a bio-oil refinery based on bio-oil hydrotreatment (Retrieved from http://www.ensyn.com/partners/uop-honeywell/).

Figure 4. Block Diagram of the PNNL two step hydrotreatment concept (Jones et al., 2009)



Business success should be premised on the development of bio-oil, biochar, and high-value products that address local needs. The development of the business model will depend on the pyrolysis technology used (slow or fast pyrolysis, mobile, transportable or stationary) (Mesa-Perez et al. 2013, Garcia-Perez and Garcia-Nunez, 2013). Success depends on obtaining a sufficient average price from a few different types of outlets (Simmons, 1957) and scaling up as demand rises. Biomass-based companies also depend on local biomass availability.

FINANCIAL ANALYSES

Several very good techno-economic analyses have been published in the last five years (Badger, Badger, Puettmann,. Steele, & Cooper, 2011; Bridgwater et al., 2002; Farag et al., 2002; Jones et al., 2009; Ringer, Putsche, & Scahill, 2006; Rogers & Brammer, 2012; Wright, Satrio, Brown, Daugaard, & Hsu, 2010). The lack of commercial pyrolysis facilities is a major hurdle to obtain reliable techno-economic data (Kuppens et al., 2010). Thus, the information provided is predicated on currently available equipment (typically costly first generation designs).

Biomass Supply Chain

Biomass supply chain analysis is needed to calculate the cost of biomass at the gate of the pyrolysis unit (Flora, 2012). The feedstock value is the price paid for biomass, standing or lying on the land. Depending on the feedstock (i.e., corn stover, cereal grain straw, sorghum stover, switchgrass, prairie grass, logging residues, forest thinnings, etc.) the price has historically varied from less than $10 US/dry ton (t) to $50 US/dry t (Perlack & Hess, 2006). In Washington State, for example, it is typical to pay $10 US/t of windrowed straw in the field. Baled straws in Idaho in 2004 cost $32 to $42 US/t. Note that the current price is likely to increase with demand increases (Grant et al., 2006). In Malasya, the the oil palm mesocarp fiber was sold in 2010 at $12.50 US/t, while the oil palm shell had a price ranged between $44 and $63 US/t (Rozario & Melssen, 2013). In Colombia, the oil palm shell has been selling at $35 US/t (Garcia-Nunez et al., 2010).

Biomass Preprocessing

The main goals of biomass pre-processing for pyrolysis are: (1) particle size reduction, (2) moisture content reduction (normally below 10%), (3) buffer storage space (short term), (4) storage space between deliveries (long term), and (5) efficient truck unloading (Rogers & Brammer, 2012). Following are key elements of biomass preprocessing operations.

Capital Costs

The most important preprocessing equipment is: chippers, grinders, dryers, optimized for the feedstock, and pyrolysis process used (Badger et al., 2011). Table 3 shows capital costs for biomass plants capable of processing 100, 450 and 680 t/day (US EPA, 2007) broken down into three parts: (1) receiving system (truck tipper, conveyor, and radial stacker), (2) processing system (reclaim feeder, conveyor, metal separator, dryer, screener and grinder), and (3) buffer storage (storage bin for 24 hours) (US EPA, 2007). In the analysis the authors considered that the small facilities (e.g., 100 t/day) will handle the feedstock manually and that large conversion systems (450 and 680 t/day) will use a fully automated preparation yard. For fast pyrolysis plants, the data provided by the US Department of Agriculture, the US Department of Energy, and National Renewable Energy Laboratory (Antares Group, 2003) (Table 3) should be complemented with drying and fine grinding costs.

Costs reported by Badger et al. (2011) are summarized in Table 4. The capital cost of biomass preprocessing units can be found elsewhere (Naimi et al., 2006; Ringer et al., 2006; Spath et al., 2005).

Operating Costs of Biomass Processing Units

Labor costs herein were calculated by the Antares Group (2003). Spath et al. (2005) provided information on salaries for thermochemical plant employees in the US.

Energy costs to reduce feedstock size, to feed the reactors, for illumination, for pumping products and fans, are additional factors in calculating operating cost (Naimi et al., 2006; Ringer et al., 2006). Particle size reduction is a critical requirement for biomass pyrolysis because the yield of bio-oil product is directly related to the particle size used (Shen et al., 2009). Depending on the material and grinding mechanism (shear, impact, attrition), the energy consumed by the grinder may vary (10-50 kW/t) (Naimi et al., 2006; Wright et al., 2010). Farag et al. (2002) estimated that grinding costs can be up to $10 US/t. Chipping branches and stumps to ~5 cm wood chips costs approximately $4 US/t. Grinding ~5 cm wood chips to ~0.1 cm costs up to $1.8-$6 USD/t.

Table 3. Capital costs (USD) associated with biomass preparation for power technology that can be applied for pyrolysis (Antares Group, 2003; US EPA, 2007)

Component	t fuel/day (as received)		
	100	**450**	**680**
Receiving System			
Truck tipper	230,000	230,000	230,000
Conveyor to wood pile		40,000	45,000
Radial stacker, adder		190,000	205,000
Front end loader, adder	100,000		
Receiving Equipment Subtotal	**330,000**	**460,000**	**480,000**
Processing System			
Reclaim feeder		230,000	230,000
Conveyor		149,000	160,000
Metal Separator	40,000	40,000	40,000
Screener	150,000	220,000	250,000
Grinder	250,000	400,000	600,000
Processing Equipment Subtotal	**440,000**	**1,039,000**	**1,280,000**
Buffer storage	**60,000**	**98,000**	**135,000**
Fuel metering	252,000	313,000	364,000
Controls	115,000	166,000	196,000
Equipment Subtotal	**1,197,000**	**2,076,000**	**2,455,000**
Equipment installation	500,000	1,093,000	1,220,000
Civil/structural work	370,000	787,000	877,000
Electrical work	170,000	275,000	305,000
Direct Cost Subtotal	**2,237,000**	**4,231,000**	**4,857,000**
Engineering (10% of direct cost)	223,700	423,100	485,700
Contingency (8% of direct cost)	178,960	338,480	388,560
Indirect Costs Subtotal	402,660	761,580	874,260
Total Prep-Yard Cost	**2,639,660**	**4,992,580**	**5,731,260**
Prep-Yard Unit Cost (USD/ton/day)	26,397	11,046	8,453

PYROLYSIS UNITS

Capital Costs

Several formulas can be used to calculate the capital investment costs of a pyrolysis unit (Kuppens et al., 2010; Siemons, 2002; Bridgwater et al., 2002). Bridgwater

Table 4. Capital cost (USD) summary including the cost of transportation trucks and driers (Badger, 2002)

	46 t/day	**230 t/day**	**460 t/day**	**818 t/day**	**2047 t/day**
Truck, small dump, 12 m^3	40,000				
Large dump trailer only, 24.5 m^3	27,000				
Self unloading trailer van only, 81 m^3	40,000				
Standard trailer van only, 80 m^3	24,000	24,000	24,000	24,000	24,000
Scales, mechanical		40,000	40,000	40,000	40,000
Scales electronic		110,000	110,000	110,000	110,000
Bar code scanner/computer system					10,000
Whole truck dumper w/hopper					604,000
Truck trailer only dumper w/hopper		234,000	234,000	234,000	
Scaling dick screen	19,100	19,100	24,750	30,900	30,900
Hammer mill (hammer hog)	49,050	49,050	50,025	59,625	59,625
Enclosed metal bin w/loader	2,041,000	4,320,000			
Metal silo, conical bottom w/ inloader	1,276,000				
Concrete silo	855,000	2,532,000			
Hopper, live-bottom, 9 mdrg chain conv	26,153	35,850	35,850	42,300	42,300
Conveyor belted (33.5 m length)	51,000	51,000	51,000	53,250	53,250
Metal bldg w/concrete pad 1-side open	62,000	244,000			
Open pile w/concrete pad	28,338	41,719	121,124	5,958	5,958
Front end loader, rubber tired, w/9 m3 bucket		250,000	250,000	250,000	250,000
Magnet bar	3,975	4,800	4,800	4,800	7,600
Magnet self cleaning bar	7,800	7,800	8,400	11,950	17,100
Magnet pulley head	2,645	2,645	4,685	5,995	
Non-ferrous metal detector	6,4785	6,475	6,475	9,965	9,965
Dryer, rotary	250,000	521,000	887,200	1,362,200	3,300,300

et al. (2002) proposed an equation (equation 1) to estimate the investment cost if the hourly mass flow rate, (ϕ, t/h) of dried and ground wood fed into the reactor is known. It is important to note that equation 1 is only valid for the construction materials, the year, the capacity and the technologies used by the authors that obtained these empirical equations.

$$I_{pyrolysis} = 5.345 \bullet 10^4 \bullet (\phi \bullet 10^3)^{0.6194} + 1.559 \bullet 10^5 \bullet (0.7\phi)^{0.4045} \quad (1)$$

Where: I = Investment cost (USD)

ϕ = hourly mass flow rate (t/h)

Siemons (2002) proposed an equation to calculate the capital investment cost ($I_{pyrolysis}$ in USD) if the reactor's thermal capacity (C) in MW is known (equation 2).

$$I_{pyrolysis} = 9.057 \bullet 10^2 \bullet C\ 0.76 \quad (2)$$

Equation 3 is formula based on an analysis of a typical fluidized bed system (Brammer, Bridgwater, Lauer, & Jungmeier, 2006). This formula depends on the moisture content of the feedstock (μ), which may require a higher consumption of heat, and the mass input flow (m) in kg s^{-1} (Kuppens et al., 2010).

$$I_{pyrolysis} = 4.744 \bullet 106 \bullet (m + 0.0921)0.504 + 1.074 \bullet 10^6 \bullet m \bullet (1+ \mu) + 824 \quad (3)$$

Equation 4 is the result of a linear regression analysis on 13 data points considering capital investment cost as the dependent and hourly mass flow of the biomass (ϕ) as the independent variable (Ringer et al., 2006; Siemons, 2002; Kuppens et al., 2010).

$$I_{pyrolysis} = (1.906 + 0.598 \bullet \phi) \bullet 10^6 \quad (4)$$

The capital plant cost of different sized pyrolysis units has been reported in the literature (Farag et al., 2002, Badger et al. 2011, Cole Hill Associates, 2004, and Ringer et al., 2006). Some of the estimates do not include the land and site preparation (Farag et al., 2002). Table 5 shows a detailed cost breakdown of the installed equipment for feedstock preparation, pyrolysis, quench system with steam, and power production for a 550 t/day unit.

Table 6. shows the capital investment cost for a 550 t/day pyrolysis plant. See Wright et al. (2010) for a detailed cost estimate of pyrolysis and hydrotreatment equipment.

Operating Costs of Pyrolysis Units

To calculate variable costs, mass and energy balances are needed (Ringer et al. 2006). Utility costs associated with a 100, 200 and a 400 t/day pyrolysis unit are shown in Table 7. The cost of electricity could represent approximately 17% of the annual operating cost (at 0.05-0.08 USD /kWh) (Wright et al. 2010).

Table 5. Installed equipment costs for 550 ton/day pyrolysis units (Ringer et al., 2006; Wright et al., 2008)

Plant Area	Installed Equipment Cost (Million USD)	%
Feedstock Handling and Drying	5.57	19.61
Pyrolysis	3.92	13.80
Quench	1.94	6.83
Heat recovery	1.14	4.01
Product Recovery and Storage	0.80	2.81
Recycle	1.38	4.86
Steam and Power Production	3.16	11.12
Utilities	3.13	11.02
Equipment Contingency – 35%	7.37	25.94
Total Installed Equipment Cost	28.41	100

Table 6. Capital investment cost for a 550 t/day (dry basis) unit (Ringer et al., 2006)

Component	Basis	Cost (USD)
Total Equipment Cost	Calculated by equations	28,410,567
Warehouse	1.5% of equipment costs	426,159
Site Development	9% of ISBL	826,448
Total Installed Cost (TIC)	**Sum of Above**	**29,663,173**
Indirect Costs	20% of TIC	5,932,635
Filed Expenses	25% of TIC	7,415,793
Home Office & Construction Fee	3% TIC	889,895
Project Contingency		
Total Capital Investment (TCI)	**Sum of Above**	**43,901,497**
Other Costs (Startup)	10% of TCI	4,390,150
Total Project Investment	**Sum of Above**	**48,291,646**

Farag et al. (2002) estimated the transportation cost for bio-oil as $0.05 US/gal of liquid oil. Estimates of labor cost can be found in the literature (Badger et al., 2011; Farag et al., 2002; Ringer et al., 2006). The wages change dramatically depending of the region where the unit is located however, in the United States a 20% labor overhead rate is commonly assumed. In the analysis conducted for a 100 t/day Dynamotive plant by Cole Hill Associates (2004) they assumed that the pyrolysis plant will be in operation 24 h/day, seven days a week with 8 hour shifts.

Table 7. Dynamotive plant utility costs (Farag et al., 2002)

Wet Wood Plant Size	100 t/day	200 t/day	400 t/day
Electricity used per operating hour (kWh)	550	962	1788
Yearly operating hours (h/year)	7920		
Electricity (USD/year) (assuming 0.065 USD/kWh)	283,140	495,238	920,462
Nitrogen* (USD/year)	80,000	160,000	320,000
Miscellaneous chemicals (USD/year)	120,000	240,000	480,000
Natural as needed (MJ/year)	13,068,000	26,136,000	52,272,000
Natural Gas** (USD/year) (assuming 0.00675 USD/MJ)	88,214	176,428	352,856

Maintenance Costs

The costs of high temperature greases, gasket material, coupling, component replacement, and other required are included in annual maintenance costs and typically represent between 2 and 10% of the capital cost of the pyrolysis unit (Badger et al., 2011, Farag et al., 2002). The distribution of the operational costs for 100, 200 and 400 t/day pyrolysis units are presented in Figure 5. Maintenance, feedstock, and labor are the most important costs. Capital and operating costs are listed in Tables 8 and 9, respectively.

Figure 5. Operational costs distribution of 100, 200, and 400 t/day pyrolysis plants, respectively (Adapted from Farag et al., 2002)

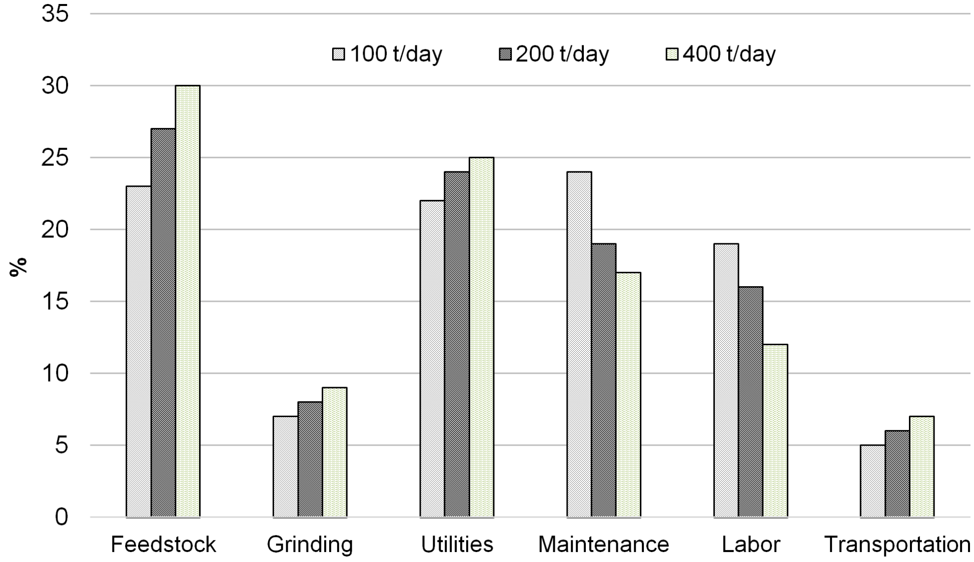


Table 8. Total capital and operating costs (in USD) (Farag et al., 2002)

Wet Wood Plant Size	100 t/day	200 t/day	400 t/day
Feedstock cost	654,772	1,309,544	2,619,089
Grinding cost	181,881	363,762	727,525
Electricity for process	283,140	495,238	920,462
Nitrogen	80,000	160,000	320,000
Miscellaneous chemicals	120,000	240,000	480,000
Natural gas	88,214	176,428	352,856
Labor	487,500	649,984	812,468
Maintenance	660,000	880,000	1,430,000
Additional non-production labor	44,196	88,393	176,786
Utilities (non-production) + potable water	19,643	39,286	78,571
Potable water, heat, exchanger water, sewage	10,000	20,000	40,000
Supplies & services	62,857	125,714	251,429
Transportation	145,049	290,099	580,197
Total Annual Operating Cost	**2,837,252**	**4,838,488**	**8,789,383**
Gallons produced	2,900,986	5,801,972	11,603,945
Dollars per gallon without capital cost payment plan	0.98 USD/ gal	0.83 USD/gal	0.76 USD/gal
Capital cost	6,600,000	8,800,000	14,300,000
Annual loan payment (equal amounts, 10 year payback period at 8%)	648,441	5,751,036	10,272,339
Total annual operating cost with loan payment	3,521,693	5,751,036	10,272,339
Dollars per gallon with capital cost payment plant	**1.21 USD/gal**	**0.99 USD/gal**	**0.89 USD/gal**

Bio-Oil Production Costs

Several technoeconomic analyses have been published to estimate the production cost of pyrolysis oils (Brammer et al., 2006; Farag et al., 2002; Ringer et al., 2006; Wright et al., 2010). Table 10 shows several estimates of crude bio-oil production cost ($0.41-3.61 US/gallon).

According to Wright et al. (2010) the commercialization of crude bio-oil at $0.86 US/gallon may be viable if petroleum prices are close to $100 US/barrel. Large units co-located with existing industry and using waste materials as feedstocks are likely to be more viable than small stand-alone units processing energy crops. Capital equipment needs can be significantly reduced by sharing existing wood handling facilities. Savings could be made by co-sharing labor.

Table 9. Breakdown of ROI operating and capital costs (USD/year), 80% online (Badger et al., 2011), based on a 100 t/day (dry basis) plant

Wet Wood Plant Size	100 t/day	200 t/day	400 t/day
Feedstock cost	654,772	1,309,544	2,619,089
Grinding cost	181,881	363,762	727,525
Electricity for process	283,140	495,238	920,462
Nitrogen	80,000	160,000	320,000
Miscellaneous chemicals	120,000	240,000	480,000
Natural gas	88,214	176,428	352,856
Labor	487,500	649,984	812,468
Maintenance	660,000	880,000	1,430,000
Additional non-production labor	44,196	88,393	176,786
Utilities (non-production) + potable water	19,643	39,286	78,571
Potable water, heat, exchanger water, sewage	10,000	20,000	40,000
Supplies & services	62,857	125,714	251,429
Transportation	145,049	290,099	580,197
Total Annual Operating Cost	**2,837,252**	**4,838,488**	**8,789,383**
Gallons produced	2,900,986	5,801,972	11,603,945
Dollars per gallon without capital cost payment plan	0.98 USD/ gal	0.83 USD/gal	0.76 USD/gal
Capital cost	6,600,000	8,800,000	14,300,000
Annual loan payment (equal amounts, 10 year payback period at 8%)	648,441	5,751,036	10,272,339
Total annual operating cost with loan payment	3,521,693	5,751,036	10,272,339
Dollars per gallon with capital cost payment plant	**1.21 USD/gal**	**0.99 USD/gal**	**0.89 USD/gal**

Hydrotreatment and Hydrocracking of Pyrolysis Oil (Bio-Oil Refining)

The data presented in this section come mostly from the work of Jones et al (2009) and corresponds to an analysis of a 2000 t/day pyrolysis unit integrated with stabilization, hydrotreatment, separation and hydrogen production units (See Figure 4). The concept studied does not produce biochar. It uses the energy of the char to run part of the unit. The authors sized the equipment with CHEMCAD and estimated the costs using ASPEN Icarus^{TM}, using quotes from vendors and the estimated made by Marker et al. (2005). The estimate for hydrogen generation by steam reforming of natural gas was done from the SRI International (2007) and Foster Wheeler (Gulf,

Table 10. Bio-oil production costs (Ringer et al., 2006)

Variable Costs (USD)	
Feedstock costs (25.00 USD/green ton)	1,460,000
Electrical utilities	104,869
Thermal utilities	0
Maintenance	91,551
Trucking costs (pyrolysis oil)	76,692
Subtotal variable costs	1,733,112
Fixed costs (USD)	
Wages & benefits & travel	565,200
Property insurance	42,113
Liability insurance	39,539
Laboratory fees	19,150
Subtotal fixed costs	666,002
Total annual operating costs (fixed + variable) (USD)	2,399,114
ROI system capital costs[1]	6,030,816
Annual loan payment 100% borrowed (9% interest, 10 year term)	916,749
Annual gallons produced (80% online), 60% yield	3,504,000
Total annual operating costs with loan payments (USD)	3,315,863
Cost per gallon of oil (USD/gal)	**0.94**

2006). Storage capacity and cooling tower capital were estimated with ASPEN Icarus™. The cost of waste water treatment was obtained from Beckman et al (1990), 15% of process contingency was added to all the new technologies. Table 11 shows the capital cost distribution for a stand-alone plant (Figure 4) (Jones et al., 2009).

Operating Costs

The assumptions made by Jones et al. (2009) to estimate the operating costs are shown in Table 12.

Jones et al (2009) estimated the selling price (Manufacturer's Suggested Retail Price - MSRP) for the gasoline and diesel blendstock following the methodology recommended by Phillips, Adem, Jechura, Dayton, & Eggman (2007). The MSRP was estimated as the selling price of the fuel that makes the net present value of the process equal to zero with a 10% discounted cash flow over a 20 years plant life (Jones et al., 2009). The economic parameters used to calculate the MSRP can be found elsewhere (Table 13) as showed the fixed operating costs of the design case for a stand-alone plant obtained by Jones et al 2009.

Table 11. Total project Investment Cost for the integrated pyrolysis based bio-refinery (Jones et al., 2009)

Study	Capacity (t/day)	Feedstock	Bio-oil cost (USD/gal)
Cottom and Bridgwater (1994)	1,000	Wood	0.41
Arthur (1991)	1000	Wood	0.41
Arthur (1991)	250	Wood	0.46
Gregorire and Bain (1994)	1,000	Wood	0.50
Gregoire (1992)	250	Wood	0.50
Solantausta et al. (1992)	1000	Wood, peat and straw	0.59 – 2.46
Radlein and Bouchard (2009) (Dynamotive)	200	Wheat straw	0.59
Badger et al. (2011)	100	Pine wood chips	0.94
Mullaney (2002) (Dynamotive)	100, 200, 400	Low-grade wood chips	1.21, 0.99, 0.89
Ismam and Ani (2000)	2.4 - 24	Rice husks	1.73-0.83
Polagye et al. (2007)	10, 100, 500, 1816	Forest thinnings	2.70, 1.32, 0.96, 0.85
Granatstein et al. (2009)	10, 100, 500, 1816	Forest thinnings	3.61, 1.44, 1.18, 1.03

Table 12. Operating Cost Assumptions (Jones et al., 2009)

	Value
Raw Materials	
Hybrid Poplar Chip, $/dry short ton	50.70
Ash Disposal, $/short ton	18
Hydrogen (refinery transfer), %/lb	0.56
Hydrotreating Catalyst, $/lb (2007)	15.5
Hydrocracking Catalyst, $/lb (2007)	15.5
Hydrogen Plant Catalyst, $/1000 scf H_2 (2007)	
Utilities	
Natural Gas, $/1000scf (1000 BTU/scf)	7.68
Electricity, $/kWh	0.0636
Labor	
Operating labor, $/hr burdened & 10% shift overlap	37.66
Maintenance and overhead	95% of labor & supervision
Materials	
Maintenance	2% of total project investment
Local Taxes and Insurance	2% of total project investment

Table 13. Cost estimations for the stand alone pyrolysis-bio-oil hydrotreatment refinery (Jones et al. 2009)

	$/gal product	Contribution %
Feedstock	0.48	23
Natural Gas	0.32	16
Catalyst & Chemicals	0.15	7
Waste Disposal	0.01	0
Utilities (Cooling water, Electricity, Steam)	0.17	8
Fixed Costs (Labor, Operating Supplies, etc)	0.22	11
Capital Depreciation	0.20	10
Average Income Tax	0.13	7
Average ROI	0.36	18
MFSP, $/gal	2.04	
MFSP Ethanol Equivalent basis, $/gal	1.34	

The average refinery price for gasoline and diesel in 2007 were $2.18 and $2.20 per gallon US (Jones et al., 2009). This result suggests that the production of transportation fuels from the pyrolysis of lignocellulosic materials could be economically viable.

LIFE CYCLE ASSESSMENT ON THE USE OF PYROLYSIS DERIVED PRODUCTS

Ideally, lignocellulosic materials should be used for bio-products as part of integrated biorefinery technologies including bio-fuel. Lippke, Wilson, Meil, & Taylor (2010) showed that using wood for bioproducts such as structural wood composites for building can be more effective for reducing carbon emissions than producing biofuels or fuel pellets. However, low quality wood residues may not be appropriate for composites, but create enormous opportunity for biofuels production.

A consistent and reliable analysis of a product or system is the Life Cycle Assessment (LCA). The International Standard Organization (14040/44) has established a framework of guidelines on how to conduct an LCA. The LCA helps identify opportunities to improve the environmental performance of different products at several stages in the products' life cycle. LCA is the ideal method to evaluate the impacts or benefits of using biomass pyrolysis derived products. This section presents a short literature review on recent LCA studies of pyrolysis processes. Since pyrolysis can be optimized for increasing the yields of solids or liquids, LCA studies are typically conducted for technologies only producing biochar (slow pyrolysis) or only bio-oil production (fast pyrolysis).

LCA of Biochar Production Business Models

Biochar is a carbon concentrate derived from lignocellulosic raw materials through pyrolysis. One of the arguments for charcoal's contribution to carbon sequestration is its stability in soil and its similarities with coal. However, there is still a debate on the real impact of charcoal as a tool to sequester carbon. For example, a literature review published by Gurwick, Moore, Kelly, and Elias (2013) on the potential environmental effects of biochar concluded that the data available are not reliable enough to support all the biochar benefits reported in the literature. The authors found that only a few of the studies reported in the literature are systematic enough to reach conclusions on the influence of biochar on ecosystem properties and its fate in the environment. The authors concluded that although there are a growing number of papers on biochar production and its material properties, the number of publications on the long-term effect of biochar on soils is very limited. Biederman and Harpole (2013) have also evaluated the impacts of applying biochar to ecosystems by conducting a meta-analysis of published literature. However, the authors concluded that, independent of soil type and climate, on average, biochar addition increased aboveground productivity, crop yield, total soil carbon compared with the control soil.

Fortunately, the topic is receiving lots of attention and a number of studies have been recently published (Case, McNamana, Reay, Whitaker, 2014; Dutta & Raghavan, 2014; Edmunds, 2012; Lugato et al. 2013; Sparrevik, Field, Martinsen, Breedveld, & Cornelissen, 2013; Wang, Dunn, Han, & Wang, 2014). These studies provide additional insights into the potential of using biochar either as a soil amendment, energy source or a tool to capture CO_2in both tropical and temperate regions. For example, Sparrevik et al. (2013) conducted a LCA for field sites in Zambia to evaluate the overall impacts of biochar for agricultural use, including ecological, health, and resource management. In the study, the authors evaluated the effect of adding biochar in conservation farming. Biochar was produced using three different methods: traditional earth-mound kilns, improved retort kilns, and micro top-lit updraft gasifier stoves. Results confirmed that biochar in conservation farming has a positive effect on climate change mitigation. Nevertheless, the authors found that particles emissions resulting from biochar production, when low-technology kilns are used, have a negative effect over the whole life cycle. Therefore, the technology for biochar production impacts the LCA results.

A recent publication (Scholz et al., 2014) showed that biochar projects in developing countries present potential to reduce GHG emissions, while offering economic benefits to local economies. In the study, the authors conducted LCA case studies in three countries: Kenya, Vietnam, and Senegal. Projects were selected based on their integration into the local economy, pyrolysis technology and scale, geographical location, data availability. Results revealed that ensuring the sustainability of the feedstock for biochar manufacture is critical for guaranteeing biochar sustainability and achieving GHG reductions. If the sustainability of the feedstock is assured, biochar can in fact sequester carbon. In Kenya, the authors showed that a household pyrolysis cookstove system with biochar returned to soil qualifies as climate change mitigation via sequestration of greenhouse emission reductions. In the study the authors added an economic analysis and found economic benefits by managing maize production with added biochar. The use of a pyrolysis cookstove for household cooking and biochar production produces a net greenhouse gasses (GHG) reduction of -1.8 tCO_2e/t of dry pyrolysis feedstock. The authors suggested that biochar use can promote social positive impacts, such as reduced indoor air pollution and related illness, less fuelwood consumption, and improved long-term soil fertility. The contribution analysis showed that the net GHG balance relies on the avoided emissions from the traditional three-stone fire and the sustainability of the primary and secondary cookstove feedstock. However, if the feedstock is harvested in an unsustainable way and does not regrow or if the emissions during cooking could not be offset by the biomass regrowth the environmental impact could be negative. The studies performed in Vietnam and Senegal analyzed the production of biochar from rice husk. In both cases the authors found that rice husk biochar has potential for climate change mitigation through carbon sequestration while providing profits to local communities. The economics of these projects will depend on the effectiveness of biochar to address soil fertility constraints, how long the effect of biochar lasts, biochar application rate, and the value of the crops obtained from soils previously amended with biochar.

The importance of feedstock harvesting sustainability and use of charcoal has also been mentioned by Ekeh, Fangmeier, & Müller, (2014). The authors conducted an LCA in another tropical country, Uganda, and quantified the emissions resulting from charcoal production using the traditional earth mound method. The result, 3 tCO_{2eq}/t of charcoal produced, has been suggested as a good approximation for other countries that produce biochar using similar technology in Africa. The authors also found that if the charcoal is used for cooking only, it could lead to increased GHG emissions and increased deforestation in the long term.

The study performed by Hammond, Shackley, Sohi, & Brownsort (2011) analyzed pyrolysis biochar systems for small, medium, and large scale process chains and ten feedstocks, assessing carbon abatement and electricity production in the UK. The authors found that pyrolysis biochar systems offer greater carbon abatement than other thermochemical technologies (e.g., combustion and gasification) and that the feedstock and the scale of the system impact the carbon abatement. Electrical production off-setting fossil fuel use accounted for 10-25% reduction, but change in soil organic carbon stocks induced by biochar is the key sensitivity. Reduction in fertilizer use and the suppression of soil N_2O emissions had little impact.

Edmunds (2012) studied the effect of incorporating switchgrass and pine biochar into agricultural soil to sequester carbon in the Southeastern United States. Biochar application to soil at a rate of 5% (wt.), Mehlich-I extractable P, K, Mn, and exchangeable K significantly increased in soil. Results also showed that biochar application increased above-ground biomass yield in both switchgrass and sorghum by up to 25%. The study concluded that charcoal produced from switchgrass at 600 °C best meets the balance between carbon sequestration and improving soil fertility and plant biomass yield. A similar conclusion on the effect of hardwood biochar amendment on *Miscanthus x Giganteus* crop under field and controlled conditions was reported by Case et al. (2014), who mentioned that biochar amendment can potentially reduce net soil CO_2e emissions from the *Miscanthus* soil crop.

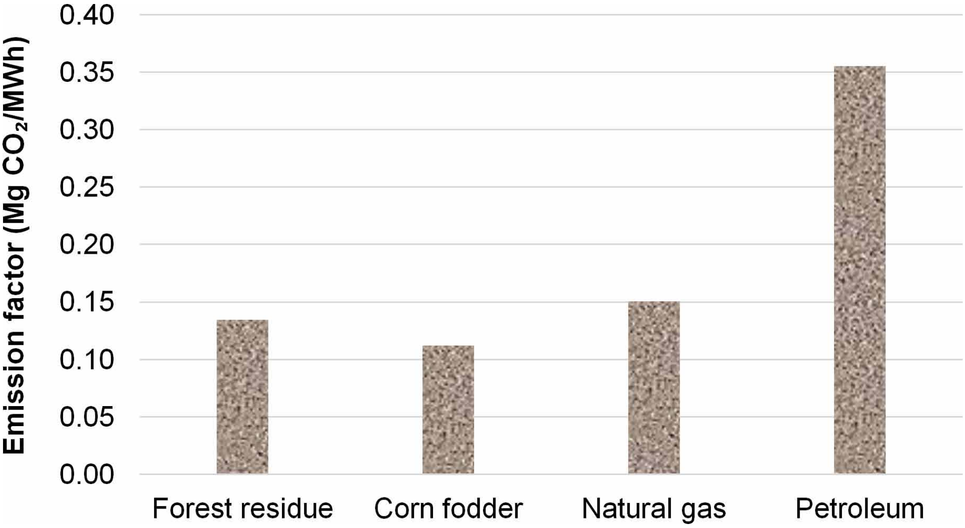
Lugato et al. (2013) conducted an LCA coupling energy production via gasification of forest materials with the resulting bio-char as soil amendment. Biochar was then applied to rice paddies. The LCA focused on the GHG balance of the supply chain, from the forest management to biochar field distribution. The authors found that gasification was responsible for the highest impact in the supply chain in terms of emissions. However, the net emissions allocated to biochar were negative and biochar had a marginal but positive effect on rice yields.

The work of Dutta and Raghavan (2014) showed that the total emissions from biochar produced from corn fodder (corn stalk without the ears; treated as waste) and forest residues were, respectively, up to 94.2% and 92.9% less than those for natural gas. Emission factors (commonly used for computing GHG) were marginally lower than that of natural gas, but appreciably lower than that of petroleum (see Figure 6). The authors found that the GHG emissions associated with the pyrolysis process are the highest, contributing for approximately 50% of the emissions of the cycle. On the other hand, the stabilized carbon in the biochar was the main contributor of GHG reduction.

LCA of Business Models Producing Biochar and Bio-Oil

LCAs of technologies producing both biochar and bio-oil have been performed by a number of researchers (e.g., Ibarrola, Shackley, & Hammond, 2012; Lippke et al., 2012; Han, Elgowainy, Dunn & Wang, 2013; Wang, Dunn, Han, & Wang, 2014). In these studies bio-oil was in most cases used as fuel for producing heat and electric-

Figure 6. Comparison of emission factors between traditional fuel sources and biochar produced from forest residue and corn fodder (Adapted from Dutta & Raghavan, 2014)



ity (Ibarrola et al., 2012). LCA considered three thermochemical processes: slow pyrolysis, fast pyrolysis, and gasification, for processing ten types of non-virgin feedstocks (urban biodegradable wastes and residues) in the UK. The objective of their study was to determine and compare the carbon abatement and the energy benefits from pyrolysis/gasification biomass systems. Results showed that the net carbon abatement (t CO_2e/t of feedstock) was positive in most materials (especially in those with higher heating value and carbon content), independent of the type of processing technology. However, slow pyrolysis systems showed the highest carbon abatement due to the carbon storage offset of biochar. The highest electricity generation, on the other hand, was achieved by gasification, which resulted from the system efficiency and because both the syngas and the bio-oil were devoted to electricity generation.

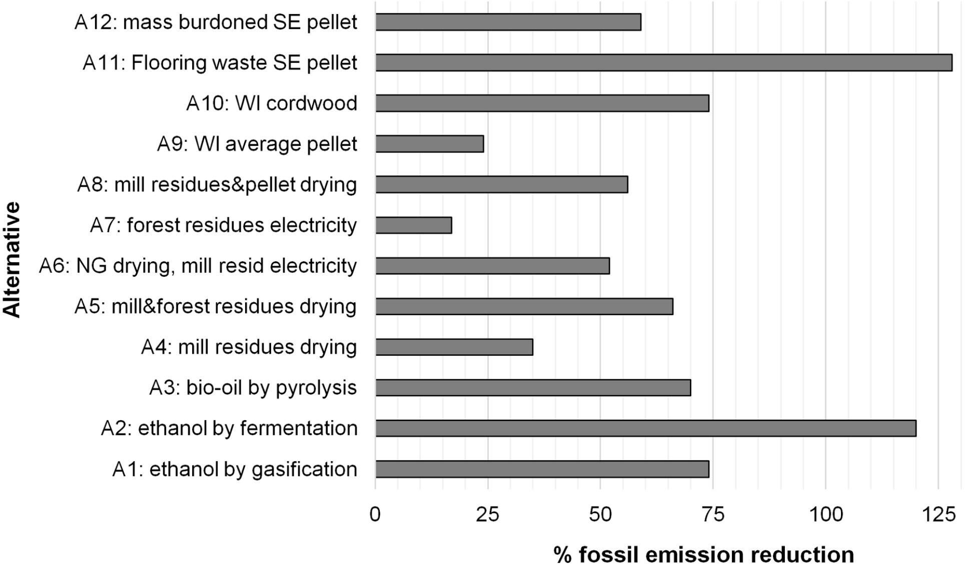
Han et al. (2013) conducted a well-to-wheels analysis of gasoline produced from pyrolysis bio-oil compared with petroleum-based gasoline produced from oil. Deviations resulting from different pathways were solved by adding probability distributions for key parameters with literature data. Since hydrogen is required for upgrading pyrolysis bio-oil, the authors assessed two different hydrogen sources: reforming of natural gas and reforming of bio-oil. The study found that the hydrogen source causes a trade-off between GHG reduction per unit fuel output and petroleum displacement per unit biomass used.

Wang et al. (2014) conducted an LCA of using both biochar and bio-oil, assuming that biochar is a byproduct of biomass pyrolysis. Varying accounting techniques for biochar benefits including soil amending can influence LCA results. In fact, the life-cycle greenhouse gas emissions for pyrolysis-based gasoline are lower when biochar is applied to soil than when it is combusted. Zhang, Hu, & Brown, (2013) have also evaluated and quantified the environmental impacts of producing hydrogen and transportation fuels from corn stover fast pyrolysis. Their results showed that co-production of hydrogen and transportation fuels have lower GHG emissions and fossil energy input than scenarios in which bio-oil was used for producing transportation fuels only. The authors also showed that bio-oil production, biomass preprocessing, and bio-oil upgrading are critical components that the environmental performance of biofuels produced from pyrolytic bio-oil.

A well-to-wheel analysis of transportation fuel from the fast pyrolysis and upgrading of forest residues, has also been carried out by Hsu (2012). An uncertainty analysis for GHG emissions was conducted as well, and found that all scenarios had lower GHG emissions than petroleum-based gasoline. Iribarren, Peters, & Doufur (2012) performed an LCA for pyrolytic bio-oil produced from short-rotation poplar biomass. A hydrotreating upgrading process was added to the process to produce gasoline and diesel. Seven impact categories were evaluated: cumulative energy demand, global warming, ozone layer depletion, photochemical oxidant formation, land competition, acidification and eutrophication. The study showed that biomass pretreatment (drying and grinding), pyrolysis process, and steam reforming of natural gas for hydrogen used in the hydroprocessing stages, had the highest environmental impact.

Lippke et al. (2012) evaluated the "comparative life-cycle impacts for a range of different biofuel alternatives on the reduction of fossil carbon emissions as well as the potential to reduce energy dependence and to understand how the use of biofuels can be most complementary to wood product opportunities for improvement." The work used a C:C displacement ratio to directly measure the efficiency to reduce fossil fuel emissions per unit of carbon in the wood. The C:C is the ratio of "input biogenic carbon" (C_{in} or CO_2 in the wood used) to the "reduction in fossil fuel emissions" (C_{out} or change in fossil CO_2 equivalent output). The alternative C:C displacement ratio is shown in Figure 7. The work also found that some of the alternatives analyzed produce better than 60% reduction in emissions per Megajoule of energy produced compared with the fossil fuel alternative.

Figure 7. Carbon emission reductions per unit of carbon in the wood used (C_{out} / C_{in}) for a range of biofuel alternatives. Note: The LCI data include three biofuel feedstock collection alternatives: forest residuals, thinnings, and short rotation woody crops serving three liquid bioprocessing alternatives: (A1) pyrolysis, (A2) gasification, and (A3) fermentation. Comparisons are also made for five alternatives using more or less woody biofuel feedstocks in solid wood mills (A4 to A8), largely for drying energy, or using the feedstocks for electrical energy to offset fossil energy uses and their emissions. Four production alternatives for pellets and cordwood are also included (A9 to A12) covering a range of purchased and mill residual pellet feedstocks(Adapted from Lippke et al., 2012). NG-natural gas SE – Southeast US, WI-Wisconsin-



CONCLUSION

Sustainability and techno-economic criteria to integrate pyrolysis, biochar activation, and bio-oil refining into sustainable business models have been discussed in this chapter. The strengths and weaknesses of several business models such as the production of biochar with heat recovery and bio-oil refining were analyzed from the lens of sustainability. A major weakness of most business models for biochar production in developing countries is that they disregard the use of the energy produced from pyrolysis vapors. One of the advantages of condensing pyrolysis vapors into liquid fuels is the possibility of using these fuels for highly efficient (28%) engines such gas turbines. Nevertheless, several limitations must be overcome prior to using crude bio-oils as fuels in gas turbines and diesel engines. The residence time in the combustion chamber of gas turbines is much smaller than for boilers and the ash content/alkalinity must be strictly controlled. Although several bio-oil refinery concepts are under laboratory study to produce fuel and chemicals from bio-oils, only the bio-oil hydrotreatment and bio-oil gasification concepts are currently being evaluated at pilot and demonstration scales. The lack of technologies at the commercialization stage to produce a stabilized bio-oil compatible with the existing petroleum refineries or large bio-oil gasification plants are the main hurdle in developing a biomass economy based on pyrolysis. The revenue resulting from commercialization of the heat, electricity or bio-oils derived from pyrolysis vapors could be critical for the success of biochar businesses when scaled for using/transforming pyrolysis gases. Cost data needed for enterprise-level financial analyses of different biomass pyrolysis economy models were presented. Life Cycle Assessment studies that have been conducted confirm that, if feedstocks are produced sustainably and pyrolysis vapors are used, both the production of biochar and its use as a soil amendment to sequester carbon and the production and refining of bio-oils to produce transportation fuels have positive environmental impacts.

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REFERENCES

Adjaye, J. D., Sharma, R. K., & Bakhshi, N. N. (1992). Characterization and stability analysis of wood derived bio-oil. *Fuel Processing Technology*, *31*(3), 241–256. doi:10.1016/0378-3820(92)90023-J

Andrews, R. G., Zukowski, S., & Patnaik, P. C. (1997). *Feasibility of firing an industrial ags turbine using a biomass derived fuel. Developments in thermochemical biomass conversion* (A. V. Bridgwater & D. G. B. Boocock, Eds.). London, England: Blackie Academic and Professional.

Anex, R. P., Lynd, L. R., Laser, M. S., Heggenstaller, A. H., & Liebman, M. (2007). Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. *Crop Science*, *47*(4), 1327–1335. doi:10.2135/cropsci2006.06.0406

Annan, K. A. (2002). A chance to secure our future. Joburg Summit. Retrived from http://www.thejakartapost.com /news/2002/05/30/joburg-summit-a-chance-secure-our-future.html

Antares Group Inc. (2003). *Assessment of power production at rural utilities using forest thinning and commercially available biomass power technologies.* Prepared for the U.S. Department of Agriculture, U.S. Department of Energy and National Renewable Energy Laboratory. Golden, CO

Assessment, M. E. (2005). *Ecosystems and human well-being: synthesis.* Washington, DC: Island Press; Retrieved from http://www.millenniumassessment.org/documents/document.356.aspx.pdf, Retrieved June 9th 2014.

AtKisson, A. (2001). *Sustainability is dead–long live sustainability. A manifesto: written to mark the end of millennium two, and the beginning of millennium three*. Retrieved from http://www.rrcap.unep. org /uneptg06/course/Robert/SustainabilityManifesto2001.pdf

Badger, P., Badger, S., Puettmann, M., Steele, P. H., & Cooper, J. (2011). Technoeconomic analysis: Preliminary assessment of pyrolysis oil production costs and material energy balance associated with a transportable fast pyrolysis system. *BioResources*, *6*(1), 34–47.

Badger, P. C. (2002). Processing cost analysis for biomass feedstock. preopared for the us department of energy. Under contract DE-AC05-00OR22725. *ORNL. U. S. Atomic Energy Commission*, *TM-2002*(199).

Baker, E. G., & Elliott, D. C. (1993). *Method of upgrading oils containing hydroxyaromatic hydrocarbons compounds to highly aromatic gasoline.* US Patent Number 5, 1800, 868, Issue January 19.

Baranick, M., McElwee, D., & Zazycki, M. (2011). *Biochar feasility study: exploring the environmental, social, and economic value of a biochar business in the methow valley*. MKTG 591: Sustainable Business Practicum, June 9, Seattle University. Retrieved from http://www.biochar-international.org/ sites/ default/files/ Biochar_Final_Paper_For_Distribution_v9.29.pdf

Beckman, D., Elliott, D. C., Gevert, B., Hornell, C., Kjellstrom, B., Ostman, A., & Solantausta, V. (1990). *Techno-economic assessment of selected biomass liquefaction processes. Research Report 697*. VTT Technical Research Center of Finland.

Biederman, L. A., & Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy*, *5*(2), 202–214. doi:10.1111/gcbb.12037

Booker, C. J., Bedmutha, R., Vogel, T., Gloor, A., Xu, R., Ferrante, L., & Briens, C. et al. (2010). Experimental investigations into the insecticidal, fungicidal and bactericidal properties of pyrolysis bio-oil from tabacco leaves using a fluidized bed pilot plant. *Industrial & Engineering Chemistry Research*, *49*(20), 10074–10079. doi:10.1021/ie100329z

Brammer, J. G., Bridgwater, A. V., Lauer, M., & Jungmeier, G. (2005). Opportunities for bio-oil in european heat and power markets. In A. V. Bridgwater (Ed.), *Fast pyrolysis of biomass: a handbook, 3* (pp. 179–204). Newbury: CPL Press.

Bridgwater, A. V., Toft, A. J., & Brammer, J. G. (2002). A Technoeconomic comparison of power production by biomass fast pyrolysis with gasification and combustion. *Renewable & Sustainable Energy Reviews*, *6*(5), 181–248. doi:10.1016/ S1364-0321(01)00010-7

Brown, N. C. (1917). *The Hardwood distillation Industry in New York. Technical Publications No. 5, 17(1)*. The New York State College of Forestry at Syracuse University.

Case, S. D. C., McNamara, N. P., Reay, D. S., & Whitaker, J. (2014). Can biochar reduce soil greenhouse gas emissions from a Miscanthus bioenergy crop? *GCB Bioenergy*, *6*(1), 76–89. doi:10.1111/gcbb.12052

Chiaramonti, D., Oasmaa, A., & Solantausta, Y. (2007). Power generation using fast pyrolysis liquids from biomass. *Renewable & Sustainable Energy Reviews*, *11*(6), 1056–1086. doi:10.1016/j.rser.2005.07.008

Cole Hill Associates. (2004). *Bio-oil Commercialization Plan*. Report prepared for the New Hampshire Office of Energy and Planning. Retrieved from http://www.nh.gov/ oep/programs/energy/ documents/appendix anhbio-oilcommercializationplan.pdf

Coutinho, A. R., Rocha, J. D., & Lungo, C. A. (2000). Preparing and characterizing biocarbon electrodes. *Fuel Processing Technology*, *67*(2), 93–102. doi:10.1016/S0378-3820(00)00091-6

Czernik, S., & Bridgwater, A. V. (2004). Overview of applications of biomass fast pyrolysis oils. *Energy & Fuels*, *18*(2), 590–598. doi:10.1021/ef034067u

Dutta, B., & Raghavan, V. (2014). A life cycle assessment of environmental and economic balance of biochar systems in Quebec. *International Journal of Energy and Environmental Engineering*, *5*(2-3), 1–11. doi:10.1007/s40095-014-0106-4

Edmunds, C. W. (2012). Effects of biochar amendment in soil on bioenergy crop yield and biomass composition, MS Thesis, University of Tennesse, Knoxville.

Ekeh, O., Fangmeier, A., & Müller, J. (2014). Quantifying greenhouse gases from the production, transportation and utilization of charcoal in developing countries: A case study of Kampala, Uganda. *The International Journal of Life Cycle Assessment*, *19*(9), 1643–1652. doi:10.1007/s11367-014-0765-7

Elliott, D. C., & Hart, T. R. (2009). Catalytic hydroprocessing of chemical models for bio-oil. *Energy & Fuels*, *23*(2), 631–637. doi:10.1021/ef8007773

Emrich, W. (1985). *Handbook of Charcoal Making: The traditional and industrial methods*. Boston, MA: D. Reidel Publishing Company. doi:10.1007/978-94-017-0450-2

Falcon-Hernandez, J., & Carbonell, M. J. (2003). Fuel emulsions using biomass pyrolysis products as an emulsifier agent. *Energy & Fuels*, *17*(2), 302–307. doi:10.1021/ef020030i

FAOSTAT. (2014). Statistics on forestry production and trade. Retrieved from http://faostat3.fao.org/ faostat-gateway/go/to/download/F/FO/E

Farag, I. H., LaClair, C. E., & Barrett, C. (2002). Technical, environmental and economic feasibility of bio-oil in New Hampshire's north county. UNH Project Number 14B316 or ABAN-URI-B043.

Flora, G. (2010a). The human dimension: building support for biomass to biochar projects. Retrieved from http://www.archive.biorenew.iastate.edu/events/biochar2010/conference-agenda/agenda-overview/creating-positive-communitysocial-impacts-with-biochar-projects.html

Flora, G. (2012). Biochar: The sustainability challenge. Retrieved from http://2012.biochar.us.com /382/biochar-sustainability-challenge

Freel, B. A., & Huffman, D. R. (1994). Applied Bio-oil Combustion. *Proceedings of the Workshop on Biomass Pyrolysis Oil Properties and Combustion*. Estes Park, CO. 1994, p. 309-315.

Galdamez, J. R., Garcia, L., & Bilbao, R. (2005). Hydrogen production by steam reforming of bio-oil using co-precipitated ni-al catalyst. Acetic acid as a model compound. *Energy & Fuels*, *19*(3), 1133–1142. doi:10.1021/ef049718g

Garcia-Nunez, J. A., Cardenas, M., & Yanez-Angarita, E. E. (2010). Generación y uso de biomasa en plantas de beneficio de palma de aceite en colombia. *Palmas*, *31*(2), 41–48.

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., Rodrigue, D., & Roy, C. (2006). Multiphase Structure of Bio-oils. *Energy & Fuels*, *20*(1), 364–375. doi:10.1021/ef050248f

Garcia-Perez, M., & Garcia-Nunez, J. A. (2013). Nuevos conceptos para biorrefinerías de aceite de palma (New Concepts of Palm Oil Mill Biorefineries). *Palmas, 34*(Especial, Tomo II), 66–84.

Garcia-Perez, M., Garcia-Nunez, J. A., Lewis, T., Kruger, C. E., & Kantor, S. (2011a). *Methods for producing biochar and advanced bio-fuels in Washington state. Part 3: Literature review of technologies for product collection and refining.* Retrieved from http://www.ecy.wa.gov/biblio/ 1207034.html

Garcia-Perez, M., Shen, J., Wang, S. X., & Li, C. Z. (2010). Production and fuel properties of fast pyrolysis oil/biodiesel blends. *Fuel Processing Technology*, *91*(3), 296–305. doi:10.1016/j.fuproc.2009.10.012

Grant, D., Hess, R. J., Kenney, K., Laney, P., Muth, D., Pryfogle, P., & Wright, C. (2006). *Feasibility of a producer owned ground straw feedstock supply system for ethanol and other products.* Idaho National Laboratory. Prepared Under Contracts: DOE Office of Biomass DE-AC07-05ID145167, USDA Rural Business Cooperative Service producer Grant 12-034-82036979. Retrieved from http://www.inl.gov/bioenergy/ projects/d/1001_feasibility.pdf

Gulf Publishing Co. (2006). *Hydrocarbon processing: Refining processes*. Houston, Texas: Gulf Publishing Co.

Gurwick, N. P., Moore, L. A., Kelly, C., & Elias, P. (2013). A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PLoS ONE*, *8*(9), 1–9. doi:10.1371/journal.pone.0075932 PMID:24098746

Gust, S. (1997). Combustion experiences of flash pyrolysis fuel in intermediate size boiler. In: A. V. Bridgwater, & D. G. B. Boocock (Eds), Thermochemical Biomass Conversion (pp. 481-488). London.England: Blackie academic & Professional. doi:10.1007/978-94-009-1559-6_37

Hammond, J., Shackley, S., Sohi, S., & Brownsort, P. (2011). Prospective life cycle carbon abatement for pyrolysis biochar systems in the UK. *Energy Policy*, *39*(5), 2646–2655. doi:10.1016/j.enpol.2011.02.033

Hsu, D. D. (2011). Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing. Technical Report NREL/TP-6A20-49341. Retrieved from http://www.nrel.gov/docs/fy11osti/49341.pdf

Ibarrola, R., Shackley, S., & Hammond, J. (2012). Pyrolysis biochar systems for recovering biodegradable materials: A life cycle carbon assessment. *Waste Management (New York, N.Y.)*, *32*(5), 859–868. doi:10.1016/j.wasman.2011.10.005 PMID:22119050

International, S. R. I. (2007). *Hydrogen Production from Natural Gas. PEP Yearbook International Vol. IE, SRI International*. Menlo Park: Calofornia.

International Biochar Initiative-IBI. (2012a). *Biochar sustainability principles.* Retrieved from http://www.biochar-International.org/sites/default/files/IBI_Biochar_Sustainability_Principles _September_2012.pdf (Retrieved June 3rd, 2014).

International Biochar Initiative-IBI. (2012b). *Standardized product definition and product testing guidelines for biochar that is used in soil.* Retrieved from http://www.biochar-international.org/ sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf

International Biochar Initiative-IBI. (2013). *Biochar and sustainability.* Retrieved from http://www.biochar-international.org/sustainability

International Biochar Initiative-IBI. (2014a). *Guiding principles for a sustainable biochar industry*. Retrieved from http://www.biochar-international.org/sustainability

Iribarren, D., Peters, J. F., & Doufur, J. (2012). Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel*, *97*, 812–821. doi:10.1016/j.fuel.2012.02.053

Jones, S. B., Valkenburg, C., Walton, C. W., Elliott, D. C., Holladay, J. E., Stevens, D. J., Kinchin, C., & Czernik, S. (2009). *Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case*. Prepared for the US Department of Energy under Contract DE-AC05-76RL01830.

Klar, M., & Rule, A. (1925). The technology of wood distillation. London, England. Chapman & Hall, LTD.

Kuppens, T., Cornelissen, T., Carleer, R., Yperman, J., Schreurs, S., Jans, M., & Thewys, T. (2010). Economic assessment of flash co-pyrolysis of short rotation coppice and biopolymer waste streams. *Journal of Environmental Management*, *91*(12), 2736–2747. doi:10.1016/j.jenvman.2010.07.022 PMID:20724061

Laird, D. (2008). The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy Journal*, *100*(1), 178–181. doi:10.2134/agrojnl2007.0161

Li, X., Gunawan, R., Lievens, C., Wang, Y., Mourant, D., Wang, Sh., & Li, C. Z. et al. (2011). Simultaneous catalytic esterification of carboxylic acidas and acetalisation of aldehydes in a fast pyrolysis bio-oil from mallee biomass. *Fuel*, *90*(7), 2530–2537. doi:10.1016/j.fuel.2011.03.025

Lian, J., Chen, S., Zhou, Z., Wang, Z., O'Fellon, J., Li, C. Z., & Garcia-Perez, M. (2010). Separation, hydrolysis and fermentation of pyrolytic sugars to produce ethanol and lipids. *Bioresource Technology*, *101*(24), 9688–9699. doi:10.1016/j.biortech.2010.07.071 PMID:20708928

Lippke, B., Puettmann, M. E., Johnson, L., Gustafson, R., Venditti, R., Steele, P., & Caputo, J. et al. (2012). Carbon emission reduction impacts from alternative biofuels. *Forest Products Journal*, *62*(4), 296–304. doi:10.13073/12-00021.1

Lippke, B., Wilson, J., Meil, J., & Taylor, A. (2010). Characterizing the importance of carbon stored in wood products. *Wood and Fiber Science*, *42*, 5–14.

Lovins, L. H. (2002). *Small is Profitable. The Hidden Economic Benefits of Making Electrical Resources the Right Size*. Snowmass, CO: Rocky Mountain Institute.

Lugato, M., Vaccari, F. P., Genesio, L., Baronti, S., Pozzi, A., Rack, M., & Miglietta, F. et al. (2013). An energy-biochar chain involving biomass gasification and rice cultivation in Northern Italy. *GCB Bioenergy*, *5*(2), 192–201. doi:10.1111/gcbb.12028

Marker, T., Petri, J., McCall, M., Mackowiak, D., Jerosky, B., Regan, B., . . . Shannard, D. (2005). Opportunities for Biorenewables in Oil Refineries. UOP Des Plaines, Illinois. Retrieved from http://www.osti.gov/energycitations/product. biblio.jsp?osti_id=861458

MBDC. 2010. Sustainable Business: Minimization vs. Optimization. Optimisation (p. 15). Charlottesville,-VA. Retrieved from http://www.globalcitizen.net/data/topic/knowledge/uploads/ 20110803114637705.pdf

McDonough, W., & Braungart, M. 2002. Beyond the Triple Bottom Line: Design for the Triple Top Line. http://www.mcdonough.com/writings/beyond_triple.htm (Retrieved June 3rd, 2014).

Medrano, J. A., Oliva, M., Ruiz, J., Garcia, L., & Arauzo, J. (2011). Hydrogen from aqueous fraction of biomass pyrolysis liquids by catalytic steam reforming in fluidized bed. *Energy*, *36*(4), 2215–2224. doi:10.1016/j.energy.2010.03.059

Mesa-Pérez, J. M., Rocha, J. D., Barbosa-Cortez, L. A., Penedo-Medina, M., Luengo, C. A., & Cascarosa, E. (2013). Fast oxidative pyrolysis of sugar cane straw in a fluidized bed reactor. *Applied Thermal Engineering*, *56*(1-2), 167–175. doi:10.1016/j.applthermaleng.2013.03.017

Mohan, D., Pittman, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy & Fuels*, *20*(3), 848–889. doi:10.1021/ef0502397

Mullaney, H., Farag, I., LaClaire, C., Batter, C., & Hall, K. (2002). Technical, environmental and economic feasibility of bio-oil in New Hampshire's north country. Retrieved from http://www.unh.edu/p2/ biooil/bounhif.pdf

Naimi, L. J., Sokhansanj, S., Mani, S., Hoque, M., Bi, T., Womac, A. R., & Narayan, S. (2006). Cost and performance of woody biomass size reduction for energy production. Annual Conference of CSBE/SCGA. Edmonton, Alberta, July 16-19.

Oasmaa, A., Kyto, M., & Silipa, K. (2001). Pyrolysis oil combustion test in an industrial boiler. in: proceedings in thermochemical biomass conversion. In A. V. Bridgwater (Ed.), *Progress in thermochemical biomass conversion* (pp. 1468–1481). Oxford, England: Blackwell Sciences. doi:10.1002/9780470694954.ch121

Olson, E. S., & Freel, B. (2007). Process for converting anhydrosugars to glucose and other fermentable sugars. US Patent Application 20070125369

Ormrod, D., & Webster, A. 2000. Progression in Utilization of Bio-oils in Diesel Engines. PyNe Newsletter, 10, 15.http://www.pyne.co.uk/Resources/user/PyNews%20 10.pdf

Patel, M., Crack, M., Dornburg, V., Hermann, B., Roes, L., Husing, B., & Recchia, E. et al. (2006). *Medium and long term opportunity and risks of biotechnological production of bulk chemicals from renewable resourses - The potential of white biotechnology. Final Report, prepared under the European Commission's GROWTH Programme*. Utrecht: DG Research.

Pelaez-Samaniego, M. R., Garcia-Perez, M., Cortez, L. B., Rosillo-Calle, F., & Mesa, J. (2008). Improvements of brazilian carbonization industry as part of the creation of a global biomass economy. *Renewable & Sustainable Energy Reviews*, *12*(4), 1063–1086. doi:10.1016/j.rser.2006.10.018

Perlack, R. D., & Hess, J. R. (2006). Biomass resources for liquid fuels production. *Proceedings of 28th. Symposium of Biotechnology for Fuels and Chemicals*. Nashville, TN.

Phillips, S., Adem, A., Jechura, J., Dayton, D., & Eggman, T. (2007). Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass. NREL/TP-510-41168. Retrieved from http://www.nrel.gov/docs/fy07osti/41168.pdf

PRWeb. (2014). Global activated carbon market to reach 2.3 million metric tons by 2017. Retrieved from http://www.prweb.com/releases/activated_carbon/water_treatment/prweb8286149.htm

Radlein, D. (1999). The production of chemicals from fast pyrolysis bio-oils. In A. Bridgwater, S. Czernik, J. Diebold, D. Meier, A. Oasmaa, C. Peacocke, & D. Radlein et al. (Eds.), *Fast pyrolysis of biomass: A handbook* (pp. 164–188). Newbury, UK: CPL Press.

Radlein, D. (2005). Chemicals and materials from bio-oil. Retrieved from http://www.pyne.co.uk/ Resources/user/PYNE%20Newsletters/Pynews%2005.pdf

Resasco, D. E., Sooknoi, T., Zhu, X., Huang, T., Lobban, L., & Mallinson, R. G. Catalytic conversion of small oxygenates from bio-oil to alkyloaromatics on zeolite. School of Chemical, Biological and Materials Engineering and Center for Biomass Refining, University of Oklahoma (2010).

Ringer, M., Putsche, V., & Scahill, J. (2006). Large-scale pyrolysis oil production: a technology assessment and economic analysis. Technical Report NREL/TP-510-37779. NREL, Golden, CO.

Rogers, J. G., & Brammer, J. G. (2012). Estimation of the Production cost of fast pyrolysis bio-oil. *Biomass and Bioenergy*, *36*, 209–217. doi:10.1016/j.biombioe.2011.10.028

Roy, C., & Morin, D. (1999). Efficient electricity production from biomass through ipcc power plants. *Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies*. Interlaken, Switzerland, Aug. 20-Sept. 2. Eds. B Eliasson, P Riemer, & A Wokaun, Pergamon, p. 729-734 doi:10.1016/B978-008043018-8/50115-6

Rozario, M., & Melssen, B. (2013). National Biomass Strategy 2020 : New wealth creation for Malaysia's biomass industry (p. 37). Retrieved from http://www.cmtevents.com/MediaLibrary/BStgy2013Rpt AIM.pdf

Salvi, G. &Salvi G Jr. (1991). Pyrolytic products assessment study. Report from Commission of European Community, Contract No. EN3B-0191-1 (CH).

Schmidt, H. P. (2012). 55 Uses of Biochar. *Ithaka Journal*, *1*, 286–289.

Scholz, S. B., Sembres, T., Roberts, K., Whitman, T., Wilson, K., & Lehmann, J. (2014). *Biochar systems for smallholders in developing countries: leveraging current knowledge and exploring future potential for climate-smart agriculture*. World Bank Publications; doi:10.1596/978-0-8213-9525-7

Shen, J., Wang, X. S., Garcia-Perez, M., Mourant, D., Rhodes, M., & Li, C. Z. (2009). Effect of particle size on the fast pyrolysis of oil mallee woody biomass. *Fuel*, *88*(10), 1810–1817. doi:10.1016/j.fuel.2009.05.001

Siemons, R. V. (2002). *A Development Perspective for Biomass-fuelled Electricity Generation Technologies e Economic Technology Assessment in View of Sustainability*. Amsterdam: Universiteit van Amsterdam.

Simmons, F. C. (1957). Guides to manufacturing and marketing charcoal in the northwestern states. USDA Forest Service Station Paper No. 95, Upper Darby, PA. Retrieved from http://web1.cnre.vt.edu/ forestry/ charcoal/documents/sp_ne05%20 reduced.pdf

Solanstausta, Y., Oasmaa, A., Sipila, K., Lindfors, C., Lehto, J., Autio, J., & Heiskanen, J. et al. (2012). Bio-oil production from biomass: Steps toward demonstration. *Energy & Fuels*, *26*(1), 233–240. doi:10.1021/ef201109t

Sparrevik, M., Field, J. L., Martinsen, V., Breedveld, G. D., & Cornelissen, G. (2013). Life cycle assessment to evaluate the environmental impact of biochar implementation in conservation agriculture in Zambia. *Environmental Science & Technology*, *47*, 1206–1215. PMID:23272937

Spath, P., Aden, A., Eggeman, T., Ringer, M., Wallace, B., & Jechure, J. (2005). Biomass to hydrogen production detailed design and economics utilizing the battelle columbus laboratory indirectly – heated gasifier. Technical Report NREL/TP-510-37408. Retrieved from http://www.nrel.gov/docs/ fy05osti/37408.pdf

US Department of Energy-DOE. (2010). Biomass multi-year program plan. Retrieved from http://www1.eere.energy.gov/ biomass/pdfs/biomass_mypp_november2010.pdf

US Environmental Protection Agency-EPA. (2007). Biomass Combined Heat and Power Catalog of Technologies. Retrieved from http://www.epa.gov/chp/documents/biomass_chp_catalog.pdf (November 1st, 2014).

Van Rossum, G., Kersten, S. R. A., & Van Swaaij, W. P. M. (2007). Catalytic and noncatalytic gasification of pyrolysis oil. *Industrial & Engineering Chemistry Research*, *46*(12), 3959–3967. doi:10.1021/ie061337y

Vitasari, C. R., de Haan, A. B., & Meindersma, G. W. (2010). Conceptual process-design of glycoaldehyde isolation from pyrolysis oil via physical extraction route. Eindhoven University of Technology. Netherlands. Retrieved from www.biocoup.com/fileadmin/user/december/00_64_TUE_ March 10.pdf (November 1st, 2014).

Wang, Z., Dunn, J. B., Han, J., & Wang, M. Q. (2014). Effects of co-produced biochar on life cycle greenhouse gas emissions of pyrolysis-derived renewable fuels. *Biofuels. Bioproducts and Biorefining*, *8*(2), 189–204. doi:10.1002/bbb.1447

Weisberg, P., Delaney, M., & Hawkes, J. (2010).Carbon market investment criteria for biochar projects. Public Interest Energy Research (PIER) Program. Retrieved from http://www.biochar-international. org/sites/default/files/WestCARB%20Biochar%20Report%20Final.pdf

Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J., & Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nature Communications*, *1*(5), 1–9. doi:10.1038/ncomms1053 PMID:20975722

Wright, M. M., Satrio, J. A., Brown, R. C., Daugaard, D. E., & Hsu, D. D. (2010). Technoeconomic analysis of biomass fast pyrolysis to transportation fuels. Technical Report NREL/TP-6A20-465886. Retreived from http://www.nrel.gov/docs/fy11osti/46586.pdf

Yu, Y., & Wu, H. (2010). Bioslurry as a fuel 2: Life-Cycle energy and carbon footprints of bioslurry fuels from malee biomass in Western Australia. *Energy & Fuels*, *24*(10), 5660–5668. doi:10.1021/ef100957a

Zhang, Y., Hu, G., & Brown, R. C. (2013). Life cycle assessment of the production of hydrogen and transportation fuels from corn stover via fast pyrolysis. *Environmental Research Letters*, *8*(2), 025001. doi:10.1088/1748-9326/8/2/025001

ADDITIONAL READING

Garcia-Perez, M., Garcia-Nunez, J. A., Lewis, T., Kruger, C., Fuchs, M. R., Flora, G., . . . Kantor, S. (2013). Methods for Producing Biochar and Advanced Biofuels in Washington State. Part 4: Literature Review. Sustainability Issues, Business Models and Financial Analysis. Retrieved from http://www.pacificbiomass.org/documents/Biochar%20Economics.pdf

Garcia-Perez, M., Kruger, C., Sokhansanj, S., Badger, P. C., Garcia-Nunez, J. A., Lewis, T., & Kantor, S. (2011). Methods for producing biochar and advanced biofuels in Washington state. Part 2: Literature review of biomass supply chain and processing technologies (from field to pyrolysis reactor). Retrieved from https://fortress.wa.gov/ecy/publications/publications/1207033.pdf

Garcia-Perez, M., Lewis, T., & Kruger, C. E. (2011). Methods for producing biochar and advanced biofuels in washington state. part 1: literature review of pyrolysis reactors. Ecology Publication Number 11-07-017. Retrieved from http://www.ecy.wa.gov/pubs/1107017.pdf

KEY TERMS AND DEFINITIONS

Combined Heat and Power: This term refers to the simultaneous generation of electricity and heat in a thermochemical system.

Greenhouse Gases: This term is used to describe a gas in an atmosphere that absorbs and emits radiation within the infrared range. The presence of these gases in the atmosphere is the main cause of global warming.

International Biochar Initiative: It is an initiative that brings together leaders in Biochar research, advocacy and technology to catalyze the implementation of biochar application as a soil amendment to fight global warming.

Compilation of References

Abbasi, T., & Abbasi, S. A. (2010). Biomass energy and the environmental impacts associated with its production and utilization. *Renewable & Sustainable Energy Reviews*, *14*(3), 919–937. doi:10.1016/j.rser.2009.11.006

Abdullah, M. Z., Hussain, Z., & Yin Pong, S. L. (2003). Analyses of cold flow fluidization test results for various biomass fuels. *Biomass and Energy*, *24*(6), 487–494. doi:10.1016/S0961-9534(02)00150-2

Aboulkas, A., & El Harfi, K. (2008). Study of the Kinetics and Mechanisms of Thermal Decomposition of Moroccan Tarfaya Oil Shale and Its Kerogen. *Oil Shale*, *25*(4), 426–443. doi:10.3176/oil.2008.4.04

Abril, D., Medina, M., & Abril, A. (2012). Sugar cane bagasse prehydrolysis using hot water. *Brazilian Journal of Chemical Engineering*, *29*(1), 31–38. doi:10.1590/S0104-66322012000100004

Abuadala, a., Dincer, I., & Naterer, G. F. (2010). Exergy analysis of hydrogen production from biomass gasification. *International Journal of Hydrogen Energy, 35*(10), 4981–4990. doi:10.1016/j.ijhydene.2009.08.025

Adapa, P. K., Tabil, L. G., & Schoenau, G. J. (2010). Compression characteristics of non-treated and steam-exploded barley, canola, oat and wheat straw grinds. *Applied Engineering in Agriculture*, *26*(4), 617–632.

Adapa, P., Tabil, L., & Schoenau, G. (2011). Grinding performance and physical properties of non-treated and steam exploded barley, canola, oat and wheat straw. *Biomass and Bioenergy*, *35*(1), 549–561. doi:10.1016/j.biombioe.2010.10.004

Adjaye, J. D., Sharma, R. K., & Bakhshi, N. N. (1992). Characterization and stability analysis of wood derived bio-oil. *Fuel Processing Technology*, *31*(3), 241–256. doi:10.1016/0378-3820(92)90023-J

Adnađević, B., Gigov, M., Sindjic, M., & Jovanović, J. (2008). Comparative study on isothermal kinetics of fullerol formation under conventional and microwave heating. *Chemical Engineering Journal*, *140*(1–3), 570–577. doi:10.1016/j.cej.2007.12.011

Adnadjevic, B. K., & Jovanovic, J. D. (2012). A comparative kinetics study on the isothermal heterogeneous acid-catalyzed hydrolysis of sucrose under conventional and microwave heating. *Journal of Molecular Catalysis A Chemical*, *356*(0), 70–77. doi:10.1016/j.molcata.2011.12.027

Adnadjević, B. K., & Jovanović, J. D. (2012). Kinetics of Isothermal Ethanol Adsorption onto a Carbon Molecular Sieve under Conventional and Microwave Heating. *Chemical Engineering & Technology*, *35*(4), 761–768. doi:10.1002/ceat.201100153

Aguilar, R., Ramírez, J. A., Garrote, G., & Vázquez, M. (2002). Kinetic study of the acid hydrolysis of sugar cane bagasse. *Journal of Food Engineering*, *55*(4), 309–318. doi:10.1016/S0260-8774(02)00106-1

Ahmed, A., Cateni, B. G., Huhnke, R. L., & Lewis, R. S. (2006). Effects of biomass-generated producer gas constituents on cell growth, product distribution and hydrogenase activity of Clostridium carboxidivorans P7T. *Biomass and Bioenergy*, *30*(7), 665–672. doi:10.1016/j.biombioe.2006.01.007

Ahmed, A., & Lewis, R. S. (2007). Fermentation of biomass-generated synthesis gas: Effects of nitric oxide. *Biotechnology and Bioengineering*, *97*(5), 1080–1086. doi:10.1002/bit.21305 PMID:17171719

Akay, G., & Jordan, C. A. (2011). Gasification of fuel cane bagasse in a downdraft gasifier: Influence of lignocellulosic composition and fuel particle size on syngas composition and yield. *Energy & Fuels*, *25*(5), 2274–2283. doi:10.1021/ef101494w

Alén, R., Kuoppala, E., & Oesch, P. (1996). Formation of the main degradation compound groups from wood and its components during pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *36*(2), 137–1148. doi:10.1016/0165-2370(96)00932-1

Alonso-Pippo, W., Luengo, C.A., Felfli, F. F., Garzone P., & Cornacchia, G. (2009). Energy recovery from sugarcane biomass residues: Challenges and opportunities of bio-oil production in the light of second generation biofuels. *Journal of Renewable and Sustainable Energy, 1,* 063-102. doi: 10.1063/1.3259170

Anca-Couce, A., Berger, A., & Zobel, N. (2014). How to determine consistent biomass pyrolysis kinetics in a parallel reaction scheme. *Fuel*, *123*, 230–240. doi:10.1016/j.fuel.2014.01.014

Andrel, H., Mory, A., & Zotter, T. (1999). Gasification of biomass and co-combustion of the gas in a pulverized-coal burner.*Proceeding of the 15th International Conference on Fluidized Bed Combustion*. Savannah, Georgia: ASME.

Andrews, R. G., Zukowski, S., & Patnaik, P. C. (1997). *Feasibility of firing an industrial ags turbine using a biomass derived fuel. Developments in thermochemical biomass conversion* (A. V. Bridgwater & D. G. B. Boocock, Eds.). London, England: Blackie Academic and Professional.

Anex, R. P., Lynd, L. R., Laser, M. S., Heggenstaller, A. H., & Liebman, M. (2007). Potential for enhanced nutrient cycling through coupling of agricultural and bioenergy systems. *Crop Science*, *47*(4), 1327–1335. doi:10.2135/cropsci2006.06.0406

Annan, K. A. (2002). A chance to secure our future. Joburg Summit. Retrived from http://www.thejakartapost.com /news/2002/05/30/joburg-summit-a-chance-secure-our-future.html

Annoussamy, M., Richard, G., & Guerif, J. (2000). Change in mechanical properties of wheat straw due to decomposition and moisture. *Applied Engineering in Agriculture*, *16*(6), 657–664. doi:10.13031/2013.5366

Antal, M. J., De Almeida, C., Sinha, S., & Mok, W. S. L. (1991). A New Technology for Manufacturing Charcoal from Biomass. In *Proceedings of the Energy from Biomass & Wastes,XV Conference*, Washington, D.C., USA.

Antares Group Inc. (2003). Assessment of power production at rural utilities using forest thinning and commercially available biomass power technologies. Prepared for the U.S. Department of Agriculture, U.S. Department of Energy and National Renewable Energy Laboratory. Golden, CO

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2012b). Syngas production from sugar cane bagasse in a circulating fluidized bed gasifier using Aspen PlusTM: Modelling and Simulation. In F. Ian David Lockhart Bogle and Michael (Ed.), Computer Aided Chemical Engineering (Vol. Volume 30, pp. 1093-1097): Elsevier.

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2012a). Simulation of the syngas production based on technologies removal of tar using Aspen PlusTM*International Symposium on Gasification and its Applications (ISGA-3)*. Vancouver.

Ardila, Y. C., Figueroa, J. E. J., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2014). Simulation of ethanol production via fermentation of the synthesis gas using Aspen PlusTM. *Chemical Engineering Transaction*, *37*, 637–642. doi:10.3303/CET1437107

Arredondo, V., Junior, O., & Medellin, S. (2009). Ethanol production from banana fruit and its lignocellulosic residues: Exergy and renewability analysis*. *International Journal of Thermodynamics*, *12*(3), 155–162.

Arsène, M.-A., Bilba, K., Savastano Junior, H., & Ghavami, K. (2013). Treatments of non-wood plant fibres used as reinforcement in composite materials. *Materials Research*, *16*(4), 903–923. doi:10.1590/S1516-14392013005000084

Arthur, J. F., Kepner, R. A., Dobie, J. B., Miller, G. E. & Parsons, P. S. (1982). Tub grinder performance with crop and forest residues. *Transactions of the ASABE, 25*(6), 1488-1494. doi:.3375110.13031/2013

Assessment, M. E. (2005). Ecosystems and human well-being: synthesis. Washington, DC: Island Press; Retrieved from http://www.millenniumassessment.org/documents/document.356.aspx.pdf, Retrieved June 9th 2014.

AtKisson, A. (2001). *Sustainability is dead–long live sustainability. A manifesto: written to mark the end of millennium two, and the beginning of millennium three*. Retrieved from http://www.rrcap.unep. org /uneptg06/course/Robert/SustainabilityManifesto2001.pdf

Ayllón, M., Aznar, M., Sánchez, J. L., Gea, G., & Arauzo, J. (2006). Influence of temperature and heating rate on the fixed bed pyrolysis of meat and bone meal. *Chemical Engineering Journal*, *121*(2-3), 85–96. doi:10.1016/j.cej.2006.04.013

Aznar, M. P., Garcia-Gorria, F. A., & Corella, J. (1992a). Minimum and maximum velocities for fluidization for mixtures of agricultural and forest residues with a second fluidized solid. I. Preliminary data and results with sand-sawdust mixtures. *International Chemical Engineering*, *32*(1), 95–102.

Aznar, M. P., Garcia-Gorria, F. A., & Corella, J. (1992b). Minimum and maximum velocities for fluidization for mixtures of agricultural and forest residues with a second fluidized solid. II. Experimental results for different mixtures. *International Chemical Engineering*, *32*(1), 103–113.

Bacon, D. W., Downie, J., Hsu, J. C., & Peters, J. (1985). Modelling of fluidized bed wood gasifiers. In R. P. Overend, T. A. Milne, & L. K. Mudge (Eds.), *Fundamentals of thermochemical biomass conversion* (pp. 717–732). London, New York: Elsevier Applied Science Publishers. doi:10.1007/978-94-009-4932-4_37

Badger, P. C. (2002). Processing cost analysis for biomass feedstock. preopared for the us department of energy. Under contract DE-AC05-00OR22725. *ORNL. U. S. Atomic Energy Commission*, *TM-2002*(199).

Badger, P., Badger, S., Puettmann, M., Steele, P. H., & Cooper, J. (2011). Technoeconomic analysis: Preliminary assessment of pyrolysis oil production costs and material energy balance associated with a transportable fast pyrolysis system. *BioResources*, *6*(1), 34–47.

Baker, E. G., & Elliott, D. C. (1993). Method of upgrading oils containing hydroxyaromatic hydrocarbons compounds to highly aromatic gasoline. US Patent Number 5, 1800, 868, Issue January 19.

Balan, V., Chiaramonti, D., & Kumar, S. (2013). Review of US and EU initiatives toward development, demonstration, and commercialization of lignocellulosic biofuels. *Biofuels. Bioproducts and Biorefining*, *7*(6), 760–760. doi:10.1002/bbb.1452

Balat, M., & Balat, H. (2009). Recent trends in global production and utilization of bio-ethanol fuel. *Applied Energy*, *86*(11), 2273–2282. doi:10.1016/j.apenergy.2009.03.015

Baleato, F. Z. (1986). *Analyse des phénomènes de mélange et de ségrégation de deux populations différentes de particules solides dans un lit fluidisé par un gaz* (Unpublished Doctoral Dissertation). National Polytechnic Institute of Toulouse, Toulouse, FR.

Baranick, M., McElwee, D., & Zazycki, M. (2011). Biochar feasility study: exploring the environmental, social, and economic value of a biochar business in the methow valley. MKTG 591: Sustainable Business Practicum, June 9, Seattle University. Retrieved from http://www.biochar-international.org/ sites/default/files/Biochar_Final_Paper_For_Distribution_v9.29.pdf

Barrio, M. (2002). *Experimental investigations of small-scale gasification of woody biomass*. (Doctoral dissertation). The Norwegian University of Science and technology.

Basu Paudel, B. E. (2011). *Experimental Study on Fluidization of Biomass, Inert Particles, and Biomass/Sand Mixtures*. (Master's thesis, University of North Texas, Denton, USA). Retrieved from http://digital.library.unt.edu/ark:/67531/metadc84265/

Basu, P. (2010). *Biomass gasification and pyrolysis - Practical design and theory*. Burlington, MA: Academic Press.

Basu, P. (2010). *Biomass Gasification and Pyrolysis Practical Design and Theory. Elsevier* (pp. 1–364). Kidlington, Oxford: Academic Press.

Basu, P. (2013). *Biomass gasification, pyrolysis and torrefaction - Practical design and theory* (2nd ed.). San Diego, California: Academic Press.

Becidan, M., Várhegyi, G., Hustad, J. E., & Skreiberg, Ø. (2007). Thermal decomposition of biomass wastes. A kinetic study. *Industrial & Engineering Chemistry Research*, *46*(8), 2428–2437. doi:10.1021/ie061468z

Beckman, D., Elliott, D. C., Gevert, B., Hornell, C., Kjellstrom, B., Ostman, A., & Solantausta, V. (1990). *Techno-economic assessment of selected biomass liquefaction processes. Research Report 697*. VTT Technical Research Center of Finland.

Bergman, P. C. A., van Paasen, S. V. B., & Boerrigter, H. (2002). The novel OLGA technology for complete tar removal from biomass producer gas. In *Proceedings of Pyrolysis and Gasification of biomass and waste*, Expert Meeting, Strasbourg, France.

Bian, J., Peng, P., Peng, F., Xiao, X., Xu, F., & Sun, R.-C. (2014). Microwave-assisted acid hydrolysis to produce xylooligosaccharides from sugarcane bagasse hemicelluloses. *Food Chemistry*, *156*(0), 7–13. doi:10.1016/j.foodchem.2014.01.112 PMID:24629931

Biederman, L. A., & Harpole, W. S. (2013). Biochar and its effects on plant productivity and nutrient cycling: A meta-analysis. *GCB Bioenergy*, *5*(2), 202–214. doi:10.1111/gcbb.12037

Bilbao, R., Lezaun, J., & Abanades, C. (1987). Fluidization velocities of sand/straw binary mixtures. *Powder Technology*, *52*(1), 1–6. doi:10.1016/0032-5910(87)80001-3

Biswas, A. K., Umeki, K., Yang, W., & Blasiak, W. (2011a). Change of pyrolysis characteristics and structure of woody biomass due to steam explosion pretreatment. *Fuel Processing Technology*, *92*(10), 1849–1854.

Biswas, A. K., Yang, W., & Blasiak, W. (2011b). Steam pretreatment of Salix to upgrade biomass fuel for wood pellet production. *Fuel Processing Technology*, *92*(9), 1711–1717. doi:10.1016/j.fuproc.2011.04.017

Biswas, R., Uellendahl, H., & Ahring, B. K. (2014). Wet explosion pretreatment of sugarcane bagasse for enhanced enzymatic hydrolysis. *Biomass and Bioenergy*, *61*(0), 104–113. doi:10.1016/j.biombioe.2013.11.027

Bitra, V. S. P., Womac, A. R., Chevanan, N., Miu, P. I., Igathinathane, C., Sokhansanj, S., & Smith, D. R. (2009). Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions. *Powder Technology*, *193*(1), 32–45. doi:10.1016/j.powtec.2009.02.010

BNDES, B., & CGEE, C. (2008). *Sugarcane-Based Bioethanol: Energy for sustainable development*. Brazil, Rio de Janeiro-RJ: Coordination BNDES and CGEE.

Booker, C. J., Bedmutha, R., Vogel, T., Gloor, A., Xu, R., Ferrante, L., & Briens, C. et al. (2010). Experimental investigations into the insecticidal, fungicidal and bactericidal properties of pyrolysis bio-oil from tabacco leaves using a fluidized bed pilot plant. *Industrial & Engineering Chemistry Research*, *49*(20), 10074–10079. doi:10.1021/ie100329z

Borges, F. C., Du, Z., Xie, Q., Trierweiler, J. O., Cheng, Y., Wan, Y., & Ruan, R. (2014). Fast microwave assisted pyrolysis of biomass using microwave absorbent. *Bioresource Technology*, *156*(0), 267–274. doi:10.1016/j.biortech.2014.01.038 PMID:24518438

Bourgeois, J. P. (1984). Torrefied wood from temperate and tropical species, advantages and prospects. In: Egneus, & Ellegard (Eds.), Bioenergy 84, v.III, 153-159. London.

Boussarsar, H., Rogé, B., & Mathlouthi, M. (2009). Optimization of sugarcane bagasse conversion by hydrothermal treatment for the recovery of xylose. *Bioresource Technology*, *100*(24), 6537–6542. doi:10.1016/j.biortech.2009.07.019 PMID:19664914

Bradbury, A. G. W., Sakai, Y., & Shafizadeh, F. (1979). A kinetic model for pyrolysis of cellulose. *Journal of Applied Polymer Science*, *23*(11), 3271–3280. doi:10.1002/app.1979.070231112

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (1997). Use of amino phase adsorbent for biomass tar sampling and separation. *Fuel*, *76*(2), 137–142. doi:10.1016/S0016-2361(96)00199-8

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (2000). Tar evolution profiles obtained from gasification of biomass and coal. *Biomass and Bioenergy*, *18*(1), 87–91. doi:10.1016/S0961-9534(99)00069-0

Brage, C., Yu, Q., Chen, G., & Sjostrom, K. (2007). A new method for the analysis of heavy tar in raw producer gases from biomass gasifiers. In *Proceedings of 15th European Biomass Conference & Exhibition*, p. 1221-1223. Berlin.

Brammer, J. G., Bridgwater, A. V., Lauer, M., & Jungmeier, G. (2005). Opportunities for bio-oil in european heat and power markets. In A. V. Bridgwater (Ed.), *Fast pyrolysis of biomass: a handbook, 3* (pp. 179–204). Newbury: CPL Press.

Branca, C., & Di Blasi, C. (2013). Char structure and combustion kinetics of a phenolic-impregnated honeycomb material. *Industrial & Engineering Chemistry Research*, *52*(41), 14574–14582. doi:10.1021/ie402470z

Braun, R. L., Burnham, A. K., Reynolds, J. G., & Clarkson, J. E. (1991). Pyrolysis kinetics for lacustrine and marine source rocks by programmed micropyrolysis. *Energy & Fuels*, *5*(1), 192–204. doi:10.1021/ef00025a033

Brazilian Energy Balance Year 2013. (2014). Retrieved from https://ben.epe.gov.br/downloads/S%C3% ADntese%20do%20Relat%C3%B3rio%20Final_2014_Web.pdf

Bridgwater, A. V. (1999). Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of Analytical and Applied Pyrolysis*, *51*(1-2), 3–22. doi:10.1016/S0165-2370(99)00005-4

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, *38*, 68–94. doi:10.1016/j.biombioe.2011.01.048

Bridgwater, A. V., Meier, D., & Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, *30*(12), 1479–1493. doi:10.1016/S0146-6380(99)00120-5

Bridgwater, A. V., Toft, A. J., & Brammer, J. G. (2002). A Technoeconomic comparison of power production by biomass fast pyrolysis with gasification and combustion. *Renewable & Sustainable Energy Reviews*, *6*(5), 181–248. doi:10.1016/S1364-0321(01)00010-7

Broido, A. (1976). Kinetics of solid-phase cellulose pyrolysis. In F. Shafizadeh, K. V. Sarkanen, & D. A. Tillman (Eds.), *Thermal uses and properties of carbohydrates and lignins* (pp. 19–36). New York: Academic Press. doi:10.1016/B978-0-12-637750-7.50006-6

Brown, N. C. (1917). *The Hardwood distillation Industry in New York. Technical Publications No. 5, 17(1).* The New York State College of Forestry at Syracuse University.

Budarin, V. L., Clark, J. H., Lanigan, B. A., Shuttleworth, P., Breeden, S. W., Wilson, A. J., & Ross, A. (2009). The preparation of high-grade bio-oils through the controlled, low temperature microwave activation of wheat straw. *Bioresource Technology*, *100*(23), 6064–6068. doi:10.1016/j.biortech.2009.06.068 PMID:19615895

Cai, J., Wu, W., Liu, R., & Huber, G. W. (2013). A distributed activation energy model for the pyrolysis of lignocellulosic biomass. *Green Chemistry*, *15*(5), 1331–1340. doi:10.1039/c3gc36958g

Campañone, L. A., & Zaritzky, N. E. (2005). Mathematical analysis of microwave heating process. *Journal of Food Engineering*, *69*(3), 359–368. doi:10.1016/j.jfoodeng.2004.08.027

Campoy, M., Go, A., Villanueva, A. L., & Ollero, P. (2008). Air - Steam Gasification of Biomass in a Fluidized Bed under Simulated Autothermal and Adiabatic Conditions. *Industrial & Engineering Chemistry Research*, *47*(16), 5957–5965. doi:10.1021/ie800220t

Cardona, C. A., Quintero, J. A., & Paz, I. C. (2010). Production of bioethanol from sugarcane bagasse: Status and perspectives. *Bioresource Technology*, *101*(13), 4754–4766. doi:10.1016/j.biortech.2009.10.097 PMID:19945863

Cardoso, C. R., Miranda, M. R., Santos, K. G., & Ataíde, C. H. (2011). Determination of kinetic parameters and analytical pyrolysis of tobacco waste and sorghum bagasse. *Journal of Analytical and Applied Pyrolysis*, *92*(2), 392–400. doi:10.1016/j.jaap.2011.07.013

Carmo, V. B. (2013). *Avaliação da eficiência energética renovável de biomassas alternativas para geração de eletricidade.* (Doctoral dissertation). University of Campinas, Campinas, Brazil. Retrieved from http://www.bibliotecadigital.unicamp.br/document/?code=000940097.

Case, S. D. C., McNamara, N. P., Reay, D. S., & Whitaker, J. (2014). Can biochar reduce soil greenhouse gas emissions from a Miscanthus bioenergy crop? *GCB Bioenergy*, *6*(1), 76–89. doi:10.1111/gcbb.12052

CEN (Ed.). (2005). Biomass Gasification — Tar and Particles in Product Gases — Sampling and Analysis CEN BT/TF 143 TC 143 WI CSC 03002.

Çengel, Y. A., & Boles, M. A. (2006). *Thermodynamics: an engineering approach.* Boston: McGraw Hill College.

Cerqueira, D. A., Rodrigues Filho, G., & Meireles, C. S. (2007). Optimization of sugarcane bagasse cellulose acetylation. *Carbohydrate Polymers*, *69*(3), 579–582. doi:10.1016/j.carbpol.2007.01.010

Ceylan, S., & Topçu, Y. (2014). Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresource Technology*, *156*, 182–188. doi:10.1016/j.biortech.2014.01.040 PMID:24508656

Chandel, A. K., Singh, O. V., Chandrasekhar, G., Rao, L. V., & Narasu, M. L. (2010). Key drivers influencing the commercialization of ethanol-based biorefineries. *Journal of Commercial Biotechnology*, *16*(3), 239–257. doi:10.1057/jcb.2010.5

Chandra Shekara, B. M., Jai Prakash, B. S., & Bhat, Y. S. (2012). Microwave-induced deactivation-free catalytic activity of BEA zeolite in acylation reactions. *Journal of Catalysis*, *290*(0), 101–107. doi:10.1016/j.jcat.2012.03.005

Chandrakant, T. (1997). *Biomass gasification. Technology and Utilization*. ARTES Institute, University of Flensburg, Flensburg, Germany. Retrieved from http://members.tripod.com/~cturare/bio.htm

Chang, C., Ma, X., & Cen, P. (2006). Kinetics of levulinic acid formation from glucose decomposition at high temperature. *Chinese Journal of Chemical Engineering*, *14*(5), 708–712. doi:10.1016/S1004-9541(06)60139-0

Chen, D., Zheng, Y., & Zhu, X. (2013). In-depth investigation on the pyrolysis kinetics of raw biomass. Part I: Kinetic analysis for the drying and devolatilization stages. *Bioresource Technology*, *131*, 40–46. doi:10.1016/j.biortech.2012.12.136 PMID:23340100

Chen, F., Wang, G., Shi, C., Zhang, Y., Zhang, L., Li, W., & Yang, F. (2013). Kinetics of glycolysis of poly(ethylene terephthalate) under microwave irradiation. *Journal of Applied Polymer Science*, *127*(4), 2809–2815. doi:10.1002/app.37608

Chen, H., Liu, N., & Fan, W. (2006). Two-step consecutive reaction model and kinetic parameters relevant to the decomposition of Chinese forest fuels. *Journal of Applied Polymer Science*, *102*(1), 571–576. doi:10.1002/app.24310

Chen, W.-H., Ye, S.-C., & Sheen, H.-K. (2012). Hydrolysis characteristics of sugarcane bagasse pretreated by dilute acid solution in a microwave irradiation environment. *Applied Energy*, *93*(0), 237–244. doi:10.1016/j.apenergy.2011.12.014

Chen, Y., Stevens, M. A., Zhu, Y., Holmes, J., Moxley, G., & Xu, H. (2012). Reducing acid in dilute acid pretreatment and the impact on enzymatic saccharification. *Journal of Industrial Microbiology & Biotechnology*, *39*(5), 691–700. doi:10.1007/s10295-011-1068-7 PMID:22167347

Cheung, S. W., & Anderson, B. C. (1996). Ethanol production from wastewater solids. *Water Environment and Technology*, *8*(5), 55–60.

Chiaramonti, D., Oasmaa, A., & Solantausta, Y. (2007). Power generation using fast pyrolysis liquids from biomass. *Renewable & Sustainable Energy Reviews*, *11*(6), 1056–1086. doi:10.1016/j.rser.2005.07.008

Chiba, S., Chiba, T., Nienow, A. W., & Kobayashi, H. (1979). The minimum fluidization velocity, bed expansion and pressure-drop profile of binary particle mixture. *Powder Technology*, *22*(2), 255–269. doi:10.1016/0032-5910(79)80031-5

Chiew, Y. L., & Shimada, S. (2013). Current state and environmental impact assessment for utilizing oil palm empty fruit bunches for fuel, fiber and fertilizer – A case study of Malaysia. *Biomass and Bioenergy*, *51*, 109–124. doi:10.1016/j.biombioe.2013.01.012

Chung , J. N. (2013). Grand challenges in bioenergy and biofuel research: engineering and technology development, environmental impact, and sustainability. *Frontiers Energy Research, 1*, 1-4. doi: 10.3389/fenrg.2013.00004

Coats, A. W., & Redfern, J. P. (1965). Kinetic parameters from thermogravimetric data. II. *Journal of Polymer Science. Part B: Polymer Letters*, *3*(11), 917–920. doi:10.1002/pol.1965.110031106

Cole Hill Associates. (2004). *Bio-oil Commercialization Plan*. Report prepared for the New Hampshire Office of Energy and Planning. Retrieved from http://www.nh.gov/oep/programs/energy/ documents/appendixanhbio-oilcommercializationplan.pdf

Collard, F. (2012).*Development of size reduction equations for calculating energy iput for grinding woody biomass with hammer mill. Internship Report*. Vancouver, Canada: Chemical and Biological Engineering Department. University of British Columbia.

Coll, R., Salvadó, J., Farriol, X., & Montané, D. (2001). Steam reforming model compounds of biomass gasification tars: Conversion at different operating conditions and tendency towards coke formation. *Fuel Processing Technology*, *74*(1), 19–31. doi:10.1016/S0378-3820(01)00214-4

Corella, J., Aznar, M.-P., Gil, J., & Caballero, M. A. (1999). Biomass gasification in fluidized bed: Where to locate the dolomite to improve gasification? *Energy & Fuels*, *13*(6), 1122–1127. doi:10.1021/ef990019r

Cortez, L. A. B., Lora, E. S., & Gómez, E. O. (2008). Caracterização da biomassa. In L. A. B. Cortez, E. E. S. Lora, & E. O. Gómez (Eds.), Biomassa para energia (pp. 31-60). Campinas, SP, Brazil: Unicamp.

Cortez, L. A. B., & Gómez, E. O. (1998). A method for exergy analysis of sugarcane bagasse boilers. *Brazilian Journal of Chemical Engineering*, *15*(1). doi:10.1590/S0104-66321998000100006

Coutinho, A. R., Rocha, J. D., & Lungo, C. A. (2000). Preparing and characterizing biocarbon electrodes. *Fuel Processing Technology*, *67*(2), 93–102. doi:10.1016/S0378-3820(00)00091-6

Cruz, F. E. (2010). *Produção de hidrogênio em refinarias de petróleo: avaliaçao exergética e custo de produção*. (Master dissertation). Universidade de São Paulo. Retrieved from http://www.teses.usp.br/teses/disponiveis/3/3150/tde-17082010-123008/pt-br.php

Cui, H., & Grace, J. R. (2007). Fluidization of biomass particles: A review of experimental multiphase flow aspects. *Chemical Engineering Science*, *62*(1-2), 45–55. doi:10.1016/j.ces.2006.08.006

Cutshall, J., Greene, D., Baker, S., & Mitchell, D. (2011). *Transpirational drying effects on energy and ash content from whole-tree chipping operations in a southern pine plantation. Paper presented at the 34th Council on Forest Engineering*. Quebec City, Canada.

Czernik, S., & Bridgwater, A. V. (2004). Overview of applications of biomass fast pyrolysis oils. *Energy & Fuels*, *18*(2), 590–598. doi:10.1021/ef034067u

Danish Technological Institute. (2012). *Guideline: Handling and Storage of Wood Pellets. Resultat Kontrakt Report*. Denmark: Taastrup.

Dantas, G. A., Legey, L. F. L., & Mazzone, A. (2013). Energy from sugarcane bagasse in Brazil: An assessment of the productivity and cost of different technological routes. *Renewable & Sustainable Energy Reviews*, *21*(0), 356–364. doi:10.1016/j.rser.2012.11.080

Dasari, R. K., & Berson, R. E. (2007). The effect of particle size on hydrolysis reaction rates and rheological properties in cellulosic slurries. *Applied Biochemistry and Biotechnology*, *136-140*(1-12), 289–299. doi:10.1007/s12010-007-9059-x PMID:18478396

de Andrade, R. R., Maugeri Filho, F., Maciel Filho, R., & da Costa, A. C. (2013). Kinetics of ethanol production from sugarcane bagasse enzymatic hydrolysate concentrated with molasses under cell recycle. *Bioresource Technology*, *130*(0), 351–359. doi:10.1016/j.biortech.2012.12.045 PMID:23313680

de Azevedo, A. L. (2013). *Análise exergética da produção de NH_3 via oxigaseificação de bagaço de cana*. (Master dissertation). Universidade Federal do Rio de Janeiro.

Demirbas, M. F., & Balat, M. (2007). Biomass pyrolysis for liquid fuels and chemicals: A review. *Journal of Scientific and Industrial Research*, *66*(10), 797–804.

Di Bari, I., Barisano, D., Cardinale, M., Matera, D., Nanna, F., & Viggiano, D. (2000). Air Gasification of Biomass in a Downdraft Fixed Bed: A Comparative Study of the Inorganic and Organic Products Distribution. *Energy & Fuels*, *14*(4), 889–898. doi:10.1021/ef990243g

Di Blasi, C. (2008). Modeling chemical and physical processes of wood and biomass pyrolysis. *Progress in Energy and Combustion Science*, *34*(1), 47–90. doi:10.1016/j.pecs.2006.12.001

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Cunha, M. P., Jesus, C. D. F., Rossell, C. E. V., & Bonomi, A. et al. (2012). Integrated versus stand-alone second generation ethanol production from sugarcane bagasse and trash. *Bioresource Technology*, *103*(1), 152–161. doi:10.1016/j.biortech.2011.09.120 PMID:22019267

Dias, M. O. S., Junqueira, T. L., Cavalett, O., Pavanello, L. G., Cunha, M. P., Jesus, C. D. F., & Bonomi, A. et al. (2013). Biorefineries for the production of first and second generation ethanol and electricity from sugarcane. *Applied Energy*, *109*(0), 72–78. doi:10.1016/j.apenergy.2013.03.081

Dias, M. O. S., Junqueira, T. L., Jesus, C. D. F., Rossell, C. E. V., Maciel Filho, R., & Bonomi, A. (2012). Improving bioethanol production – Comparison between extractive and low temperature fermentation. *Applied Energy*, *98*(0), 548–555. doi:10.1016/j.apenergy.2012.04.030

Dincer, I., & Rosen, M. A. (2013). *Exergy: energy, environment and sustainable development (Second.)*. San Diego: Elsevier Science.

Doat, J. (1985). CTFT Research into wood pyrolysis. In: *Proceedings of Symposium Forest Products Research International Achievements and the Future*, 12-24.

Dogan, H., & Hilmioglu, N. D. (2009). Dissolution of cellulose with NMMO by microwave heating. *Carbohydrate Polymers*, *75*(1), 90–94. doi:10.1016/j.carbpol.2008.06.014

Doherty, W., Reynolds, A., & Kennedy, D. (2009a). Computer simulation of a biomass gasification-solid oxide fuel cell power system using Aspen Plus. *Energy*, *35*(12), 4545–4555. doi:10.1016/j.energy.2010.04.051

Doherty, W., Reynolds, A., & Kennedy, D. (2009b). The effect of air preheating in a biomass CFB gasifier using ASPEN Plus simulation. *Biomass and Bioenergy*, *33*(9), 1158–1167. doi:10.1016/j.biombioe.2009.05.004

Domínguez, A., Menéndez, J. A., Fernández, Y., Pis, J. J., Nabais, J. M. V., Carrott, P. J. M., & Carrott, M. M. L. R. (2007). Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *Journal of Analytical and Applied Pyrolysis*, *79*(1–2), 128–135. doi:10.1016/j.jaap.2006.08.003

Donohoe, B. S., Decker, S. R., Tucker, M. P., Himmel, M. E., & Vinzant, T. B. (2008). Visualizing lignin coalescence and migration through maize cell walls following thermochemical pretreatement. *Biotechnology and Bioengineering*, *101*(5), 913–925. doi:10.1002/bit.21959 PMID:18781690

Doyle, C. D. (1961). Kinetic Analysis of Thermogravimetric Data. *Journal of Applied Polymer Science*, *5*(15), 285–292. doi:10.1002/app.1961.070051506

Dufour, A., Girods, P., Massonc, E., Normanda, S., Rogaumeb, Y., & Zoulalian, A. (2007). Comparison of two methods of measuring wood pyrolysis tar. *Journal of Chromatography. A*, *1164*(1-2), 240–247. doi:10.1016/j.chroma.2007.06.049 PMID:17628580

Durka, T., Van Gerven, T., & Stankiewicz, A. (2009). Microwaves in Heterogeneous Gas-Phase Catalysis: Experimental and Numerical Approaches. *Chemical Engineering & Technology*, *32*(9), 1301–1312. doi:10.1002/ceat.200900207

Dusan, S. (2011). *Black pellets verification programme*. Retrieved June 9, 2014, from http://www.solandersciencepark.se/sites/default/files/media/pdf_filer_sv/stefandusan.pdf

Dutta, B., & Raghavan, V. (2014). A life cycle assessment of environmental and economic balance of biochar systems in Quebec. *International Journal of Energy and Environmental Engineering*, *5*(2-3), 1–11. doi:10.1007/s40095-014-0106-4

Earle, R. L., & Earle, M. D. (1983). *Unit Operations in Food Processing*. NZIFST(Inc) The web Edition. Retrieved from http://www.nzifst.org.nz/unitoperations

Ebrahimi-Kahrizsangi, R., & Abbasi, M. H. (2008). Evaluation of reliability of Coats-Redfern method for kinetic analysis of non-isothermal TGA. *Transactions of Nonferrous Metals Society of China*, *18*(1), 217–221. doi:10.1016/S1003-6326(08)60039-4

Edmunds, C. W. (2012). Effects of biochar amendment in soil on bioenergy crop yield and biomass composition, MS Thesis, University of Tennesse, Knoxville.

Ekeh, O., Fangmeier, A., & Müller, J. (2014). Quantifying greenhouse gases from the production, transportation and utilization of charcoal in developing countries: A case study of Kampala, Uganda. *The International Journal of Life Cycle Assessment*, *19*(9), 1643–1652. doi:10.1007/s11367-014-0765-7

El harfi, K., Mokhlisse, A., Chanâa, M. B., & Outzourhit, A. (2000). Pyrolysis of the Moroccan (Tarfaya) oil shales under microwave irradiation. *Fuel, 79*(7), 733-742. doi: 10.1016/s0016-2361(99)00209-4

Elliott, D. C., & Hart, T. R. (2009). Catalytic hydroprocessing of chemical models for bio-oil. *Energy & Fuels*, *23*(2), 631–637. doi:10.1021/ef8007773

Emrich, W. (1985). *Handbook of Charcoal Making: The traditional and industrial methods*. Boston, MA: D. Reidel Publishing Company. doi:10.1007/978-94-017-0450-2

Ergun, S. (1952). Fluid flow through packed columns. *Chemical Engineering Progress*, *48*(2), 89–94.

Erlich, C., & Fransson, T. H. (2011). Downdraft gasification of pellets made of wood, palm oil residues respective bagasse: Experimental study. *Applied Energy*, *88*(3), 899–908. doi:10.1016/j.apenergy.2010.08.028

Esteban, L. S., & Carrasco, J. E. (2006). Evaluation of different strategies for pulverization of forest biomasses. *Powder Technology*, *166*(3), 139–151. doi:10.1016/j.powtec.2006.05.018

Falcon-Hernandez, J., & Carbonell, M. J. (2003). Fuel emulsions using biomass pyrolysis products as an emulsifier agent. *Energy & Fuels*, *17*(2), 302–307. doi:10.1021/ef020030i

FAOSTAT. (2014). Statistics on forestry production and trade. Retrieved from http://faostat3.fao.org/ faostat-gateway/go/to/download/F/FO/E

Farag, I. H., LaClair, C. E., & Barrett, C. (2002). Technical, environmental and economic feasibility of bio-oil in New Hampshire's north county. UNH Project Number 14B316 or ABAN-URI-B043.

Farag, S. (2013). *Production of chemicals by microwave thermal treatment of lignin* (Philosophiae Doctor), Montreal University, École Polytechnique de Montréal

Farag, S., & Chaouki, J. (2014). A Modified Microwave Thermogravimetric-Analyzer for Kinetic Purposes. *Applied Thermal Engineering*.

Farag, S., Fu, D., Jessop, P. G., & Chaouki, J. (2014). Detailed Compositional Analysis and Structural Investigation of a Bio-oil from Microwave Pyrolysis of Kraft Lignin. *Journal of Analytical and Applied Pyrolysis*, (0). doi:10.1016/j.jaap.2014.06.005

Farag, S., Kouisni, L., & Chaouki, J. (2014). Lumped Approach in Kinetic Modeling of Microwave Pyrolysis of Kraft Lignin. *Energy & Fuels*, *28*(2), 1406–1417. doi:10.1021/ef4023493

Farag, S., Sobhy, A., Akyel, C., Doucet, J., & Chaouki, J. (2012). Temperature profile prediction within selected materials heated by microwaves at 2.45GHz. *Applied Thermal Engineering*, *36*(0), 360–369. doi:10.1016/j.applthermaleng.2011.10.049

Felfli, F. F. (2003). *Torrefação de Biomassa, Viabilidade Técnica e Potencial de Mercado*. (Doctoral Thesis). Retrieved from Acervus Unicamp dissertations and Theses database. (vtls000321223)

Felfli, F. F., Luengo, C. A., Beaton, P., & Suarez, A. (1999). Efficiency test for bench unit torrefaction and characterization of torrefied biomass. In *Proceedings of the 4th Biomass Conference of Americas*, *1*, 589-592. California, USA.

Felfli, F. F., Luengo, C. A., Suarez, J. A., & Soler, B. (2005). Wood briquette torrefaction. *Energy Sustainable Development*, *9*(3), 19–22. doi:10.1016/S0973-0826(08)60519-0

Figueroa, J. E. J., Ardila, Y. C., Filho, R. M., & Maciel, M. R. W. (2014). Fluidized bed reactor for gasification of sugarcane bagasse: Distribution of syngas, bio-tar and char. *Chemical Engineering Transactions*, *37*, 229–234. doi:10.3303/CET1437039

Figueroa, J. E. J., Ardila, Y. C., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2013a). Evaluation of pyrolysis and steam gasification processes of sugarcane bagasse in a fixed bed reactor. *Chemical Engineering Transactions*, *32*, 925–930. doi:10.3303/CET1332155

Figueroa, J. E. J., Ardila, Y. C., Lunelli, B. H., Maciel Filho, R., & Wolf Maciel, M. R. (2013b). Evaluation of pyrolysis and steam gasification processes of sugarcane bagasse in a fixed bed reactor*AIDIC Conference Series*.

Fiori, L., Valbusa, M., Lorenzi, D., & Fambri, L. (2012). Modeling of the devolatilization kinetics during pyrolysis of grape residues. *Bioresource Technology, 103*(1), 389–397. doi:. 09.11310.1016/j.biortech.2011

FitzPatrick, M., Champagne, P., Cunningham, M. F., & Whitney, R. A. (2010). A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technology, 101*(23), 8915-8922. doi:. 2010.06.12510.1016/j.biortech

Flora, G. (2010a). The human dimension: building support for biomass to biochar projects. Retrieved from http://www.archive.biorenew.iastate.edu/events/biochar2010/conference-agenda/agenda-overview/creating-positive-communitysocial-impacts-with-biochar-projects.html

Flora, G. (2012). Biochar: The sustainability challenge. Retrieved from http://2012.biochar.us.com/382/biochar-sustainability-challenge

Flynn, J. H., & Wall, L. A. (1966). General Treatment of the Thermogravimetry of Polymers. *Journal of Research of the National Bureau of Standards*, *70*(6), 487–523. doi:10.6028/jres.070A.043

Formisani, B., Girimonte, R., & Longo, T. (2008). The fluidization process of binary mixtures of solids: Development of the approach based on the fluidization velocity interval. *Powder Technology*, *185*(2), 97–108. doi:10.1016/j.powtec.2007.10.003

Foust, A. S., Clump, C. W., & Wenzel, L. A. (1982). *Princípio das operações unitárias*. Rio de Janeiro, BR: Livros Técnicos e Científicos Press.

Freel, B. A., & Huffman, D. R. (1994). Applied Bio-oil Combustion.*Proceedings of the Workshop on Biomass Pyrolysis Oil Properties and Combustion*. Estes Park, CO. 1994, p. 309-315.

Freeman, M. C., O'Dowd, W. J., Brown, T. D., Hargis, R. A. Jr, James, R. A., Plasynski, S. I., & Battista, J. J. Jr et al.. (2000). Pilot-scale air toxics R&D assessment of creosote-treated and PCP-treated wood cofiring for pulverized coal utility boiler applications. *Biomass and Bioenergy*, *19*(6), 447–456. doi:10.1016/S0961-9534(00)00055-6

Friedman, H. L. (1964). Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *Journal of Polymer Science Part C: Polymer Symposia*, *6*(1), 183–195. doi:10.1002/polc.5070060121

Fukushima, J., Kashimura, K., Takayama, S., Sato, M., Sano, S., Hayashi, Y., & Takizawa, H. (2013). In-situ kinetic study on non-thermal reduction reaction of CuO during microwave heating. *Materials Letters*, *91*(0), 252–254. doi:10.1016/j.matlet.2012.09.114

Gaddy, J. L. (2000). US 6136577 United StatesMon Apr 09 07:57:11 EDT 2007CHO-English.

Gaggioli, R. A. (1980). Thermodynamics: second law analysis. In American chemical Society, Symposium Series (p. 52). Whashington, ACS Symposium Series. Retrieved from http://pubs.acs.org/isbn/9780841205413

Gaggioli, R. A., & Petit, P. J. (1977). Use the second law first. *Chemtech*, *7*, 496–506.

Galdamez, J. R., Garcia, L., & Bilbao, R. (2005). Hydrogen production by steam reforming of bio-oil using co-precipitated ni-al catalyst. Acetic acid as a model compound. *Energy & Fuels*, *19*(3), 1133–1142. doi:10.1021/ef049718g

Gámez, S., González-Cabriales, J. J., Ramírez, J. A., Garrote, G., & Vázquez, M. (2006). Study of the hydrolysis of sugar cane bagasse using phosphoric acid. *Journal of Food Engineering*, *74*(1), 78–88. doi:10.1016/j.jfoodeng.2005.02.005

Gao, Y., Xu, J., Zhang, Y., Yu, Q., Yuan, Z., & Liu, Y. (2013). Effects of different pretreatment methods on chemical composition of sugarcane bagasse and enzymatic hydrolysis. *Bioresource Technology*, *144*(0), 396–400. doi:10.1016/j.biortech.2013.06.036 PMID:23891836

Garcia-Nunez, J. A., Cardenas, M., & Yanez-Angarita, E. E. (2010). Generación y uso de biomasa en plantas de beneficio de palma de aceite en colombia. *Palmas*, *31*(2), 41–48.

Garcia-Perez, M., & Garcia-Nunez, J. A. (2013). Nuevos conceptos para biorrefinerías de aceite de palma (New Concepts of Palm Oil Mill Biorefineries). *Palmas, 34*(Especial, Tomo II), 66–84.

Garcia-Perez, M., Garcia-Nunez, J. A., Lewis, T., Kruger, C. E., & Kantor, S. (2011a). Methods for producing biochar and advanced biofuels in Washington state. Part 3: Literature review of technologies for product collection and refining. Retrieved from http://www.ecy.wa.gov/biblio/ 1207034.html

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., Rodrigue, D., & Roy, C. (2006). Multiphase Structure of Bio-oils. *Energy & Fuels*, *20*(1), 364–375. doi:10.1021/ef050248f

Garcia-Perez, M., Chaala, A., Pakdel, H., Kretschmer, D., & Roy, C. (2007). Characterization of bio-oils in chemical families. *Biomass and Bioenergy*, *31*(4), 222–242. doi:10.1016/j.biombioe.2006.02.006

Garcia-Perez, M., Shen, J., Wang, S. X., & Li, C. Z. (2010). Production and fuel properties of fast pyrolysis oil/biodiesel blends. *Fuel Processing Technology*, *91*(3), 296–305. doi:10.1016/j.fuproc.2009.10.012

Gauder, M., Graeff-Hönninger, S., & Claupein, W. (2011). The impact of a growing bioethanol industry on food production in Brazil. *Applied Energy*, *88*(3), 672–679. doi:10.1016/j.apenergy.2010.08.020

Geldart, D. (1973). Types of gas fluidization. *Powder Technology*, *7*(5), 285–292. doi:10.1016/0032-5910(73)80037-3

Gil, M., Gonzalez, A., & Gil, A. (2008). Evaluation of milling energy requirements of biomass residues in a semi-industrial pilot plant for co-firing. In *Proceedings of 16th European Biomass Conference and Exhibition*. Retrieved from: http://teide.cps.unizar.es:8080/pub/publicir.nsf/ codigospub/0497/$FILE/cp0497a.pdf

Glicksman, L. R. (1999). Fluidized bed scale-up. In W. C. Yang (Ed.), Fluidization solid handling and processing (1-42). Westwood, New Jersey, USA: Noyes Publications.

Gómez, E. (1996). *Projeto, construção e avaliação preliminar de um reator de leito fluidizado para gaseificação de bagaço de cana-de-açúcar.* (Master dissertation). Universidade Estadual de Campinas. Retrieved from Acervus Unicamp Dissertations and Theses Database. (D/UNICAMP OL4p)

Gómez, E. O., Mesa-Pérez, J. M., & Brossard-Perez, L. E. (2008). Pirólise rápida de materiais lignocelulósicos para a obtenção do bioóleo. In L. A. B. Cortez, E. O. Gómez, & E. E. S. Lora (Eds.), *Biomassa para energia* (pp. 395–396). Campinas, BR: University of Campinas Press.

Goossens, W. R. A., Dumont, G. L., & Spaepen, G. L. (1971). Fluidization of binary mixtures in the laminar flow region.*Chemical Engineering Progress Symposium Series*, *67*(116), 38–45.

Govin, A., Repellin, V., Rolland, M., & Duplan, J. (2009). Effect of torrefaction on grinding energy requirement for thin wood particle production. Presented at Nicolas Roche. *XII ° Congrès de la Société Française de Génie des Procédés Pour relever les défis industriels du XXI° siècle A la croisée des Sciences et des Cultures*, Marseille, France.

Gräbner, M., & Meyer, B. (2014). Performance and exergy analysis of the current developments in coal gasification technology. *Fuel*, *116*, 910–920. doi:10.1016/j.fuel.2013.02.045

Grace, J. R. (1982). Fluidized-bed hydrodynamics. In G. Hetsroni (Ed.). Handbook of multiphase systems (pp. 8: 5-64). Washington, US: Hemisphere Publishing.

Grant, D., Hess, R. J., Kenney, K., Laney, P., Muth, D., Pryfogle, P., & Wright, C. (2006). Feasibility of a producer owned ground straw feedstock supply system for ethanol and other products. Idaho National Laboratory. Prepared Under Contracts: DOE Office of Biomass DE-AC07-05ID145167, USDA Rural Business Cooperative Service producer Grant 12-034-82036979. Retrieved from http://www.inl.gov/ bioenergy/projects/d/1001_feasibility.pdf

Grønli, M. G., Várhegyi, G., & Di Blasi, C. (2002). Thermogravimetric analysis and devolatilization kinetics of wood. *Industrial & Engineering Chemistry Research*, *41*(17), 4201–4208. doi:10.1021/ie0201157

Guiotoku, M., Rambo, C. R., Hansel, F. A., Magalhães, W. L. E., & Hotza, D. (2009). Microwave-assisted hydrothermal carbonization of lignocellulosic materials. *Materials Letters*, *63*(30), 2707–2709. doi:10.1016/j.matlet.2009.09.049

Gulf Publishing Co. (2006). *Hydrocarbon processing: Refining processes*. Houston, Texas: Gulf Publishing Co.

Gunarathne, D. S., Mueller, A., Fleck, S., Kolb, T., Chmielewski, J. K., Yang, W., & Blasiak, W. (2014). Gasification characteristics of steam exploded biomass in an updraft pilot scale gasifier. *Energy*, *71*, 496–506. doi:10.1016/j.energy.2014.04.100

Güneş, M., & Güneş, S. (2002). A direct search method for determination of DAEM kinetic parameters from nonisothermal TGA data (note). *Applied Mathematics and Computation*, *130*(2-3), 619–628. doi:10.1016/S0096-3003(01)00124-2

Guo, W. (2013). *Self-heating and spontaneous combustion of wood pellets during storage*. (Doctoral dissertation). Available from The University of British Columbia, Vancouver.

Gupta, M., & Eugene, W. W. L. (2007). Microwaves and metals. Singapore: John Wiley & sons (Asia) Pte Ltd doi:10.1002/9780470822746

Gurgel, L. V. A., Marabezi, K., Zanbom, M. D., & Curvelo, A. A. S. (2011). Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic Study of cellulose saccharification and glucose decomposition. Part I: Sulfuric acid as the catalyst. *Industrial & Engineering Chemistry Research*, *51*(3), 1173–1185. doi:10.1021/ie2025739

Gurgel, L. V. A., Pimenta, M. T. B., & Curvelo, A. A. S. (2014). Enhancing liquid hot water (LHW) pretreatment of sugarcane bagasse by high pressure carbon dioxide (HP-CO2). *Industrial Crops and Products*, *57*(0), 141–149. doi:10.1016/j.indcrop.2014.03.034

Gurwick, N. P., Moore, L. A., Kelly, C., & Elias, P. (2013). A systematic review of biochar research, with a focus on its stability in situ and its promise as a climate mitigation strategy. *PLoS ONE*, *8*(9), 1–9. doi:10.1371/journal.pone.0075932 PMID:24098746

Gust, S. (1997). Combustion experiences of flash pyrolysis fuel in intermediate size boiler. In: A. V. Bridgwater, & D. G. B. Boocock (Eds), Thermochemical Biomass Conversion (pp. 481-488). London.England: Blackie academic & Professional. doi:10.1007/978-94-009-1559-6_37

Haider, A., & Levenspiel, O. (1989). Drag coefficient and terminal velocity of spherical and non-spherical particles. *Powder Technology*, *58*(1), 63–70. doi:10.1016/0032-5910(89)80008-7

Hakkila, P. (1989). *Utilization of residual forest biomass*. Heidelberg, Berlin: Springer-Verlag. doi:10.1007/978-3-642-74072-5

Hammond, J., Shackley, S., Sohi, S., & Brownsort, P. (2011). Prospective life cycle carbon abatement for pyrolysis biochar systems in the UK. *Energy Policy*, *39*(5), 2646–2655. doi:10.1016/j.enpol.2011.02.033

Haro, P., Ollero, P., Perales, Á. L. V., & Vidal-barrero, F. (2013). Potential routes for thermochemical biorefi neries, 551–572. doi:10.1002/bbb

Henstra, A. M., Sipma, J., Rinzema, A., & Stams, A. J. M. (2007). Microbiology of synthesis gas fermentation for biofuel production. *Current Opinion in Biotechnology*, *18*(3), 200–206. doi:10.1016/j.copbio.2007.03.008 PMID:17399976

Hepbasli, A. (2008). A key review on exergetic analysis and assessment of renewable energy resources for a sustainable future. *Renewable & Sustainable Energy Reviews*, *12*(3), 593–661. doi:10.1016/j.rser.2006.10.001

He, X., Lau, A. K., Sokhansanj, S., Lim, C. J., Bi, X. T., & Melin, S. (2014). Investigating gas emissions and dry matter loss from stored biomass residues. *Fuel*, *134*, 159–165. doi:10.1016/j.fuel.2014.05.061

Holtzapple, M. T., Humphrey, A. E., & Taylor, J. D. (1989). Energy requirements for the size reduction of Poplar and Aspen wood. *Biotechnology and Bioengineering*, *33*(2), 207–210. doi:10.1002/bit.260330210 PMID:18587902

Horn, S. J., Estevez, M. M., Nielsen, H. K., Linjordet, R., & Eijsink, V. G. H. (2011). Biogas production and saccharification of *Salix* pretreated at different steam explosion conditions. *Bioresource Technology*, *102*(17), 7932–7936. doi:10.1016/j.biortech.2011.06.042 PMID:21727002

Horowitz, H. H., & Metzger, G. (1963). A new analysis of thermogravimetric traces. *Analytical Chemistry*, *35*(10), 1464–1468. doi:10.1021/ac60203a013

Hsu, D. D. (2011). Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing. Technical Report NREL/TP-6A20-49341. Retrieved from http://www.nrel.gov/docs/fy11osti/49341.pdf

Huang, J., & Dincer, I. (2014). Parametric analysis and assessment of a coal gasification plant for hydrogen production. *International Journal of Hydrogen Energy*, *39*(7), 3294–3303. doi:10.1016/j.ijhydene.2013.12.054

Huang, J., Liu, C., Tong, H., Li, W., & Wu, D. (2014). A density functional theory study on formation mechanism of CO, CO_2 and CH_4 in pyrolysis of lignin. *Computational and Theoretical Chemistry*, *1045*, 1–9. doi:10.1016/j.comptc.2014.06.009

Huang, Y. F., Kuan, W. H., Lo, S. L., & Lin, C. F. (2010). Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. *Bioresource Technology*, *101*(6), 1968–1973. doi:10.1016/j.biortech.2009.09.073 PMID:19836946

Husain, Z., Zainac, Z., & Abdullah, Z. (2002). Briquetting of palm fibre and shell from the processing of palm nuts to palm oil. *Biomass and Bioenergy*, *22*(6), 505–509. doi:10.1016/S0961-9534(02)00022-3

Ibarrola, R., Shackley, S., & Hammond, J. (2012). Pyrolysis biochar systems for recovering biodegradable materials: A life cycle carbon assessment. *Waste Management (New York, N.Y.)*, *32*(5), 859–868. doi:10.1016/j.wasman.2011.10.005 PMID:22119050

IEA. (2014). *Key World Energy Statistics 2014*. Retrieved from http://www.iea.org/publications/freepublications/publication/KeyWorld2014.pdf

International Biochar Initiative-IBI. (2012a). Biochar sustainability principles. Retrieved from http://www.biochar-International.org/sites/default/files/IBI_Biochar_Sustainability_Principles _September_2012.pdf (Retrieved June 3rd, 2014).

International Biochar Initiative-IBI. (2012b). Standardized product definition and product testing guidelines for biochar that is used in soil. Retrieved from http://www.biochar-international.org/ sites/default/files/Guidelines_for_Biochar_That_Is_Used_in_Soil_Final.pdf

International Biochar Initiative-IBI. (2013). Biochar and sustainability. Retrieved from http://www.biochar-international.org/sustainability

International Biochar Initiative-IBI. (2014a). Guiding principles for a sustainable biochar industry. Retrieved from http://www.biochar-international.org/sustainability

International, S. R. I. (2007). *Hydrogen Production from Natural Gas. PEP Yearbook International Vol. IE, SRI International*. Menlo Park: Calofornia.

IPCC. (2001). *Summary for policymakers, concentrations of atmospheric greenhouse gases*. Retrieved June 10, 2014, from http://www.grida.no/climate/ipcc_tar/wg1/006.htm

Iribarren, D., Peters, J. F., & Doufur, J. (2012). Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel*, *97*, 812–821. doi:10.1016/j.fuel.2012.02.053

Iribarren, D., Susmozas, A., Petrakopoulou, F., & Dufour, J. (2014). Environmental and exergetic evaluation of hydrogen production via lignocellulosic biomass gasification. *Journal of Cleaner Production*, *69*, 165–175. doi:10.1016/j.jclepro.2014.01.068

Jones, S. B., Valkenburg, C., Walton, C. W., Elliott, D. C., Holladay, J. E., Stevens, D. J., Kinchin, C., & Czernik, S. (2009). Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case. Prepared for the US Department of Energy under Contract DE-AC05-76RL01830.

Jones, J. M., Kubacki, M., Kubica, K., Ross, A. B., & Williams, A. (2005). Devolatilisation characteristics of coal and biomass blends. *Journal of Analytical and Applied Pyrolysis*, *74*(1-2), 502–511. doi:10.1016/j.jaap.2004.11.018

Jönsson, L. J., Alriksson, B., & Nilvebrant, N.-O. (2013). Bioconversion of lignocellulose: inhibitors and detoxification. *Biotechnology for Biofuels, 6*(1), 16-. doi: 10.1186/1754-6834-6-16

Jordan, C. A., & Akay, G. (2012). Occurrence, composition and dew point of tars produced during gasification of fuel cane bagasse in a downdraft gasifier. *Biomass and Bioenergy*, *42*(0), 51–58. doi:10.1016/j.biombioe.2012.03.014

Jordan, P. D. (1992). *Class Notes of Macroscopic Thermodynamic, Draft 1, Part B. Department of Mechanical Engineering, Class Handbook*. Lubbock, Texas, USA: Texas Tech University.

Kajaste, R. (2014). Chemical from biomass-managing greenhouse gas emissions in biorefinery production chains-a review. *Journal of Cleaner Production*, *75*, 1–10. doi:10.1016/j.jclepro.2014.03.070

Kanaujia, P. K., Sharma, Y. K., Garg, M. O., Tripathi, D., & Singh, R. (2014). Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. *Journal of Analytical and Applied Pyrolysis*, *105*, 55–74. doi:10.1016/j.jaap.2013.10.004

Kang, Y., Bansal, P., Realff, M. J., & Bommarius, A. S. (2013). SO_2- catalyzed steam explosion: The effects of different severity on digestibility, accessibility, and crystallinity of lignocellulosic biomass. *Biotechnology Progress*, *29*(4), 909–916. doi:10.1002/btpr.1751 PMID:23749425

Karmakar, M. Kr, Haldar, S., & Chatterjee, P. Kr. (2013). Studies on fluidization behaviour of sand and biomass mixtures[Special issue]. *International Journal of Emerging Technology and Advanced Engineering*, *3*(3), 180–185.

Karthikeyan, S., Balasubramanian, R., & See, S. W. (2006). Optimization and validation of a low temperature microwave-assisted extraction method for analysis of polycyclic aromatic hydrocarbons in airborne particulate matter. *Talanta*, *69*(1), 79–86. doi:10.1016/j.talanta.2005.08.060 PMID:18970535

Kasim, N. B. (2009). *Separation technique of crude palm oil at clarification area via optimum parameters* (Bachelor of Chemical Engineering Thesis). Available from Universiti Malaysia Pahang, Malaysia.

Kemippainen, K., Inkinen, J., Uusitalo, J., Setala, T. N., & Siika-aho, M. (2012). Hot water extraction and steam explosion as pretreatments for ethanol production from spruce bark. *Bioresource Technology*, *117*, 131–139. doi:10.1016/j.biortech.2012.04.080 PMID:22613888

Kerdsuwan, S., & Laohalidanond, K. (2011). Renewable energy from palm oil empty fruit bunch. In M. Nayeripour & M. Kheshti (Eds.), *Renewable energy – trends and applications* (pp. 123–150). Croatia: InTech. doi:10.5772/25888

Kettunen, P. O. (2006). *Wood, Structure and Properties*. Zuerich, Switzerland: Trans Tech Publications Ltd.

Khuong, L. D., Kondo, R., De Leon, R., Kim Anh, T., Shimizu, K., & Kamei, I. (2014). Bioethanol production from alkaline-pretreated sugarcane bagasse by consolidated bioprocessing using Phlebia sp. MG-60. *International Biodeterioration & Biodegradation*, *88*(0), 62–68. doi:10.1016/j.ibiod.2013.12.008

Kissinger, H. E. (1957). Reaction kinetics in differential thermal analysis. *Analytical Chemistry*, *29*(11), 1702–1706. doi:10.1021/ac60131a045

Klar, M., & Rule, A. (1925). The technology of wood distillation. London, England. Chapman & Hall, LTD.

Klasson, K. T., Ackerson, M. D., Clausen, E. C., & Gaddy, J. L. (1993). Biological conversion of coal and coal-derived synthesis gas. *Fuel*, *72*(12), 1673–1678. doi:10.1016/0016-2361(93)90354-5

Klinbun, W., & Rattanadecho, P. Analysis of microwave induced natural convection in a single mode cavity (Influence of sample volume, placement, and microwave power level). *Applied Mathematical Modelling*(0). doi: 10.1016/j.apm.2011.07.003

Knoef, H. A. M., & Koele, H. J. (2000). Survey of tar measurement protocols. *Biomass and Bioenergy*, *18*(1), 55–59. doi:10.1016/S0961-9534(99)00067-7

Köpke, M., Held, C., Hujer, S., Liesegang, H., Wiezer, A., Wollherr, A., & Dürre, P. et al. (2010). Clostridium ljungdahlii represents a microbial production platform based on syngas.*Proceedings of the National Academy of Sciences*. doi:10.1073/pnas.1004716107

Koroneos, C., Spachos, T., & Moussiopoulos, N. (2003). Exergy analysis of renewable energy sources. *Renewable Energy*, *28*(2), 295–310. doi:10.1016/S0960-1481(01)00125-2

Kotas, T. J. (1995). *The exergy method of thermal plant analysis*. Malabar: Krieger Publishing Company.

Krishnan, C., Sousa, L. C., Jin, M., Chang, L., Dale, B. E., & Balan, V. (2010). Alkali-based AFEX pretreatment for the conversion of sugarcane bagasse and cane leaf residues to ethanol. *Biotechnology and Bioengineering*, *107*(3), 441–450. doi:10.1002/bit.22824 PMID:20521302

Krzan, A., & Zagar, E. (2009). Microwave driven wood liquefaction with glycols. *Bioresource Technology*, *100*(12), 3143–3146. doi:10.1016/j.biortech.2009.01.057 PMID:19261468

Kumar, L., Arantes, V., Chandra, R., & Saddler, J. (2012a). The lignin present in steam pretreated softwood binds enzymes and limits cellulose accessibility. *Bioresource Technology*, *103*(1), 201–208. doi:10.1016/j.biortech.2011.09.091 PMID:22047660

Kumar, L., Chandra, R., Chung, P. A., & Saddler, J. (2010). Can the same steam pretreatment conditions be used for most softwoods to achieve good, enzymatic hydrolysis and sugar yields? *Bioresource Technology*, *101*(20), 7827–7833. doi:10.1016/j.biortech.2010.05.023 PMID:20570139

Kumar, L., Tooyserkani, Z., Sokhansanj, S., & Saddler, J. (2012b). Does densification influence the steam pretreatment and enzymatic hydrolysis of softwoods to sugars? *Bioresource Technology*, *121*, 190–198. doi:10.1016/j.biortech.2012.06.049 PMID:22858485

Kunii, D., & Levenspiel, O. (1991). *Fluidization Engineering*. Newton, MA: Butterworth-Neinemann Ltda Press.

Kuppens, T., Cornelissen, T., Carleer, R., Yperman, J., Schreurs, S., Jans, M., & Thewys, T. (2010). Economic assessment of flash co-pyrolysis of short rotation coppice and biopolymer waste streams. *Journal of Environmental Management*, *91*(12), 2736–2747. doi:10.1016/j.jenvman.2010.07.022 PMID:20724061

Laird, D. (2008). The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agronomy Journal*, *100*(1), 178–181. doi:10.2134/agrojnl2007.0161

Lam, P. S. (2011). *Steam explosion of biomass to produce durable wood pellets* (Doctoral dissertation). Available from The University of British Columbia.

Lam, P. Y. (2013). *Steam pre-treatment and leaching for the production of high quality oil palm residue pellets* (Master dissertation). Available from The University of British Columbia, Vancouver.

Lam, P. S., Lam, P. Y., Sokhansanj, S., Bi, X. T., & Lim, C. J. (2013). Mechanical and compositional characteristics of steam-treated Douglas fir (*Pseudotsuga menziesii L.*) during pelletization. *Biomass and Bioenergy*, *56*, 116–126. doi:10.1016/j.biombioe.2013.05.001

Lam, P. S., Lam, P. Y., Sokhansanj, S., Lim, C. J., Bi, X. T., Stephen, J. D., & Mabee, W. E. et al. (2015). Steam explosion of oil palm residues for the production of durable pellets. *Applied Energy*, *141*, 160–166. doi:10.1016/j.apenergy.2014.12.029

Lam, P. S., Sokhansanj, S., Bi, X. T., & Lim, C. J. (2012a). Colorimetry applied to steam-treated biomass and pellets made from western Douglas fir (Pseudotsuga Menziesii L.). *Transactions of the ASABE*, *55*(2), 673–678. doi:10.13031/2013.41368

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., & Larsson, S. H. (2012b). Drying characteristics and equilibrium moisture content of steam-treated Douglas fir (*Pseudotsuga menziesii L.*). *Bioresource Technology*, *116*, 396–402. doi:10.1016/j.biortech.2012.03.093 PMID:22542137

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., & Melin, S. (2011). Energy input and quality of pellets made from steam-exploded Douglas fir (*pseudotsuga menziesii*). *Energy & Fuels*, *25*(4), 1521–1528. doi:10.1021/ef101683s

Lam, P. S., Sokhansanj, S., Bi, X. T., Lim, C. J., Naimi, L. J., Hoque, M., & Ye, X. P. et al. (2008). Bulk Density of wet and dry wheat straw and switchgrass particles. *Applied Engineering in Agriculture*, *24*(3), 351–358. doi:10.13031/2013.24490

Lam, P. Y., Lim, C. J., Sokhansanj, S., Lam, P. S., Stephen, J. D., Pribowo, A., & Mabee, W. E. (2014). Leaching characteristics of inorganic constituents from oil palm residues by water. *Industrial & Engineering Chemistry Research*, *53*(29), 11822–11827. doi:10.1021/ie500769s

Lanzetta, M., & Di Blasi, C. (1998). Pyrolysis kinetics of wheat and corn straw. *Journal of Analytical and Applied Pyrolysis*, *44*(2), 181–192. doi:10.1016/S0165-2370(97)00079-X

Lavarack, B. P., Griffin, G. J., & Rodman, D. (2002). The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. *Biomass and Bioenergy*, *23*(5), 367–380. doi:10.1016/S0961-9534(02)00066-1

Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., & House, J. I., … Zeng N. (2012). The global carbon budget 1959–201. *Earth System Science Data Discussions*, *5*(2), 1107–1157.

Lee, D., Owens, V. N., Boe, A., & Jeranyama, P. (2007). *Composition of herbaceous biomass feedstocks.* Sun Grant Initiative, North Central Center, South Dakota State University. Retrieved from http://ncsungrant.sdstate.org/uploads/publications/SGINC1-07.pdf

Lenihan, P., Orozco, A., O'Neill, E., Ahmad, M. N. M., Rooney, D. W., & Walker, G. M. (2010). Dilute acid hydrolysis of lignocellulosic biomass. *Chemical Engineering Journal*, *156*(2), 395–403. doi:10.1016/j.cej.2009.10.061

Lian, J., Chen, S., Zhou, Z., Wang, Z., O'Fellon, J., Li, C. Z., & Garcia-Perez, M. (2010). Separation, hydrolysis and fermentation of pyrolytic sugars to produce ethanol and lipids. *Bioresource Technology*, *101*(24), 9688–9699. doi:10.1016/j.biortech.2010.07.071 PMID:20708928

Li, D., Zhang, Y., Quan, X., & Zhao, Y. (2009). Microwave thermal remediation of crude oil contaminated soil enhanced by carbon fiber. *Journal of Environmental Sciences (China)*, *21*(9), 1290–1295. doi:10.1016/S1001-0742(08)62417-1 PMID:19999979

Liew, W. H., Hassim, M. H., & Ng, D. K. S. (2014). Review of evolution, technology and sustainability assessments of biofuel production. *Journal of Cleaner Production*, *71*, 11–29. doi:10.1016/j.jclepro.2014.01.006

Li, J., Henriksson, G., & Gellerstedt, G. (2007). Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion. *Bioresource Technology*, *98*(16), 3061–3068. doi:10.1016/j.biortech.2006.10.018 PMID:17141499

LINDANA. (2008). *TP Wood Chippers for Work in Green Areas*. Retrieved from http://www.machinerie.com/FedereePamphlet/Linddana/eNGLbrochure.pdf

Lior, N. (2011). Sustainable energy development: The present situation and possible paths to the future. *Energy*, *43*(1), 174–191. doi:10.1016/j.energy.2011.11.038

Lippke, B., Puettmann, M. E., Johnson, L., Gustafson, R., Venditti, R., Steele, P., & Caputo, J. et al. (2012). Carbon emission reduction impacts from alternative biofuels. *Forest Products Journal*, *62*(4), 296–304. doi:10.13073/12-00021.1

Lippke, B., Wilson, J., Meil, J., & Taylor, A. (2010). Characterizing the importance of carbon stored in wood products. *Wood and Fiber Science*, *42*, 5–14.

Lipska-Quinn, A. E., Zeronian, S. H., & Mc Gee, K. M. (1985). Thermal degradation of rice straw and its components. In R. P. Overend, T. A. Milne, & L. K. Mudge (Eds.), *Fundamentals of Thermochemical Biomass Conversion* (pp. 453–471). London: Elsevier App. Sc. Pub. doi:10.1007/978-94-009-4932-4_26

Lisbôa, A. C. L., & Watkinson, A. P. (1999). Operating conditions for oil shale thermogravimetry. *Powder Technology*, *101*(2), 151–156. doi:10.1016/S0032-5910(98)00166-1

Liu, Q., Zhong, Z., Wang, S., & Luo, Z. (2011). Interactions of biomass components during pyrolysis: A TG-FTIR study. *Journal of Analytical and Applied Pyrolysis, 90*(2), 213–218. doi:. 2010.12.00910.1016/j.jaap

Liu, C., Huang, J., Huang, X., Li, H., & Zhang, Z. (2011). Theoretical studies on formation mechanisms of CO and CO_2 in cellulose pyrolysis. *Computational and Theoretical Chemistry*, *964*(1-3), 207–212. doi:10.1016/j.comptc.2010.12.027

Liu, K., Atiyeh, H. K., Stevenson, B. S., Tanner, R. S., Wilkins, M. R., & Huhnke, R. L. (2014). Continuous syngas fermentation for the production of ethanol, n-propanol and n-butanol. *Bioresource Technology*, *151*(0), 69–77. doi:10.1016/j.biortech.2013.10.059 PMID:24211485

Liu, Z., Quek, A., & Balasubramanian, R. (2014). Preparation and characterization of fuel pellets from woody biomass, agro-residues and their corresponding hydrochars. *Applied Energy*, *113*, 1315–1322.

Li, X., Gunawan, R., Lievens, C., Wang, Y., Mourant, D., Wang, Sh., & Li, C. Z. et al. (2011). Simultaneous catalytic esterification of carboxylic acidas and acetalisation of aldehydes in a fast pyrolysis bio-oil from mallee biomass. *Fuel*, *90*(7), 2530–2537. doi:10.1016/j.fuel.2011.03.025

Lora, E. E. S., Andrade, R. V., Sanchez, C. G., Gómez, E. O., & Sales, C. A. V. B. (2008). Gaseificação. In L. A. B. Cortez, E. E. S. Lora, & E. O. Gómez (Eds.), *Biomassa para energia*. Campinas: Editora Unicamp.

Lourenço, J. B. (2012). *Estudo das características fluidodinâmicas de misturas da madeira de eucalipto e do caroço do fruto do tucumã com inerte visando aplicação em processos de termoconversão.* (Master's thesis). Retrieved from Acervus Unicamp Dissertations and Theses database. (T/UNICAMP L934e)

Lourenco, J. B., Mitri, A. G., & Tannous, K. (2012). Fluid dynamic and mixing characteristics in fluidized beds of inerts and biomass - *Eucalyptus grandis* and *Cariniana legalis*. In *Proceedings of the 3nd International Symposium on Gasification and Its Applications ISGA-3* [CD]. Vancouver, CA.

Lovins, L. H. (2002). *Small is Profitable. The Hidden Economic Benefits of Making Electrical Resources the Right Size*. Snowmass, CO: Rocky Mountain Institute.

Lozano, M. A., & Valero, A. (1988). Methodology for calculating exergy in chemical process. In W. Wepfer, G. Tsatsaronis, & R. A. Bajura (Eds.), *Thermodynamic analysis of chemically systems*. Zaragoza: ASME Book.

Lua, A. C., & Su, J. (2006). Isothermal and non-isothermal pyrolysis kinetics of Kapton® polyimide. *Polymer Degradation & Stability*, *91*(1), 144–153. doi:10.1016/j.polymdegradstab.2005.04.021

Lu, C., Song, W., & Lin, W. (2009). Kinetics of biomass catalytic pyrolysis. *Biotechnology Advances*, *27*(5), 583–587. doi:10.1016/j.biotechadv.2009.04.014 PMID:19393731

Lucas, A., Arnaldos, J., Casal, J., & Puigjaner, L. (1986). High temperature incipient fluidization in mono and polydisperse systems. *Chemical Engineering Communications*, *41*(1-6), 121–132. doi:10.1080/00986448608911715

Lucchesi, M. E., Chemat, F., & Smadja, J. (2004). Solvent-free microwave extraction of essential oil from aromatic herbs: Comparison with conventional hydro-distillation. *Journal of Chromatography. A*, *1043*(2), 323–327. doi:10.1016/j.chroma.2004.05.083 PMID:15330107

Lugato, M., Vaccari, F. P., Genesio, L., Baronti, S., Pozzi, A., Rack, M., & Miglietta, F. et al. (2013). An energy-biochar chain involving biomass gasification and rice cultivation in Northern Italy. *GCB Bioenergy*, *5*(2), 192–201. doi:10.1111/gcbb.12028

Lupa, C. J. R., Wylie, S., Shaw, A., Al-Shamma'a, A. J., Sweetman, A., & Herbert, B. M. J. (2012). Experimental analysis of biomass pyrolysis using microwave-induced plasma. *Fuel Processing Technology*, *97*(0), 79–84. doi:10.1016/j.fuproc.2012.01.015

Macedo, I. C., Seabra, J. E. A., & Silva, J. E. A. R. (2008). Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: The 2005/2006 averages and a prediction for 2020. *Biomass and Bioenergy*, *32*(7), 582–595. doi:10.1016/j.biombioe.2007.12.006

Makray, Z. T. (1984). *Gaseificação de biomassa em gaseificador co-corrente para a produção de gás de médio poder calorífico e gás de síntese* (Doctoral dissertation). Faculdade de Engenharia de Alimento, Universidade Estadual de Campinas, Campinas, SP.

Mando, M., & Rosendahl, L. (2010). On the motion of non-spherical particles at high Reynolds number. *Powder Technology*, *202*(1), 1–13. doi:10.1016/j.powtec.2010.05.001

Mani, S., Tabil, L. G., & Sokhansanj, S. (2004). Grinding performance and physical properties of wheat and barley straws, corn stover, and switchgrass. *Biomass and Bioenergy*, *27*(4), 339–352. doi:10.1016/j.biombioe.2004.03.007

Marker, T., Petri, J., McCall, M., Mackowiak, D., Jerosky, B., Regan, B., . . . Shannard, D. (2005). Opportunities for Biorenewables in Oil Refineries. UOP Des Plaines, Illinois. Retrieved from http://www.osti.gov/energycitations/product. biblio.jsp?osti_id=861458

Martin-Davison, J. S., Ballesteros, M., Manzanares, P., Sepulveda, P. X., & Fernandez, A. V. (2015). Effects of temperature on steam explosion pretreatment of Poplar Hybrids with different lignin contents in bioethanol production. *International Journal of Green Energy*, *12*(8), 832–842. doi:10.1080/15435075.2014.887569

Mayerhofer, M., Fendt, S., Spliethoff, H., & Gaderer, M. (2014). Fluidized bed gasification of biomass - In bed investigation of gas and tar formation. *Fuel*, *117*, 1248–1255. doi:10.1016/j.fuel.2013.06.025

Mazo, P., Estenoz, D., Sponton, M., & Rios, L. (2012). Kinetics of the Transesterification of Castor Oil with Maleic Anhydride Using Conventional and Microwave Heating. *Journal of the American Oil Chemists' Society*, *89*(7), 1355–1361. doi:10.1007/s11746-012-2020-3

MBDC. 2010. Sustainable Business: Minimization vs. Optimization. Optimisation (p. 15). Charlottesville,-VA. Retrieved from http://www.globalcitizen.net/data/topic/knowledge/uploads/ 20110803114637705.pdf

McDonough, W., & Braungart, M. 2002. Beyond the Triple Bottom Line: Design for the Triple Top Line. http://www.mcdonough.com/writings/beyond_triple.htm (Retrieved June 3rd, 2014).

McKendry, P. (2002). Energy production from biomass (part 1): Overview of biomass. *Bioresource Technology*, *83*(1), 37–46. doi:10.1016/S0960-8524(01)00118-3 PMID:12058829

McKendry, P. (2002). Energy production from biomass (Part 3): Gasification technologies. *Bioresource Technology*, *83*(1), 55–63. http://www.ncbi.nlm.nih.gov/pubmed/12058831 doi:10.1016/S0960-8524(01)00120-1 PMID:12058831

Medrano, J. A., Oliva, M., Ruiz, J., Garcia, L., & Arauzo, J. (2011). Hydrogen from aqueous fraction of biomass pyrolysis liquids by catalytic steam reforming in fluidized bed. *Energy*, *36*(4), 2215–2224. doi:10.1016/j.energy.2010.03.059

Menéndez, J. A., Domínguez, A., Inguanzo, M., & Pis, J. J. (2004). Microwave pyrolysis of sewage sludge: Analysis of the gas fraction. *Journal of Analytical and Applied Pyrolysis*, *71*(2), 657–667. doi:10.1016/j.jaap.2003.09.003

Menéndez, J. A., Inguanzo, M., & Pis, J. J. (2002). Microwave-induced pyrolysis of sewage sludge. *Water Research*, *36*(13), 3261–3264. doi:10.1016/S0043-1354(02)00017-9 PMID:12188123

Menon, N. R., Rahman, Z. A., & Bakar, N. A. (2003). Empty fruit brunches evaluation: Mulch in plantation vs. fuel for electricity generation. *Oil Palm Industry Economic Journal*, *3*, 15–20.

Menon, V., & Rao, M. (2012). Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science*, *38*(4), 522–550. doi:10.1016/j.pecs.2012.02.002

Mesa, L., González, E., Cara, C., González, M., Castro, E., & Mussatto, S. I. (2011). The effect of organosolv pretreatment variables on enzymatic hydrolysis of sugarcane bagasse. *Chemical Engineering Journal*, *168*(3), 1157–1162. doi:10.1016/j.cej.2011.02.003

Mesa-Pérez, J. M., Cortez, L. A. B., Marín-Mesa, H. R., Rocha, J. D., Peláez-Samaniego, M. R., & Cascarosa, E. (2014). A statistical analysis of the auto thermal fast pyrolysis of elephant grass in fluidized bed reactor based on produced charcoal. *Applied Thermal Engineering, 65*(s 1–2), 322–329. doi: 10.1016/j.applthermaleng.2013.12.072

Mesa-Perez, J. M., Cortez, L. A. B., Rocha, J. D., Brossard-Perez, L. E., & Olivares-Gómez, E. (2005). Unidimensional heat transfer analysis of elephant grass and sugar cane bagasse slow pyrolysis in a fixed bed reactor. *Fuel Processing Technology*, *86*(5), 565–575. doi:10.1016/j.fuproc.2004.05.014

Mesa-Pérez, J. M., Rocha, J. D., Barbosa-Cortez, L. A., Penedo-Medina, M., Luengo, C. A., & Cascarosa, E. (2013). Fast oxidative pyrolysis of sugar cane straw in a fluidized bed reactor. *Applied Thermal Engineering*, *56*(1-2), 167–175. doi:10.1016/j.applthermaleng.2013.03.017

Metaxas, A. C., & Meredith, R. J. (2008). *Industrial Microwave Heating*. London, United Kingdom: The Institution of Engineering and Technology.

Mettler, M. S., Vlachos, D. G., & Dauenhauer, P. J. (2012). Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy and Environmental Science, 5*(7), 7797–7809. doi: 79E10.1039/C2EE216

Miao, Z., Grift, T. E., Hansen, A. C., & Ting, K. C. (2011). Energy requirement for comminution of biomass in relation to particle physical properties. *Industrial Crops and Products*, *33*(2), 504–513. doi:10.1016/j.indcrop.2010.12.016

Mitri, A. G., Lourenço, J. B., & Tannous, K. (2011). Comportamento fluidodinâmico e velocidades características de misturas binárias de biomassa (C*ariniana legalis*) e areia. In *Proceeding of the XXXV Congresso Brasileiro de Sistemas Particulados* (pp.100-109) [CD]. Vassouras, BR.

Miura, M., Kaga, H., Sakurai, A., Kakuchi, T., & Takahashi, K. (2004). Rapid pyrolysis of wood block by microwave heating. *Journal of Analytical and Applied Pyrolysis*, *71*(1), 187–199. doi:10.1016/S0165-2370(03)00087-1

Mobini, M., Sowlati, T., & Sokhansanj, S. (2013). A simulation model for the design and analysis of wood pellet supply chains. *Applied Energy*, *111*, 1239–1249. doi:10.1016/j.apenergy.2013.06.026

Mohammadi, M., Najafpour, G. D., Younesi, H., Lahijani, P., Uzir, M. H., & Mohamed, A. R. (2011). Bioconversion of synthesis gas to second generation biofuels: A review. *Renewable & Sustainable Energy Reviews*, *15*(9), 4255–4273. doi:10.1016/j.rser.2011.07.124

Mohammadi, M., Younesi, H., Najafpour, G., & Mohamed, A. R. (2012). Sustainable ethanol fermentation from synthesis gas by Clostridium ljungdahlii in a continuous stirred tank bioreactor. *Journal of Chemical Technology and Biotechnology (Oxford, Oxfordshire)*, *87*(6), 837–843. doi:10.1002/jctb.3712

Mohan, D., Pittman, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy & Fuels*, *20*(3), 848–889. doi:10.1021/ef0502397

Monsef-Mirzai, P., Ravindran, M., McWhinnie, W. R., & Burchill, P. (1995). Rapid microwave pyrolysis of coal: Methodology and examination of the residual and volatile phases. *Fuel*, *74*(1), 20–27. doi:10.1016/0016-2361(94)P4325-V

Moran, M. J., & Shapiro, H. N. (2006). *Fundamentals of engineering thermodynamics* (5th ed.). England: John Wiley & Sons Ltd.

Morrow, C. T., & Mohsenin, N. N. (1966). *Food engineering. Principles and selected applications*. New York: Academic Press.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, *96*(6), 673–686. doi:10.1016/j.biortech.2004.06.025 PMID:15588770

Motasemi, F., & Afzal, M. T. (2013). A review on the microwave-assisted pyrolysis technique. *Renewable & Sustainable Energy Reviews*, *28*(0), 317–330. doi:10.1016/j.rser.2013.08.008

Motasemi, F., Afzal, M. T., Salema, A. A., Mouris, J., & Hutcheon, R. M. (2014). Microwave dielectric characterization of switchgrass for bioenergy and biofuel. *Fuel*, *124*(0), 151–157. doi:10.1016/j.fuel.2014.01.085

Mourad, M., Hemati, M., & Laguerie, C. (1994). Hydrodynamique d'un séchoir à lit fluidisé à flottation: Détermination dês vitesses caractéristiques de fluidisation de mélanges de maïs et de sable. *Powder Technology*, *80*(1), 45–54. doi:10.1016/0032-5910(94)87004-7

Mullaney, H., Farag, I., LaClaire, C., Batter, C., & Hall, K. (2002). Technical, environmental and economic feasibility of bio-oil in New Hampshire's north country. Retrieved from http://www.unh.edu/p2/ biooil/bounhif.pdf

Munasinghe, P. C., & Khanal, S. K. (2010). Biomass-derived syngas fermentation into biofuels: Opportunities and challenges. *Bioresource Technology*, *101*(13), 5013–5022. doi:10.1016/j.biortech.2009.12.098 PMID:20096574

Muzamal, M., Gamstedt, E. K., & Rasmuson, A. (2014). Modeling wood fiber deformation caused by vapor expansion during steam explosion of wood. *Wood Science and Technology*, *48*(2), 353–372. doi:10.1007/s00226-013-0613-0

Muzamal, M., Jedvert, K., Theliander, H., & Rasmuson, A. (2015). Structural changes in spruce wood during different steps of steam explosion pretreatment. *Holzforschung*, *69*(1), 61–66. doi:10.1515/hf-2013-0234

Nagano, M. S., Stefanovitz, J. P., & Vick, T. E. (2014). Innovation management processes, their internal organizational elements and contextual factors: An investigation in Brazil. *Journal of Engineering and Technology Management*, *33*(7-9), 63–92. doi:10.1016/j.jengtecman.2014.02.004

Naimi, L. J., Sokhansanj, S., Mani, S., Hoque, M., Bi, T., Womac, A. R., & Narayan, S. (2006). Cost and performance of woody biomass size reduction for energy production. Annual Conference of CSBE/SCGA. Edmonton, Alberta, July 16-19.

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C. J., Lau, A., Melin, S., & Pelz, S. et al. (2012). Size reduction and fractionation to reduce the ash content of biomass. In the *62nd Chemical Engineering conference*. Vancouver, BC, Canada.

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C. J., Womac, A. R., Lau, A. K., & Melin, S. (2013). Development of size reduction equations for calculating energy input for grinding lignocellulosic particles. *Applied Engineering in Agriculture*, *29*(1), 93–100. doi:10.13031/2013.42523

Naimi, L. J., Sokhansanj, S., Bi, X., Lim, C., Womac, A. R., Lau, A., & Melin, S. (2011). Development of population balance model to simulate fractionation of ground switchgrass. *Transactions of the ASABE*, *54*(1), 219–227. doi:10.13031/2013.36239

Nascimento, V. F. (2012). *Caracterização de biomassas amazônicas - ouriço de castanha do brasil, ouriço de sapucaia e caroço do fruto do tucumã - visando sua utilização em processos de termoconversão.* (Master dissertation). University of Campinas, Campinas, Brazil. Retrieved from http://www.biblioteca digital.unicamp.br/document/?code= 000881657

Nascimento, V. F. (2012). *Caracterização de biomassas amazônicas-ouriço de castanha do brasil, ouriço de sapucaia e caroço do fruto do tucumã-visando sua utilização em processos de termoconversão.* (Master dissertation). Retrieved from Acervus Unicamp dissertations and Theses database. (T/UNICAMP N17C)

Nexterra. (2012). *UBC biomass fuel specification for i.c. engine systems*. Nexterra Corp.

Nigam, P. S., & Singh, A. (2011). Production of liquid biofuels from renewable resources. *Progress in Energy and Combustion Science*, *37*(1), 52–68. doi:10.1016/j.pecs.2010.01.003

Nussenzveig, H. M. (2002). *Curso de física básica: fluidos oscilações e ondas de calor. Volume number two* (4th ed.). Rio de Janeiro: Editora Blucher.

Oasmaa, A., Kyto, M., & Silipa, K. (2001). Pyrolysis oil combustion test in an industrial boiler. in: proceedings in thermochemical biomass conversion. In A. V. Bridgwater (Ed.), *Progress in thermochemical biomass conversion* (pp. 1468–1481). Oxford, England: Blackwell Sciences. doi:10.1002/9780470694954.ch121

Oasmaa, A., & Meier, D. (2005). Norms and standards for fast pyrolysis liquids:1. Round robin test. *Journal of Analytical and Applied Pyrolysis*, *73*(2), 323–334. doi:10.1016/j.jaap.2005.03.003

Olivares-Gómez, E. (2002). Study Of The Elephant Grass Fast Pyrolysis In A Bubbling Fluidized Bed Reactor Throught The Fine Charcoal Characterization (Doctoral Thesis) Retrieved from Acervus Unicamp dissertations and Thesis database. (T/UNICAMP OL4e).

Oliveira, C. R. M., & Tannous, K. (2009). Fluidodinâmica de biomassa em leito fluidizado gasoso. In *Proceedings of the VIII Congresso Brasileiro de Engenharia Química* [CD]. Uberlândia, BR. Retrieved from http://www.cobeqic2009.feq.ufu.br/uploads/media/84220321.pdf

Oliveiras Júnior, S. (2013). *Exergy – production, cost and renewability*. London: Springer-Verlag.

Olson, E. S., & Freel, B. (2007). Process for converting anhydrosugars to glucose and other fermentable sugars. US Patent Application 20070125369

Omar, R., Idris, A., Yunus, R., Khalid, K., & Aida Isma, M. I. (2011). Characterization of empty fruit bunch for microwave-assisted pyrolysis. *Fuel*, *90*(4), 1536–1544. doi:10.1016/j.fuel.2011.01.023

Orfão, J. J. M., Antunes, F. J. A., & Figueiredo, J. L. (1999). Pyrolysis kinetics of lignocellulosic materials - three independent reactions model. *Fuel*, *78*(3), 349–358. doi:10.1016/S0016-2361(98)00156-2

Ormrod, D., & Webster, A. 2000. Progression in Utilization of Bio-oils in Diesel Engines. PyNe Newsletter, 10, 15.http://www.pyne.co.uk/Resources/user/PyNews%2010.pdf

Orozco, A., Ahmad, M., Rooney, D., & Walker, G. (2007). Dilute Acid Hydrolysis of Cellulose and Cellulosic Bio-Waste Using a Microwave Reactor System. *Process Safety and Environmental Protection*, *85*(5), 446–449. doi:10.1205/psep07003

Oveisi, E., Lau, A., Sokhansanj, S., Lim, C. J., Bi, X. T., Larsson, S. H., & Melin, S. (2013). Breakage behavior of wood pellets due to free fall. *Powder Technology*, *235*, 493–499. doi:10.1016/j.powtec.2012.10.022

Overend, R. P., Chornet, E., & Gascoigne, J. A. (1987). Fractionation of lignocellulosics by steam aqueous pretreatments. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, *321*(1561), 523–536. doi:10.1098/rsta.1987.0029

Ozawa, T. (1965). A new method of analizing thermogravimetric data. *Bulletin of the Chemical Society of Japan*, *38*(11), 1881–1886. doi:10.1246/bcsj.38.1881

Painuly, J. P. (2001). Barriers to renewable energy penetration; a framework for analysis. *Renewable Energy*, *24*(1), 73–89. doi:10.1016/S0960-1481(00)00186-5

Paixão, V., Monteiro, R., Andrade, M., Fernandes, A., Rocha, J., Carvalho, A. P., & Martins, A. (2011). Desilication of MOR zeolite: Conventional versus microwave assisted heating. *Applied Catalysis A, General*, *402*(1–2), 59–68. doi:10.1016/j.apcata.2011.05.025

Palma, C. F., & Martin, A. D. (2013). Model based evaluation of six energy integration schemes applied to a small-scale gasification process for power generation. *Biomass and Bioenergy*, *54*(0), 201–210. doi:10.1016/j.biombioe.2013.03.024

Panopoulos, K. D., Fryda, L. E., Karl, J., Poulou, S., & Kakaras, E. (2006). High temperature solid oxide fuel cell integrated with novel allothermal biomass gasification: Part I: Modelling and feasibility study. *Journal of Power Sources*, *159*(1), 570–585. doi:10.1016/j.jpowsour.2005.12.024

Pan, R., Wu, Y., Wang, Q., & Hong, Y. (2009). Preparation and catalytic properties of platinum dioxide nanoparticles: A comparison between conventional heating and microwave-assisted method. *Chemical Engineering Journal*, *153*(1–3), 206–210. doi:10.1016/j.cej.2009.06.009

Park, S. R., Pandey, K., Tyagi, V. V., & Tyagi, S. K. (2014). Energy and exergy analysis of typical renewable energy systems. *Renewable & Sustainable Energy Reviews*, *30*, 105–123. doi:10.1016/j.rser.2013.09.011

Parthasarathy, P., & Narayanan, S. K. (2014). Determination of kinetic parameters of biomass samples using thermogravimetric analysis. *Environmental Progress & Sustainable Energy*, *33*(1), 256–266. doi:10.1002/ep.11763

Patel, M., Crack, M., Dornburg, V., Hermann, B., Roes, L., Husing, B., & Recchia, E. et al. (2006). *Medium and long term opportunity and risks of biotechnological production of bulk chemicals from renewable resourses - The potential of white biotechnology. Final Report, prepared under the European Commission's GROWTH Programme*. Utrecht: DG Research.

Patil, P., Gude, V. G., Pinappu, S., & Deng, S. (2011). Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions. *Chemical Engineering Journal*, *168*(3), 1296–1300. doi:10.1016/j.cej.2011.02.030

Pelaez-Samaniego, M. R., Garcia-Perez, M., Cortez, L. B., Rosillo-Calle, F., & Mesa, J. (2008). Improvements of brazilian carbonization industry as part of the creation of a global biomass economy. *Renewable & Sustainable Energy Reviews*, *12*(4), 1063–1086. doi:10.1016/j.rser.2006.10.018

Pella, E., & Colombo, B. (1973). Study of carbon, hydrogen and nitrogen determination by combustion-gas chromatography. *Mikrochimica Acta*, *61*(5), 697–719. doi:10.1007/BF01218130

Pellegrini, L., & Oliveira Júnior, S. (2007). Exergy analysis of sugarcane bagasse gasification. *Energy*, *32*(4), 314–327. doi:10.1016/j.energy.2006.07.028

Penã, J. A. P. (2011). Bubbling fluidized bed (BFB), when to use this technology? In *Industrial Fluidization South Africa* (pp. 1–12). Johannesburg, South Africa: The Southern African Institute of Mining and Metallurgy.

Perlack, R. D., & Hess, J. R. (2006). Biomass resources for liquid fuels production.*Proceedings of 28th. Symposium of Biotechnology for Fuels and Chemicals*. Nashville, TN.

Petersson, A., Thomsen, M. H., Hauggaard-Nielsen, H., & Thomsen, A. B. (2007). Potential bioethanol and biogas production using lignocellulosic biomass form winter rye, oilseed rape and fababean. *Biomass and Bioenergy*, *31*(11-12), 812–819. doi:10.1016/j.biombioe.2007.06.001

Phan, D. T., & Tan, C.-S. (2014). Innovative pretreatment of sugarcane bagasse using supercritical CO2 followed by alkaline hydrogen peroxide. *Bioresource Technology*, *167*(0), 192–197. doi:10.1016/j.biortech.2014.06.006 PMID:24983689

Phanphanich, M., & Mani, S. (2011). Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology*, *102*(2), 1246–1253. doi:10.1016/j.biortech.2010.08.028 PMID:20801023

Phillips, S., Adem, A., Jechura, J., Dayton, D., & Eggman, T. (2007). Thermochemical ethanol via indirect gasification and mixed alcohol synthesis of lignocellulosic biomass. NREL/TP-510-41168. Retrieved from http://www.nrel.gov/docs/fy07 osti/41168.pdf

Phillips, J. R., Clausen, E. C., & Gaddy, E. (1994). Synthesis gas as substrate for the biological production of fuels and chemicals. *Applied Biochemistry and Biotechnology*, *45-46*(1), 145–157. doi:10.1007/BF02941794

Phillips, J. R., Klasson, K. T., Clausen, E. C., & Gaddy, E. (1993). Biological production of ethanol from coal synthesis gas. *Applied Biochemistry and Biotechnology*, *39-40*(1), 559–571. doi:10.1007/BF02919018

Piarpuzan, D., Quintero, J. A., & Cardona, C. A. (2011). Empty fruit bunches from oil palm as a potential raw material for fuel ethanol production. *Biomass and Bioenergy*, *35*(3), 1130–1137. doi:10.1016/j.biombioe.2010.11.038

Pippo, W. A., Luengo, C. A., Alberteris, L. A. M., Garzone, P., & Cornacchia, G. (2011). Energy recovery from sugarcane-trash in the light of 2nd generation biofuels. Part 1: Current situation and environmental aspects. *Waste and Biomass Valorization*, *2*(1), 1–16. doi:10.1007/s12649-010-9048-0

Prado, J. M., Follegatti-Romero, L. A., Forster-Carneiro, T., Rostagno, M. A., Maugeri Filho, F., & Meireles, M. A. A. (2014). Hydrolysis of sugarcane bagasse in subcritical water. *The Journal of Supercritical Fluids*, *86*(0), 15–22. doi:10.1016/j.supflu.2013.11.018

Prins, M. J. (2005). *Thermodynamic analysis of biomass gasification and torrefaction* (Doctoral dissertation). Technische Universiteit Eindhoven, Netherlands.

Prins, M., J., Ptasinski, K., & J. J. G. Janssen, F. (. (2003). Thermodynamics of gas-char reactions: First and second law analysis. *Chemical Engineering Science*, *58*(3-6), 1003–1011. doi:10.1016/S0009-2509(02)00641-3

PRWeb. (2014). Global activated carbon market to reach 2.3 million metric tons by 2017. Retrieved from http://www.prweb.com/releases/activated_carbon/water_treatment/prweb8286149.htm

Punčochář, M., Drahoš, J., Čermák, J., & Selucký, K. (1985). Evaluation of minimum fluidization velocity in gaz fluidized bed from pressure fluctuations. *Chemical Engineering Communications*, *35*(1-6), 81–87. doi:10.1080/00986448508911219

Rabelo, S. C., Maciel Filho, R., & Costa, A. C. (2013). Lime pretreatment and fermentation of enzymatically hydrolyzed sugarcane bagasse. *Applied Biochemistry and Biotechnology*, *169*(5), 1696–1712. doi:10.1007/s12010-013-0097-2 PMID:23334836

Radlein, D. (2005). Chemicals and materials from bio-oil. Retrieved from http://www.pyne.co.uk/ Resources/user/PYNE%20Newsletters/Pynews%2005.pdf

Radlein, D. (1999). The production of chemicals from fast pyrolysis bio-oils. In A. Bridgwater, S. Czernik, J. Diebold, D. Meier, A. Oasmaa, C. Peacocke, & D. Radlein et al. (Eds.), *Fast pyrolysis of biomass: A handbook* (pp. 164–188). Newbury, UK: CPL Press.

Rajagopalan, S., Datar, R. P., & Lewis, R. S. (2002). Formation of ethanol from carbon monoxide via a new microbial catalyst. *Biomass and Bioenergy*, *23*(6), 487–493. doi:10.1016/S0961-9534(02)00071-5

Ramakers, B. J., Ridder, R., & Kerkhof, P. J. A. M. (2004). Fluidization behavior of wood/sand mixtures. *Maderas. Ciencia y Tecnología*, *6*(2), 145–153. doi:10.4067/S0718-221X2004000200005

Ramos, L. P. (2003). The chemistry involved in the steam treatment of lignocellulosic materials. *Quimica Nova*, *26*(6), 863–871. doi:10.1590/S0100-40422003000600015

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., & Sommariva, S. (2008). Chemical Kinetics of Biomass Pyrolysis. *Energy & Fuels*, *22*(6), 4292–4300. doi:10.1021/ef800551t

Rao, K. V. N. S., & Reddy, G. V. (2010). Cold flow studies of rice husk, sawdust, and groundnut shell fuels in a fluidized bed. *Energy Source Part A: Recovery, Utilization, and Environmental Effects*, *32*(18), 1701–1711. doi:10.1080/15567030902882893

Rao, T. R., & Bheemarasetti, J. V. R. (2001). Minimum fluidization velocities of mixtures of biomass and sands. *Energy*, *26*(6), 633–644. doi:10.1016/S0360-5442(01)00014-7

Rasul, M. G., & Rudolph, V. (2000). Fluidized bed combustion of Australian bagasse. *Fuel*, *79*(2), 123–130. doi:10.1016/S0016-2361(99)00144-1

Raveendran, K., & Ganesh, A. (1996). Heating value of biomass and biomass pyrolysis products. *Fuel*, *75*(15), 1715–1720. doi:10.1016/S0016-2361(96)00158-5

REN21. (2014). *Renewables 2014: Global Status Report*. Retrieved from http://www.ren21.net/portals/0/documents/resources/gsr/2014/gsr2014_full%20report_low%20res.pdf

Repellin, V., Govin, A., Rolland, M., & Guyonnet, R. (2010). Energy requirement for fine grinding of torreifed wood. *Biomass and Bioenergy*, *34*(7), 923–930. doi:10.1016/j.biombioe.2010.01.039

Resasco, D. E., Sooknoi, T., Zhu, X., Huang, T., Lobban, L., & Mallinson, R. G. Catalytic conversion of small oxygenates from bio-oil to alkyloaromatics on zeolite. School of Chemical, Biological and Materials Engineering and Center for Biomass Refining, University of Oklahoma (2010).

Rezende, C., de Lima, M., Maziero, P., deAzevedo, E., Garcia, W., & Polikarpov, I. (2011). Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for Biofuels*, *4*(1), 1–19. doi:10.1186/1754-6834-4-54 PMID:22122978

Riley, N. A. (1941). Projection sphericity. *Journal of Sedimentary Research*, *11*(2), 94–95.

Ringer, M., Putsche, V., & Scahill, J. (2006). Large-scale pyrolysis oil production: a technology assessment and economic analysis. Technical Report NREL/TP-510-37779. NREL, Golden, CO.

Rocha, G. J. M., Martín, C., da Silva, V. F. N., Gómez, E. O., & Gonçalves, A. R. (2012). Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification. *Bioresource Technology*, *111*(0), 447–452. doi:10.1016/j.biortech.2012.02.005 PMID:22391588

Rocha, G. J. M., Martin, C., Soares, I. B., Souto Maior, A. M., Baudel, H. M., & Moraes de Abreu, C. A. (2011). Dilute mixed-acid pretreatment of sugarcane bagasse for ethanol production. *Biomass and Bioenergy*, *35*(1), 663–670. doi:10.1016/j.biombioe.2010.10.018

Rocha, G. J. M., Silva, V. F. N., Martín, C., Gonçalves, A. R., Nascimento, V. M., & Souto-Maior, A. M. (2013). Effect of xylan and lignin removal by hydrothermal pretreatment on enzymatic conversion of sugarcane bagasse cellulose for second generation ethanol production. *Sugar Tech*, *15*(4), 390–398. doi:10.1007/s12355-013-0218-9

Rodrigues, S. J., & Gaggioli, A. R. (1980). Second-law efficiency analysis of a coal gasification process. *Canadian Journal of Chemical Engineering*, *58*(3), 376–381. doi:10.1002/cjce.5450580314

Rogers, J. G., & Brammer, J. G. (2012). Estimation of the Production cost of fast pyrolysis bio-oil. *Biomass and Bioenergy*, *36*, 209–217. doi:10.1016/j.biombioe.2011.10.028

Rowe, P. N., Nienow, A. W., & Agbim, A. J. (1972). A preliminary quantitative study of particle segregation in gas fluidized beds – Binary systems of near spherical particles. *Transactions of the Institution of Chemical Engineers*, *50*, 324–333.

Roy, C., & Morin, D. (1999). Efficient electricity production from biomass through ipcc power plants.*Proceedings of the 4th International Conference on Greenhouse Gas Control Technologies*. Interlaken, Switzerland, Aug. 20-Sept. 2. Eds. B Eliasson, P Riemer, & A Wokaun, Pergamon, p. 729-734 doi:10.1016/B978-008043018-8/50115-6

Rozario, M., & Melssen, B. (2013). National Biomass Strategy 2020 : New wealth creation for Malaysia's biomass industry (p. 37). Retrieved from http://www.cmtevents.com/MediaLibrary/BStgy2013Rpt AIM.pdf

Rueda-Ordóñez, Y. J., Olivares-Gómez, E., & Tannous, K. (2013). Thermogravimetric study and kinetic analysis of sugarcane straw. In *Proceedings of the 22nd International Congress of Mechanical Engineering* (*COBEM, 2013*). Ribeirão Preto, SP, Brazil. ABCM.

Salema, A. A., & Ani, F. N. (2011). Microwave induced pyrolysis of oil palm biomass. *Bioresource Technology*, *102*(3), 3388–3395. doi:10.1016/j.biortech.2010.09.115 PMID:20970995

Salema, A. A., & Ani, F. N. (2012). Pyrolysis of oil palm empty fruit bunch biomass pellets using multimode microwave irradiation. *Bioresource Technology*, *125*(0), 102–107. doi:10.1016/j.biortech.2012.08.002 PMID:23026320

Salema, A. A., Yeow, Y. K., Ishaque, K., Ani, F. N., Afzal, M. T., & Hassan, A. (2013). Dielectric properties and microwave heating of oil palm biomass and biochar. *Industrial Crops and Products*, *50*(0), 366–374. doi:10.1016/j.indcrop.2013.08.007

Salomon, M., Gomez, M. F., Erlich, C., & Martin, A. (2013). Pelletization: An alternative for polygeneration in the palm oil industry. *Biomass Conversion and Biorefinery*, *3*(3), 213–229. doi:10.1007/s13399-013-0075-5

Salvi, G. &Salvi G Jr. (1991). Pyrolytic products assessment study. Report from Commission of European Community, Contract No. EN3B-0191-1 (CH).

Sánchez, C. G. (1994). *Estudo da volatilização e da gaseificação de biomassa em leito fluidizado* (Doctoral dissertation). Universidade Estadual de Campinas, Faculdade de Engenharia Mecânica, Campinas.

Sánchez, C. G., Silva, E. L., & Olivares-Gómez, E. (1997). Gaseificação. In: L. A. B. Cortez, & E. L. Silva (Ed.), Tecnologias de Conversão Energética da Biomassa (pp. 255-347).Universidade de Manaus-EFEI, Manaus, Série Sistemas Energéticos II.

Sanchez, M. E., Otero, M., Gómez, X., & Morán, A. (2009). Thermogravimetric kinetic analysis of the combustion of biowastes. *Renewable Energy*, *34*(6), 1622–1627. doi:10.1016/j.renene.2008.11.011

Sanchez-Silva, L., López-González, D., Villaseñor, J., Sánchez, P., & Valverde, J. L. (2012). Thermogravimetric-mass spectrometry analysis of lignocellulosic and marine biomass pyrolysis. *Bioresource Technology*, *109*, 163–172. doi:10.1016/j.biortech.2012.01.001 PMID:22297048

Sankey, H. R. (1898). Introductory note on the thermal efficiency of steam-engines. *The Engineer*, *86*, 236–237.

Santos, E. S. (1997). *Estudo dos fenômenos de mistura e segregação em leitos fluidizados de partículas polidispersas*. (Master's thesis). Retrieved from Acervus Unicamp Dissertations and Theses database. (T/UNICAMP Sa59e)

Santos, F. J. (2010). Fluidodinâmica do leito fluidizado aplicada à gaseificação. In C. G. Sánchez (Ed.), *Tecnologia da gaseificação de biomassa* (pp. 263–275). Campinas, BR: Átomo Press.

Saxena, R., Adhikari, D., & Goyal, H. (2009). Biomass-based energy fuel through biochemical routes: A review. *Renewable & Sustainable Energy Reviews*, *13*(1), 167–178. doi:10.1016/j.rser.2007.07.011

Sbirrazzuoli, N., Vincent, L., Mija, A., & Guigo, N. (2009). Integral, differential and advanced isoconversional methods - Complex mechanisms and isothermal predicted conversion–time curves. *Chemometrics and Intelligent Laboratory Systems, 96*(2), 219–226. doi:. 02.00210.1016/j.chemolab.2009

Schmidt, H. P. (2012). 55 Uses of Biochar. *Ithaka Journal*, *1*, 286–289.

Schmidt, M. (2008a). The Sankey Diagram in Energy and Material Flow Management. *Journal of Industrial Ecology*, *12*(1), 82–94. doi:10.1111/j.1530-9290.2008.00004.x

Scholz, S. B., Sembres, T., Roberts, K., Whitman, T., Wilson, K., & Lehmann, J. (2014). *Biochar systems for smallholders in developing countries: leveraging current knowledge and exploring future potential for climate-smart agriculture*. World Bank Publications; doi:10.1596/978-0-8213-9525-7

Schwob, Y. (1985). Process for converting ligneous matter from vegetable origin by torrefaction, and product obtained thereby. US patent. 4553978.

Shamsudin, S., Shah, U. K. M., Zainudin, H., Aziz, S. A., Kamal, S. M. M., Shirai, Y., & Hassan, M. A. (2012). Effect of steam pretreatment on oil palm empty fruit bunch for the production of sugars. *Biomass and Bioenergy*, *36*, 280–288. doi:10.1016/j.biombioe.2011.10.040

Shen, J., Wang, X. S., Garcia-Perez, M., Mourant, D., Rhodes, M., & Li, C. Z. (2009). Effect of particle size on the fast pyrolysis of oil mallee woody biomass. *Fuel*, *88*(10), 1810–1817. doi:10.1016/j.fuel.2009.05.001

Si, C., & Guo, Q. (2008). Fluidization characteristics of binary mixtures of biomass and quartz sand in an acoustic fluidized bed. *Industrial & Engineering Chemistry Research*, *47*(23), 9773–9782. doi:10.1021/ie801070z

Siegle, V., Schweitzer, B., Splethoff, H., & Hein, K. R. G. (1996). Preparation and co-combustion of cereals with hard coal in a 500 kW pulverized-fuel test unit. In *Proceedings of the 9th European Bioenergy Conference*, Vol. II, Elsevier Oxford, UK, 1027-1032.

Siemons, R. V. (2002). *A Development Perspective for Biomass-fuelled Electricity Generation Technologies e Economic Technology Assessment in View of Sustainability*. Amsterdam: Universiteit van Amsterdam.

Silva, F. S., & Tannous, K. (2012). *APOGEO - Analisador de Partículas e Formas Geométricas* [Computer software and manual]. Rio de Janeiro, BR: Brazilian National Institute of Industrial Property.

Silva, V. F. N., Arruda, P. V., Felipe, M. G. A., Gonçalves, A. R., & Rocha, G. J. M. (2011). Fermentation of cellulosic hydrolysates obtained by enzymatic saccharification of sugarcane bagasse pretreated by hydrothermal processing. *Journal of Industrial Microbiology & Biotechnology*, *38*(7), 809–817. doi:10.1007/s10295-010-0815-5 PMID:20740373

Simmons, F. C. (1957). Guides to manufacturing and marketing charcoal in the northwestern states. USDA Forest Service Station Paper No. 95, Upper Darby, PA. Retrieved from http://web1.cnre.vt.edu/ forestry/ charcoal/ documents/sp_ne05%20reduced.pdf

Sing, C. Y., & Aris, M. S. (2012). An experimental investigation on the handling and storage properties of biomass fuel briquettes made from oil palm mill residues. *Journal of Applied Science*, *12*(24), 2621–2625. doi:10.3923/jas.2012.2621.2625

Singh, P. S., Weil, A. S., & Babu, P. S. (1980). Thermodynamic Analysis of Coal Gasification Processes. *Energy*, *5*(8-9), 905–914. doi:10.1016/0360-5442(80)90106-1

Sipila, K., Kuoppala, E., Fagernas, L., & Oasmaa, A. (1998). Characterization Of Biomass-Based Flash Pyrolysis Oils. *Biomass and Bioenergy*, *14*(2), 103–113. doi:10.1016/S0961-9534(97)10024-1

Sithambaram, S., Nyutu, E. K., & Suib, S. L. (2008). OMS-2 catalyzed oxidation of tetralin: A comparative study of microwave and conventional heating under open vessel conditions. *Applied Catalysis A, General*, *348*(2), 214–220. doi:10.1016/j.apcata.2008.06.046

Smith, J. M., & Van Ness, H. C. (1987). *Introduction to chemical engineering thermodynamics*. New York: McGraw-Hill Book Company.

Smook, G. A. (1992). *Handbook for Pulp and Paper Technologists*. Vancouver, BC: Angus Wilde Publication.

Sokhansanj, S., & Turhollow, A. F. (2004). Biomass densification – Cubing operations and costs for corn stover. *Applied Engineering in Agriculture*, *20*(4), 459–499. doi:10.13031/2013.16480

Solanstausta, Y., Oasmaa, A., Sipila, K., Lindfors, C., Lehto, J., Autio, J., & Heiskanen, J. et al. (2012). Bio-oil production from biomass: Steps toward demonstration. *Energy & Fuels*, *26*(1), 233–240. doi:10.1021/ef201109t

Sparrevik, M., Field, J. L., Martinsen, V., Breedveld, G. D., & Cornelissen, G. (2013). Life cycle assessment to evaluate the environmental impact of biochar implementation in conservation agriculture in Zambia. *Environmental Science & Technology*, *47*, 1206–1215. PMID:23272937

Spath, P., Aden, A., Eggeman, T., Ringer, M., Wallace, B., & Jechure, J. (2005). Biomass to hydrogen production detailed design and economics utilizing the battelle columbus laboratory indirectly – heated gasifier. Technical Report NREL/TP-510-37408. Retrieved from http://www.nrel.gov/docs/fy05osti/37408.pdf

Spath, P. L., & Dayton, D. C. (2003). *Preliminary Screening—Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas* (p. 142). Golden: National Renewable Energy Laboratory. doi:10.2172/15006100

Sricharoenchaikul, V., Frederick, Wm. J. Jr, & Agrawal, P. (2002). Black Liquor Gasification Characteristics. 2. Measurement of Condensable Organic Matter (Tar) at Rapid Heating Conditions. *Industrial & Engineering Chemistry Research*, *41*(23), 5650–5658. doi:10.1021/ie020208o

Starink, M. (1996). A new method for the derivation of activation energies from experiments performed at constant heating rate. *Thermochimica Acta*, *288*(1-2), 97–104. doi:10.1016/S0040-6031(96)03053-5

Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., & Ptasinski, K. J. (2011). Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Bioenergy*, *35*(9), 3748–3762. doi:10.1016/ j.biombioe.2011.06.023

Stockholm University. (n.d.). *Planetary Boundaries Research*. Stockholm Resilience Centre. Retrieved from http://www.stockholmresilience.org/

Stokes, B. J., McDonald, T. P., & Kelley, T. (1993) Transpirational drying and costs for transporting woody biomass - a preliminary review. IEA/BA Task IX, Activity 6: Transport and Handling. New Brunswick, CN: IEA pp. 76-91.

Stokes, B. J., Watson, W. F., & Sirois, D. L. (1987). Factors affecting power requirements for chipping whole trees. Paper No. 87-6012. *American Society of Agricultural Engineers Summer Meeting*, Baltimore, Maryland.

Sues, A., Juraščík, M., & Ptasinski, K. (2010). Exergetic evaluation of 5 biowastes-to-biofuels routes via gasification. *Energy*, *35*(2), 996–1007. doi:10.1016/j.energy.2009.06.027

Sun, J., Wang, W., Liu, Z., Ma, Q., Zhao, C., & Ma, C. (2012). Kinetic Study of the Pyrolysis of Waste Printed Circuit Boards Subject to Conventional and Microwave Heating. *Energies*, *5*(9), 3295–3306. doi:10.3390/en5093295

Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technology*, *83*(1), 1–11. doi:10.1016/S0960-8524(01)00212-7 PMID:12058826

Swain, P. K., Das, L. M., & Naik, S. N. (2011). Biomass to liquid: A prospective challenge to research and development in 21st century. *Renewable & Sustainable Energy Reviews*, *15*(9), 4917–4933. doi:10.1016/j.rser.2011.07.061

Szargut, J., Morris, R. D., & Steward, R. F. (1988). *Exergy analysis of thermal chemical and metallurgical processes*. Berlin: Springer – Verlag.

Tang, W., Liu, Y., Zhang, H., & Wang, C. (2003). New approximate formula for Arrhenius temperature integral. *Thermochimica Acta*, *408*(1-2), 39–43. doi:10.1016/S0040-6031(03)00310-1

Tannous, K., & Mizonov, V. (2009). Comportamento da biomassa na fluidodinâmica em leitos fluidizados cônico e cilíndrico. In *Proceedings of the XXXIV Congresso Brasileiro de Sistemas Particulados* (pp. 171-181) [CD]. Campinas, BR.

Tannous, K., Hemati, M., & Laguerie, C. (1994). Caractéristiques au minimum de fluidisation et expansion des couches fluidisées de particules de la catégorie D de Geldart. *Powder Technology*, *80*(1), 55–72. doi:10.1016/0032-5910(94)02841-9

Tannous, K., Hemati, M., & Laguerie, C. (1998). Hydrodynamic characteristics of fluidized beds containing large polydispersed particles. *Brazilian Journal of Chemical Engineering*, *15*(1), 67–76. doi:10.1590/S0104-66321998000100007

Tannous, K., Lam, P. S., Sokhansanj, S., & Grace, J. R. (2013). Physical properties for flow characterization of ground biomass from Douglas fir wood. *Particulate Science and Technology*, *31*(3), 291–300. doi:10.1080/02726351.2012.732676

Tavares, J. R., Sthel, M. S., Campos, L. S., Rocha, M. V., Lima, G. R., da Silva, M. G., & Vargas, H. (2011). Evaluation of pollutant gases emitted by ethanol and gasoline powered vehicles. *Procedia Environmental Sciences*, *4*(0), 51–60. doi:10.1016/j.proenv.2011.03.007

Temur Ergan, B., & Bayramoğlu, M. (2011). Kinetic Approach for Investigating the "Microwave Effect": Decomposition of Aqueous Potassium Persulfate. *Industrial & Engineering Chemistry Research*, *50*(11), 6629–6637. doi:10.1021/ie200095y

Thompson, J., & Sprinkle, W. (2013). Production, cost and chip characteristics of in-wood microchipping. In *2013 Council on Forest engineering Annual Meeting. Missoula, Montana, USA*.

Thonglimp, V., Hiquily, N., & Laguerie, C. (1984). Vitesse minimale de fluidization et expansion de couches de mélanges de particules solides fluidisés par un gaz. *Powder Technology*, *39*(2), 223–239. doi:10.1016/0032-5910(84)85040-8

Tiangco, M. V., Jenkins, M. B., Goss, R. J., Chancellor, J. W., & Camacho, R. I. (1990). Variation of engine performance with reactor size for rice hull fueled gasification system. *American Society of Agricultural Engineers*, paper (6076) presented at 1990 International Summer Meeting.

Tiango, M. V., Jenkins, M. B., Goss, R. J., & Chancellor, W. J. (1986). Design and development of a continuous small-scale rice hull gas producer. *American Society of Agricultural Engineers*, paper (3070) presented at ASAE Summer Meeting.

Timms, R. (2007). Palm oil – The oil for the 21st century? *European Journal of Lipid Science and Technology*, *109*(4), 287–288. doi:10.1002/ejlt.200700047

Tonbul, Y. (2008). Pyrolysis of pistachio shell as a biomass. *Journal of Thermal Analysis and Calorimetry*, *91*(2), 641–647. doi:10.1007/s10973-007-8428-6

Tooyserkani, Z., Kumar, L., Sokhansanj, S., Saddler, J., Bi, X. T., Lim, C. J., & Melin, S. et al. (2013). SO_2- catalyzed steam pretreatment enhances the strength and stability of softwood pellets. *Bioresource Technology*, *130*, 59–68. doi:10.1016/j.biortech.2012.12.004 PMID:23347905

Tooyserkani, Z., Sokhansanj, S., Bi, X. T., Lim, C. J., Saddler, J., Lau, A., & Kumar, L. et al. (2012). Effect of steam treatment on pellet strength and the energy input in pelleting of softwood particles. *Transactions of the ASABE*, *55*(6), 2265–2272. doi:10.13031/2013.42484

Torres, W., Pansare, S. S., & Goodwin, J. G. Jr. (2007). Hot gas removal of tars, ammonia, and hydrogen sulfide from biomass gasification gas. *Catalysis Reviews*, *49*(4), 407–456. doi:10.1080/01614940701375134

Tovar, L. P., dos Santos, R. A., Maciel, M. R. W., & Filho, R. M. (2013). Experimental evaluation and kinetic modeling studies on the hydrothermal and H2SO4-catalyzed hydrothermal pretreatments of sugarcane bagasse: Focusing on pretreatment at low temperature and batch process for high-solids loading *35th Symposium on Biotechnology for Fuels and Chemicals* (pp. 196). Hilton Portland: Portland, OR.

Tovar, L. P., Maciel, M. R. W., & Filho, R. M. (2014a). Optimizing dilute H2SO4-hydrolysis/pretreatment in a batch reactor at high solids loading to enhance pentose sugars recovery and enzymatic digestibility: a critical step for 2G ethanol production from sugarcane bagasse *36th Symposium on Biotechnology for Fuels and Chemicals* (pp. 68). Hilton Clearwater Beach: Clearwater Beach, FL.

Tovar, L. P., Maciel, M. R. W., & Filho, R. M. (2014b). Plug flow reactor model to analyse operating conditions on the dilute H2SO4-acid hydrolysis of sugarcane bagasse at high-solids loading. *Chemical Engineering Transactions*, *37*, 325–330. doi:10.3303/CET1437055

Tsai, W. T., Lee, M. K., & Chang, Y. M. (2006). Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*, *76*(1-2), 230–237. doi:10.1016/j.jaap.2005.11.007

U.S. Environmental Protection Agency. (2014). *Climate change indicators in the United States, 2014. 3rd edition. EPA 430-R-14-004*. Retrieved April 7, 2015, from www.epa.gov/climatechange/indicators

US Department of Energy-DOE. (2010). Biomass multi-year program plan. Retrieved from http://www1.eere.energy.gov/ biomass/pdfs/biomass_mypp_november2010.pdf

US Environmental Protection Agency-EPA. (2007). Biomass Combined Heat and Power Catalog of Technologies. Retrieved from http://www.epa.gov/chp/documents/biomass_chp_catalog.pdf (November 1st, 2014).

Van de Velden, M., Baeyens, J., Brems, A., Janssens, B., & Dewil, R. (2010). Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy*, *35*(1), 232–242. doi:10.1016/j.renene.2009.04.019

Van Dranen, A., & Mello, S. (1997). *Production of ethanol from biomass*. U.S. Patent No. 5677154.

Van Krevelen, D., Van Heerden, C., & Huntjens, F. (1951). Physicochemical aspects of the pyrolysis of coal and related organic compounds. *Fuel*, *30*, 253–259.

Van Rossum, G., Kersten, S. R. A., & Van Swaaij, W. P. M. (2007). Catalytic and noncatalytic gasification of pyrolysis oil. *Industrial & Engineering Chemistry Research*, *46*(12), 3959–3967. doi:10.1021/ie061337y

Várhegyi, G., Antal, M. J. Jr, Jakab, E., & Szabó, P. (1997). Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *42*(1), 73–87. doi:10.1016/S0165-2370(96)00971-0

Várhegyi, G., Antal, M. J. Jr, Szekely, T., & Szabó, P. (1989). Kinetics of the thermal decomposition of cellulose, hemicellulose, and sugar cane bagasse. *Energy & Fuels*, *3*(3), 329–335. doi:10.1021/ef00015a012

Várhegyi, G., Czégény, Z., Jakab, E., McAdam, K., & Liu, C. (2009). Tobacco pyrolysis. Kinetic evaluation of thermogravimetric–mass spectrometric experiments. *Journal of Analytical and Applied Pyrolysis*, *86*(2), 310–322. doi:10.1016/j.jaap.2009.08.008

Várhegyi, G., Jakab, E., & Antal, M. J. Jr. (1994). Is the Broido-Shafizadeh model for cellulose pyrolysis true? *Energy & Fuels*, *8*(6), 1345–1352. doi:10.1021/ef00048a025

Vassilev, S. V., Baxter, D., Andersen, L. K., Vassileva, C. G., & Morgan, T. J. (2012). An overview of the organic and inorganic phase composition of biomass. *Fuel, 94*, 1–33. doi:. 2011.09.03010.1016/j.fuel

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913–933. doi:10.1016/j.fuel.2009.10.022

Vitasari, C. R., de Haan, A. B., & Meindersma, G. W. (2010). Conceptual processdesign of glycoaldehyde isolation from pyrolysis oil via physical extraction route. Eindhoven University of Technology. Netherlands. Retrieved from www.biocoup.com/fileadmin/user/december/00_64_TUE_ March 10.pdf (November 1st, 2014).

Vlaev, L. T., Markovska, I. G., & Lyubchev, L. A. (2003). Non-isothermal kinetics of pyrolysis of rice husk. *Thermochimica Acta*, *406*(1–2), 1–7. doi:10.1016/S0040-6031(03)00222-3

Vyazovkin, S., Burnham, A. K., Criado, J. M., Pérez-Maqueda, L. A., Popescu, C., & Sbirrazzuoli, N. (2011). ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica Acta*, *520*(1–2), 1–19. doi:10.1016/j.tca.2011.03.034

Wadell, H. (1935). Volume, shape and roundness of quartz particles. *The Journal of Geology*, *43*(3), 250–280. doi:10.1086/624298

Wan Rosli, W. D., Law, K. N., Zainuddin, Z., & Asro, R. (2004). Effect of pulping variables on the characteristics of oil palm frond fiber. *Bioresource Technology*, *93*(3), 233–240. doi:10.1016/j.biortech.2003.11.016 PMID:15062817

Wang, Z., Dunn, J. B., Han, J., & Wang, M. Q. (2014). Effects of co-produced biochar on life cycle greenhouse gas emissions of pyrolysis-derived renewable fuels. *Biofuels. Bioproducts and Biorefining*, *8*(2), 189–204. doi:10.1002/bbb.1447

Wanjun, T., Cunxin, W., & Donghua, C. (2005). Kinetic studies on the pyrolysis of chitin and chitosan. *Polymer Degradation & Stability*, *87*(3), 389–394. doi:10.1016/j.polymdegradstab.2004.08.006

Watson, W. F., Sabo, R. F., & Stokes, B. J. (1986). Productivity of in-woods chippers processing understory biomass. In *Proceedings of the Council on Forest Engineering, Improving Productivity through Forest Engineering*. Academic Press.

Weber, C., Farwick, A., Benisch, F., Brat, D., Dietz, H., Subtil, T., & Boles, E. (2010). Trends and challenges in the microbial production of lignocellulosic bioalcohol fuels. *Applied Microbiology and Biotechnology*, *87*(4), 1303–1315. doi:10.1007/s00253-010-2707-z PMID:20535464

Wei, L., Prodesimo, L. O., Igathinathane, C., & Batchelor, W. D. (2009). Process engineering evaluation of ethanol production from wood through bioprocessing and chemical catalysis. *Biomass and Bioenergy*, *33*(2), 255–266. doi:10.1016/j.biombioe.2008.05.017

Weisberg, P., Delaney, M., & Hawkes, J. (2010).Carbon market investment criteria for biochar projects. Public Interest Energy Research (PIER) Program. Retrieved from http://www.biochar-international. org/sites/default/files/WestCARB%20Biochar%20Report%20Final.pdf

Wen, C. Y., & Yu, Y. H. (1966). Mechanics of fluidization.*Chemical Engineering Progress Symposium Series*, *62*(62), 100-111.

White, J. E., Catallo, W. J., & Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 1–33. doi:10.1016/j.jaap.2011.01.004

Woolf, D., Amonette, J. E., Street-Perrott, F. A., Lehmann, J., & Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nature Communications*, *1*(5), 1–9. doi:10.1038/ncomms1053 PMID:20975722

Woudstra, N. (2012). *Sustainable energy systems: limitations and challenges based on exergy analysis.* (Doctoral dissertation). Delft University of Technology, Delft, Netherlands.

Wright, M. M., Satrio, J. A., Brown, R. C., Daugaard, D. E., & Hsu, D. D. (2010). Technoeconomic analysis of biomass fast pyrolysis to transportation fuels. Technical Report NREL/TP-6A20-465886. Retreived from http://www.nrel.gov/docs/fy11osti/46586.pdf

Wu, C., Budarin, V. L., Gronnow, M. J., De Bruyn, M., Onwudili, J. A., Clark, J. H., & Williams, P. T. (2014). Conventional and microwave-assisted pyrolysis of biomass under different heating rates. *Journal of Analytical and Applied Pyrolysis*, *107*(0), 276–283. doi:10.1016/j.jaap.2014.03.012

WWF. (2014). Living[*Species and spaces, people and places*. Available at: http://wwf.panda.org/about_our_earth/all_publications/living_planet_report/]. *The Planetary Report, 2014*.

Wyman, C. E. (1994). Ethanol from lignocellulosic biomass: Technology, economics, and opportunities. *Bioresource Technology*, *50*(1), 3–15. doi:10.1016/0960-8524(94)90214-3

Xu, D., Tree, D. R., & Lewis, R. S. (2011). The effects of syngas impurities on syngas fermentation to liquid fuels. *Biomass and Bioenergy*, *35*(7), 2690–2696. doi:10.1016/j.biombioe.2011.03.005

Xu, R., Ferrante, L., Briens, C., & Berruti, F. (2011). Bio-oil production by flash pyrolysis of sugarcane residues and post treatments of the aqueous phase. *Journal of Analytical and Applied Pyrolysis*, *91*(1), 263–272. doi:10.1016/j.jaap.2011.03.001

Yadav, G. D., & Borkar, I. V. (2006). Kinetic modeling of microwave-assisted chemoenzymatic epoxidation of styrene. *AIChE Journal. American Institute of Chemical Engineers*, *52*(3), 1235–1247. doi:10.1002/aic.10700

Yan, W., Hu, X., Zhang, G., Deng, M., Yi, C., & Xu, Z. (2012). Microwave assisted preparation of monodisperse polymeric microspheres and its morphologies and kinetics. *Journal of Wuhan University of Technology-Mater. Science Editor*, *27*(6), 1100–1104. doi:10.1007/s11595-012-0609-x

Yao, F., Wu, Q., Lei, Y., Guo, W., & Xu, Y. (2008). Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. *Polymer Degradation & Stability*, *93*(1), 90–98. doi:10.1016/j.polymdegradstab.2007.10.012

Yazadanpanah, F., Sokhansanj, S., Lim, C. J., Lau, A., Bi, X. T., Lam, P. Y., & Melin, S. (2013). Potential for flammability of gases emitted from stored wood pellets. *Canadian Journal of Chemical Engineering*, *92*(4), 603–609. doi:10.1002/cjce.21909

Ye, N., Li, D., Chen, L., Zhang, X., & Xu, D. (2010). Comparative studies of the pyrolytic and kinetic characteristics of maize straw and the seaweed *ulva pertusa. Journal PLOS ONE*, *5*(9), 1–6. doi:10.1371/journal.pone.0012641 PMID:20844751

Younesi, H., Najafpour, G., & Mohamed, A. R. (2005). Ethanol and acetate production from synthesis gas via fermentation processes using anaerobic bacterium, Clostridium ljungdahlii. *Biochemical Engineering Journal*, *27*(2), 110–119. doi:10.1016/j.bej.2005.08.015

Younesi, H., Najafpour, G., & Mohamed, A. R. (2006). Liquid Fuel Production from Synthesis Gas via Fermentation Process in a Continuous Tank Bioreactor (CSTBR) Using Clostridium ljungdahlii. *Iranian Journal of Biotechnology*, *4*(1), 45–53.

Yuan, H. R., & Liu, R. H. (2007). Study on pyrolysis kinetics of walnut shell. *Journal of Thermal Analysis and Calorimetry*, *89*(3), 983–986. doi:10.1007/s10973-006-7688-x

Yu, Q., Brage, C., Chen, G., & Sjostrom, K. (2007). The fate of fuel-nitrogen during gasification of biomass in a pressurised fluidised bed gasifier. *Fuel*, *86*(4), 611–618. doi:10.1016/j.fuel.2006.08.007

Yu, Y., & Wu, H. (2010). Bioslurry as a fuel 2: Life-Cycle energy and carbon footprints of bioslurry fuels from malee biomass in Western Australia. *Energy & Fuels*, *24*(10), 5660–5668. doi:10.1021/ef100957a

Zhang, M., Sword, M., Buckmaster, W. D., & Cauffman, D. R. (2003). Design and evaluation of a corn silage harvester using shredding and flail cutting. *Transactions of American Society of Agricultural and Biological Engineers*, *46*(6), 1503–1511. doi:10.13031/2013.15633

Zhang, Y., Hu, G., & Brown, R. C. (2013). Life cycle assessment of the production of hydrogen and transportation fuels from corn stover via fast pyrolysis. *Environmental Research Letters*, *8*(2), 025001. doi:10.1088/1748-9326/8/2/025001

Zhang, Z., & Zhao, Z. K. (2010). Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. *Bioresource Technology*, *101*(3), 1111–1114. doi:10.1016/j.biortech.2009.09.010 PMID:19800219

Zhou, L., Puri, V. M., Anantheswaran, R. C., & Yeh, G. (1995). Finite element modeling of heat and mass transfer in food materials during microwave heating - Model development and validation. *Journal of Food Engineering*, *25*(4), 509–529. doi:10.1016/0260-8774(94)00032-5

Zhu, S., Wu, Y., Yu, Z., Liao, J., & Zhang, Y. (2005). Pretreatment by microwave/alkali of rice straw and its enzymic hydrolysis. *Process Biochemistry*, *40*(9), 3082–3086. doi:10.1016/j.procbio.2005.03.016

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