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ELÉM PATRÍCIA ALVES ROCHA

MELHORIA DO CONHECIMENTO ATUAL DAS PROPRIEDADES E PROCESSOS DE CONVERSÃO TÉRMICA DE UMA GRANDE VARIEDADE DE BIOMASSAS LIGNOCELULÓSICAS BRASILEIRAS

IMPROVING CURRENT KNOWLEDGE OF THE PROPERTIES AND THERMAL CONVERSION PROCESSES OF A WIDE VARIETY OF BRAZILIAN LIGNOCELLULOSIC BIOMASSES

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Supervisor: Prof. Dr. Marcelo Cardoso

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to my family

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CHAPTER 1

1. General Introduction

1.1 Background

Energy sources are indispensable for a country's development. In addition, the quality and capacity of a region's energy sources are indicative of its degree of development. The Brazilian energy sector has developed as the country has modernized. The main sources of energy in Brazil are hydroelectric power, petroleum, coal and biofuels, and some others used on a smaller scale, such as natural gas and nuclear energy.

A report from the National Energy Balance (EPE, 2016) estimates that the electricity generation in the Brazilian public service and independent power plants reached 581.5 TWh in 2015. It is known that the Brazilian energy matrix is largely dominated by hydroelectric power (more than 80 GW generated) and 75.5 % of electricity in Brazil comes from renewable sources as shown in figure 1.1. The production of electricity from wind power reached 21,626 GWh and from fossil fuels accounted for 26.0% of the national total in 2015. In the same year, the independent producers' generation, like Pulp and Paper and sector, Steel, Sugar and Alcohol, Chemical and oil exploitation, refining and production segment, participated reached 96.6 TWh which represents 16.6% of total production in the country. Further, net imports of 34.4 TWh, added to internal generation, allowed a domestic electricity supply of 615.9 TWh, and the final consumption was 522.8 TWh (EPE, 2016). The electricity generation from biomass accounted for 8.0% of the national total (EPE, 2016), and is mainly extracted from the sugar–ethanol sector (Tolmasquim, 2016).

In Brazil, the domestic production of oil reaching an average of 2.44 million barrels per day in 2015 representing an increase of 8 % in this year. However, according to EPE (2016), a decrease of 5.2 % for diesel and 9.5 % for automotive gasoline. The decrease in diesel consumption was due to the reduction of economic activity in Brazil the year before. The decline in automotive gasoline consumption was associated with the hydrous ethanol and natural gas with more competitive prices. Natural gas is usually produced together with oil and its share in the national energy matrix reached the level of 13.7% in 2015. The average daily production of natural gas was 96.2 million m^3/day, and the volume of imported was an average of 50.4 million m^3/day (EPE, 2016). It is used for domestic heating and cooking, industrial activities and thermoelectric plants supply and

in the production of motor fuels (Godemberg and Lucon, 2007). Highlighted is the demand of steam coal for electricity generation which increased 9,4% in 2015 compared to 2014 (EPE, 2016).

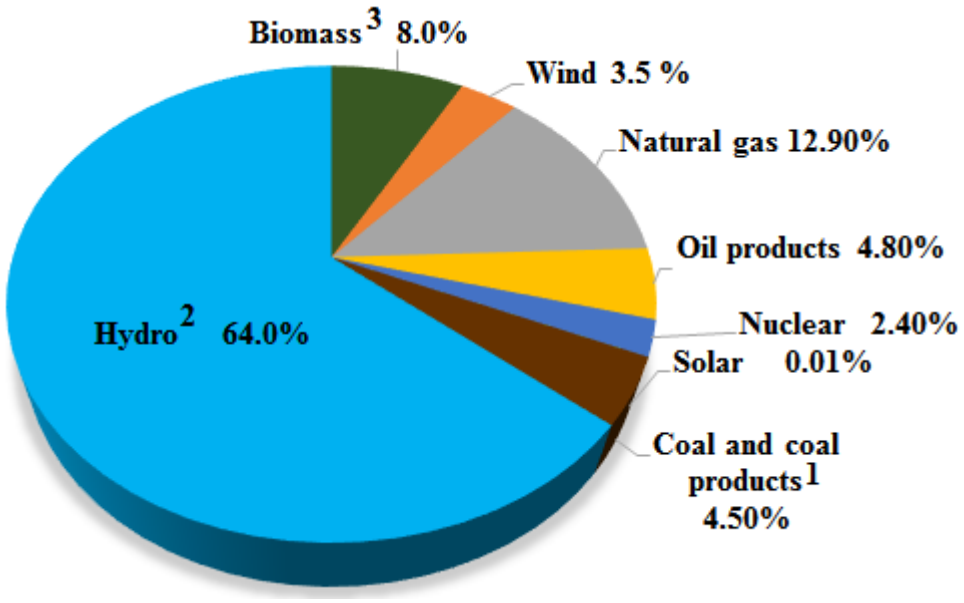

Figure 1.1. Domestic Electricity Supply by Source (1-Includes coke oven gas; 2-Includes electricity imports; 3- Includes firewood, sugarcane bagasse, black-liquor and other primary sources) (EPE, 2016).

Biofuels are energy sources from natural biomass products which are successfully deployed in the country. Ethanol, biogas and biodiesel are most common biofuels used in Brazil. In 2015 the amount of biodiesel (B100) produced in Brazil reached 3,937,269 m^3 in which the main raw material was the soybean oil (70%), followed by tallow (16%). The production of ethanol, from sugarcane, increased by 6.0%, yielding the amount of 30,249 thousand m^3 (EPE, 2016).

Biomass stands as a renewable alternative with a high potential and it is considered as a clean source of renewable energy whose exploitation contributes to the reduction of environmental pollution. For example, in Brazil, São Paulo and Minas Gerais states are the major producers of sugarcane with around two thirds of the whole production in the country. These states are committed to the total removal of burning process in the farms until 2018. This process has been controlled by the Brazilian government by law No. 11241 (September 19th, 2002) to promote the gradual reduction of sugarcane burning until 2031. Due to the high generation of this agricultural residue in

ethanol production, it has become necessary to find one or more energetic applications for sugarcane straw. Brazil produces a substantial amount of lignocellulosic agricultural and industrial waste such as rice husks, wheat straw, sugar cane bagasse and straw that can produce various sustainable bioproducts, biofuels and energy (Fernandes et al., 2016; Sellin et al. 2016). According to Rambo et al. (2015), in 2014, forestry industries in Brazil generated around 47.0 million tons of solid waste, 33.60 million tons (71.5%) of which were generated in forestry activities and 13.40 million tons (28.5%) by forest industrial activities. Bracepa has reported that in 2010, the total production of pulp and paper in Brazil was 22.7 million tones. This generated 11 million tonnes of waste, representing about 48% in relation to the total paper and pulp production.

The use of lignocellulosic biomass for the production of heat, power, transportation fuels, and chemicals has increased in recent years for a number of different reasons, the main ones being:

- the desired reduction of green house gas emissions to the atmosphere;
- the threat of depletion of traditional fossil fuels;
- policies to secure the energy supply by diversification of the resources.

Brazil has natural and geographical conditions favorable to the production of biomass and it is also an important producer of fast-growing woods, such as eucalyptus, which is cultivated in the country for many industrial purposes (González-García et al., 2012). Because of this, research efforts are important for the development and implementation of thermal biomass conversion technologies, given the huge demand for obtaining energy in a cleaner way. At the same time, the use of lignocellulosic biomass for energy purposes is subjected to some uncertainties, mainly concerning the harvesting costs. In addition, biomass in its original form is not ideal for fuel use. Therefore, comprehensive understanding of the thermal behavior of each biomass feedstock, and the major characteristics and overall environmental impact of their use in the long term is important for proper implementation in renewable energy applications.

The growing interest in the use of lignocellulosic biomasses for renewable energy production together with a few gaps in the thermal biomass conversion technologies were the chief motivations for this thesis.

1.2 Objectives

1.2.1 General Objectives

The objective of this thesis is to improve the understanding of thermal biomass conversion process and widen the Brazilian lignocellulosic biomasses database.

1.2.2 Specific Objectives

- Conduct the analysis of physicochemical characteristics of nine types of important lignocellulosic biomasses widely available in Brazil, including five types of eucalyptus wood chips derived from different clones, sugar cane bagasse (industrial residues of ethanol and sugar mills), elephant grass, bamboo, and fibers of coconut fruit (husk).
- Proposal of a new analysis procedure to obtain the kinetic parameters of nine Brazilian lignocellulosic biomasses pyrolysis assuming first order reactions.
- Analyze the fast oxidative pyrolysis of residues from coffee and eucalyptus plantations as a renewable alternative to add value to waste.
- Select agro-industrial solid residues from coffee crops (parchment and coffee bush, i.e., stem, primary branch, secondary branch and leaves) to characterize as solid fuels and an evaluation of their properties by analysis of proximate and ultimate composition, energy content, several chemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl group), drying and thermogravimetric analysis.
- Estimate the potential of main Brazilian biomasses for generating renewable energy in Brazil such as sugarcane straw, sugarcane bagasse, coffee husks, banana leaves, banana stalk, coconut husk, coconut shell, soybean straw, soybean husk, corn straw, corn cob, rice straw, rice husk, orange bagasse, bamboo, elephant grass, eucalyptus and pinus. by their important fuel and other physicochemical properties, and annual production. This study adopts a resource-based assessment that takes into account the main characteristics of biomass feedstocks to estimate the renewable energy potential. The information obtained from the literature of the agro-industrial residues studied has been initially applied to evaluating the technical and environmental feasibility of their use as alternative energy sources

in thermochemical processes. Then, the biomass data were used to calculate the carbon stock and carbon sequestration potential of the biomass in renewable energy practices by the thermochemical conversion.

1.3 Contributions of this thesis

The main contribution of the thesis can be summarized as follows:

Improve the current knowledge of Brazilian lignocellulosic biomasses database for thermal biomass conversion. The studies developed allow valorization of agricultural and agro-industrial residues reducing landfill waste and improving sustainability. Additionally, the use of residual biomass has environmental and social benefits at current biomass processing sites. This can also mean development of new biotechnology based businesses.

The main contributions of the Chapters included in the thesis according to the related research objectives are presented here

- **Chapter 2** presents the analysis of physicochemical characteristics of nine types of important lignocellulosic biomasses widely available in Brazil, including five types of eucalyptus wood chips derived from different clones, sugar cane bagasse (industrial residues of ethanol and sugar mills), elephant grass, bamboo, and fibers of coconut fruit (husk). These results are useful for individuals and institutions which are considering using Brazilian biomass for thermochemical conversion because the data studied in this manuscript is not readily available in the literature to assess potential crop variability and the full range of important properties.
- **Chapter 3** shows the determination pyrolysis kinetic parameters of nine Brazilian lignocellulosic biomasses, including five types of eucalyptus wood derived from different clones, sugarcane bagasse (industrial residues of ethanol and sugar mills), elephant grass, bamboo and fibers of coconut fruit (husk). Kinetic parameters were obtained for the purpose of representing the kinetic mechanism of biomass carbonization by a general equation. The results are expected to provide useful information for individuals and institutions who are interested in using Brazilian biomass for thermochemical conversion, since limited amount of studies of the Brazilian biomass has been conducted so far and the data found in this manuscript are still not readily available in the literature.

- **Chapter 4** presents an extensive characterization of residual biomasses from the coffee production chain for energy purposes, increasing knowledge about the alternatives applicable to the energy matrix of countries where the coffee industry is a major agricultural activity, through physical and chemical analyzes that identify the most important quality indices, the interactions between them, as well as the quantification of its importance. In this sense, agro-industrial solid residues from coffee crops were selected being previously classified as parchment and coffee bush, i.e., stem, primary branch, secondary branch and leaves. Then, an extensive characterization of the solid fuel was performed, evaluating the evolution of their properties, including proximate and ultimate composition, energy content, several biochemical composition (polysaccharides, lignin, extractives, uronic acids and acelyl group), drying and thermogravimetric analysis of each residue group. It is important to note that the extensive characterization of the residues presented in this work is not readily available in the literature and these results are fundamental tools for the qualification and quantification of the effects of residues properties on conversion technologies that include thermochemical processes such as pyrolysis, gasification, and combustion, and physical processes such as briquetting and pelletizing
- **Chapter 5** analyzes the fast oxidative pyrolysis of residues from coffee and eucalyptus plantations as a renewable alternative to add value to waste. The eucalyptus and coffee plantations are of great importance for the Brazilian economy and they generating a large quantity of lignocellulosic biomass residues. These biomasses can be used to generate bio-oil, which are much easier to handle and transport than solid or gaseous fuels. In the literature we find articles of fast pyrolysis with inert gases, such as nitrogen, for eucalyptus wood and for coffee grounds, or household residues after coffee infusion. There are no literature data for the oxidative fast pyrolysis of eucalyptus residues from the pulp industry and pyrolysis data of the woody residue of the coffee crop.
- The successful exploitation of the agro-industrial solid residues as a substitute and alternative fuels in thermochemical processes constitutes an effective option to reduce energy costs in the Brazilian agro-industry and the environmental problems associated with waste disposal. As the evaluation of the residue properties constitutes an important step in defining the thermochemical process to be applied, **the chapter 6** is important for estimating the agro-industrial

potential for generating renewable energy in Brazil. Thus, the valorization of these abundant and low-cost residues could give a substancial positive contribution to the agro-industrial sector in Brazil.

1.4 Author's contribution

Prof. Marcelo participated actively in and contributed significantly to the research and preparation of these Chapters. The work presented in **chapters 2 and 3** are associated with a partnership formed between two Brazilian universities, University Federal of Minas Gerais (UFMG) and University Federal of Viçosa (UFV), and two Finnish universities, Lappeenranta University of Technology (LUT) and University of Jyväskylä (JYU) aiming to improve current knowledge of the thermal conversion processes of a wide variety of biomass feedstocks. For the choice of biomasses, the study developed by Fernando José Borges Gomes from the Federal University of Viçosa was taken into account which eighteen eucalypt clones obtained from the Brazilian Genolyptus project were investigated regarding their potential characteristics for pulp production. Aiming at the same goal, two species of elephant grass were also evaluated as an alternative source for the pulp industry. The characterization of the biomass samples was realized with help of prof. Fernando José Borges Gomes (from UFV), prof. Jorge Luiz Colodette (from UFV), MS. Ekaterina Sermyagina (from LUT) and the autor (from UFMG). Thus, Ekaterina Sermyagina assisted the autor with preparation of **chapters 2 and 3.**

For the choice of biomasses described in **chapters 4**, it was take in account the large amount of residues obtained from the coffee production that the extensive characterization of the residues was not readily available in the literature. Mrs. Clara Mendoza Martinez is the first author of **chapter 4** and was responsible for most of the characterization analyzes. The author took part in the biomass thermogravimetric analyzes, and then assisted in the data analysis and preparation of the paper.

The student Vinícius Ramos conducted the pyrolysis tests for chapter 5, and assisted in the pyrolysis material analysis. The autor processed the experimental results which are presented in **chapter 5**. Further, **chapters 5** and **3** are associated with a study aiming to develop a computational framework for simulating biomass fast pyrolysis. The computational framework will help in the understanding of complex physical phenomena, design and optimize biomass conversion processes in fluidized bed reactors. In this study, the pyrolyzer modeling was carried out and the simulator is in the

implementation phase. However, this work is not described in this thesis because the computational framework is being developed. Thus, the computer code will be validated by the information from the chapters 3 and 5.

For **chapter 6** the studies carried out in previous chapters were considered, as well as the information known about the large amount of residues generated by the agro-industry in Brazil. In this way, the author and student Matheus Fiuza generated an extensive database for biomass aims to estimate the potential of main Brazilian biomasses for generating renewable energy in Brazil.

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CHAPTER 2

An Analysis of Brazilian Biomass Focusing on Thermochemical Conversion for Energy Production

Elém Patrícia Alves Rocha[1], Fernando José Borges Gomes[2], Ekaterina Sermyagina[3], Marcelo Cardoso[1],Jorge Luiz Colodette[2]

[1]Federal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901

[2]Federal University of Viçosa (UFV), Viçosa, MG Brazil, 36.570-000

[3]Lappeenranta University of Technology (LUT), Lappeenranta, FIN-53851

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Abstract: Concerns about climate change and other issues mostly related to the reduction of fossil fuel usage have increased the demand for renewable energy sources. The possibility of using lignocellulosic biomass for energy generation is gaining interest in many countries worldwide. Current paper presents the analysis of physicochemical characteristics of nine lignocellulosic biomasses: five types of eucalyptus wood chips, sugarcane bagasse, elephant grass, bamboo, and coconut husk. Selection of a thermal conversion technology depends on the knowledge of important biomass characteristics in relation to thermal conversion: density and productivity, proximate and ultimate analysis, heating value, ash and polysaccharides`s compositions, and thermogravimetric analysis. In regards to the annual energy potential and density, it was suggested that the *E. urophylla (Flores IP) x E. urophylla (Timor)* and bamboo have the greatest potential for energy application, which reduces transport and storage costs. Moreover, the eucalyptus has desirable characteristics in thermal conversion processes: low ash content that results in lesser damage to the equipment, low content of sulfur and nitrogen that lead to better environmental performance and product quality. Obtained information could be used as a basis for a more comprehensive database of biomass properties that will help to evaluate various biomasses with respect to renewable energy potential.

2.1 Introduction

The composition of raw biomass depends on various factors, such as plant species, part of plant, growth processes, soil type, growing region and fertilizer treatment, etc. Biomass materials can be divided into four main types, namely: woody plants, herbaceous plants/grasses, aquatic plants and manures. Woody biomass, such as eucalyptus, is widely and quite efficiently used as a feedstock for Brazilian pulp and steel industries. At the same time, eucalyptus is a relatively expensive option, and alternative sources (e.g., grasses) are being investigated. High productivity plants such as elephant grass (30−45 bone dry t/ha/yr) could potentially supply biomass at a low cost to meet the current demand needed for energy production (Gomes, 2013).

The objective of this study was to conduct the analysis of physico-chemical characteristics of nine types of important lignocellulosic biomasses widely available in Brazil, including five types of eucalyptus wood chips derived from different clones, sugarcane bagasse (industrial residues of ethanol and sugar mills), elephant grass, bamboo and fibers of coconut fruit (husk). These results are useful for individuals and institutions who are considering using Brazilian biomass for thermochemical conversion because the data studied in this manuscript is not readily available in literature to assess potential crop variability and the full range of important properties.

2.1.1 The main Brazilian plants species

The current study focuses on most common Brazilian woody and non-woody biomass species.

2.1.1.1 Woody species

The eucalyptus plantations owned by the Brazilian pulp & paper industry (1.8 million ha) represent the largest industrial eucalyptus plantation base in the world. These include plantations with the highest growth rates and lowest production cost, which were achieved after many years of genetic improvements. The Brazilian steel industry owns more than 1 million ha of eucalyptus plantations used for charcoal (pig iron) production. At the same time, in Brazil, significant amount of land is still available for expanding the eucalyptus forest for bioenergy use (Lora et al, 2009).

The coconut tree or coconut palm, is an agricultural crop widely spread out through the tropics. In Brazil, coconut plantations are found mainly along the coast throughout the northeastern and southeastern parts of the country. Brazilian coconut production in 2011 was 1.9 billion fruit, with a total plantation area of 270,000 ha, of which it is estimated that 20% are represented by the variety of dwarf coconut, 10% by hybrid coconut tree and 70% by giant coconut (Embrapa, 2007). The dwarf coconut is the variety of coconut that is more commercially used in Brazil, and according to Embrapa (2007) more than 57,000 ha of these species are planted in Brazil. Under good conditions, a pure stand of dwarf coconut palms should annually produce at least 130 nuts per palm, or 120,000 nuts per hectare. Most coconut fruit processing generates residue (fibrous parts) which after removing the solids for shredded coconut and coconut water accounts for 35% of the fruit mass. Moreover, the coconut husk is constituted of 30% fiber and 70% pitch material (Grimwood et al., 1975). Since only a small part of the available coconut material is currently utilized, alternative outlets, such as energy applications, are attracting increasing interest.

Bamboo represents another wood type widespread in Brazil. There are over 1200 species of bamboo in the world, which are typically associated with tropical and subtropical forests and are found natively on every continent except Europe (Calderón and Soderstrom, 1980). Brazil has the greatest diversity with about 34 genera and 232 species of which about 204 are endemic (Figueiras et al., 2004). Calderón and Soderstrom (1980) have divided bamboos into two groups, *Bambuseae bamboos* (or timber) and *Olyreae* (or herbaceous). The *Dendrocalamus giganteus* also known as Giant Bamboo studied in current work is one of the largest bamboo trees in the world (reaching heights of 30 to 40 m).

2.1.1.2 Non-woody species

Sugarcane plant, a worldwide commodity, first emerged from Oceania (New Guinea) and Asia (mainly India and China). It is basically composed of the stalk - formed by several nodes, which are made up of fibers (cellulose, hemicelluloses and lignin), sugar (sucrose, fructose and lactose) and the leaf - green leafs and dry leaf sheaths, commonly called straw. In Brazil, ethanol fuel is produced from sugarcane which can be harvested mechanically using harvesting machines or manually; the straw that surrounds the base

of the plant is removed (and in most cases burnt), and the stalk is cut. The sugarcane stalk is then crushed and ground in mills and power plants extracting the juice that serves as raw material for ethanol production. The bagasse from the grinding is burned to produce the electricity used by the plant and for export to the grid. The sugarcane grown for ethanol production represents about 1% of the Brazilian arable land, or about 9.5 million hectares (representing 7 million tons of processed sugarcane per year) (Santos et al., 2012).

Elephant grass (*Pennisetum purpureum, Schumach*), originates from Africa and is one of the most important and widespread species of grass in all tropical and subtropical regions of the world. This grass is an important source of food for livestock, principally for feeding dairy cattle. Elephant grass has the ability to produce from 30 to 50 t of dry matter per hectare per year in regions with abundant and well-distributed rain throughout the year (Gomes, 2013). It has been considered as an alternative source of energy due its low cost, high fiber content, and potential for two harvests per year.

2.1.2 The main characteristics of biomass for thermochemical conversion processes

Direct combustion, gasification and pyrolysis present the most common and available for thermochemical conversion of biomass. In general terms, gasification is applied to convert solid material into gas phase by partial oxidation with generation of gases (CO, H2, CH4 and lighter hydrocarbons), ash, char, tar and other minor contaminants. Tar and char are the result of incomplete conversion of biomass, and the gasification temperature needs to be high enough (above 750–1000 °C) for the steam reforming and water-gas reactions to be favorable (Souza-Santos, 2010; McKendry, 2002). Combustion is similar to gasification process in which fuel can be completely oxidized and converted to hot flue gasses. Pyrolysis is a thermal decomposition of biomass components that starts at 350-550 °C and goes up to 700-800°C in the absence of air/oxygen (Basu, 2010). Depending on the operating condition, pyrolysis can be classified into three main categories: convertional, fast and flash pyrolysis.

The choice of the most suitable solid fuel is influenced by the thermochemical conversion process specific features (Souza-Santos, 2010). At the same time, the inherent

properties of the biomass are essential in choosing the conversion process depending on subsequent processing difficulties that might arise (Basu, 2010).

The main biomass properties considered important for thermochemical conversion are the following: productivity, density, moisture content, elemental composition, calorific value, proportions of fixed carbon to volatile matter, ash/residue content, alkali metal content and cellulose/lignin ratio.

Density, productivity and energy potential of biomass are important parameters for analysis of the viability of thermochemical conversion processes. Biomass density and calorific value can influence economic and logistic considerations, such as shipping, handling and storage costs (Basu, 2010). Elemental composition of both feedstock material and ash provides an important information for prediction of thermochemical conversions (Vassilev et al., 2010; Demirbas, 2004). Higher ash content contributes to reducing the heating value of the material because the minerals do not have energy value in thermochemical conversion processes. The reaction of alkali metals with silica to form alkali silicates that melt or soften at low temperatures results in a sticky and mobile liquid phase; the reaction of alkali metals with sulfur forms alkali sulfates, which fouls heat transfer surfaces and may lead to operational problems during the thermochemical conversion process. These problems are aggravated by the presence of chlorine being a major factor in sticky ash formation (Lv et al., 2010).

Another important characteristic of biomass is its composition in terms of the plant`s structural chemical compounds. The dried biomass is generally composed of about 40 to 60% of cellulose which forms the skeletal structure of the plant and is composed of glucose molecules joined linearly. It also contains 15 to 30% hemicelluloses, which is a polymer similar to cellulose, but with heterogeneous branched chains composed mainly of: xylose, glucose, mannose, galactose, arabinose and others. Finally, it has from 20 to 35% lignin, a polymer completely different from cellulose and hemicelluloses, and is composed of a three-dimensional polymer which has irregular phenyl-propane units operating in the cell walls as a support material (Demirbas, 2010; Basu, 2010). Structural components that form plant cell (cellulose, hemicelluloses and lignin) illustrate quite different decomposition behavior during thermal treatments (Mckendry, 2002). As a

result, knowledge of lignocellulosic components content for a specific biomass type is essential for comprehensive understanding and control of biomass treatment.

2.2 Methodology

Five eucalyptus clones wood samples from commercial harvesting at seventh year growth, bamboo and elephant grass (150 days old), sugarcane from the industrial residues of ethanol and sugar mills, and coconuts husks were collected from Minas Gerais state in southeast of Brazil, and used as the test samples. The biomass samples were divided into representative specimens by quartering on a flat surface. In this process, the samples were thoroughly mixed and then sectioned into four approximately equal quarters. Opposite quarters were then combined and the process was repeated until sufficiently small specimens were obtained for each analytical technique. The samples were chipped, mixed and screened to produce the particles sizes below 0.42 mm, according to SCAN-CM 40:94 procedures (1993). After that, the biomasses were dried to about 15% moisture and stored in large plastic bags.

The measurements for basic density were performed according to SCAN CM-46:92 standard procedures (1993). The biomass productivity was calculated using the medium annual increase (MAI) and basic density, by the simple relation: biomass productivity (ton/ha/yr) = MAI (m^3/ha/yr) x basic density (t/m^3).

The proximate analysis aims to quantify the moisture, volatiles (condensable and non-condensable), fixed carbon and ash contained in a biomass sample. According to the standard EN 14774-2 (2009) for moisture analysis, biomass samples were weighed in dry containers and then kept in the oven at a temperature of 105 ± 2 °C for a certain period of time until biomass mass remained constant. For the volatile matter analysis, samples were prepared and placed in a muffle furnace at a temperature of 900 °C for 7 minutes, according to standard EN 15148 (2010). According to standard EN 14775 (2010), ash content is determined from the mass of the inorganic residue remaining after heating the biomass sample in air under controlled conditions of time to a temperature of 550 ± 10 °C.

The ultimate analysis shows the content of five major elements: carbon (C), oxygen (O), hydrogen (H), nitrogen (N), and sulphur (S) in the organic phase. Content of these elements was measured using a TruSpec Micro - Leco Instruments 628 Series C/H/N elemental analyzer with oxygen and sulfur module. All measurements were repeated in triplicate and a mean value corrected for moisture content is reported.

The higher heating value (HHV) of biomass samples was determined by combustion of the sample under specific conditions in a bomb calorimeter (Parr 6300 Calorimeter) according to DIN 51900-1 (2000) and Biomass energy potential (GJ/ha/yr) = MAI (m^3/ha/yr) x basic density (t/m^3) x HHV (GJ/t).

The analyses of ash with respect to contents of silica, chloride, iron, copper, manganese, potassium, calcium and magnesium were carried out directly on raw sawdust in accordance with standard methods for the examination of water and waste water (2000) by anatomic absorption spectrophotometer, Perkin Elmer - AA Analyst 200 series, except for chloride, which was determined according to Tappi T256 cm-97 standard procedure (2000).

Chemical composition of studied biomass samples was evaluated within the following procedure. The total extractives were determined in three steps, an extraction in ethanol toluene (1:2), an extraction in ethanol and a hot water extraction, according to T204 cm-97 standard procedures (2007). The content of biomass extractable in acetone was determined according to TAPPI T280 pm-99 standard procedure (2006). In order to determine biomass main cell wall components, a 200g sample of extractive free biomass (TAPPI T204 cm-97, 2007) was conditioned in a temperature and humidity controlled room (23 ± 1 ^{o}C, 50 ± 2 % RH) until an equilibrium moisture was achieved (~10 %). The contents of uronic acids, acetyl groups and sugars (glucans, mannans, galactans, xylans and arabinans) in the extractives-free biomass were determined according to Scott (1979), Solar et al. (1987) and Wallis et al. (1996), respectively. On the same extractives-free wood sample, the content of acid insoluble lignin, acid soluble lignin and lignin syringyl/guaiacyl (S/G) was determined according to TAPPI T 222 om-97 standard procedure (2011).

Thermogravimetric analysis was applied to study the transformations of chemical components when the biomass is subjected to a heat treatment in an inert atmosphere

(pyrolysis). Tests were performed using a TGA analyzer (SHIMADZU DTG60 Series), by heating a typical sample mass of 6 mg in a purge of nitrogen (100 ml/min), at heating rates of 5, 15 and 25 K/min with final temperature at 1173 K.

2.3 Results and discussion

2.3.1 Density, productivity and energy potential of biomass.

The basic density, productivity and energy potential data of the biomass samples are shown in Table 2.1.

Table 2.1. Basic density, productivity and energy potential of the biomass samples.

Sample Code	Sample	Basic Density (kg/m^3)	Productivity (ton/ha/yr)	Energy Potential (GJ/ha/yr)
E-U1xU2	*E. urophylla (Flores IP) x E. urophylla (Timor)*	504	43.3	801.0
E-U2xC1	*E. urophylla (Timor) x E. camaldulensis (VM1)*	547	29.6	553.5
E-G1xGL	*E. grandis (Coffs Harbour)x E. globulus (R)*	530	20.8	376.5
E-DGxC1	*[E. dunnii*(R) x *E. grandis (R)] x E. camaldulensis (VM1)*	500	36.3	667.9
E-GL	*Eucalytous globulus*	618	20.0	372.0
SCB	Sugar cane bagasse	131	12.0	229.2
EG	Elephant grass (*Penisetum purpureum*)	216	32.0	595.2
BB	Bamboo (*Bambusea gigantea*)	610	40.0	785.0
DCH	Dwarf coconut husk	348	3.37*	67.1

* Based on Brazilian coconut production in 2011 (FAOSTAT, 2015).

The eucalyptus wood samples presented a high value of basic density (504−610 kg/m^3) in relation to the grass species, expect for the bamboo sample that also showed a high value. Sugar cane bagasse (SCB) had the lowest basic energy density (131 kg/m^3) of all tested species.

The energy performance of each species can be evaluated by combining the amount of biomass produced per unit area with its heating value (HHV). The results show that the potential energy production of biomass ranges from 67.1 to 801.0 GJ/ha/yr. The result is mainly determined by the potential of Brazilian energy farming that is the result

of land availability and biomass productivity. The greatest potential of energy production were calculated for the *E. urophylla (Flores IP) x E. urophylla (Timor)* (E-U1xU2) and Bamboo (BB) (801.0 and 785.0 GJ/ha/yr) and the lowest values were calculated for the Sugar cane bagasse (SCB) and Dwarf coconut husk (DCH) (229.2 and 67.1 GJ/ha/yr). However, the energy value of SCB and DCH should not be underestimated, since these materials are agro-industrial waste.

2.3.2 Heating value, proximate and ultimate analysis

Table 2.2 includes the results of proximate analysis, ultimate, and heating values of the biomass collected. It was observed that the woody and non-woody species have high levels of volatile matter (69.20−79.72%) and low ash content (0.10−6.74%), which are typical values for biomass coming from wood and agricultural waste. In terms of ash, that is, total minerals in the biomass of different compositions, the species SCB, EG and BB showed more significant levels. However, these samples had very low levels of ash when compared, for example, to the Brazilian coal.

Table 2.2. Heating value, proximate and ultimate analysis.

	Sample code								
	E-U1xU2	E-U2xC1	E-G1xGL	E-DGxC1	E-GL	SCB	EG	BB	DCH
	Ultimate analysis(% mass, dry ash free basis)								
N	0.09	0.08	0.09	0.08	0.09	0.73	0.53	0.09	0.21
C	48.75	49.39	49.29	48.97	49.50	50.57	51.39	52.48	53.56
H	5.93	5.96	5.91	5.88	5.90	6.05	5.77	5.92	5.78
S	0.03	0.03	0.03	0.03	0.02	0.10	0.08	0.05	0.04
O	45.21	44.54	44.68	45.05	44.49	42.55	42.23	41.47	40.42
H/C	1.45	1.44	1.43	1.43	1.42	1.43	1.34	1.34	1.29
O/C	0.70	0.68	0.68	0.69	0.67	0.63	0.62	0.59	0.57
	Proximate analysis (% mass)								
M	10.53	9.03	13.18	11.05	12.33	11.86	10.18	9.09	10.24
Ash	0.19	0.25	0.10	0.19	0.21	6.74	4.48	2.04	1.16
V	78.02	79.72	75.21	76.36	75.27	70.42	69.20	70.91	74.76
FC	11.26	11.0	11.52	12.41	12.19	10.98	16.14	17.96	13.84
	Heating value (MJ/kg)								
HHV	18.5	18.7	18.1	18.4	18.6	19.1	18.6	19.6	19.9

M – moisture; V – volatiles; FC – fixed carbon; HHV – higher heating value.

In Table 2.2 it can be observed that all samples have quite low moisture content, with the *E. grandis (Coffs Harbour) x E. globulus (R)* (B3) having the highest moisture contents, 13 and 18%, respectively. The fixed carbon content for Sugarcane bagasse (SCB) stood at 10.98%, consistent with published values. For the Elephant grass (EG), the fixed carbon content was found 16.14%, while 16.55% and 14.66% were reported by Assis et al. (2014) and Braga et al. (2014), respectively. For the several eucalypt clones, the fixed carbon content mentioned in the literature is approximately 12 % (Souza-Santos, 2010), similar to the value found in this study.

According to Nogueira and Lora (2003) fuels with high fixed carbon content and low levels of volatile materials tend to burn more slowly, requiring longer residence time in the thermochemical equipment compared to fuels with a low fixed carbon content.

As for the heating value, Table 2.2 shows mean values of about 18.7 MJ/kg for all species, wherein the highest values found were from the biomasses SCB, BB and DCH. The heating value is directly related to the fixed carbon content and is associated with volatile and ash content. Given these relationships, it was noted that although the EG biomass has a high fixed carbon content, it did not maintain the expected relationship and presented the lowest volatile content and higher ash content, which reduces the heating value of this biomass.

For the studied biomasses, the main constituent is carbon (48.75−53.56%, dry basis). For eucalyptus, regardless of the type, the elemental composition on a dry basis showed approximately 0.09% of nitrogen, 49.29% of carbon, 5.91% of hydrogen, 44.68% of oxygen and 0.03% of sulfur.

The presence of nitrogen in the composition of biomass results in the formation of nitrogen oxides after thermochemical conversion process. All the nitrogen oxides enhance the greenhouse effect, thus minimal amounts of nitrogen are desirable in thermochemical processes. In addition, the nitrogen content does not present a positive relationship with the heating value. Therefore, low nitrogen values found for all eucalyptus species imply a smaller amount of nitrogen released into the environment after thermochemical conversion. The highest levels of nitrogen were found for the species SCB, EG and DCH (0.21−0.73%), but these values do not compromise the energy use of these species.

The contents of sulfur observed in the elemental composition of biomass were very low (0.03−0.1%), which is an advantage when using these species in thermochemical processes. Low sulfur values are always desired because sulfur oxides are strong pollutants. Generally, the S content in biomass varies in the interval of 0.01–2.3% and normally decreases in the order: animal biomass > contaminated biomass> herbaceous and agricultural residue > herbaceous and agricultural grass > woody biomass. This order is the same for N and indicates the close association of both N and S (Vassilev et al., 2010).

As for the content of oxygen, the highest values were observed in the species E-U1xU2 (45.21%) and E-DGxGL (45.05%), and the lowest values in the species BB (40.42%) and DCH (40.42%). For thermochemical conversion processes, knowing the ratios of H/C and O/C is more important than only H, O and C contents separately. In most cases, biomasses are characterized by larger O/C and H/C ratios compared to fossil fuels, such as coals (Figure 2.1). Cellulose is the most oxygenated and saturated constituent of wood (H/C and O/C ratios equal to 1.8 and 0.9 respectively) while lignin is the most unsaturated (H/C and O/C ratios equal to 1.2 and 0.35 respectively). For the studied samples, a higher H/C ratio (1.42−1.45) and O/C (0.67−0.70) can be observed in the samples of eucalyptus and sugar cane bagasse (H/C=1.43 and O/C=0.63). The sample of coconut husk showed the lowest values (H/C=1.29 and O/C=0.57). Comparison of biomass with fossil fuels, such as coal, shows clearly that the higher proportion of oxygen and hydrogen, compared with carbon, reduces the heating value of the fuel, due to the fact that energy found in carbon - oxygen and carbon - hydrogen bonds is lower than carbon - carbon bonds (Basu, 2010). The high values of the atomic H/C ratio for all samples agree with the high volatile content found by proximate analysis (69.2−79.72%). The values obtained for these parameters are relatively similar to those reported for *Eucalyptus globules bark* in the literature (Girón el al., 2012) and for other biomass species such as bamboo and sugarcane bagasse (Gang el at., 2007; Turn el al., 2004).

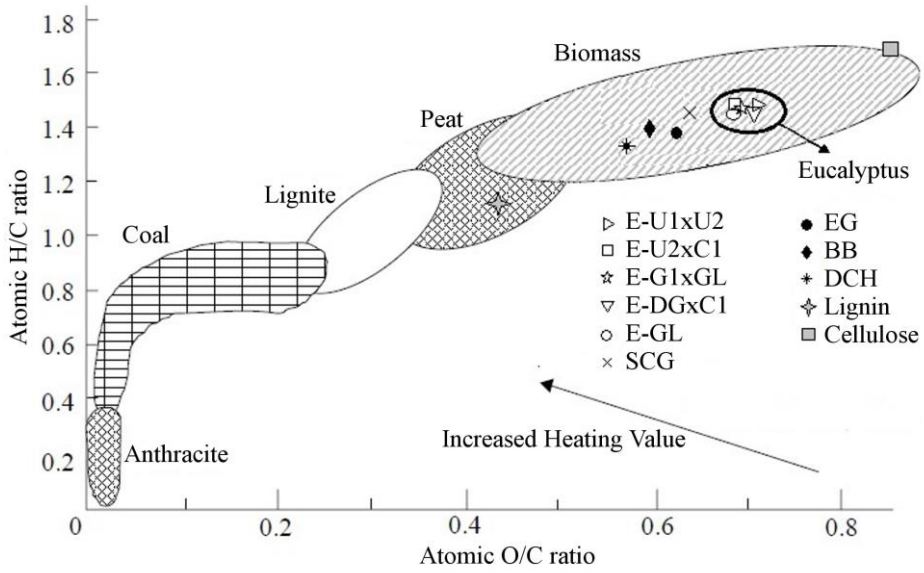

Figure 2.1. The Van Krevelen diagram for lignin, cellulose and studied biomass samples.

The Van krevelen diagram has now been used by a number of research groups and can be used in the prediction of different properties, such as Higher Heating Value, and potentially in predicting lignin. However, other parameters, such as volatile matter or fixed carbon, slightly correlate, because these parameters may be influenced by ash content (and metal composition) ash as described later.

2.3.3 Chemical composition

Table 2.3 shows the complete chemical characterization of the biomass species.

In the sugar cane bagasse (SCB), a lower lignin content (21.4%) was found, whereas *E. urophylla (Timor) x E. camaldulensis (VM1)* (E-U2xC1) showed a higher lignin content (32%). *Eucalyptus globulus* (E-GL) showed significantly higher amounts of cellulose contents (52.9%), while Coconout husk (DCH) showed the lowest value (35.1%). E-GL and SCB were found to have the highest total-carbohydrate content (69.7 and 70.7%, respectively), whereas the DCH had the lowest content (52.6%). The other six species had similar carbohydrate contents at approximately 63%.

Table 2.3. Chemical composition of the biomass species evaluated. All properties are reported on an extractive-free basis, except for extractives and ash contents, which are expressed on a dry biomass basis.

	Sample code								
	E-U1xU2	E-U2xC1	E-G1xGL	E-DGxC1	E-GL	SCG	EG	BB	DCH
Polysaccharides (% mass)									
Glucans	47.9	47.1	47.8	48.2	52.9	41.8	47.4	47.9	35.1
Xylans	12.2	11.1	14.6	11.0	12.9	24.8	16.6	13.5	15.3
Galactans	0.8	1.2	1.0	1.2	2.1	0.9	0.6	0.4	0.4
Mannans	0.8	1.1	0.8	0.9	0.8	0.9	0.0	0.1	0.9
Arabinans	0,2	0.2	0.3	0.3	0.3	2.3	1.3	0.7	0.9
Total sugar	62.0	60.8	64.5	61.6	69.0	70.7	65.8	62.6	52.6
Uronic acids (% mass)									
	3.9	4.1	4.1	4.1	2.0	1.5	1.6	1.2	3.2
Acetyl group (% mass)									
	2.2	2.0	3.1	1.8	1.5	3.0	2.5	2.9	2.9
Lignin (% mass)									
S/G	3.0	2.8	3.6	2.9	4.1	1.0	1.1	1.2	1.3
Insoluble lignin	27.0	27.2	22.8	26.9	24.0	19.5	21.1	26.8	31.7
Soluble lignin	4.5	4.8	5.2	4,8	3.1	1.9	2.8	0.8	1.4
Total lignin	31.5	32.0	28.0	31.7	27.1	21.4	23.9	27.6	33.1
Chloride (mg/kg)									
	260	328	446	701	417	340	663	111	529
Ash (% mass)									
	0.10	0.19	0.18	0.14	0.20	2.31	6.01	1.10	0.85
Extractives (% mass)									
In acetone	1.7	1.1	1.2	0.9	3.8	3.2	3.9	2.6	0.8
Total	3.6	3.4	2.8	1.9	5.4	15.0	14.8	7.8	3.3
Total (% mass)									
	99.6	99.0	99.7	99.3	99.8	99.0	99.8	95.8	92.9

Analysis of the matrix polysaccharides in each extracted biomass sample consistently showed the presence of xylans, arabinans, mannans, and galactans. Xylans were the most predominant hemicelluloses in all samples ranging from 11% (E-DGxGL) to 24.8% (SCB). However, the amount of others non-cellulosic derived sugar were relatively low in all sample.

The total extractive content for the species analyzed ranged from 1.9 to 15.0%. As can be seen in Table 2.3, SCB and EG species showed the highest levels of total extractives. Furthermore, these species have high levels of total sugar (70.7 and 65.8%, respectively), lower lignin content (21.4 and 23.9%, respectively) and lower densities (131 and 216 kg/m^3, respectively).

The chemical composition can be used as a method of classification of fuel. In this approach the classification considers that the biomass behaviour can be predicted based on knowledge of the pure component behaviour. This type of classification is shown in Figures 2.2 and 2.3 for all samples. Figure 2.2 shows a relationship between components of the chemical composition of the samples, wherein the species in the top right hand corner (SCB and EG) would have low lignin concentrations. This may be used as an indicator of the tendency to form low levels of volatile and of high reactivity. However, because of the influence of the minerals present, this was not observed.

When the lignin content was compared with an ash content (dry basis), there was a clear inverse relationship such that as lignin content increased, ash content decreased. This is a consequence of samples biology. For example, eucalyptus contained more lignin and less metal than the sugar cane bagasse and elephant grass. Lignification provides the plant with mechanical strength and the ability to withstand aggressive environmental conditions. This is less important for the grass, where the accumulation of metals was more pronounced. Further, extractive and ash content was directly proportional, such that, as extractive increased, ash content increased (Table 2.3).

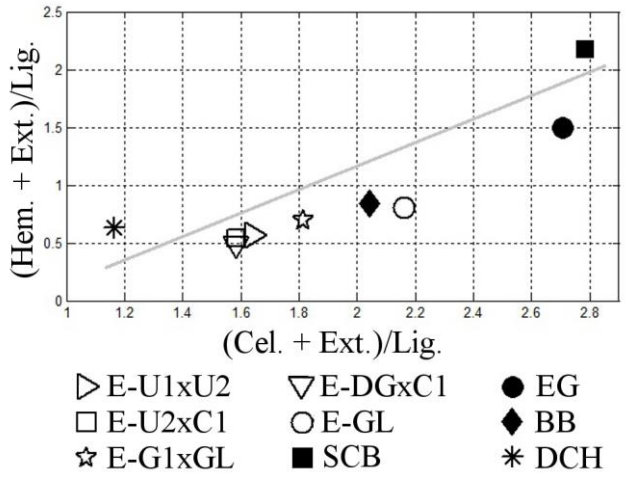

Figure 2.2. Plot based on chemical composition of samples.

2.3.4 Ash characterization

Table 2.4 shows the ash composition of the biomass species. Potassium, calcium and magnesium were present in higher levels in the ashes and manganese, iron, copper appeared in small quantities. In regards to the silica content in the studied biomasses, SiO_2 was not measured for eucalyptus samples because they are present in very low contents. High SiO_2 contents were identified in samples EG (1.5%) and SCB (1.44%).

Table 2.4. Ash composition of the biomass species evaluated.

	Sample code								
	E-U1xU2	E-U2xC1	E-G1xGL	E-DGxC1	E-GL	SCG	EG	BB	DCH
	Metals (mg kg^{-1})								
Cu	0.8	0.7	0.6	0.9	2.4	2.3	8.8	2.1	2.4
Fe	15.5	12.3	19.5	10.6	9.8	163	11.2	10.7	178
Ca	307	384	525	263	323	431	423	456	488
Mn	9.5	16.0	18.9	11.2	48.0	30.3	11.1	21.2	2.5
Mg	81.2	146	129	128	282	686	490	548	519
K	194	265	450	252	248	3185	21194	32478	1282
	Silica (%)								
SiO_2	BDL	BDL	BDL	BDL	BDL	1.44	1.5	0.30	0.30

BDL, below detectable limit.

2.3.5 TGA and DTG experiments

The TG and DTG curves of all biomass are shown in Figures 2.3 and 2.4 where characteristic curves of pyrolysis can be observed. This type of characterization of biomass is useful for several reasons including understanding the reactivity of a biomass but also the char and volatile forming tendency.

A quite marked similarity can be observed between the TG and DTG curves of woody species and marked differences with non-woody species, which may be associated with chemical composition of species. In this study, a subset of points was used as presented in Figure 2.5, wherein mass loss (X%) and the derivative of mass loss (dX/dt) curves obtained during the pyrolysis of E-U1xU2 under inert atmosphere at a heating rate of 25 K/min are shown. According to this Figure during thermal degradation of E-U1xU2, two distinct pyrolysis zones were observed. After the loss of water stage, there was a sharp drop in the mass loss of the samples up to T_{offset} (the extrapolated offset temperature

of the (-dX/dt) curves). This region corresponds to the active pyrolysis zone. The second pyrolysis zone is characterized by a slight change in mass loss curves, it was referred to the passive stage.

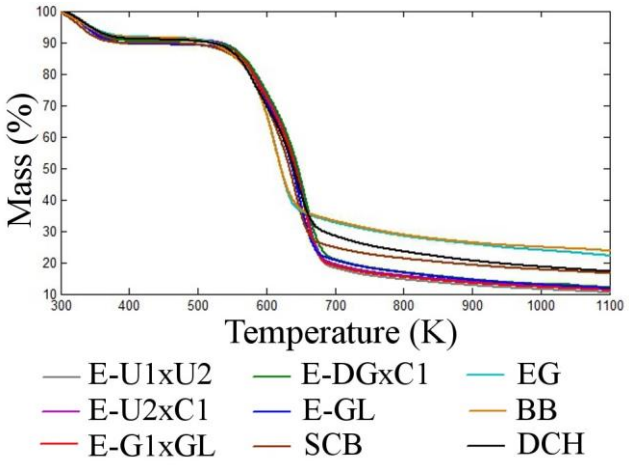

Figure 2.3. TG Dynamic of the biomass species evaluated (25 K/min).

The analysis of the curve of the mass loss rate shows that during the active pyrolysis zone two different peaks appear that can be associated with degradation of hemicelluloses and cellulose, respectively. Given the first peak or a shoulder, $(-dX/dt)_{sh}$ and T_{sh} are the characteristics overall maximum of the hemicelluloses decomposition rate and the corresponding temperature, respectively. Furthermore, $(-dX/dt)_{peak}$ and T_{peak} are the characteristics overall maximum of the mass loss rate and the corresponding temperature, respectively.

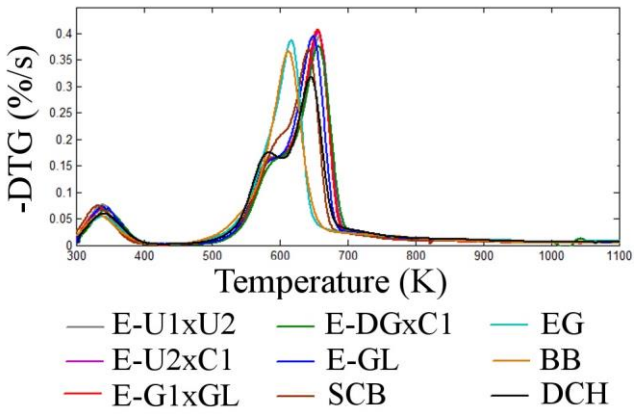

Figure 2.4. DTG Dynamic of the biomass species evaluated (25 K/min).

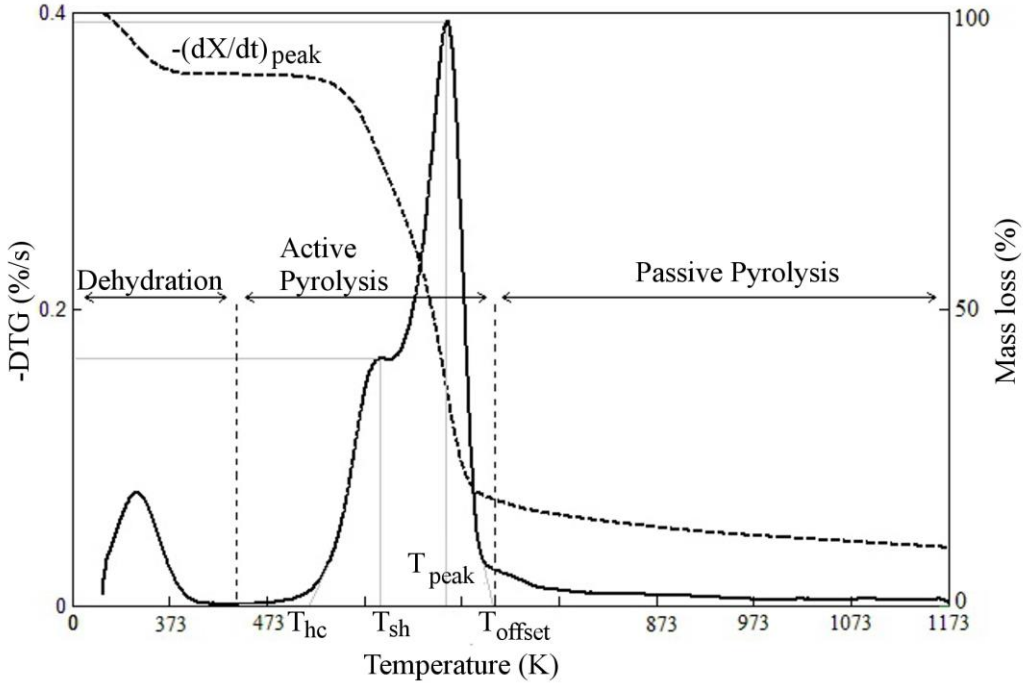

Figure 2.5. Characteristics of the pyrolysis of E-U1xU2 heated at 25 K/min.

A summary of the thermogravimetric properties of the samples is given in Table 2.5. The first weight loss appears at a temperature below 442 K for all samples due to evaporation of water. The temperatures for the onset of active pyrolysis occurs in a range between 486 and 509 K and range of temperatures for the conclusion of active pyrolysis is 617-704 K for the samples. A noticeable feature of TGA data are that the hemicelluloses peak merges with the cellulose peak in the EG and BB (Samples with higher potassium content).

The characteristic temperatures, T_{sh} and T_{peak}, presented higher values as heating rate increased. This effect indicates that it takes some time to transmit heat from the surface to the interior of the biomass and release volatiles from the interior to the particle surface, then the pyrolysis process may exhibit a temperature delay with the the higher heating rate.

The composition of each sample is different and, therefore, the thermogravimetric properties at same heating rate are also different. Figure 2.6 shows the relationship between residual weight after pyrolysis of biomass and fixed carbon plus ash obtained from the approximate analysis. A good relationship was observed between the results of

the two methodologies, and the small quantitative variations found may be associated with the different experimental conditions laid down in the adopted techniques.

Table 2.5. Thermogravimetric properties of the samples.

	Thermogravimetric properties of the samples									
Sample	Rate (K/min)	T_{hc} (K)	T_{sh} (K)	$-(dXdt)_{sh}$ (%/s)	X_{sh} (%)	T_{peak} (K)	$-(dXdt)_{peak}$ (%/s)	X_{peak} (%)	T_{offset} (K)	X_{offset} (%)
E-U1xU2	5	497.9	553.6	0.035	75.0	626.6	0.096	31.2	651.9	16.6
	15	497.9	575.5	0.102	76.8	645.8	0.265	36.4	680	21.1
	25	497.9	590.3	0.167	75.2	658.7	0.394	35.9	701.7	18.8
E-U2xC1	5	509.1	555.3	0.034	77.1	624.7	0.097	33.4	649.2	18.1
	15	505.9	576.6	0.101	79.0	646.9	0.265	36.1	678.3	19.5
	25	505.9	592.2	0.165	76.5	657.4	0.403	37.8	697	19.7
E-G1xGL	5	504	552.9	0.033	76.0	624.3	0.099	32.3	648.1	17.7
	15	508.8	575	0.099	80.4	644.9	0.276	37.3	677.3	19.9
	25	508.7	591.6	0.164	75.6	656.1	0.409	37.4	696.1	19.2
E-DGxC1	5	501.3	554.2	0.032	77.5	622.8	0.097	36.1	647.3	21.7
	15	507.3	580	0.097	75.4	644.8	0.261	36.1	677.3	19.4
	25	509.2	596.1	0.133	75.9	657.6	0.377	40.1	704.8	20.7
E-GL	5	503.2	555	0.033	74.4	612.6	0.093	40.8	671.6	18.5
	15	498.5	576.4	0.096	73.7	637.9	0.252	36.9	673.5	19.7
	25	498.5	589.2	0.162	75.3	649.1	0.395	39.1	693.4	21.2
SGB	5	499.1	567.9	0.041	72.2	611	0.090	41.1	637.2	26.2
	15	498.9	591.5	0.124	70.1	632.4	0.246	41.6	664.8	28.9
	25	498.8	601.3	0.207	69.3	642.6	0.370	42.5	682.6	25.8
EG	5	492	-	-	-	589.4	0.084	49.6	617.3	35.2
	15	494.3	-	-	-	609.1	0.244	50.5	641.5	35.7
	25	493.1	-	-	-	616.9	0.387	53.9	660.4	35.4
BB	5	488.2	-	-	-	583.1	0.075	49.6	627.9	35.8
	15	486.7	-	-	-	613.1	0.374	58.1	671.4	35.4
	25	486.7	-	-	-	613.1	0.367	56.9	668.2	35.1
DCH	5	496.8	553	0.035	75.6	615.9	0.073	42.7	643.8	29.5
	15	504.3	572.2	0.104	77.1	635	0.205	45.4	673.3	30.2
	25	495.4	584.4	0.175	76.3	646	0.318	45.5	690.4	29.2

- It can not be measured.

The relationship between the amount of hemicelluloses in the samples against the height of the shoulder ($(-dX/dt)_{sh}$) in the active pyrolysis characteristic is shown in Figure 2.7-a and the relationship between the amount of celluloses in the samples against the height of the peak ($(-dX/dt)_{peak}$) in the active pyrolysis is shown in Figure 2.7-b. These results confirm that cellulose and hemicelluloses amounts affect biomass thermal degradation.

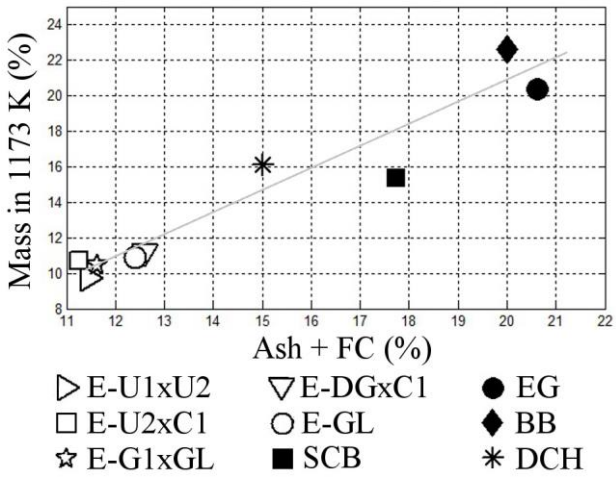

Figure 2.6. Residual mass (%) after pyrolysis (at 25 K/min) of biomass and fixed carbon plus ash (%) obtained from the approximate analysis.

A lower conversion temperature is observed in EG and BB than in other species. In addition, higher rates could be observed for EG, E-G1xGL and BB (Table 2.5). This behavior can be attributed to the higher proportion of alkali metal in species EG and BB, particularly K. The influence of the potassium content in pyrolysis is illustrated in Figure 2.8. It was clear from these plots that the alkali metal content of the biomass fuel has a significant effect on the volatile release during the pyrolysis of the samples, there was a negative relationship. This suggests that the potassium increases the char formation as well as lowering the temperature of degradation. According to Jones et al. (2014)[34], the uncatalysed process favours the generation of sugar-type monomers from the carbohydrates, but the presence of potassium changes the mechanism to one that involves ring cracking causing gases to polymerize to char. Consequently, the addition of potassium to biomass pyrolysis aids the production of charcoal. Thus, the effect of potassium on the pyrolysis mechanism and the influence of that would have to be included in any complete prediction scheme. This helps in the prediction of the quality and quantity of bio-products in a larger scale process. Also these results indicated that potassium composition affects the biomass thermal temperature (Figure 2.8-b).

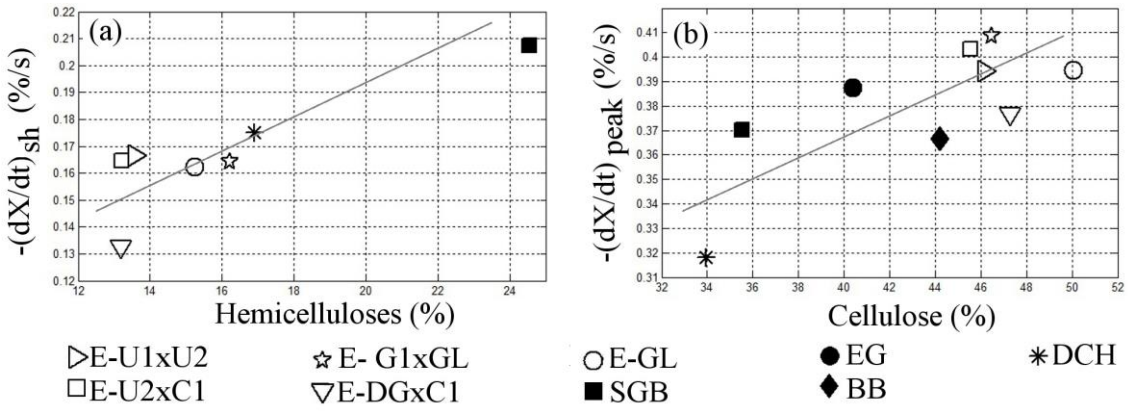

Figure 2.7. a) A plot of hemicelluloses content against the $(-dX/dt)_{sh}$ and (b) a plot of cellulose content against the $(-dX/dt)_{peak}$ (at 25K/min).

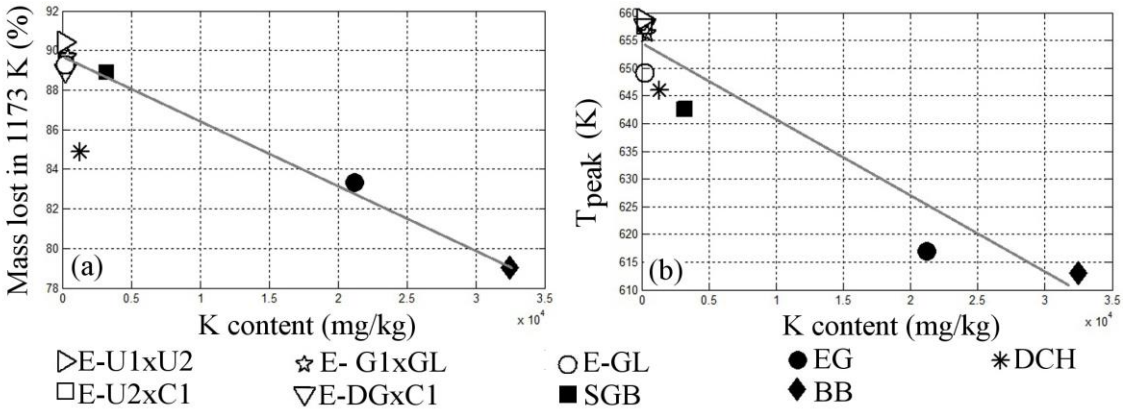

Figure 2.8. (a) A plot of K content (mg/Kg) against the mass lost during the TG analysis (in ash-free basis) and (b) relationship between the T_{peak} of cellulose against K contents of samples (at 25 K/min).

2.3.6 Thermochemical conversion and biomass properties

When dry biomass is obtainable, enhancement in the many conversion processes for fuel production are available or under development. Knowing the biomass characteristics is important in order to understand its influence on the thermochemical conversion process. The following section describes the effects of the main evaluated biomass properties on the quantity and composition of the product and its impurities from combustion, gasification and pyrolysis and on the economic and operational parameters:

First, from the annual energy potential, it is shown that the *E. urophylla (Flores IP) x E. urophylla (Timor)* has the greatest economic potential for energy application followed by

bamboo and then by the other species of Eucalyptus. The density of E. U1xU2 and BB are relatively high, which reduces transport and storage costs.

- In fast pyrolysis for liquid production, biomass is rapidly heated to a high temperature, very short vapor residence time and rapid cooling of vapors. Consequence of high ash content is secondary cracking of vapors and reducing liquid yield and liquid quality (Demirbas, 2010). Moreover, the presence of inorganic compounds such as K favors the formation of char (Girón el al., 2012). High K content of species EG and BB make them desirable as feedstock for fast pyrolysis process.

- Generally the gasification requires a feedstock of at less the 5% ash content, preferably less the 2%, in order to prevent the formation of clinkers. Accordingly, the SCB and EG species are least suitable for the gasification of the evaluated biomass.

- Due to the aromatic content of lignin, it degrades slowly on heating and contributes to a major fraction of the char and tar formation (Basu, 2010). However, pyrolysis of biomass with a high percentage of lignin can produce bio-oil with lower oxygen content and therefore a higher energy density (Demirbas et al., 2010). In this sense, the eucalypts and coconut husk are more suitable for the bio-oil production of the evaluated biomass.

- Most species contains very little sulfur (<0.1%), which, during gasification and combustion, is converted to H_2S and SO_2, and fast pyrolysis. Because of the low sulfur content in the evaluated biomass, as compared to coal, the gas sulfur content in the product is low enough to meet the needs of most applications. But for a few applications, such as methanol synthesis, even a low sulfur of gas level can irreversibly inactivate the catalysts. Fuel cells and some fast pyrolysis catalysts are also sensitive to sulfur. In this sense, B6 and B7 species, which have the highest content of sulfur, are the least qualified feedstock. Additionally, these species also showed the highest nitrogen content.

A comprehensive data table showing the inherent properties of each biomass and ranking its potential use in the various thermochemical conversion processes has not been found in the literature due to the complexity of the relationship of

the characteristic and the processes. However, building a database that can analyze and establish the relationships between the various characteristics of the biomass and the thermochemical conversion processes is now possible.

2.4 Conclusions

The understanding of the biomass thermal behavior, properties and their environmental impact in the long-term represents an important factor for the development of renewable energy applications. For this reason, we have characterized the most common species of Brazilian biomasses. In general, the proximate and ultimate analysis showed relatively similar values between studied species. Only sugarcane bagasse and elephant grass were distinguished with significantly higher values for fixed carbon content. In regards to the annual energy potential and density, it was suggested that the E. urophylla (Flores IP) x E. urophylla (Timor) and bamboo have the greatest potential for energy application, which reduces transport and storage costs. Moreover, the eucalyptus has undesirable characteristics in thermal conversion processes: low ash content that results in lesser damage to the equipment, low content of sulfur and nitrogen that lead to better environmental performance and product quality.

Finally, the TG and DTG curves of all biomass characteristic curves of pyrolysis could be observed. The research confirms that other constituents, such as mineral matter, modify the thermal behavior of the main components. Potassium catalyzed pyrolysis resulted in increased char yields and reduced degradation temperatures. The result of proximate analysis on samples can be used to predict the product yield produced during pyrolysis.

The data demonstrate significant diversity in composition amongst studied species that will be important in selecting candidates for the development of feedstocks for thermal conversion processes.

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CHAPTER 3

Kinetics of pyrolysis of some biomasses widely available in Brazil

Elém Patrícia Alves Rocha[1], Ekaterina Sermyagina[2], Esa Vakkilainen[2], Marcelo Cardoso[1], Jorge Luiz Colodette[3], Idalmo Montenegro de Oliveira[1]

[1] Federal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901

[2] Lappeenranta University of Technology (LUT), Lappeenranta, FIN-53851

[3] Federal University of Viçosa (UFV), Viçosa, MG Brazil, 36.570-000

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Abstract. Biomass conversion via thermal processes to generate energy will be an important part of the future energy landscape. The objective of this study was to determine the kinetic parameters of pyrolysis of five types of eucalyptus wood derived from different clones, sugarcane bagasse, elephant grass, bamboo and fibers of coconut fruit. The framework to describe the kinetic pyrolysis consists of a fuel model including four constituents, namely hemicelluloses, cellulose, lignin and extractives. Each pseudo-component was converted via two competing reactions into volatile and char. A statistical fit was achieved with mass loss rate data, obtained from the pyrolysis modeling and the thermogravimetric analysis, providing satisfactory statistical variance. In the end of the kinetic parameters optimization: the activation energies for reaction of hemicelluloses, cellulose and lignin were obtained as 179.98, 130.0 and 40 kJ mol^{-1}, respectively, whereas the decomposition of the pseudo-components resulted in relatively similar values of pre-exponential factor for all biomasses evaluated. The experimental results and kinetic parameters provide useful data to improve design of thermochemical conversion units.

3.1 Introduction

The notable consequences of global warming, such as atypical droughts and floods, strong hurricanes and storms, can be already observed in different parts of the planet. The effect of climate change coupled with the outcomes of intensive deforestation can result in significant economic losses currently and in a long-term perspective.

The power supply system in Brazil is mainly composed of hydropower, according to the report of Brazilian Ministry of Mines and Energy, generating about 65% of the country´s electricity (EPE, 2015). The electricity system is thus vulnerable to droughts. During dry season, it is necessary to implement conservation measures which not always avoid blackouts. In the Southeast Brazil, for instance, which is the wealthiest and populous region in Brazil, the water volume in the rivers has a systematic downward trend in the last three decades. This has a major impact on the economy of the region since the main urban centers actively use water from rivers for consumption, irrigation, industrial activities and power generation. Furthermore, it is estimated that the growth of the Brazilian energy demand will be 106% by 2040 and the growth of the electricity demand will be 150% in the same period (EPE, 2014).

Such situation requires a new approach to the energy production and water distribution strategy in Brazil, with measures to expedite the implementation of projects and increase the supply, such as the construction of new reservoirs. In this context, it is urgent to search for alternative energy generation processes. One of the most viable solutions is to produce electricity from local biomass. Energy from wastes, particularly lignocellulosic-based materials (forestry waste, agricultural residues and agro-industrial waste), is advantageous due to their wide availability, distribution, low environmental pollution, etc. At the same time, residual biomass also represents an important element of waste management and economics aspects (Demirbas, 2010, 2008). According to the Brazilian Ministry (MMA, 2011) of the Environment, industrial and agro-industrial activities in Brazil produce 97.7 and 290.8 million tons of waste per year, respectively. As a consequence, it is highly relevant to develop in-depth studies of enhanced energy production from biomass, combined with the efficient use of energy conversion processes, with minimum environmental impact.

Considering the technological development requirements a partnership was formed between two Brazilian universities, University Federal of Minas Gerais (UFMG)

and University Federal of Viçosa (UFV), and two Finnish universities, Lappeenranta University of Technology (LUT) and University of Jyväskylä (JYU) aiming to improve current knowledge of the thermal conversion processes of a wide variety of biomass feedstocks. Among other subjects, this partnership put resources to develop a study on the pyrolysis process. More specifically, the objective of this study was to determine the kinetic parameters of nine Brazilian lignocellulosic biomasses, including five types of eucalyptus wood derived from different clones, sugarcane bagasse (industrial residues of ethanol and sugar mills), elephant grass, bamboo and fibers of coconut fruit (husk). Kinetic parameters were obtained for the purpose of representing the kinetic mechanism of biomass carbonizing by a general equation. The results are expected to provide useful information for individuals and institutions who are interested in using Brazilian biomass for thermochemical conversion, since limited amount of studies of the Brazilian biomass have been conducted so far and the data found in this manuscript still not readily available in the literature.

3.1.1 Thermochemical processes

A wide variety of biomasses can be converted into fuel or energy using thermochemical pathways, such as combustion, gasification and pyrolysis. While combustion presents the complete oxidation of the fuel, gasification is a partial combustion of biomass in order to produce combustible gas mixtures (known as synthesis gas or syngas). The main components of this gas are CO, H_2, CO_2, CH_4, H_2O and N_2. A variety of tars is also produced during the gasification reaction depending on the reactor design and operating conditions (Basu, 2010; Demirbas, 2010).

Pyrolysis, similar to gasification, is a quite complex process of biomass conversion through heating, with high-temperature decomposition of organic materials in a reducing (absence or limited oxygen supply) atmosphere. It involves a series of reactions and could be operated in varying process conditions. Process performance is affected by several factors such as reaction temperature, residence time, heating rate and composition of the feedstock (Bridgwater, 2012). Three product streams are generated: viscous oil, light gases, and carbon-rich char. The operation parameters can be set to enhance the yield in liquid versus gaseous products. The lignocellulosic biomass when subjected to high temperatures under an inert atmosphere experiences the thermal cracking of its components, such as hemicelluloses, cellulose and lignin, through a

process of carbonization. Each lignocellulosic component volatilizes within different temperature ranges: hemicelluloses - between 423 and 623 K; cellulose - between 548 and 623 K, and lignin - between 523 and 773 K (Basu, 2010). The decomposition mechanism of biomasses is still unknown due to the significant variations in biomass composition and complexity of occurring chemical reactions during pyrolysis. Understanding the decomposition mechanism of each structural component is key for a better evaluation of the potential of the conversion processes. Some researchers have been studying these mechanisms for lignocellulosic biomass conversion (Burhenne et al., 2013; Quan et al., 2016) and suitable equipment design are being proposed based on the knowledge of pyrolysis mechanisms and consistent kinetic parameters (Blanco and Chejne, 2016; Fateh et al., 2013).

3.1.2 Thermogravimetric analysis

Thermogravimetric analysis (TG) is a simple and effective technique widely used to evaluate the material decomposition as the mass-loss in a function of time and temperature during biomass thermal treatment (Ferrara et al., 2014; Pasangulapati et al., 2012). TG is also an excellent tool for determining the kinetics of thermochemical conversion process for solid fuels. Pyrolysis behavior is assessed by performing the analysis in an inert atmosphere (nitrogen or argon), whereas the combustion behavior is determined with an oxidant gas (usually air). The thermogravimetric (TG) curve shows the mass-loss of the biomass as a function of temperature, whereas the derivative of TG profile (DTG curve) highlights the ongoing chemical processes more clearly (Ferrara et al., 2014).

The biomass type influences the pyrolysis behavior significantly: cellulose and hemicelluloses are found to contribute notably to the liquid product yield, while high lignin content leads on larger proportion of solid char (Akhtar and Saidina Amin, 2012). Wang et al. (Wang et al., 2011) reported that the extractives in biomass could increase the bio-oil yield and suppress the char and gas production when using corn stalk and wheat straw as the feedstocks for pyrolysis. In other words, it should be noted that the presence of certain inorganic components within the lignocellulosic structure may affect quite significantly the decomposition pathways. Consequently, the accurate prediction of real biomass degradation on the basis of experimental data from pyrolytic behavior of pure lignocellulosic constituents can be rather problematic.

Due to the relatively complex chemical composition of biomass, the conventional linearization techniques to determine kinetic parameters are not suitable for the evaluation of the TG experiments. Therefore, the experimental data from pyrolysis experiments is generally evaluated by the nonlinear method of least-squares, assuming more than one reaction. Burhennea et al. (2013) developed a theoretical one-step multi-component pyrolysis model to estimate the pyrolysis behavior of each lignocellulosic component for wheat straw, rape straw and spruce wood on the basis of TG analysis and evaluated the findings in laboratory-scale reactor to check the applicability for industrial processes. It was shown that the high cellulose and hemicellulose content in herbaceous species leads to faster decomposition in comparison with woody biomass which characterized with a higher lignin content. Another model was created and described by Sungsuk et al. (2016): the response surface methodology and simplex-lattice mixture design methods were applied to predict the pyrolysis behavior of the legume tree (*L. leucocephala*). The statistical analysis of the proposed model showed that the cellulose has the strongest effect on the activation energy and the interaction between cellulose and lignin has the biggest impact on the reaction order. Another group of researchers has modeled the thermal degradation of pistachio shells by a system of coupled differential conservation equations for mass, momentum, species, and energy for a pistachio shell particle (Peters, 2011).

Even though numerous studies on the thermal decomposition of various biomasses are currently available, scientific knowledge on the pyrolysis behavior of certain Brazilian biomasses is still relatively limited. Several studies reported on the evaluation of pyrolysis potential for sugarcane bagasse: pyrolysis kinetics of sugarcane bagasse and additionally cotton stalk powders were studied in Pyrolysis characteristics and kinetic parameters determination of biomass fuel powders by differential thermal gravimetric analysis (TG/DTG) by El-Sayed and Mostafa (2014) (El-Sayed and Mostafa, 2014); optimization of bio-oil production from sugarcane bagasse and palm empty fruit bunch by intermediate pyrolysis was carried out in a laboratory-scale pilot unit by Mantilla et al. (2014). Empty fruit bunch from oil palm as one of the perspective biomasses for biofuels production with slow/fast pyrolysis or solvolysis process was reviewed by Chang S.H. (2014). In another study, the potential of several Brazilian biomasses (water hyacinth, sugarcane bagasse, castor meal, coconut pericarp, and Eucalyptus crop residues) was investigated with respect to slow pyrolysis applications for production of soil fertilizers and energy (Doumer et al., 2015). The coconut pericarp, Eucalyptus residues and sugarcane bagasse

exhibited rather suitable decomposition behavior to produce biochar with low ash contents and high calorific values. Moreover, studied biomasses generated quite sufficient quantities of bio-oil, and can be effectively used for biofuel production or in the chemical industry. There are also studies on slow pyrolysis evaluation for such biomass types as bamboo (*Bambusa chungii*), rice husk and pine wood (Hu et al., 2016); sugarcane bagasse, cocopeat, paddy straw, palm kernel shell, and umbrella tree (Y. Lee et al., 2013); corn stalks, poplar, switchgrass "Alamo" and switchgrass "Trailblazer" (Basile et al., 2016).

3.2 Materials and Methods

3.2.1 Material and Experimental method

Nine species of lignocellulosic biomasses were studied. Five samples of seven years old eucalyptus wood E. urophylla (Flores IP) x E. urophylla (Timor) (E-U1xU2); E. urophylla (Timor) x E. camaldulensis (VM1) (E-U2xC1), E. grandis (Coffs Harbour)x E. globulus (R) (E-G1xGL); [E. dunnii (R) x E. grandis (R)] x E. camaldulensis (VM1) (E-DGxC1) and E. globulus (E-GL), provided by Genolyptus project, located in Minas Gerais state. Samples of elephant grass (EG) and bamboo (BB) (150 days old) were obtained from the experimental plantation of UFV. The coconut husk sample (DCH) was from a coconut company located in Minas Gerais state. The characterization of the samples comprised of the proximate analysis, elemental composition, heating value, density, ash composition and is available in published work (Rocha et al., 2015). For important characteristics of the samples (Table 1) used in this study, the extractives were firstly removed and determined according to TAPPI T264 cm-97 and TAPPI T280 pm-99 standards, respectively. The contents of cellulose and hemicelluloses in the extractive-free biomass were analyzed according to Gomes (2013). The extraction in ethanol toluene (1:2), extraction in ethanol and a hot water extraction were determined according to T204 cm-97 standard procedures (2007). According to TAPPI T280 pm-99 standard procedure (2006), the content of biomass extractable in acetone was determined. Ash chemical analysis was done using anatomic absorption spectrophotometer, Perkin Elmer-AA Analyst 200 series.

Pyrolysis characteristics of the biomass under non-isothermal conditions were determined with the TG analyzer (SHIMADZU DTG60 Series). Each biomass sample was crushed in a laboratory chipper (Chogokukikai model, equipped with 3 knives) and

sieved to the particle size less than 0.42 mm. The samples were then dried in the oven at a constant temperature of 105 ± 2 °C for at least 24 h and stored in the desiccators to prevent moisture absorption from atmosphere. The initial weight of biomass used in the study was 0.6 ± 0.05 mg. In the TG analyzer, the sample was heated from room temperature to 1127 K with different heating rates of 5, 15 and 25 K min^{-1} under a high purity nitrogen flow (100 ml min^{-1}).

Table 3.1. Composition of investigated biomass species.

Code sample	Cellulose %	Hemicelluloses %	Lignin %	Extractives %	Ash %
E-U1xU2	49.38	14.53	32.44	3.56	0.10
E-U2xC1	49.00	14.22	33.23	3.36	0.19
E-G1xGL	50.17	17.51	29.33	2.81	0.19
E-DGxC1	50.62	14.11	33.25	1.88	0.15
E-GL	51.97	15.82	26.62	5.40	0.20
SCB	37.66	26.01	19.25	15.00	2.08
EG	42.18	16.39	21.28	14.81	5.35
BB	48.37	14.87	27.87	7.77	1.12
DCH	39.23	19.54	36.99	3.29	0.95

3.2.2 Model Formulation

3.2.2.1 Kinetic Mechanism

As already mentioned, the thermal decomposition of lignocellulosic materials takes place via complex mechanisms that are greatly influenced by heat and mass transfer processes (Demirbas, 2010; Fateh et al., 2013). The main components of biomass are cellulose, hemicelluloses and lignin, in addition to extractives and mineral matter. The thermal decomposition of biomass involves a large number of reactions occurring in parallel and series. In this work, biomass pyrolysis has been modeled using pseudo-components: cellulose (*C*), hemicelluloses (*H*), lignin (*L*) and extractive (*E*). The following assumptions were employed:

- There is no moisture content (samples are assumed to be completely dry);
- Inert atmosphere surrounds the sample;
- When pyrolysis starts, *char* is not present in the biomass, but it is gradually created from thermal degradation of pseudo-components;
- Produced char consists completely of carbon.

Based on the above assumptions, the proposed reaction model contains the following steps:

$$\rho_C \xrightarrow{r_1} \rho_{vol,C} \tag{3.1}$$

$$\rho_C \xrightarrow{r_2} \rho_{char,C} \tag{3.2}$$

$$\rho_H \xrightarrow{r_3} \rho_{vol,H} \tag{3.3}$$

$$\rho_H \xrightarrow{r_4} \rho_{char,H} \tag{3.4}$$

$$\rho_L \xrightarrow{r_5} \rho_{vol,L} \tag{3.5}$$

$$\rho_L \xrightarrow{r_6} \rho_{char,L} \tag{3.6}$$

$$\rho_E \xrightarrow{r_7} \rho_{vol,E} \tag{3.7}$$

$$\rho_E \xrightarrow{r_8} \rho_{char,E} \tag{3.8}$$

where ρ_e, $\rho_{vol,e}$ and $\rho_{Char,e}$ are respectively the instantaneous mass, volatiles (gas + tar) and char of the pseudo-component.

Conversion of pseudo-component e α_e is defined as the conversion of pseudo-component '*e*', and kinetics of pyrolysis of biomass by TG was assumed to comply with the following equation:

$$r_i = \frac{d\alpha_e}{dt} = k_i(1-\alpha_e)^n \tag{3.9}$$

where *n* is the order of reaction. Under the conditions of thermal analysis in an inert atmosphere, the cellulose, hemicelluloses and lignin decomposition is usually approximated by first-order kinetics (Grønli et al., 2002; Mui et al., 2008). Thus, this work has adopted the first-order kinetic for all components of the biomass to avoid numerical problems. The Arrhenius relation was used to model the dependence of each rate constant (k_i, in s^{-1}) to the temperature (T, in K):

$$k_i = k_{0,i} \exp\left(\frac{-E_{a,i}}{RT}\right) \tag{3.10}$$

where $k_{0,i}$ (s^{-1}) is the pre-exponential factor and $E_{a,i}$ (J mol^{-1}) is the activation energy. Equation (10) can be converted into the following logarithmic form:

$$k_i = \exp\left(A_i - \frac{B_i}{T}\right) \tag{3.11}$$

where $k_{0,i} = \exp A_i$ and $B_i = E_{a,i}/R$.

3.2.2.2 Material balance

The mechanisms and rate equations described in the previous sections can be used to express the material balance over all species, as follows:

$$\frac{1}{\rho_{0,C}}\frac{d\rho_C}{dt} = -r_1 - r_2 \tag{3.12}$$

$$\frac{1}{\rho_{0,H}}\frac{d\rho_H}{dt} = -r_3 - r_4 \tag{3.13}$$

$$\frac{1}{\rho_{0,L}}\frac{d\rho_L}{dt} = -r_5 - r_6 \tag{3.14}$$

$$\frac{1}{\rho_{0,E}}\frac{d\rho_E}{dt} = -r_7 - r_8 \tag{3.15}$$

$$\frac{1}{\rho_{0,C}}\frac{d\rho_{vol,C}}{dt} = r_1 \tag{3.16}$$

$$\frac{1}{\rho_{0,H}}\frac{d\rho_{vol,H}}{dt} = r_3 \tag{3.17}$$

$$\frac{1}{\rho_{0,L}}\frac{d\rho_{vol,L}}{dt} = r_5 \tag{3.18}$$

$$\frac{1}{\rho_{0,E}}\frac{d\rho_{vol,E}}{dt} = r_5 \tag{3.19}$$

$$\frac{1}{\rho_{0,C}}\frac{d\rho_{char,C}}{dt} = r_2 \tag{3.20}$$

$$\frac{1}{\rho_{0,H}}\frac{d\rho_{char,H}}{dt} = r_4 \tag{3.21}$$

$$\frac{1}{\rho_{0,L}}\frac{d\rho_{char,L}}{dt} = r_6 \tag{3.22}$$

$$\frac{1}{\rho_{0,E}}\frac{d\rho_{char,E}}{dt} = r_8 \tag{3.23}$$

$$\frac{d\rho}{dt} = -\frac{d\rho_{vol,C}}{dt} - \frac{d\rho_{vol,H}}{dt} - \frac{d\rho_{vol,L}}{dt} - \frac{d\rho_{vol,E}}{dt} \tag{3.24}$$

where $\rho_{0,e}$ is the is the initial mass of pseudo-components "e" in biomass.

3.2.3 Model integration and parameter estimation methods

The dynamic system (equations: 3.12–3.24) with the initial conditions was solved numerically using Forward Euler algorithm. The integration algorithm was written in the vector form, i.e., the entire state vector was integrated in parallel as described by Cellier and Kofman (2006). This procedure generates the simulated evolution of each state variable, but the dynamic is dependent on the set of kinetic parameters (A_i and B_i). For the regression model, a maximum likelihood statistical criterion was applied. Maximum likelihood estimation is a method to seek the probability distribution that makes the observed data most probable, which means that one must seek the value of the parameter vector that maximizes the likelihood function or minimize the negative log-likelihood (T.-S. Lee et al., 2013; Varziri et al., 2008). Therefore, the objective function to minimize was:

$$\hat{\beta} = \min_{\{\beta\}} \left[\frac{d\underline{\rho}}{dt}^{\exp} - \frac{d\underline{\rho}}{dt}(\beta) \right]^t \underline{\underline{W}} \left[\frac{d\underline{\rho}}{dt}^{\exp} - \frac{d\underline{\rho}}{dt}(\beta) \right] \tag{3.25}$$

Here, $\underline{\underline{W}}$, $\frac{d\underline{\rho}}{dt}^{\exp}$ and $\frac{d\underline{\underline{\rho}}}{dt}(\beta)$ are the diagonal matrix of weights, the experimental and calculated mass loss rates (DTG), respectively, for N points experiment.

The computational iterative method was implemented in MATLAB R2015a. The estimates were obtained computationally by applying the Quasi-Newton method. This method requires an initial value for the parameters, and in every interaction, the algorithm determines and evaluates a new value of the objective function until a satisfactory minimum value of the objective function is found.

3.3 Results and discussion

3.3.2 TG of biomass species degradation under inert atmosphere

The mass loss and DTG curves evolutions of biomass under inert atmosphere, which were obtained at heating rate of 15 K min^{-1}, are plotted in Figure 3.1 and 3.2, respectively.

As can be observed, from the room temperature to 350–400 K (depending of the sample), around 9% of the initial mass is lost, corresponding to the moisture evaporation. The mass loss rate evolutions peaks differ in position and height (Figure 3.2). It could be seen that the thermal degradation starts at the same temperature (around 470 K) for all samples of eucalyptus, where the reaction rate increased linearly to approximately 580 K and stays constant for a small period until it rose sharply to the peak at about 650 K and went down. The reaction rate curve became flat after 700 K, revealing a slower decomposition that was attributed to a component such as lignin. Similar behavior can be observed for samples of coconut husk (DCH) and sugar cane bagasse (SCB). Eucalyptus samples showed higher generation of volatiles among all species: 83–85.5% mass is lost before reaching 800 K. For elephant grass (EG) and bamboo (BB) samples, the devolatilization with maximum rate occurs between 500 and 660 K and is essentially completed by about 690 K. This is followed by a further slow mass loss up to the final temperature. Until 800 K, a mass loss of around 71% are observed for EG and BB.

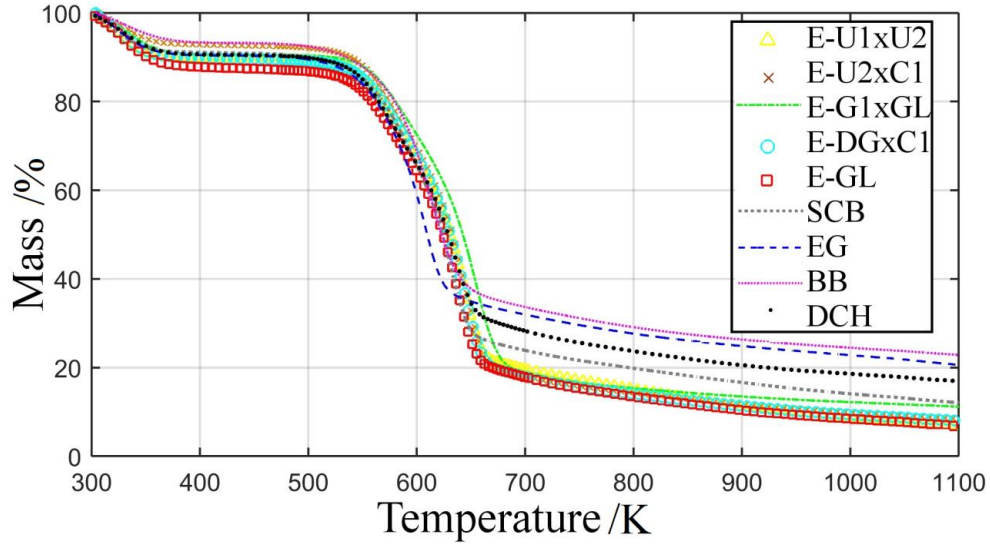

Figure 3.1. Mass evolutions of the biomass species evaluated (15 K min^{-1}).

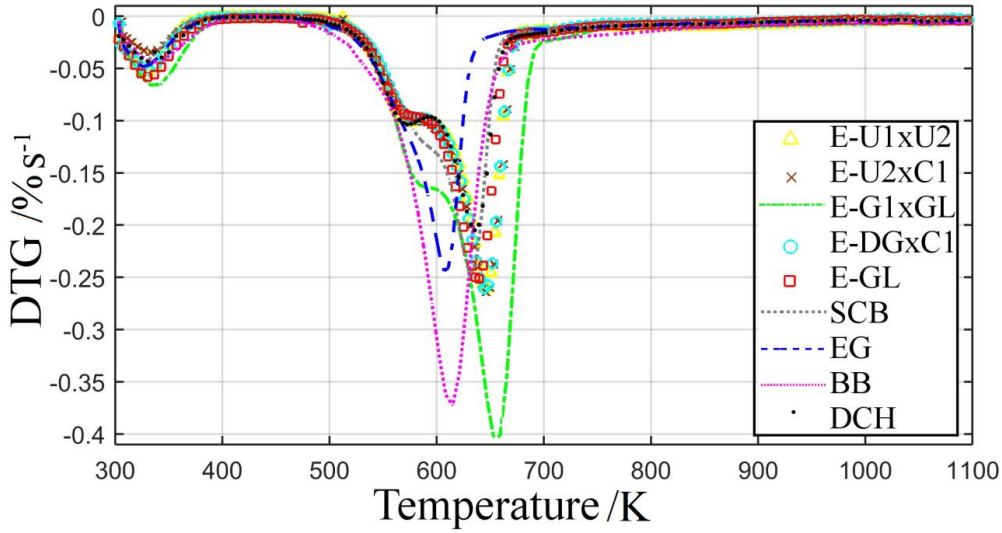

Figure 3.2. DTG evolutions of the biomass species evaluated.

Considering similar experimental conditions applied (i.e. rate of heating, temperature, pressure, particle size and inert environment), the difference in the thermal degradation profiles and apparent kinetic trends between the samples can be attributed to the differences in the relative composition and nature of these components. In addition, the amount and composition of ash contained within biomass may influence its devolatilization (Basu, 2010; Mui et al., 2008).Taking into account the shape of the DTG and lost weight curves, the main devolatilization for all samples can be observed at the

temperatures 400–850 K. Consequently, the kinetic analysis was carried out in this temperature range.

3.3.3 Kinetic parameters

The kinetic constants of each pseudo-component in the parallel reaction scheme were estimated by Maximum Likelihood (ML) regression of the TG data for each stage using MATLAB R2015a, and the initial values for the kinetic parameters were obtained from Li et al. (2014) and Grønli et al. (2002). First, the initial values for kinetic parameters were used to calculate approximated pre-exponential factors and activation energies considering the DTG data from all the samples together in the optimization program. Thus it was obtained the same values for the parameters for all samples. In the second step, the parameters determined in the previous step were used as the initial values of kinetic parameters to minimize the objective function for each sample separately. The second step allowed the determination of the kinetic parameter values for each species.

Table 3.2. Calculated kinetic parameters for the pyrolysis of biomass materials

	Code sample								
	E-U1xU2	E-U2xC1	E-G1xGL	E-DGxC1	E-GL	SCB	EG	BB	DCH
***Ln*(A_i / s^{-1})**									
1	29.5	29.5	29.2	29.3	31.1	29.8	31.1	31.1	31.7
2	26	25.9	26	26	29	27.9	29	29.6	29.4
3	22.51	22.51	22.51	22.51	22.4	22.9	22.4	22.51	22.7
4	19.03	19	19	18	22.1	18.59	22.1	22.1	20.4
5	1	1.1	1.1.	1.1.	1.2	0.1	1.2	1	0.7
6	0.1	0.09	0.1	0.1	0.5	0.1	0.5	0.5	0.19
7	20	20	17	20	19.5	19.8	19.5	20.9	20.5
8	15	15	15	17	19.4	17.5	19.4	20.9	18.2
$E_{a,i}$ /kJ mol^{-1}									
1	179.98	179.98	179.98	179.98	179.98	179.98	179.98	179.98	179.98
2	179.98	179.98	179.98	179.98	179.98	179.98	179.98	179.98	179.98
3	130	130	130	130	130	130	130	130	130
4	130	130	130	130	130	130	130	130	130
5	40	40	40	40	40	40	40	40	40
6	40	40	40	40	40	40	40	40	40
7	115	115	115	115	115	115	115	115	115
8	115	115	115	115	115	115	115	115	115
S^2y x10^6 /mg^2 s^{-2}									
	1.55	1.08	0.47	0.68	0.46	0.27	0.59	0.87	0.24

The results of the kinetic parameters (pre-exponential factors and activation energies) and the model variance, S2y at three heating rates, are reported for every sample in Table 3.2. The model variance between $2.3x10^{-7}$ and $1.5x10^{-6}$ $(mg\ s^{-1})^2$ were estimated, denoting low uncertainties of predicted values, while having the experimental maximum rate at 0.02 mg s^{-1}. To check the pyrolysis model, the DTG curves are reproduced using solutions in Table 3.2 as inputs and compared against the experimental data. Figure 3.3 presents the experimental DTG curve with the predicted DTG curves for all samples. As can be seen, the shape of the curves and position of the peaks stayed basically unaltered, confirming the good obtained settings. Furthermore, the kinetic constants were obtained to represent the thermal decomposition of biomass at different heating rates. Figure 3.4 compares the experimental and calculated DTG curves for DCH at 5, 15 and 25 K min^{-1}.

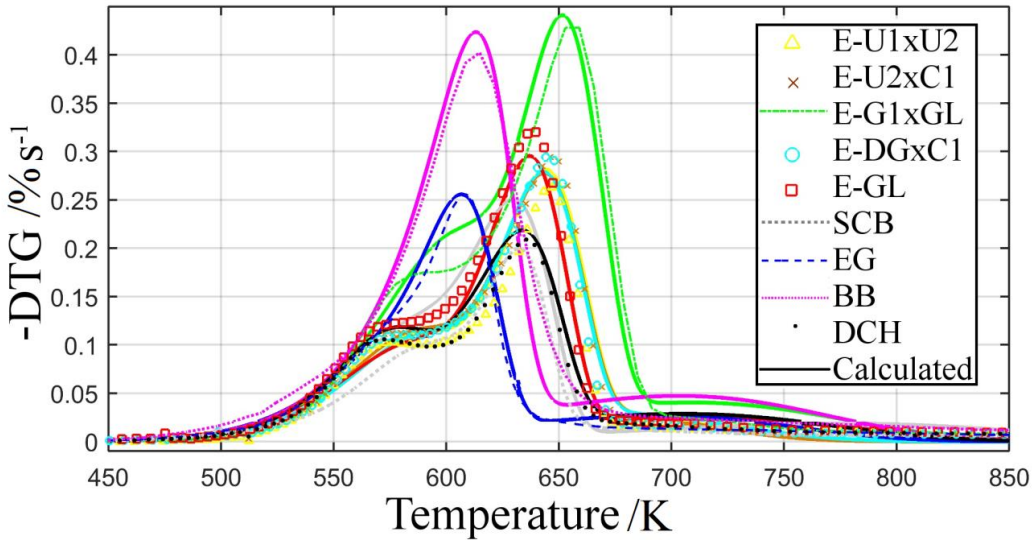

Figure 3.3. Comparison between experimental and calculated DTG curves for all samples

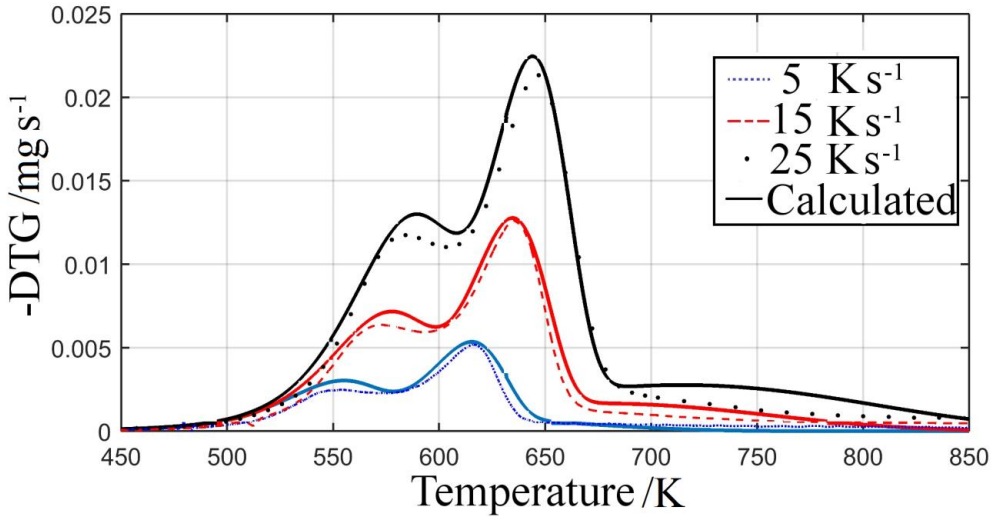

Figure 3.4. Comparison between experimental and calculated DTG curves for DCH at 5, 15 and 25 K min^{-1}

In Table 3.2 it can be observed that the same activation energies were obtained for all species at the end of the optimization of kinetic parameters and the decomposition of the pseudo-components resulted in relatively similar values of activation energies for all biomass, such tendencies proves the similarities in the kinetic behavior of the samples. The pre-exponential factor are higher for the biomasses that have higher potassium content in its composition, such as EG and BB, and this behavior can be attributed to the higher proportion of alkali metal in species, particularly K (Rocha et al., 2015). According to Nowakowski and Jones (2005) the presence of potassium has a significant influence on the rates and form of evolution of gas components generated during the pyrolysis processes and catalytic effect of potassium has a profound influence on the char formation stage; generally increasing the char yields. Furthermore, the ratio between the pre-exponential factor of reactions generation of char and reactions generation of volatile for each biomass component increase with the potassium content of the samples (Table 3.2 and Rocha et al. (2015)).

Comprehensive understanding of the cellulose pyrolysis is especially important as it has the highest mass fraction in the studied biomasses (Rocha et al., 2015). For a first order reaction of cellulose, Li et al. (2014) found the values for activation energy and pre-exponential factor of cellulose to be 173. 5 kJ mol^{-1} and 12.3 (*ln* (*A*, s^{-1})) correspondingly, while Branca et al. (2003) reported 76.2 and 10.2 (ln (*A*, s^{-1})). Becidan et al. (2007) conducted DTG thermal analysis of biomass wastes and came up with an activation

energy of 180−224 kJ mol^{-1} and a pre-exponential factor of 12.93−17.39 (*ln* (*A*, s^{-1})), while Grønli et al. (2002) proposed the higher values of 236 kJ mol^{-1} and 17.36−17.97 (*ln* (*A*, s^{-1}) for the two properties for nine wood species. Consequently, the values found in this study for the activation energy (179.98 kJ mol^{-1}) and pre-exponential factor (25.9–31.1 (*ln* (*A*, s^{-1})) of cellulose are consistent with values found in the literature.

The activation energy of 40 kJ mol^{-1} for the conversion reactions of the lignin estimated in the current work are comparable with generally reported in literature (20–65 kJ mol^{-1}) (Grønli et al., 2002; Li et al., 2014; Medrano et al., 2016).

About the kinetic constants for hemicelluloses, many previous kinetic studies show some dissimilarity among the results. Wang et al. (2008) obtained that the activation energy of xylan in a range of 156.0–250.1 kJ mol^{-1} and the pre-exponential factor was in a range of $3.6x10^{11}$–$3.4x10^{22}$ s^{-1} (*A*), while Jeguirim and Trouvé (2009) measured that the activation energy and the pre-exponential factor of hemicelluloses were 110 kJ mol^{-1} and 20 s^{-1} (*ln A*) according to the global independent reactions model. Calculated by the genetic algorithm, Li et al (2013) obtained the *E* and *ln* (*A*) values equal to 87.5 kJ mol^{-1} and 5.51 (*ln* (*A*, s^{-1})). For the nine species studied, activation energy for hemicelluloses volatilization was found 130 kJ mol^{-1} and pre-exponential factor in a range 18.0−22.9 (*ln* (*A*, s^{-1})). The activation energy values were in agreement with values obtained from Vamvuka et al. (2013) for different biomass materials. Some variations found in the kinetic parameters can be attributed to heterogeneous chemical composition of hemicelluloses used in the experiment.

Finally, according to the regression model, the extractives volatilization are characterized by a pre-exponential factor close to 15−20.9 *ln* (*A*, s^{-1}), an activation energy was 115 kJ mol^{-1}. The activation energy remained within the initial values in range 105−127 kJ mol^{-1}, while the pre-exponential factor were outside the initial values (9.29−10.22 (*ln* (*A*, s^{-1})), all obtained from Grønli et al. (2002).

3.3.3 Kinetic simulation of the thermal degradation

It is widely recognized that the thermal degradation behavior of lignocellulosic biomass is strongly dependent on the behavior of their pseudo-components (Basu, 2010; Jeguirim and Trouvé, 2009). The proposed model for lignocellulosic biomass pyrolysis is the sum of the degradation of its components. As shown in the simulated curves,

remarkable differences were found among thermal decomposition behaviors of extractives, cellulose, hemicelluloses and lignin. It was expected that the first peak would be hemicelluloses, and then cellulose would exhibit a tall narrow peak, while the lignin would produce a lower peak with a flat tailing. It is admitted that the main peak, resulting from the cellulose volatilization, is accompanied by a shoulder at low temperature, which is associated to degradation of hemicelluloses, and a tail at high temperature related to lignin volatilization. The devolatilization of extractives occurs in the same range of temperature as hemicelluloses and parts of cellulose, consistent with the results reported by Aboyade et al (2011) and Li et al. (2013). This qualitative interpretation can be observed in Figure 3.5 for the specific heating rate of 15 K min^{-1}. Under these results, we can observe the simulation of biomass pyrolysis comparing the experimental and calculated DTG curves and including the volatilization curves for each pseudo-component. Furthermore, these results provide a clear idea of the temperature ranges where the conversion of each pseudo-component takes place. The profiles obtained at this specific condition are representative of the ones obtained for the other heating rates.

The kinetic characteristics of pseudo-components decomposition are identical for eucalyptus samples, in contrast to those of Elephant grass and Bamboo. This may be due to differences in their compositions. In addition, the Elephant grass and Bamboo have high content of metals in the ashes, such as potassium and calcium, which can act as catalysts in the pyrolysis. Even though the polysaccharides compositions of Coconut husk and eucalyptus differ quite significantly (Rocha et al., 2015), they present relatively similar kinetic behaviors. The similarity between the location of the maximum of the peaks for hemicelluloses (595 K in Coconut husk and about 585 K in eucalyptus, at 15 K min^{-1}) and cellulose (595 K in Coconut husk and about 640 K in eucalyptus, 15 K min^{-1}), supports this finding.

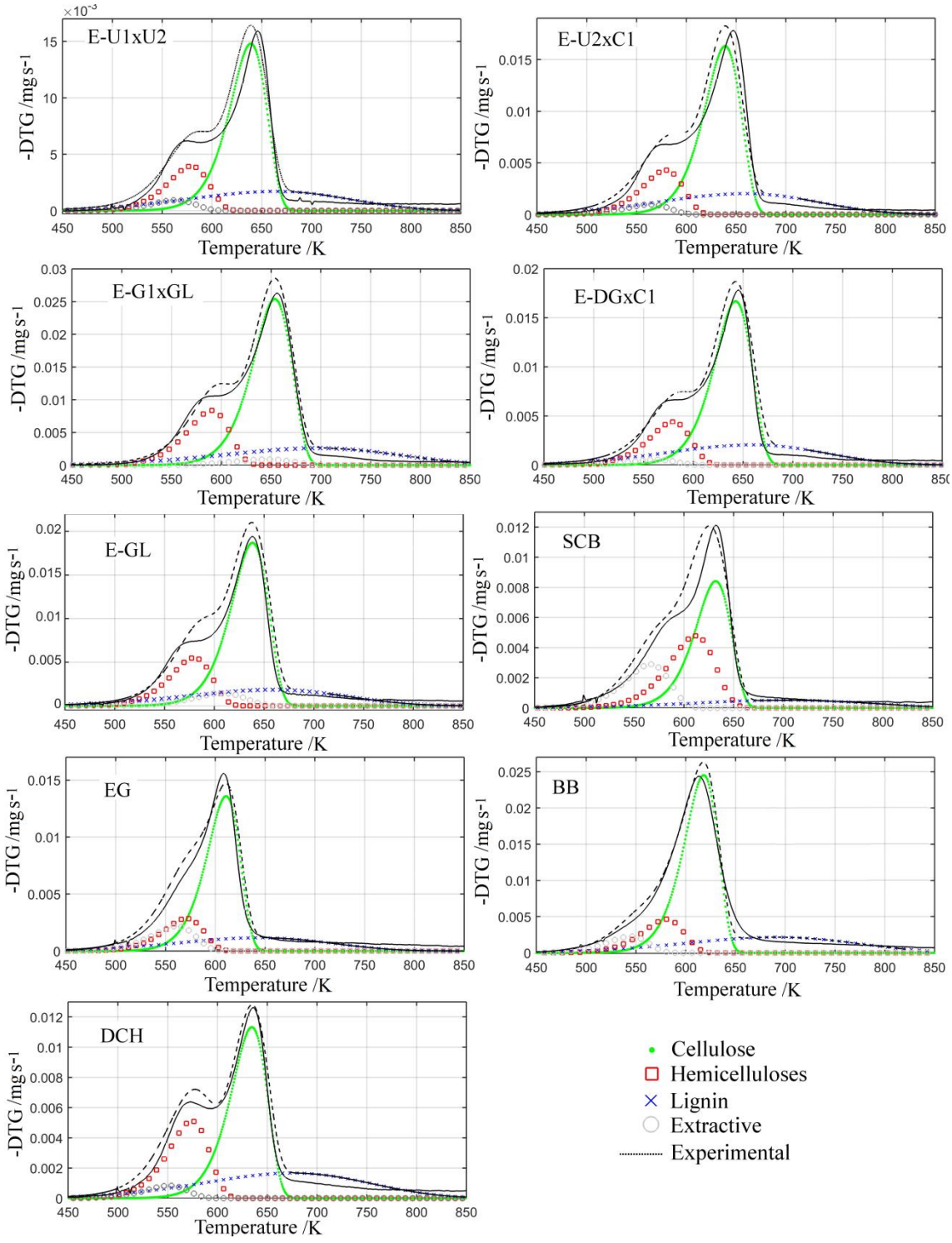

Figure 3.5. Simulated profile for the degradation of pseudo biomass components at 15 K min^{-1}

3.4 Conclusions

The devolatilization behavior of several lignocellulosic biomasses grown in Brazil, was investigated by thermogravimetry. The kinetics model is able to deal with

varying heating rates through the different reaction paths, and is sensitive to deal with variations in fuel composition since it considers the pseudo-components of sample instead of one model specie for lignocellulosic biomass. The kinetic constants of each pseudo-component in reaction scheme were estimated by Maximum Likelihood (ML) regression of the TG data for each stage using MATLAB R2015a. The stability of kinetic parameters shows that pyrolysis model describes the thermal degradation of biomass quite adequately for the samples studied. The same activation energies were obtained for all species at the end of the optimization of kinetic parameters and the decomposition of the pseudo-components resulted in relatively similar values of activation energies for all biomass, such tendencies proves the similarities in the kinetic behavior of the samples. The kinetic parameters estimated with the model were comparable with those reported in the literature, and were used to simulate decomposition curves of pseudo-components at different heating rates. Through the methodology used, kinetic parameters were obtained that may provide useful data for effective design and improvement of thermochemical conversion units.

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CHAPTER 4

Characterization of residual biomasses from the coffee production chain for energy purposes

Clara Lisseth Mendoza Martinez[1], Elém Patrícia Alves Rocha[1], Angélica de Cassia Oliveira Carneiro[2], Fernando José Borges Gomes[2], Larisse Aparecida Ribas Batalha[2], Marcelo Cardoso[1]

[1]Federal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901
[2]Federal University of Viçosa (UFV), Viçosa, MG Brazil, 36.570-000

Abstract. Characterization of biomass relevant to thermochemical conversion processes and other applications is critical to the design and proper operation of energy conversion, biorefining, and other facilities, especially for adding value to waste. In the present work, selected agro-industrial solid residues from coffee crops – and – were characterized as solid fuels and an evaluation of their properties, including proximate and ultimate composition, energy content, several biochemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl group) and thermogravimetric analysis. Results showed that moisture content ranged 8.69 % to 18.46 %, carrying an average higher heating value of 18.3 MJ kg^{-1}–19.45 MJ kg^{-1}, and volatile matter content of 74.07 %-83.70 %. The silica (0 %–0.4 %) contents are quite small for all biomass samples. Glucans is the dominant component in the carbohydrate fraction of all studied samples (17.90 %-33.25 %). Additionally, the high content of extractives (10.57 %-24.72 %) and lignin (26.59 %-43.17 %) of the samples found in this study, reveals that the biomasses are more suitable for charcoal production than cellulose pulp production. The extensive residue characterization provided valuable data that helped in outcome of the evaluation of different conversion technologies as being an environmentally friendly alternative, contributing to upgrading the large quantity of waste generated by the coffee industry into energetic valued residues, and improving their management.

4.1 Introduction

The coffee production chain derivate a large quantity of residues obtained from the cherries and shrub, as it is produced in large scale around the world. It is estimated that over ten million tons of residues are produced yearly (solid and liquid) in relation to the annual world production of coffee. This amount excludes the residues of cultivation (pruning leaves) because is difficult to estimate due to the differences in agronomic management practices (Echeverria et al., 2017). These residues represent a serious source of environmental contamination, if discarded inadequately and without any management. Brazil, Vietnam, Colombia and Indonesia are the largest coffee producers in the world, responsible for more than 50 % of world production. South America maintained both species, *Coffea Arábica* L. and *Coffea Robusta*, estimating, in 2016, an average yield of 1.5 ton ha^{-1}; *Coffea Arábica* L. and *Coffea Robusta* production was 81.09 % and 18.91 %, respectively (CONAB, 2016).

With exports amounting to 35.23 million bags of 60 kg in May/2016, Brazil is the largest producer and exporter of coffee in the world (USDA, 2016). The gross amount of coffee (*Coffea Arábica L*. and *Coffea Robusta*) produced in Brazil (May 2015/2016) was 3.04 million tonnes according to IBGE (2017), and the total area planted in the country with coffee (*Coffea Arábica L*. and *Coffea Robusta*) was 2.28 million hectares, where 2.09 million hectares (91.7%) were in production. As can be seen in Table 4.1, Southeastern Brazil, is the main region of coffee production (89.7 % of total coffee produced) where the environment and climate provide ideal growing conditions for coffee plant.

Table 4.1. Planted area, harvested area, amount of coffee produced and amount of waste generated in coffee plantation in Brazil (2015/2016).

Region	Planted area (hec) (IBGE, 2017).	Harvested area (hec) (IBGE, 2017).	Coffee produced (ton) (IBGE, 2017).	Waste generated	
				Wood (ton)	Parchment (ton)
Brazil	2296476.0	1993926.0	3047665.0	3444714.0	664945.1
North	98324.0	81569.0	93361.0	147486.0	20369.7
Northeast	180974.0	166218.0	135744.0	271461.0	29616.9
Southeast	1946029.0	1678506.0	2733060.0	2919043.5	596304.0
South	44082.0	44020.0	62299.0	66123.0	13592.5
Midwest	27067.0	23613.0	23201.0	40600.5	5062.0

An adult coffee plant weighs on average 15 kg (dry wood) and approximately 25 % of coffee plant is converted into solid waste, after pruning, which occurs approximately every five years (de Oliveira et al., 2013), and this means an average generation of 291.65 million tons per year of residual wood from coffee plantations in Brazil. Furthermore, in coffee production, approximately 55 % of the coffee cherry is converted into grain, and the parchment represents 12 % of the fruit on a dry basis (Heuzé et al., 2015). Consequently, the estimated production of parchment was 664.94 thousand tons in 2016 in Brazil (May 2015/2016). Therefore, the coffee production represents over 4.1 million tons of solid residues being generated per year. As a result of having the greatest coffee production, southeastern Brazil is the region with the highest waste generation from coffee plantations, producing more the 80 % of the total amount of waste produced in the country. This amount excludes the leaves (Fallen and pruning) whose amount is difficult to estimate due to the differences in agronomic management practices. However, under normal cultivation conditions, coffee leaves have an average duration of 1.5 years, with defoliation caused by different factors such as inadequate nutrition, water deficiency in the soil, excessive plant burden, disease and crop. In the condition of coffee cultivation in full sun, as in Brazil, in the post-harvest period, the occurrence of leaf defoliation in plants with a 30-70% drop in leaves is normal (Matiello et al., nd). Thus, the Procafe foundation, in a survey in the state of Minas Gerais (Brazil), estimated that on average 5500 kg (dry basis) per hectare of leaves fall annually in different conditions of Arabica coffee plantations.

The large amount of waste generated by the agricultural industries is a problem that exists in almost all regions of Brazil. Thus, the waste management is often considered potentially problematic, because its disposal or proper use usually generates high costs that producers often want to avoid. The thermochemical conversion technologies for recovery of energy from wastes can play a vital role in mitigating the problems caused by the large amount of residual waste. In this sense, the residues from coffee production can be used to generate thermal energy to dry agricultural products or to heat animal facilities, or as fuel to generate mechanical or electrical energy. However, knowledge of the quantity, physical and chemical characteristics and technologies available for use of residues can produce an alternative that conserves energy and contributes to sustainable development.

The concern with the increase of coffee bean productivity has ignore the implementation of technological characteristics to the residues provided by the coffee production chain, additionally, little or partial information exist about its use in the generation of value-added products. In order to solve some limitations in relation to the use of residual coffee biomass in nature, such as low energetic density, high content of moisture, high heterogeneity that leads to difficulties in handling, transport and storage, agricultural / forestry companies and research centers, suggests solutions for reducing these problems, trough treatments that produce homogeneous, high yielding, high quality and low cost products, such as biodiesel (Caetano et al., 2012), biogas (Jayachandra et al., 2011), source of sugars (Mussatto et al., 2011), and precursor for production of activated carbon (Kante et al.,2012;Pappa et al., 2012).

The aim of this study is to present an extensive characterization of residual biomasses from the coffee production chain for energy purposes, increasing knowledge about the alternatives applicable to the energy matrix of countries where the coffee industry is a major agricultural activity, through physical and chemical analyzes that identify the most important quality indices, the interactions between them, as well as the quantification of its importance. It is important to note that the extensive characterization of the residues presented in this work is not readily available in the literature and these results are fundamental tools for the qualification and quantification of the effects of residues properties on conversion technologies that include thermochemical processes such as pyrolysis, gasification, and combustion, and physical processes such as briquetting and pelletizing.

4.2 Methodology

4.2.1. Sampling and preparation for characterization process

Residues from coffea (*Coffea Arabica* L.) cultivation: parchment, leaves and wood, provided by a rural farm in the municipality of Paula Cândido – MG - Brazil (20°49'50.0" S 42°55'03.3" W) were used. The plantation was established in 1986, and due to low productivity, pruning of new plant formation was required, making the cuts at the base of the stem. The wood collected from this pruning was 11 years old (from after the last pruning period), and from a bush in which the base and the roots have been conserved since it was planted 30 years ago.

The biomasses was ground in an industrial mincing Lippel® brand, and posteriorly in an electric hammer mill, motor Weg® mark of 10 CV and 3520 rpm, which was coupled with a screen opening of 2 mm. For samples intended for chemical analysis it was necessary to further reduce the particle size, using a knife mill type Wiley® Mill Model 4. The biomasses were finally classified into superposed screen with openings of 40 mesh and 60 mesh according to ASTM (1982).

The experiment was conducted according to a randomized design with six biomasses and two replicates for each characterization. Data were subjected to analysis of variance (ANOVA), and when significant differences were established, treatments were compared through Tukey test at 5% probability level.

Statistical analyzes were performed with the help of the Statistica 8.0 program Soft (2007).

4.2.2. Stock estimation of the coffee shrub wood parts

The wood samples were previously separated into (I) stem, (II) primary branch and (III) secondary branch according to their diameter for individual properties analysis and stock estimation.

4.2.3. Laboratory procedures for biomass characterization

An extensive characterization of the solid fuel was performed, evaluating the evolution of their properties, including proximate and ultimate composition, energy content, several biochemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl group) and thermogravimetric analysis of each residue group.

4.2.3.1. Basic density.

The measurement for basic density of wood sample (stem) was determined according to SCAN CM 43:95 standard procedures of 25 disks obtained from different cut sections on the main axis of the shrub. The drying analysis of wood parts of the coffee shrub, (stem, primary branch and secondary branch) with dimensions of 30 cm length and variation of the diameter for each wood part, was conduct in a climate-controlled room with temperature (23 °C - 24°C) and relative moisture (60 %-70% U) control. The mass loss of the samples was monitored by periodic weightings until reaching anhydrous mass.

4.2.3.2. Ultimate analysis.

The ultimate analysis shows the content of five major elements: Carbon (C), oxygen (O), Hydrogen (H), Nitrogen (N) and Sulphur (S) in the organic phase. The content of these elements was measurement using a Vario Micro Cube CHNS-O equipment with helium as a carrier gas and oxygen as an ignition gas according to DIN EN 15104 standard procedure. The molar ratios of oxygen and hydrogen to carbon were determined.

4.*2.3.3. Proximate analysis*

The equilibrium hygroscopic moisture content (EHM) was determined by the mass difference according to DIN EN 14774-1 standard procedure. The volatile matter analysis was performed according to methodology DIN EN 15148 standard procedure. Ash content was determinate according to DIN EN 14775 standard procedure. Fixed carbon was calculated of the difference among 100 and the sum of volatiles and ash biomass content. The silica content of the biomasses was measured according to TAPPI T245 cm-98 and the content of sodium, iron, copper, manganese, potassium, calcium and magnesium was determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 procedures.

4.2.3.4. Heating value.

The higher heating value (HHV) has determined according to DIN EN 14918 standard procedure, in duplicate, using a bomb calorimeter adiabatic IKA300. The lower heating value (LHV) was determined according to equation (1) of the annex E of the DIN EN 14918 standard procedure.

$$LHV\ (J\ g^{-1}) = (HHV\ (J\ g^{-1}) - 212.2 * Hydrogen\ content\ (\%) - 0.8 * (Oxygen\ content\ (\%) + Nitrogen\ content\ (\%)) * (1 - 0.01 * EHM\ (\%)) - (24.43 * EHM\ (\%)) \quad (4.1)$$

4.*2.3.5. Chemical composition*.

The chemical composition of studied biomass samples was evaluated within the following procedure. The milled samples were extracted successively with ethanol/toluene (1:2 v/v), ethanol and finally water following the TAPPI method T264 cm-97. This extracted sample (extractive free sawdust) was conditioned in a temperature and relative humidity controlled room (23±1˚C, 50±2% RH) until an

equilibrium moisture was achieved. The extractions were carried out in duplicate, and the extraction yields were expressed in percentage in relation to the biomasses's dry weight. The contents of Uronic acids and Acetyl groups and anhydrosugars (Anhydroglucose, Anhydromannose, Anhydrogalactose, Anhydroxylose and Anhydroarabinose) in the extractive-free biomass were determined according to Scott (1979), Solar *et al.* (1987) and SCAN-CM 71:09 standard procedure, respectively. Sugars were measured by a Shimadzu HPLC, coupled to a refractive index detector (RID-10 A), equipped with a Bio-Rad Aminex HPX-87H column (300 x 7.8 mm), and operated at 60°C with a mobile phase of sulfuric acid 5mM at rate of 0.6 mL min^{-1}. On the extractives-free biomass, the acid insoluble lignin and acid soluble lignin were determined according to TAPPI T 222 om-11 standard procedure and Goldschinid (1971), respectively.

4.*2.3.6. Thermogravimetric analysis*.

Thermogravimetric analysis was applied to study the transformations of chemical components when the biomass is subjected to a heat treatment in an inert atmosphere. Tests were performed using a TGA analyzer (SHIMADZU DTG60 Series), by heating a typical sample mass of 4 mg in a purge of nitrogen (30 ml min^{-1}), at heating rates of 10 ºC min^{-1} with final temperature at 1000 ºC.

4.3 Results and Discussion

4.3.1 Stock estimation of the coffee shrub woods parts

Table 4.2 shows stock estimation of the biomass (stem, primary branch and secondary branch) in the coffee shrub.

Table 4.2. Stock estimation of the woods parts (stem, primary branch and secondary branch) in the coffee shrub.

	Wood Parts of coffee shrub			
Estimation	Stem	Primary Branch	Secondary Branch	Total
Diameter (cm)	9.8a	2.3b	1.8b	
Biomass (Kg coffee $shrub^{-1}$)	4.10a	2.24b	2.54b	8.88
Biomass (%)	46.17a	25.22b	28.61b	100

Averages followed by the same letter among biomasses do not differ by Tukey test at 5% of significance.

The analysis of variance presented significant difference between the stem and the branches for diameter and proportion characteristics. The stem presents greater diameter considering that is responsible for sustaining the plant, supporting the weight of the branches with its foliage and fruit. The coffee shrub represents on average 8.88 Kg of wood.coffee shrub^{-1}, the greater contribution is from the stem, followed by secondary branches and primary branches, respectively. The branches represent more than 50% of the total weight of the shrub, fact that explains the great importance of the branches in the structure of the system, as it is on which the fruits grow. In Viçosa, southeastern Brazil, shoot growth of the *Coffea Arabica* shrub is slow during the dry, cool season, and rapid in the rainy, warm season (Barros et al., Da Matta et al., 1999). The growth of the shrub is also influenced by age, planting density, cultural practices and weed competitions (Da Matta et al., 2017). The pruning of the shrub occurs approximately every five years to increase the shrub productivity (de Oliveira et al., 2013). For energy, the transport of the raw material is a fundamental stage in the chain of energy production, in this way, the stem provides more amount of stacked biomass than the branches, as a result of the significant difference between the densities.

3.2 Characterization of residual biomasses from the coffee production chain

Table 4.3 shows a chemical analysis of the residual biomasses from the coffee production chain.

Table 4.3. Characterization of residual biomasses from the coffee production chain.

Components	**Biomasses**					
	Leaves	Primary branch	Secondary branch	Bark	Stem	Parchment
Basic density (kg m^{-3})	*nd*	*nd*	*nd*	*nd*	598.7	*nd*
Ultimate elemental[b] (wt %)						
C	53.97 a	50.31 c	51.82 b	54.41 a	50.64 c	50.69 c
H	6.55 ab	6.13 d	6.40 bc	6.59 a	6.12 d	6.23 cd
O	35.50 e	42.28 a	40.06 c	36.66 d	41.16 b	42.05 a
N	3.54 a	0.92 d	1.51 c	2.13 b	1.86 b	0.82 d
S	0.43 a	0.36 a	0.21 b	0.21 b	0.21 b	0.20 b
H/C	1.46 a	1.46 a	1.48 a	1.45 a	1.48 a	1.45 a
O/C	0.49 c	0.63 a	0.58 b	0.50 c	0.62 a	0.61 a
Proximate composition(wt %)						
Moisture	16.35 b	8.70 d	9.28 d	18.11 a	10.96 c	11.09 c
Volatile Matter[a]	74.71 c	80.62 b	75.31 c	75.63 c	83.70 a	74.07 c
Fixed Carbon[a]	18.12 bc	16.95 cd	21.23 a	20.03 ab	14.62 d	20.09 ab
Ash[a]	7.17 a	2.42 e	3.45 d	4.33 c	1.67 f	5.84 b
Silica (% of ash)	0.10 b	0.10 b	0.10 b	0.40 a	0.15 b	0.35 a

continuation of the table 4.3

			Minerals[c] (g Kg^{-1})			
Ca	4.65 cd	4.49 d	6.41 b	20.96 a	6.29 bc	3.73 d
Fe	0.18 b	0.05 d	0.11 c	0.57 a	0.07 cd	0.24 b
Mn	0.03 c	0.04 a	0.02 d	0.01 e	0.01 e	0.03 b
Mg	2.05 ac	1.17 b	1.68 c	2.23 a	1.07 b	1.77 c
Cu	0.05 ab	0.02 cd	0.04 bcd	0.06 a	0.02 d	0.04 bc
K	10.86 b	6.74 d	7.96 c	2.94 f	4.06 e	12.20 a
Na	1.19 a	0.36 c	0.69 d	0.95 b	0.68 d	0.73 d
Heating value (MJ kg^{-1})						
HHV	19.45 a	19.20 ab	19.20 ab	19.20 ab	19.00 b	18.30 c
LHV	14.68 c	16.10 a	15.92 a	14.11 d	15.44 b	14.81 c
Chemical composition (%)						
Extractive	24.72 a	13.09 d	13.95 c	12.19 e	10.58 f	21.95 b
Insoluble Lignin[b]	35.52 b	26.73 de	29.32 c	40.98 a	27.33 cd	24.52 e
Soluble Lignin[b]	3.59 a	3.12 b	2.93 b	2.19 c	2.24 c	2.07 c
Total Lignin[b]	39.11 b	29.85 d	32.25 c	43.17 a	29.57 d	26.59 e
AnhydroGlucose[b]	19.65 c	33.25 a	29.05 b	17.90 c	31.65 ab	29.60 ab
AnhydroXylose[b]	5.30 e	11.85 b	10.30 c	6.25 d	12.20 b	14.55 a
AnhydroGalactose[b]	2.50 a	1.15 cd	1.45 bc	1.20 cd	0.90 d	1.65 b
AnhydroMannose[b]	1.10 d	2.55 b	1.70 c	0.90 d	3.30 a	1.00 d
AnhydroArabinose[b]	4.50 a	1.55 d	2.90 c	4.25 a	1.35 d	3.45 b
Uronicacids[b]	4.80 b	3.80 c	4.70 b	5.20 a	3.30 c	5.50 a
Total sugars[b]	37.85 b	54.15 a	50.10 a	35.70 b	52.70 a	55.75 a
Acetyl group[b]	1.00 c	1.8 b	1.8 b	1.00 c	2.80 a	2.85 a
***Others*[b]**	14.87	11.78	12.40	15.80	13.26	8.97

[a]dry basis. [b]dry ash free basis. *nd*-not determined. HHV-Higher Heating Value. LHV-Lower Heating Value.

4.3.2.1 Basic density of coffee wood

In the average value of basic density of coffee wood, negligible variations between the base and the top of the stem were observed. The value collected (598.7 kg.m^{-3}) shows that the use of coffee wood can be attractive for the production of charcoal, because higher wood density is preferred, resulting in higher mass production for a given volume of wood (Temmerman et al., 2016). In addition, the charcoal apparent density will be higher, attaining greater strength and higher heat capacity per volume, generating operational advantages, such as gains in harvesting and forest transport processes due to the fact that larger volumes of timber harvested will generate greater specify mass values (Assis et al., 2016). According to the measures suggested by

Brito *et al.* (1982) and Lima *et al.* (2001), the wood basic density for charcoal production should exceed 500 kg m^{-3}. Likewise, for direct combustion, wood with high basic density results in more concentrated fuel energy, due to the greater mass of fuel contained in the same unit volume. The value found is similar to sighted in the literature for Eucalyptus wood, that presents basic density between 436 kg m^{-3} and 668 kg m^{-3} for the species *E. pellita, E. urophylla* and *E. grandis*, traditionally used for energy conversion, including firewood and charcoal (Ribeiro et al., 1993).

4.3.2.2. Ultimate analysis

The biomasses collected are basically composed of Carbon (50.26 %– 54.41 %, dry basis), Hydrogen (6.13 %- 6.59 %, dry basis) and Oxygen (35.52 %-42.29 %, dry basis). Traces of nitrogen and sulfur were also verified. For energy generation from biomass, either through combustion, pyrolysis, or gasification, it is desirable that the biomass present high values of carbon and hydrogen, considering that these elements contribute the most to the calorific value of the fuel (Dermirbas, 2004). The energy generated by thermal degradation is associated with the enthalpy of carbon, hydrogen and sulfur (Trugilho et al., 2012). The presence of nitrogen and sulfur in the biomass have a direct impact on the environmental pollution, due to the volatile compounds resulting in the formation of toxic oxides (NO_x, SO_x) after thermochemical conversion processes (Dermirbas, 2004). The content of sulfur observed in the elemental composition was low (0.20 %-0.43 %), being a favorable characteristic of the biomasses when used in thermochemical processes. Generally, the S content in biomass varies in the interval of 0.01 %–2.3 % (Vassilev et al, 2010).

The coffee shrub are highly N-demanding, the nitrogen requirements increases with shrub age especially at the beginning of grain production (Catini et al., 1985). If there are not limiting factor, the nitrogen will promote rapid plant development specifically through the increase in number of plagiotropic branches per shrub, number of nodes per branch, and number of fruiting nodes, flowers and leaves per node, which, taken together, are associated with higher yields in coffee (Nazareno et al., 2003; Carelli et al., 2006). Hence the coffee shrub presents high potential for nitrate assimilation in leaves as well as in roots, that's the reason of the highest levels of nitrogen in leaves with significant difference between the other biomasses. The nitrogen content in biomasses varies in the interval of 0.10 %–12 % (Vassilev et al, 2010; Manyà et al.,

2008). Then, the values of nitrogen and sulfur found in this study do not compromise the energy use of the samples and its use will be environmentally more advantageous than other sources of energy such mineral coal.

The molar ratios of oxygen and hydrogen to carbon for the residues studied are shown in Figure 1. Oxygen is generally present in plant-based fuels, and its presence decreases the calorific value[31]. Therefore, low H/C and O/C ratios are desirable for the use of biomass for energy. The samples with low O/C ratio, also have more energetic content because C-C bonds have higher chemical energy than C-O bonds (McKENDRY, 2002). In the biomasses collected, higher O/C ratio can be observe in the primary branch (O/C = 0.63) with no significant difference between stem and parchment, and in H/C ratio, secondary branch and stem have the highest value (H/C =1.48) with no significant difference between the other biomasses. Parchment appears to have a low value for the heating value considering the relatively high O/C ratio. This fact may be also associated with high ash content. According to Demirbas (2004) higher proportion of oxygen, hydrogen and inorganic elements, compared with carbon, tends to decrease the heating value of the fuel.

4.3.2.3. Heating value

Dogru *et al.* (2002) reported that heating value is one of the most important parameters for energy audit and modelling in thermochemical conversion processes. For the high heating value (HHV), Table 4.3 shows mean values between 18.30-19.45 MJ kg^{-1}, similar sighted in literature (18.60 MJ kg^{-1}-19.02 MJ kg^{-1})(Paula, 2010) for residues from coffee production chain and analogous to biomasses commonly used in energy generation (19.50 MJ kg^{-1}–21.00 MJ kg^{-1})(de Oliveira et al., 2013; Keipi et al., 2014; Doumer et al., 2015). LHV shows mean values between 14.11 MJ kg^{-1}-16.10 MJ kg^{-1}. Primary branch has the higher value of LHV with no significant difference with secondary branch, mainly due to its low moisture content and its high HHV, influenced by low ash content and metal composition.

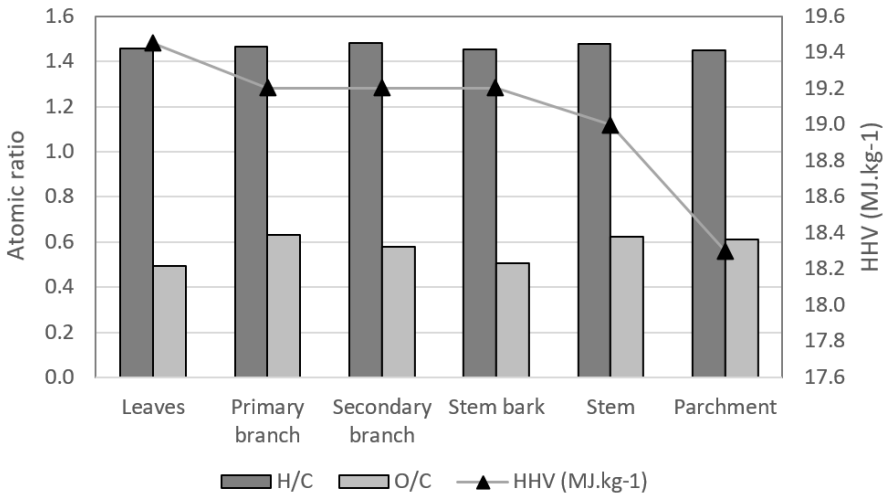

Figure 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain

4.3.2.4. Proximate analysis

The proximate analysis aims to quantify the moisture, volatiles (condensable and non-condensable), fixed carbon and ash biomass content. The fixed carbon (FC) content is of special interest since this indicates the potential for charcoal generation by devolatilized biomass (Raj et al., 2015). The FC content in the samples varies in the interval of 14.62 %-21.23 %; secondary branch presents the highest values of FC content with no significant difference between bark and parchment. The biomasses studied presents high values of FC, similar to FC content mentioned in the literature for biomasses commonly used in energy generation, such eucalyptus wood (de Souza-Santos, 2010; Dermibas, 2003). For volatile matter (V), the range of values was 74.07 %-83.70 %. The primary branch presents the highest volatile matter content (83.7 %), with significance difference between the other biomasses, and similar to solid fuels as eucalyptus (82.62 %) and bamboo (84.65 %) (Donahue et al., 2009; Parikh et al., 2007). Solid fuels with high contents of volatile matter and low levels of fixed carbon are more susceptible to thermal degradation during combustion and pyrolysis (Fernandes et al., 2013), requiring less residence time in the thermochemical equipment compared to fuels with high fixed carbon and low volatile content (Nogueira et al, 2003). Ash is the inorganic solid residue left after the fuel is completely burned (Basu, 2010). In the data obtained for ash content, it was observed that residual biomasses from the coffee

production chain presented low ash content in the range of 1.67 %-4.33 % except for parchment and leaves, which had higher values of 5.84 % and 7.17 %, respectively.

The mineral composition of ash (Table 4.3) shows that potassium, calcium and magnesium present dominants levels in the ashes, and manganese, iron, copper and sodium appeared in small quantities. The values of the minerals show a significant difference in the analysis of variance between the biomasses. These compositions indicate potential ash deposition problems at high or moderate thermal conversion temperatures (Shao et al., 2012). It was also found that silica contents are quite small for all biomass samples (0 %–0.4 %). The influence of the silica on combustion and gasification processes has been reported at temperatures higher than 873 °C because of the ash deposition propensity in thermal fuel conversion systems. The appearance of the metal increase both the tendency for ash particles to stick to heat-transfer surfaces and the subsequent rate of strength build-up in ash deposits. These operational problems are closely related to the chemical compositions of the ash. The gasification process requires a feedstock with less than 5 % ash content, preferably less the 2 %, in order to prevent the formation of clinkers (Rocha et al., 2015).

3.2.5. Chemical composition

Another important characteristic of biomass is the composition in terms of the structural chemical compounds. Obtained data of chemical composition are presented in Table 4.3. The dried biomass is composed mainly of about 40 % to 60 % of cellulose (composed of units of Anhydroglucose linked by glycosidic bonds β1-4), 15 % to 30 % of hemicelluloses and 4 %-35 % of lignin (Basu, 2010; Sjostrom, 2013). However, residues from coffee production chain are constituted by several other components, including lipids, tannin, polyphenols, fiber and nitrogenous compounds (Farah, 2012; Oestreich-Janzen, 2010), these latter components were not evaluated in this study, but were considered in the mass balance presented in the Table 4.3.

The carbohydrate fraction range for the studied samples were 17.90 %-33.25 %; 5.30 %-14.55 %; 0.90 %-2.50 %; 0.90 %-3.30 %; 1.35 %-4.50 % for anhydroglucose, anhydroxylose, anhydrogalactose, anhydromannose and anhydroarabinose, respectively. These values are within in the ranges found in studies carried out for biomasses implemented in energy production, where the anhydroglucose represent, on average, 46.6% of the chemical composition of biomass, varying from 44.5% to 50%, the

anhydroxylose are the dominant fraction of the hemiceluloses and represent 10.8% to 13.2% on average of 12.2% of the biomass, and the other carbohydrates (anhydrogalactose, anhydromannose and anhydroarabinose) contributed with approximately 0.7%, 0.6% and 0.2%, respectively (Gomide et al., 2005).

The chemical composition of the biomass exerts a great influence on the results of energy conversion, affecting the thermogravimetric performance of the process. The hemicelluloses are more susceptible to the reactions of thermal degradation because of the presence of hydroxyls connected to its main chain and the absence of crystalline agglomerates (Santos et al., 2013). The branched chains of the hemicelluloses and cellulose are easily degraded at low temperatures, having maximum peaks loss at approximately 275°C for hemicelluloses and 350°C for cellulose (Shen et al., 2010). In this sense, for the charcoal production, biomass with lower percentages of cellulose and hemiceluloses should be preferred. The parchment of coffee cherry, stem, primary and secondary branch of coffee shrub reveal a greater thermal degradation than the other biomasses at low temperatures, probably of the high anhydrosugars content in its chemical composition.

For lignin, higher content in biomass are more sustainable for energy production, because lignin is the chemical component that has a greater thermal stability due to the C-C bonds linkages between monomeric units of phenyl-propane, and consequently has more stability in its aromatic matrix contributing for charcoal and products like methanol and bio-oleo formation (Sen et al., 2015). The acid insoluble lignin content of the samples evaluated in this study varied from 24.52% to 40.98% and soluble solids from 2.07% to 3.59%, similar to the values for soluble and insoluble lignin from biomasses used in energy production such *Eucalyptus grandis, Eucalyptus globulus, Eucalyptus dunnii and Eucalyptus urophylla* wood found in the literature (Gomes et al., 2015) and higher values than those reported in the literature for *Coffea Arabica* residues (Rowell et al., 2005). In this case, the high total lignin values of the biomasses presented in this study make them an attractive raw material for the production of carbon with high calorific value, however, its use in processes such as the production of cellulose pulp is not attractive due to the increase in the expense of reagents.

The total extractive content ranged from 10.57 % to 24.72 %. Leaves of the shrub of *Coffea arábica* present a total extractive significantly higher than the other

lignocellulosic materials (Table 4.3). The high extractive content of the leaves (24.72%) is mainly due to the residual fraction of amino acids, sugars and mucilage of low molar mass not removed during the milling of the biomass, because the extraction with ethanol / toluene only extracts substances such as waxes, fats, resins, phytosterols and non-volatile hydrocarbons (Rowell et al., 2005). The lowest levels of total extractives were found in the samples of the coffee shrub wood, corresponding to approximately 50% of the total extractives verified for the leaves.

The extractives play an important role in the use of biomass, because they influence their physical and energetic properties and depending on their thermal stability, these substances can contribute to the increase in the yield of charcoal. Some of the extractives are volatile and therefore they are important in the direct burning of the biomass, because they degrade faster and help to maintain the combustion flame, however, for the production of charcoal, the high volatile extractive content in the biomass is detrimental because it provides lower gravimetric yield in coal due to the degradation of these substances at low temperatures (Santos et al., 2011).

The evaluated biomasses, with respect to the macromolecular chemical composition, present high potential as biofuel, since they present higher lignin contents than those found in the literature for ideal materials for this purpose.

4.3.2.6. Thermogravimetric analysis

Figure 2 shows the thermal behavior of the residual biomasses of the coffee production chain by Thermogravimetric analysis (TG) and Differential thermogravimetric analysis (DTG).

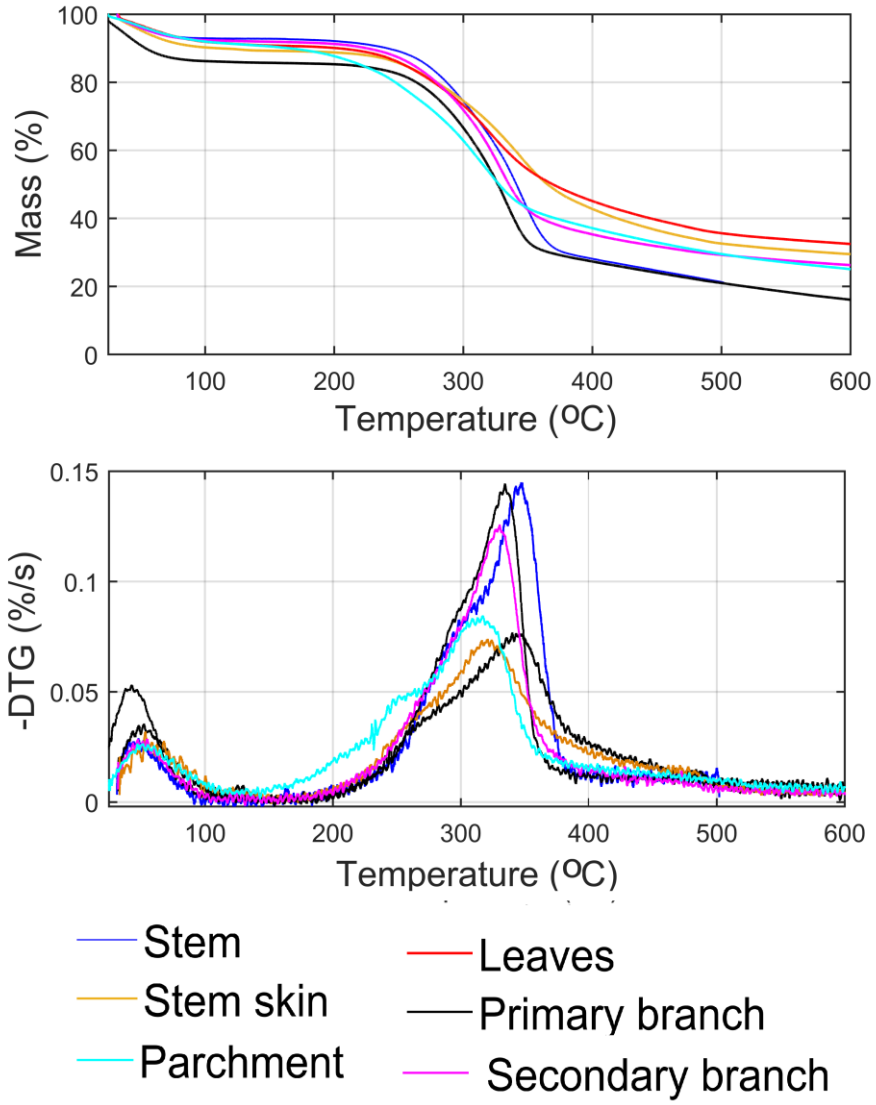

Figure 2. TG and DTG of the residual biomasses of the coffee production chain.

It is observed that the thermal degradation profiles of the biomasses were similar, with small differences in the temperatures corresponding to the maximum peaks of the curve, mainly related to the degradation of the hemicelluloses and cellulose. The thermogravimetric data (TG) curves and the first derivate data (DTG) curves, usually show three bands of thermal degradation, the first being attributed to the drying of the biomasses and the other two to the degradation of its main components; it should be emphasized that each biomass components degrades in different temperature ranges. The second temperature range corresponds mainly to the thermal degradation of the hemicelluloses and of cellulose and lignin in smaller proportions. The third thermal degradation range was then initiated, this temperature range corresponded mainly to the degradation of the cellulose. The loss of mass for the cellulose needs a greater amount

of energy than the hemicelluloses, due to the depolymerization of the cellulose chain and the breakdown of its monomer (Luo et al., 2004), that is the reason the degradation of the cellulose occurs after the degradation of the hemicelluloses. The degradation peak of lignin is absent, due to the fact that its thermal decomposition occurs in a wide temperature range (Santos et al., 2013; Yang et al., 2007). The table 4.4 shows the measurements of the mass losses (%) obtained for each biomass, according to the temperature ranges from Ti °C (Initial temperature) to 600 °C, with intervals of 100 °C.

Table 4.4.Values of mass loss of biomasses in function of the temperature ranges, in percentage.

Biomasses	Temperature rates (°C)						Residual mass (%)
	Ti - 100	100-200	200-300	300-400	400-500	500-600	
	Mass lost (%)						
Leaves	8.04	1.85	16.94	28.08	9.47	3.16	32.46
Primary branch	13.76	0.92	18.68	39.32	6.34	4.90	16.08
Secondary branch	7.63	1.08	19.45	36.54	6.02	3.00	26.26
Bark	9.73	1.49	14.22	31.78	10.17	3.13	29.47
Stem	7.04	0.82	17.66	46.35	6.86	4.99	16.00
Parchment	8.00	4.31	24.80	25.77	7.61	4.44	25.07

As present in figure 2, the combustion process of the samples could be divided into two stages. The first stage extended from 33.26 °C-127.16 °C; 23.73 °C- 105.15°C; 32.02 °C-107.01 °C; 31.27 °C-101.49 °C; 27.18 °C-121.38 °C; 24.85 °C-101.75 °C for leaves, primary branch, secondary branch, stem, bark and parchment, respectively, which represented the dehydration by evaporation. The second stage was from 232.76 °C-424.05 °C; 243.11 °C-379.57 °C; 237.41 °C-422.24 °C; 242.49 °C-383.62 °C; 233.08 °C-463.52 °C; 279.64 °C-363.91 °C for leaves, primary branch, secondary branch, stem, bark and parchment, respectively, which represent the liberation of the volatile compounds. A similar phenomenon was shown in the combustion characteristics of oil palm fiber and eucalyptus in torrefaction (Chen et al., 2014). From Table 4.4, the mass loss percentage of the first and second stage in the total mass loss was approximately 8.04% and 45.02 %; 13.76 % and 58 %; 7.63 % and 55.99%; 9.73 % and 46 %; 7.04 % and 64.01 %; 8 % and 50.57 % for leaves, primary branch, secondary branch, stem, bark and parchment, in the first and second stage, respectively. As coffee

residues are biomasses, the main composition of the biomasses are cellulose, hemicellulose and lignin. Therefore, the combustion of coffee residues corresponds to the combustion of these materials. Cellulose rapidly decomposed between 300 °C and 350 °C; lignin decomposed between 410 °C and 540 °C and hemicellulose decomposed between 198 °C and 398 °C (Yang elt al., 2007; Lu et al., 2013). Therefore, the mass loss in the second stage of the thermal degradation samples was because of the decomposition of cellulose and hemicellulose. The stem and primary branch of the coffee shrub presents higher mass losses in the second stage, probably these biomasses have higher rates of cellulose crystallite. The opposite is observed for leaves, which has the lowest degradation rate and is responsible for the greatest residual mass.

4.4 Conclusions

Residual biomasses from the coffee production chain could be classified as suitable feedstock for thermochemical conversion processes with the moisture content ranged 8.70 % to 18.11 %, carrying an average higher heating value of 18.30 MJ kg^{-1}– 19.45 MJ kg^{-1}, and volatile matter content of 74.07 %-83.70 %. Additionally, it was also found that silica (0–0.4 %) contents are quite small for all biomass samples.

The total extractive content ranged from 10.58 % to 24.72 %, and for lignin, total values found in this study were 26.59 %-43.17 %. In these aspects, the coffee biomass is not very different from more traditional wood fuels.

Data from the ash composition can be used to predict the degree of biomass ash fouling and slagging during thermochemical conversion, and can aid to avoid the occurrence of operating problems in the application of such residues in combustion, pyrolysis, and gasification equipment.

From TG and DTG curves of all biomasses, it was observed that the mass loss profile of the samples could be divided into two stages, the first one associated to the dehydration by evaporation and the second one associated to decomposition of cellulose and hemicellulose.

The characterization of the samples shows that the thermochemical conversion is an environmentally alternative contributing to upgrading the large quantity of waste generated by the coffee industry into energetic valued residues and the improvement of their management.

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CHAPTER 5

Fast oxidative pyrolysis as a sustainable way for residues from pulp industry and coffee plantation to a renewable fuel

Elém Patrícia Alves Rocha[1], Vinícius Ramos[1], Clara Lisseth Mendoza Martinez[1], Fernando José Borges Gomes[2], Marcelo Cardoso[1]

[1]Federal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901

[2]Federal University of Viçosa (UFV), Viçosa, MG Brazil, 36.570-000

Abstract. The present study aims to analyze the fast oxidative pyrolysis of eucalyptus wood (EW), from pulp industry and coffee shrub (CS), from coffee plantations as a renewable alternative to add value to waste. The feedstocks were previously characterized by proximate and elemental chemical analyses, higher and lower heating value and density and submitted to oxidative fast pyrolysis in a fluidized bed reactor. Furthermore, the pyrolytic behavior of biomasses were investigated under inert and oxidative conditions at the heating rates of 10, 25 and 50 ^{o}C/min. The processes produced gases, heavy bio-oil, light bio-oil and bio-char. As the fast pyrolysis occurred in oxidative atmosphere, the overall results for liquid yield were good compared to the other biomasses. The bio-oils have a bigger energy density than the raw materials (6.3 times bigger for EW and 3.5 bigger for CS). The bio-char presented the higher heating value (26.1 MJ/kg for CS and 26.2 MJ/kg for EW), enabling it to be used as fuel. All of these results indicate that the residues are potential candidates for bioenergy production by fast pyrolysis.

5.1 Introduction

The use of fuels derived from fossil resources leads to global warming due to high levels of CO_2 emission in atmosphere. About 98% of carbon emissions result from fossil fuel combustion (Demirbas, 2008). Thus, reducing the use of fossil fuels would considerably reduce the amount of carbon dioxide and other pollutants produced, and thereby to mitigate climate change. Lignocellulosic materials are considered as one of the most promising alternatives for the production of fuels and chemical (Basu, 2013; Baskar et al., 2016) Brazil produces a substantial amount of lignocellulosic agricultural and industrial that can produce various sustainable bioproducts, biofuels and energy (Rocha et al., 2015; Fernandes et al., 2016; Sellin et al., 2016).

According to Rambo et al. (2015), in 2014, companies in the planted tree industry in Brazil generated around 47.0 million tons of solid waste, 33.60 million tons (71.5%) of which were generated in forestry activities and 13.40 million tons (28.5%) by forest industrial activities. Bracepa has reported that in 2010, the total production of pulp and paper in Brazil was 22.7 million tones. This generated 11 million tonnes of waste, representing about 48% in relation to the total paper and pulp production. Wood and forest waste from eucalyptus plantations for the pulp and paper industry in southeastern Brazil has received increasing interest as a raw material for the production of bioenergy (Rambo et al., 2015). The high density, rapid growth rates of wood and the homogeneity of Eucalyptus species and the large generation of residues provide a real advantage for the conversion of this biomass to biofuels.

Another source of potential feedstock is coffee which is one of the globe's largest agricultural commodities. At different stages, from harvesting to processing and consumption, several forms of residues, such as leaf, pulp, husk and wood are produced (Gouvea et al., 2009). Brazil is known as the world’s largest producer and exporter of coffee (*Coffea arabica L.*), with a total plantation area of 2.21 million ha (Queiroz, 2016). The estimated production for 2016 was 2.3 million tons (IBGE, 2016) (9.4 million tons were produced in the world in 2016 (USDA, 2016)).

Biomass in its original form is not an ideal for fuel use. High water content that can reduces the net heat available by as much as 20% in direct combustion (Demirbas, 2009). Low energy density means the transportation of biomass is expensive. Pyrolysis

can transform solid low energy density biomass into high energy density liquid which is easy transport. Biomass energy especially if it is from residues generates far less harmful greenhouse emissions than fossil fuels, reduces the amount of waste sent to landfills and decreases reliance on oil. Emission benefits depend on fossil-fuels replaced. Biomass energy also creates thousands of jobs and helps revitalize rural communities (Edenhofer, 2011). Biomass can be thermochemically converted into liquid fuel, such as pyrolysis oil and further to transportation. The oil, which is easier to store and transport than solid biomass material, is then burned like petroleum to generate electricity. It is possible to make transportation fuels using hydrogenation from biomass pyrolysis oil. They can be used in pure form or blended with gasoline (Demirbas, 2009). Fast pyrolysis for the production of bio-oil has been considered for large-scale production as a very advantageous process as it involves several advantages such as simplicity, low energy consumption, low investment. Although the fuel produced is acidic and requires care for handling and transport (Oasmaa et al, 2009). Additionally, fast pyrolysis of agro-industrial residues does not compete with food security (Trippe et al., 2010; Anex et al., 2010).

Pyrolysis is the thermochemical decomposition of the biomass by heating in the absence of oxygen, generating solid, gaseous and liquid fractions (bio-oil). Slow pyrolysis has been used mainly for the production of charcoal (Klass et al, 1998). In fast pyrolysis, the system operates continuously in moderate temperatures generally in the range 400 to 650 °C and residence times from a few seconds to a fraction of a second. Fast pyrolysis of biomass can provide up to 70% by weight of yields of liquid (Klass et al, 1998). Pyrolysis in inert atmospheres requires heat. Therefore conducting biomass pyrolysis in oxygen containing atmosphere where partial oxidation occurs called oxidative pyrolysis can be simple and efficient way to sustain pyrolyis, by providing the energy needed for heating, drying, and endothermic reactions of the conversion, and to allow the process to be autothermal (Daouk et al., 1998).

Fast pyrolysis of woody biomass has been extensively studied using fluidized bed reactors of various plant scales, ranging from 0.15 to 20 kg/h (Joubert et al., 2015), but a direct comparison of the reactor scale and the configurations used have demonstrated that use of fluidized bed reactors, or fluid bed reactor variations, are most common used for the production of fast pyrolysis biofuels in research and industrial applications (Butler et al, 2011; Dahmen et al., 2012). Fluid bed reactors are often selected because of their

superior mass and heat transfer properties and the efficient blending of biomass and heat carrier particles, which can be achieved by fluidization (Joubert et al., 2015).

Bio-oils from the fast pyrolysis of lignocellulosic biomasses are very different from fossil oils. These differences occur in both chemical composition and physical properties. The liquids have a high amount of oxygen, around 35 to 45% by mass, while in mineral oils this amount is in the ppm level. The high amount of oxygen in the bio-oils is due to the presence of the same in the more than 300 compounds identified in the bio oil and especially in the presence of the high content of water. This high water content of the bio oil contributes to a higher density compared to the fossil fuel, lower energy density and consequently a decreased adiabatic flame temperature and combustion temperature. In addition, the high water content causes ignition problems in motors. On the other hand, the presence of water reduces viscosity, improves atomization properties and reduces NOx emission in combustion processes. Fast pyrolysis bio-oils are not thermally stable and their calorific value is half compared to petroleum fuel oils. However, bio-oil production can be is economical and as it is a renewable source, its use is much more environmentally friendly than the use of fossil fuels.

In biomass oxidative pyrolysis, the gas has less oxygen than in the biomass combustion. Kim (2015) investigated the fast pyrolysis of biomass in a reactor with addition of oxygen in the gas in concentrations ranging from 0 to 8.40% (v/v). The yields of bio-oil in all cases of partial oxidative pyrolysis were similar to the control run without oxygen. However, the total yield of organic compounds in the bio-oil decreased and water content increased as oxygen in the gas increased. The yield of non-condensable gas increased with increasing oxygen, which was mainly attributed to enhanced production of CO_2 and CO by the reaction of the added oxygen with the pyrolyzing biomass.

The objective of this work is to analyze the fast oxidative pyrolysis of residues from coffee and eucalyptus plantations as a renewable alternative to add value to waste.

The eucalyptus and coffee plantations are of great importance for the Brazilian economy and they generate a lot of lignocellulosic residues. These biomasses can be used to generate bio-oil, which are much easier to handle and transport than solid or gaseous fuels. In the literature we find articles of fast pyrolysis with inert gases, such as nitrogen, for eucalyptus wood and for coffee grounds, or household residues after coffee infusion. There are no literature data for the oxidative fast pyrolysis of eucalyptus residues from the pulp industry and pyrolysis data of the woody residue of the coffee crop. Therefore,

it is important to obtain data on the bio-oil generated by the oxidative pyrolysis of residues from the coffee and eucalyptus plantations so that their suitability to bio-oil generation can be ascertained.

5.2 Methodology

5.2.1 Feedstock characterization

Coffee shrub (CS). The residues from coffea (Coffea Arabica L. with about 11 years of growth) processing were provided by a rural farm in the municipality of Paula Cândido in Minas Gerais state, Brazil. Once collected, the samples with basic density of 598.7 kg/m^3 were chopped in a crusher Lippel® brand, model TNF 2660 and submitted to granulometric analysis according to ASTM E828-81 (2004) using Tyler series sieves of different meshes. The particles presented fractions between 0.25 and 1.2 mm.

Waste of eucalyptus wood (EW). The residues of eucalyptus wood (*Eucalyptus grandis x Eucalyptus urophylla*) studied were collected from the paper and pulp mills in the state of São Paulo, Brazil. The samples were sawdust waste from the cutting of wood for the production of pulp which were classified according to ASTM E828-81 (2004) using Tyler series sieves of different meshes. The particle size distribution was not uniform, around 67% of the particles presented diameters of less than 0.71 mm and the rest between 0.71 and 1.41 mm.

To evaluate the potential of the biomasses for the fast oxidative pyrolysis process, the samples particles were characterized by chemical and physical analyses. Moisture (%M), volatile (%VM) and ash contents were determined by proximate chemical analysis according to procedures described, respectively, in the EN 14774-217, EN 15148.18 and EN 14775.19 standards. Fixed carbon content (%FC) was determined using the data previously obtained in the proximate analysis using the formula % FC = 100 - (% Ash + %VM). The higher heating value (HHV) of samples was determined in a bomb calorimeter, Parr 6300 Calorimeter, according to DIN51900-1.

Ultimate analysis was performed using a TruSpec Micro - Leco Instruments 628 Series C/H/N elemental analyzer with oxygen and sulfur module.

The thermal behavior of the biomass materials was studied under inert (N_2) and oxidative (Air) atmospheres using a DTG60H-SHIMADZU. TGA and DTG experiments were performed at heating rates of 5, 25 and 50^{o}C/min (gas flow of 30 ml/min) from room temperature to 500 ^{o}C.

5.2.2 Pyrolysis Plant and Experixmental Procedure.

Fast oxidative pyrolysis experiments have been performed in a fully controlled, continuously operated pilot-scale plant (SDB-20) as shown in Figure 5.1. It mainly consists of the fluidized bed reactor, with systems for biomass feeding, char collection, vapor condensation and bio-oil recovery. The pyrolysis of feedstock takes place inside the fluidized bed reactor of 200 mm of inner diameter and 935 heights, whereby bio-char, bio-oil, and gas are produced. The char particles are collected by cyclone after the reactor. The condensable vapors generated were cooled and condensed with shell and tube heat exchanger. A centrifugal device on top of the condenser collected the heavy phase of the bio-oil, enabling the organic and aqueous liquid phases to be collected separately. This type of reactor has been previously tested with other materials (Sellin et al., 2016; Mesa-Péres et al., 2013; Demirbas, 2004).

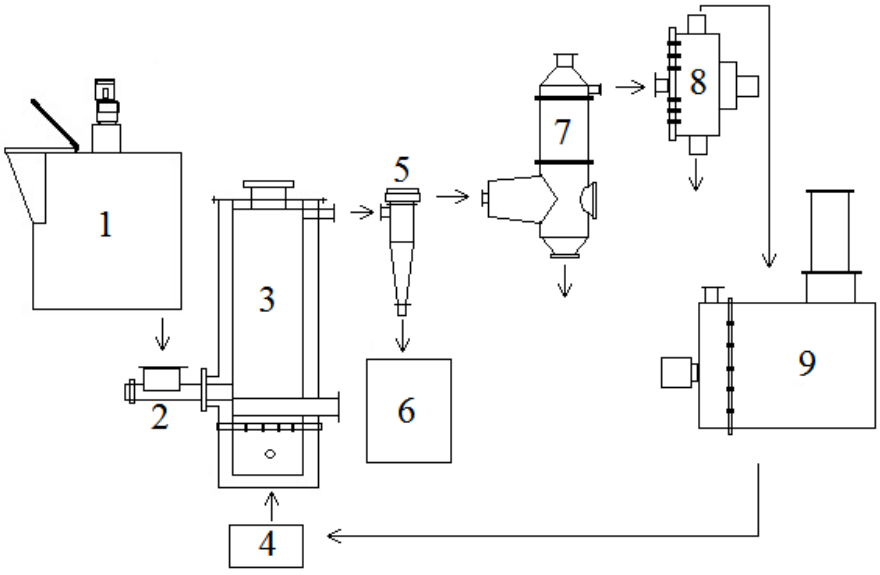

Figure 5.1. Scheme of the SDB-20 pilot plant, flow diagram. 1) Hopper/silo; 2) screw feeder; 3) fluidized bed reactor; 4) compressor; 5) cyclone; 6) char storage system; 7) and 8) bio-oil extraction system; 9) combustion chamber.

Before each experiment, the gas flow rates and the bed reactor temperature were set to the desired values. The biomass was fed to the reactor by a screw at the feed rate of 23.79 kg/h for the CS and 15.06 kg/h for the EW, which could be determined by measuring the mass difference between feedstock in the storage hopper, before and after each experiment. The pyrolysis temperature was kept about 500 ± ^{o}C and the fluidization agents were air and recirculation gases in all experiments. A blower supplied the air flow which is mixed with recirculation gases (supplied by a fan) and goes into the reactor through a dispersion plate. The flow rates of the fluidizing agents were 13 Nm^3/h for air and 7 Nm^3/h for reticulating gases. Farther, the noncondensable gases directly burned in the combustion chamber to heat the fluidizing air in a continuous process. Quartz sand (Quartzo Brasil Minas 403/050) with a mean diameter of 50 mm and a particle density of 2600 kg/m^3 was used as the bed material in the fast pyrolysis experiments.

The pressure and temperature were registered using pressure transducers and thermocouples located along the reactor height. Thus, it was possible to obtain a behavior of the profiles of temperature and static pressure during operation of the pyrolyzer. At the end of the pyrolysis process, after cooling the system, the solid and liquid fractions generated were removed and weighed.

5.2.3 Product Analysis

The procedures for determining the higher heating value and proximate analysis were very similar to those previously described for the raw biomasses. The size distribution of the char samples were measured using Tyler series sieves of different meshes.

The bio-oil products were analyzed by the higher heating value, measured by a bomb calorimeter (Parr 6300 Calorimeter) and density, measured using a scale and graduated cylinder.

5.2.4 Energy efficiency

The mass yield (%) of product was obtained using the ratio between the quantity of each product produced by the fast pyrolysis and the amount of fed biomass. The quantities of bio-char and liquid were determined by weighing the respective mass obtained after experiments. The noncondensable gases were directly burned in the

combustion chamber to heat the fluidizing air in a continuous process. The flow rate of noncondensable gases was not quantified after its generation. For that reason, the mass flow rate of non-condensable gases was measured from the sum of the amounts of feedstock and the air supplied less the amounts of liquid and solid generated. The energy balance was done considering the mass balance and higher heating value of the feed material and products from fast pyrolysis.

In this study, all the analyses were performed at least in triplicate and averaged data are reported.

5.3 Results and Discussion

After analyzing the properties of used biomass resources, the pyrolysis of eucalyptus wood and coffee shrub in the pilot-scale plant was successfully carried out. The pressure and temperature were monitored during the tests in order to control and maintain the variables close to the desirable value. In the EW pyrolysis, the temperature was kept at 476 ± 8,4 ^{o}C and in the CS pyrolysis the temperature was around 485 ± 19.9 ^{o}C. The CS pyrolysis had bigger variations of the temperature, but it was still possible to keep it around 485 ^{o}C. The pressure values on the reactor and the condenser were registered along the tests in order to check for instabilities or obstructions in the condenser.

5.3.1 Biomass Analyses

The results of the proximate analysis, ultimate analysis, and ash composition of residual biomasses studied are presented in Table 5.1. The proximate analysis shows that the biomasses evaluated contains high amount of volatile matter (86.35 and 80.63% for CS and EW, respectively). The volatile matter is related to the lignocellulosic fractions of the biomass, which during heating is thermally degraded generating vapors and gases, inducing the formation of liquid and gaseous products seen in fast pyrolysis (Basu, 2013). Fixed carbon indicates the extent of nonvolatile organic matter present in the biomass. Between species of the table 5.1, coffee shrub contains the highest fixed carbon (17.88%). Eucalyptus wood waste also has high fixed carbon, i.e., 12.89%, close to those found in vegetable biomasses, which are generally in the range of 10- 25% (Rocha et al., 2015; Amutio et al., 2012).

Table 5.1. Heating Value, Proximate and Ultimate Analysis.

	Eucalyptus wood	Coffee shrub	Sugar cane straw (Mesa-Pérez et al., 2013)	Elephant grass (Mesa-Pérez et al., 2014)	Wheat straw (Greenhalf et al., 2013)	Banana leaves (Sellin et al., 2016)	Sugar cane bagasse (Rocha et al. 2015)
proximate analysis (% mass)							
M	16.56	8.42	10.4	12.2	4.6	7.8	11.9
V [a]	86.35	80.63	74	63.3	79.9	78.2	90.35
FC [a]	17.88	12.89	11.3	15.5	15.2	15.6	1.02
ash [a]	1.5	0.76	16.4	4.9	4.9	6.2	8.74
calorimetric analysis (MJ/kg)							
HHV	18.1	19	18.0	14.7	13.3	17.1	19.1
LHV	16.4	17.5	16.3	13.2	12.0	15.6	17.5
ultimate analysis [b] (% mass)							
C	49.6	50.6	43.2	41.2	44.9	43.5	50.57
H	5.98	6.12	6.7	5.5	5.71	6.2	6.05
O	44.1	41.16	33.2	46.6	43.8	42.3	42.55
N	0.071	1.86	0.3	1.8	0.63	0.86	0.73
S	0.032	0.21	0.2	-	-	0.95	0.1
O/C	0.71	0.62	0.58	0.85	0.73	0.73	0.63
H/C	1.52	1.48	1.85	1.59	1.52	1.7	1.43

[a] dry basis; [b] dry ash free basis
M − moisture; V − volatiles; FC − fixed carbon; HHV − higher heating value; LHV− lower heating value

Moisture in the EW was 16.56%. This value is outside the recommended range for the pyrolysis process, between 7% and 15% (Fernandes, 2013). The CS presented Moisture value (8.42%) within the recommended range for the pyrolysis process. The high percentage of moisture in the EW can have further influence on the product yields and on the characteristics of bio-oil and bio-char obtained in the fast pyrolysis (Dermirbas, 2009). The higher heating values (HHV) of samples are similar to other lignocellulosic biomasses which, nowadays, are being evaluated as raw materials in pyrolysis (Sellin et al., 2016; Mesa-Pérez et al., 2013; Mesa-Pérez et al. 2014; Greenhalf et al., 2013). The ash content of the samples CS and EW are 0.76% and 1.5%, respectively. These values are similar to the contents generally found for woody biomass (Basu, 2013; Rocha et al., 2015), which are below the values normally found for nonwoody biomass as presented in Table 5.1. The ultimate analysis indicates that residues are environmental friendly, with only trace amounts of nitrogen and sulfur. For thermochemical conversion processes, knowing the ratios of H/C (1.52 for EW and 1.48

for CS) and O/C (0.71 for EW and 0.62 for CS) are more important than only H, O, and C contents separately. The high values of the atomic H/C ratio for samples agree with the high volatile content found by proximate analysis. The values obtained for these parameters are relatively similar to those reported for other biomass species such as elephant grass, sugar cane bagasse and banana leaves.

The TG and DTG curves in inert and oxidative atmosphere of eucalyptus wood and coffee shrub are shown in Figure. 5.2. Thermal analysis is a useful method for studying thermal stability of materials, in order to understand the thermal decomposition of the biomass but also the char and volatile forming tendency. A quite marked similarity can be observed between the TG and DTG curves of residues, which may be associated with similar chemical compositions of these lignocellulosic residues. The first weight loss appears at a temperature below 140 ^{o}C for all analysis (inert and oxidative) due to evaporation of water. Following the evaporation of water stage, there is a weight loss called active pyrolysis, the hemicelluloses and cellulose are decomposed, while lignin is decomposed hardly. For DTG in nitrogen atmosphere, the last stage, called passive pyrolysis, the lignin continues its decomposition without characteristic peaks. For DTG in oxidative atmosphere, there is an additional peak between 450 and 550 ^{o}C that is associated to the char combustion.

From TGA and DTG curves some characteristic points can be identified (Table 5.2):

- T_{onset} is the temperatures for the onset of active pyrolysis.
- $(-dX/dt)_{sh}$ and T_{sh} are the characteristics overall maximum of the hemicelluloses decomposition rate and the corresponding temperature, respectively.
- $(-dX/dt)_{peak}$ and T_{peak} are the characteristics overall maximum of the mass loss rate and the corresponding temperature, respectively.

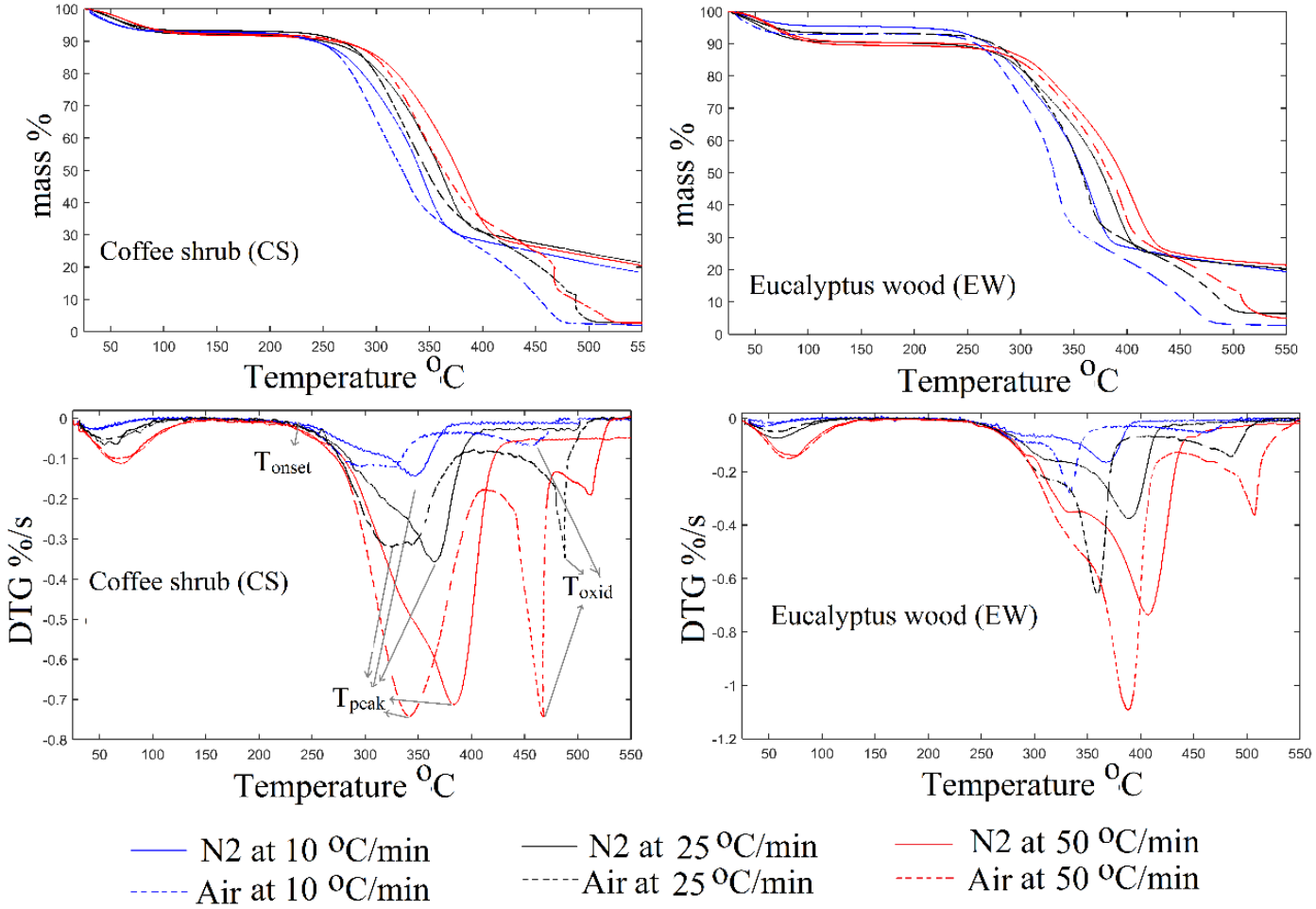

Figure 5.2. Thermal behavior of eucalyptus wood and coffee shrub by TGA and DTA.

Table 5.2. Thermogravimetric Properties of the Samples.

	Eucalyptus wood (EW)					
	Inert (N_2) atmospheres			**Oxidative (Air) atmospheres**		
rate ($^oC\ min^{-1}$)	10	25	50	10	25	50
T_{onset}	240	240	240	240	240	240
$(-dX/dt)sh$ ($\%\ s^{-1}$)	0.07	0.15	0.35	0.09	0.22	0.49
T_{sh}	306	315	333	293	308.8	340
X_{sh} (%)	77.8	77.4	77	76.9	78.5	72
$(-dX/dt)_{peak}$ ($\%\ s^{-1}$)	0.16	0.37	0.74	0.27	0.66	1.09
T_{peak}	366.7	389	407.4	333.9	358	388
X_{sh} (%)	43	39,7	40.9	46.6	49.1	46
T_{offset}	394.9	421.8	459.7	-	-	-
X_{offset} (%)	27.4	25.2	24.3	-	-	-
T_{oxid}	-	-	-	463	485	507.3
$(-dX/dt)_{oxid}$ ($\%\ s^{-1}$)	-	-	-	0.05	0.14	0.36
X_{550} (%)	19.5	20.3	21.4	2.6	6.4	4.9
	Coffee shrub (CS)					
	Inert (N_2) atmospheres			**Oxidative (Air) atmospheres**		
rate ($^oC\ min^{-1}$)	10	25	50	10	25	50
T_{onset}	233	224	223	233	224	223
$(-dX/dt)sh$ ($\%\ s^{-1}$)	0.08	0.19	0.5	-	-	-
T_{sh}	298	313.8	345	-	-	-
X_{sh} (%)	75	76.5	68,7	-	-	-
$(-dX/dt)_{peak}$ ($\%\ s^{-1}$)	0.14	0.36	0.71	0.12	0.31	0.74
T_{peak}	347	364.7	383.1	312	328	340.3
X_{sh} (%)	44.9	46.9	45.1	57.9	62.3	64.9
T_{offset}	381	404.8	434.4	-	-	-
X_{offset} (%)	29.4	30.16	27	-	-	-
T_{oxid}	-	-	-	455.8	487.4	468
$(-dX/dt)_{oxid}$ ($\%\ s^{-1}$)	-	-	-	0.07	0.39	0.73
X_{550} (%)	19.5	21	20.4	1.99	2.75	2.75

The temperatures for the onset of active pyrolysis occurs in a range between 223 and 240 ^oC. For analysis in an inert atmosphere, the characteristic temperatures, T_{sh} and T_{peak}, presented higher values as heating rate increased. This effect indicates that it takes some time to transmit heat from the surface to the interior of the biomass and release volatiles

from the interior to the particle surface, then the pyrolysis process may exhibit a temperature delay with the higher heating rate.

In an oxidative atmosphere the different decomposition stages have occurred at lower temperatures than decomposition in nitrogen atmosphere. This is due to the quick evolution of the reactions of volatiles at biomass particle surface which increases particle temperatures (Daouk et al., 2015). Besides that, it was observed not only the difference in the temperatures previously described, but also the high reaction rate in air atmosphere. These facts, lower temperatures and higher rates of decomposition in oxidative atmosphere, are more pronounced for the eucalyptus residues, which has higher volatile content (table 5.1).

For oxidative thermal degradation analysis, the greatest weight loss occurs at active pyrolysis phase, 60%, and it is higher than the weight loss under inert atmosphere. The mass loss in the combustion phase was about 24% and the final residue at 550 ºC was in range 2.6 - 6.4% for EW and 1.99-2.75% for CS, composed by the mineral matter (ash) and carbonized biomass. In nitrogen atmosphere, the behavior was quite different, above 550 °C the carbonaceous solid was reacting and the residual mass was higher (about 20% mass for studied species) due to the char formed and unburned after biomasses pyrolysis.

3.2 Yield of Products

The Table 5.3 shows the product yields obtained in the experiments carried out are expressed on basis of the dry biomass, being the pyrolyzed biomass the total biomass excluding moisture. As the biomass pyrolysis occurred in oxidative atmosphere, the overall results for liquid yield were good compared to the other biomasses (Rocha et al., 2015; Mesa-Pérez et al., 2013) [6,24]. The highest liquid yield was found for the EW. The liquid fraction yield was 39.71% (14.69% for heavy bio-oil and 23.2% for light bio-oil). However, the highest heavy bio-oil fraction was found for EW (22.64%) during conditions that produced 37.89% of liquid product. Sellin et al. (2016) obtained 27.0% liquid fraction yield (10% light bio-oil and 17% heavy bio-oil) from oxidative fast

pyrolysis of dried banana leaves. In an experimental plant (auto-thermal process) similar to that used in this study. Mesa-Pérez et al. (2013) evaluated the influence of the temperature (470, 550 and 600 ^{o}C) on the liquid yield from oxidative fast pyrolysis of sugar cane straw. The authors have concluded that the liquid yield (35.5 %) was optimized at temperature of 470 ^{o}C. Under higher temperature the bio-oil yield decreased, resulting in an increase of the gas yield. Similar yields (between 31 and 40%) of liquid product from oxidative fast pyrolysis of several other wastes such as sugar cane bagasse, orange bagasse and tobacco waste using roughtly the same operational conditions were described by the same authors (Mesa-Pérez et al., 2013). Therefore, the heavy bio-oil yield obtained for eucalyptus wood and coffee shrub from pyrolysis process may point out the oxidative fast pyrolysis is a suitable way to manage these wastes. In an oxidative atmosphere, part of the formed char by pyrolysis is burnt and contributed to the formation of gases. In addition, the combustion reactions of condensable volatiles are favored in an oxidative atmosphere and this contributes to the formation of gases. The light bio-oil can be used for other purposes, like catalytic craking to produce hydrocarbons or steam reforming to produce hydrogen. The light fraction can be destilled to produce Coke and acidic extract.

5.3.3 Characterization of bio-oil

According to the characterization results, the heavy bio-oil obtained from EW and CS by means of fast pyrolysis in fluidized bed, reached characteristic densities values of these types of substances (1127.9 kg/m^3 for EW and 1028.1 kg/m^3 for CS) and significantly higher than that of the original biomass. Demirbas (2007), for different biomasses species, found densities in the range 1170-1230 kg/m^3. The heavy bio-oils showed reasonable higher heating value of 21.8 and 27.8 MJ/kg for biomasses from pulp industry and coffee plantation, respectively.

The energy properties of the bio-oil from EW and CS are compared with their respective biomasses in Figure 5.3. As it was feasible to observe, the bio-oils have a bigger energy density than the biomasses (6.3 times bigger for EW and 3.5 bigger for CS).

Table 5.3 Mass yield for products generated in pyrolysis of wastes evaluated and other biomasses described in literature.

Feedstock	Fast pyrolysis reactor [a]			Product yields [b]			
				Liquid			
	Reactor capacity	Process temperature	Fluidization agent	Heavy bio-oil or organics	Light bio-oil or reaction water	Char	Gas
	kg h^{-1}	°C		% mass	% mass	% mass	% mass
Coffee shrub	20	500	Air	14.69	23.20	14.75	47.35
Eucalyptus Wood waste	20	500	Air	22.65	17.07	15.35	37.70
Banana leaves (Sellin et al., 2006)	12	500	Air	17	10	23.3	49.6
Wheat straw (Westerhof et al., 2010)	1	525	Nitrogen	21.39	12.54	28.05	26.99
Pine wood (Greenhalf et al., 2012)	1	480	Nitrogen	47	11	15	23
Willow SRC (Demirbas, 2007)	1	500	Nitrogen	40.51	10.81	19.28	19.89

a - Bubbling fluidized bed reactor
b - Product yields on dry feed basis

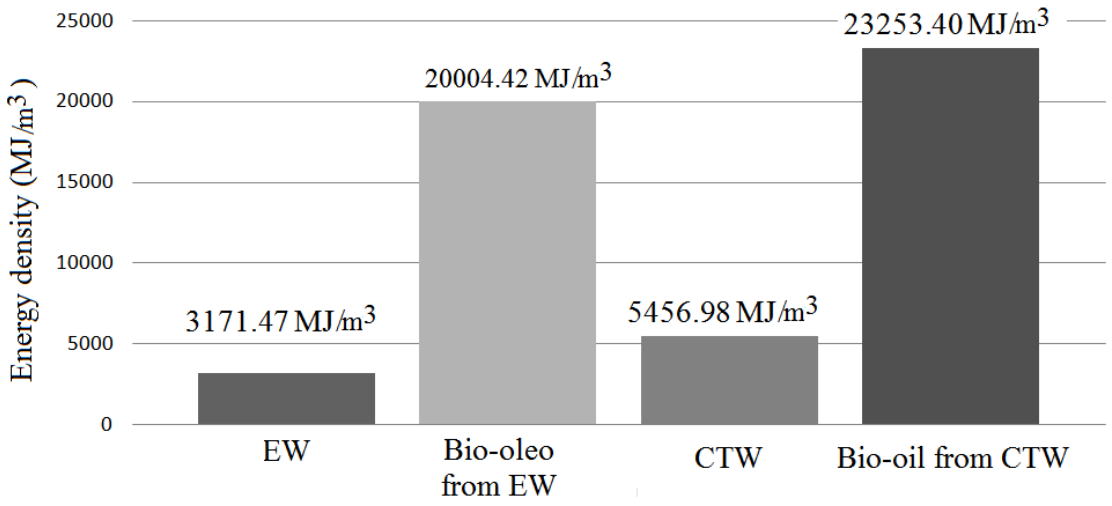

Figure 5.3. Comparison between the energy density (MJ m^{-3}) of bio-oils and biomasses.

5.3.4. Characterization of Bio-char

The proximate and calorimetric analysis of the bio-char samples and other biomasses described in literature are shown in Table 5.4. The bio-char generated in oxidative fast pyrolysis of residues from pulp industry (EW) and coffee plantation (CS) presented the

higher heating value (26.06 MJ/kg for CS and 27.16 MJ/kg for EW) inside the range found for vegetal biomasses as showed in table 5.4.

Table 5.4. Analyses of the bio-char from oxidative pyrolysis.

	Bio-char from				
	Coffee shrub	Eucalyptus wood waste	Banana leaves (Rocha et al., 2015)	Sugar cane straw (Amutio et al., 2012)	*Pinus insignis* (Demirbas, 2004)
proximate analysis (% mass)					
M	2.58	3.45	1.68	1.9	-
V [a]	19.93	35.58	53.2	36.4	27.2
FC [a]	53.67	59.51	23.2	30.1	67.8
ash [a]	26.4	4.91	23.5	33.8	5.0
calorimetric analysis (on MJ kg^{-1})					
HHV	26.06	27.16	18.2	14.15	20.9

a dry basis
M − moisture; V − volatiles; FC − fixed carbon; HHV − higher heating value

5.3.5. Energy efficiency

Table 5.5 presents the energy efficiency and energy density for products from oxidative fast pyrolysis. The total useful energy obtained from pyrolysis process were 50845 kcal/h for EW and 14412 kcal/h for CS for the total biomass fed at each operation of the plant. The higher energy efficiencies were obtained for gases and bio-char. The results reached reveal the the potential of using the wastes of eucalyptus wood and coffee shrub in the fast oxidative pyrolysis process, and considering this a pioneering study, greater heavy bio-oil fraction yields could be obtained if process conditions were adapted to improve the energy yield.

Furthermore, the results showed that the mass of residue used to produce 1 m^3 of heavy bio-oil from EW and CS was about 4 and 6 ton, respectively (4119 MJ/m^3 EW and 5105 MJ/m^3 for CS).

Table 5.5. Energy efficiency for products from pyrolysis of studied.

Products	Energy of products (kcal h^{-1})	Energy efficiency based on TPE[a] (%)	Energy efficiency based on TUE[b] (%)	Energy density (MJ m^{-3})
Procucts from waste of eucalyptus wood				
Bio-Char	9767.61	18.26	19.21	4118.89
Heavy Bio-oil	8086.37	15.11	15.90	24605.45
Light Bio-oil	1496.10	2.80	2.94	-
Gases	36808.61	68.80	72.39	-
Products from coffee shrub				
Bio-Char	3291.46	19.28	22.84	5104.92
Heavy Bio-oil	5183.43	30.37	35.97	6712.07
Light Bio-oil	273.19	1.60	1.90	-
Gases	10977.72	64.31	76.17	-

a Total primary energy (TPE, 53502 kcal h^{-1} for EW and 17069 for CS).
b Total useful energy (TUE, 50845 kcal h^{-1} for EW and 14412 for CS)

5.4. Conclusion

The characterization of raw materials indicated that in general, all of the residues exhibit different important parameters for fast pyrolysis technology, such as high calorific value, high carbon content, and low ash content. Furthermore, the pyrolytic behavior of woods were investigated under inert and oxidative conditions at the heating rates of 10, 25 and 50 ^{o}C/min. The thermal decomposition of samples presented three stages in the two atmospheres analyzed. In nitrogen, were drying, active pyrolysis (devolatilization), and passive pyrolysis (carbonization). In oxidative atmosphere, were drying, active oxidative pyrolysis (devolatilization), and char combustion. In oxidative atmosphere the different decomposition stages have occurred at lower temperatures and more higher rate of decomposition than decomposition in nitrogen atmosphere that were more pronounced for the eucalyptus residues.

The pyrolysis of eucalyptus wood and coffee shrub in the pilot-scale plant (feed rate capacity of about 20 kg/h) was successfully carried out. For eucalyptus wood, the process produced 37.7 % gases, 22.64% heavy bio-oil, 17.07% light bio-oil and 15.35% bio-char, and for coffee shrub, the process produced: 47.35% gases, 14.67% heavy bio-oil, 23.2% light bio-oil, and 14.75% bio-char. As the biomass pyrolysis occurred in oxidative atmosphere, the overall results for liquid yield were good compared to the other

biomasses in literature. The bio-oils have a bigger energy density than the raw materials (6.3 times bigger for EW and 3.5 bigger for CS). The bio-char presented the higher heating value (26.1 MJ/kg for CS and 26.2 MJ/kg for EW), enabling it to be used as fuel.

In conclusion, the characterization of Brazilian residues and products from oxidative fast pyrolysis ensures that these biomasses are potential candidates for bioenergy production by fast pyrolysis. Therefore, the Brazilian residues has the potential to favorably compete with other conventional biomass sources such as sugar cane straw, pine wood and banana leaves and in thermochemical conversion technologies.

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CHAPTER 6

The potential of main Brazilian Biomasses as a renewable energy source

Elém Patrícia Alves Rocha[1], Matheus Fiuza[1], Jorge Luiz Colodette [2], Esa Vakkilainen [3], Marcelo Cardoso[1]

[1]Federal University of Minas Gerais (UFMG), Belo Horizonte, MG Brazil, 31270-901

[2]Federal University of Viçosa (UFV), Viçosa, MG Brazil, 36.570-000

[3]Lappeenranta University of Technology (LUT), Lappeenranta, Finland 53851

Abstract. The present study aims to estimate the potential of main Brazilian biomasses for generating renewable energy in Brazil such as sugarcane straw, sugarcane bagasse, coffee husks, banana leaves, banana stalk, coconut husk, coconut shell, soybean straw, soybean husk, corn straw, corn cob, rice straw, rice husk, orange bagasse, bamboo, elephant grass, eucalyptus and pinus. The four main parameters evaluated were chemical composition, heating value, proximate and ultimate compositions in which the knowledge is important in order to understand these influences on the thermochemical conversion process. Among the biomasses, forest biomass and sugar cane residues exhibited higher total sugar content (63.7 -70.7%). The highest lignin contents were observed in forest biomasses (27.1-30.1) and coconut residues (25.4-34.5%) and the minimum in orange bagasse (2.8%). The lower heating value of the biomasses ranged from 14.0 MJ kg-1 to 19.4 MJ kg-1, on a dry and ash free basis, and most biomasses have a quite suitable content of moisture (<11 %), except for orange bagasse and banana stem. The low ash contents were found in forest biomass (0.2-2.1%), corn cob (1.2) and coconut husk (1.3%). In agro-industrial activities in Brazil, over 679.5 million tones of agricultural residues were generated in 2016 which means an energy potential of 12.1 million PJ. The fouling and slagging tendency of the ashes, based on the fuel ash composition and on the ash fusibility correlations proposed in the literature was predicted. The overall carbon content from these agroindustrial residues is approximately 276 Tg, which has the potential to generate approximately 1014.2 Tg carbon dioxide by uncontrolled burning of residues. The potential for application of the main Brazilian biomasses studied as alternative energy sources in thermochemical processes has been

identified, especially concerning for the potential of agro-industrial residues to provide considerable carbon credits for sustainable agricultural development.

6.1 Introduction

Lignocellulosic biomass consist of fibrous plant material containing a combination of and extractives, cellulose, hemicelluloses and lignin polymers interconnected (Ullah et al., 2015). Biomass, along with solar, wind and hydropower, has been regarded as one of the most promising alternatives for energy generation replacing fossil fuels with renewable sources (Mehmood et al., 2017). The Brazilian agro-industrial sector generate biomass residue that can be used in electricity generation or produce fuels through the biorefining concept (Rambo et al., 2015). In this concept, the biomass is used as a raw material for conversion processes, thermochemical or the biochemical processing pathways, to produce chemicals, power and multiple fuels (Ullah et al., 2015). Biorefinery allows diversify and decentralization, and it creates energy self-sufficiency in some industrial activities and micro-regions in the country. The use of forest and agricultural residues do not compete with food production and also minimize environmental impacts and increase the profitability of planting areas (Rambo et al., 2015).

Brazil is the world's second highest agricultural residue generator, generating 600 million tons of agricultural waste per year, superseded only by China (Ullah et al., 2015), and is the world leader in power generation from renewable sources such as biomass conversion and energy generation through hydropower. In 2016, the increase in hydropower in Brazil was 7.0% compared to the previous year. The growth in water supply and the expansion of wind power contributed to the growth of the renewable energy participation in the electricity matrix from 75.5% to 81.7%. During this year, there was a strong drop in thermal generation from oil and natural gas (EPE, 2017).

However, the share of renewables in the Brazilian energy matrix was falling year after year, due to reduced water levels in the hydroelectric plant reservoirs, caused by a decrease in rainfall in parts of the country as a result of climate change, and restrictions on new hydroelectric projects due to environmental associated problems arising from their

construction (Portugal-Pereira et al., 2015), which increased the awareness in the Brazilian energy sector that Brazil must diminish its dependence on large hydropower.

Banana, orange and coconut residues (Stems and stalks) are a potential feedstock in Brazil, as they are cultivated throughout all regions of the federation (IBGE, 2017). Brazil is also the largest coffee producer and exporter in the world with an output of 2.8 million tons and exports amounting to 35.23 million bags of 60 kg in 2016 (IBGE, 2017; USDA, 2016). In coffee crops, a large quantity of residue is obtained from the cherries and shrub, as it is produced in large scale around the world (Murthy and Naidu, 2012). In Brazil, rice and wheat have long been key crops agricultural landscape and livelihood both in terms of their production value and their, and they are very important for agribusiness trade balance in Brazil. Soybean is a highly important commodity for the Brazilian economy as the second largest producer of soybean in the world, behind only the United States. The sugar cane residues are notable because of their importance in energy production in the country (Pighinelli et al., 2014), in which the sugarcane is the raw material in the production of ethanol and sugar.

Another's potential renewable energy feedstocks are elephant grass and bamboo. The cultivation of bamboo receives the most attention due to the high growth rate, the short renovation period under various soil and climate conditions and easy propagation (Sun et al., 2013). Elephant grass is one of the most important and widespread species of grass in all tropical and subtropical regions of the world, and it has a high productivity with an estimated yield of 30 to 50 tons of dry matter per hectare per year (Gomes, 2013). It is considered an excellent alternative energy due to low costs and because it produces two crops a year (Rambo et al., 2015).

The Brazilian agro-industrial industry produces large amount of residues and by-products that can potentially be used as energy sources, which the main ones are soybean, corn, sugarcane, rice, wheat, coffee, banana, orange, and coconut crops. Agricultural waste comes from the agricultural phase of the cultivation of evaluated biomasses, while agro-industrial residues result from industrial processing of biomass. In sugarcane industry, bagasses and straw generates are generally used as a source of energy through direct combustion in boiler furnaces. Currently, second generation ethanol plants are starting to

operate. Behind that, the Brazilian planted tree industry is a worldwide reference for its performance, and with 7.84 million hectares of planted trees, this sector is responsible for 91% of all wood produced for industrial purposes in the country (IBÁ, 2017). According to the IBÁ (2017), the Brazilian planted tree sector has the greatest potential to help build a green economy between Brazilian industries. In Brazil, an estimated 1.1 million hectares of plantations are reserved for charcoal production used in the steel industry, and 2.7 million hectares for pulp mills. In 2016, Brazilian pulp production, which included chemically-processed short-fiber pulp (from eucalyptus), long-fiber pulp (from pine), and high-yield pulp, was 18.8 million tons. Thus, the planted tree sector generated 47.8 million tons of solid waste, 33.7 million tons (70.5%) of which resulted from forestry activities and 14.1 million tons (29.5%) from industrial activities in 2016 (IBÁ, 2017). About the consumption of charcoal, one of the main inputs of the steel industry was 4.5 million tons that wood from planted trees was the raw material used to produce 84% of all the charcoal consumed in the country in 2016.

There are different production routes in which biofuels can be produced from lignocellulosic biomass such as agro-industrial waste. These routes include biochemical or thermochemical processing pathways. The thermochemical routes are gasification, pyrolysis, liquefaction, combustion and hydrothermal. An example is through gasification of biomass residues generating syngas which can be used as combustion in the furnace or be processed and converted into liquid fuels. The other routes are biochemical conversions, including anaerobic digestion and fermentation. A classic example is the conversion of sugar cane to produce ethanol or conversion of agricultural residues such as bagasse and cane straw in second generation ethanol. It is believed that in the near future they will be very important in the generation of clean and renewable fuels for the transport sector (Ullah et al., 2015).

Assessing the bioenergy potential from waste biomass is, therefore, essential to know the characteristics of feedstocks both qualitatively and quantitatively and to prospect the potential substitution of fossil fuels and the associated reduction in GHG emissions. In this sense, a small number of studies can be found in the literature that touches on this subject, and at overcoming this gap. The present study aims to identify the main biomasses available in Brazil such as sugarcane straw, sugarcane bagasse, coffee husks, banana leaves, banana

stalk, coconut husk, coconut shell, soybean straw, soybean husk, corn straw, corn cob, rice straw, rice husk, orange bagasse, bamboo, elephant grass, eucalyptus and pinus by their important fuel and other physicochemical properties, and annual production.

6.2 Methodogy

6.2.1 Brazilian biomass data collection

6.2.1.1 Biomass characteristics

Several studies have been conducted and extensive data for biomass have been generated (Ferreira-Leitão et al., 2010; Pighinelli et al., 2014; Rambo et al., 2015; Rocha et al., 2015). To extend and improve the basic knowledge on composition and properties, and to apply this knowledge for the most advanced and environmentally safe utilization - a detailed review of the proximate and ultimate analysis, heating value, ash and chemical composition of biomasses from the scientific literature was conducted.

6.2.1.2 Ash composition and ash fusibility trends.

In the thermochemical conversion of biomass, the mineral matter composition of ash produced during the process may create various problems which can affect the reactor operation or make the thermochemical conversion process in conventional systems unprofitable. As described by Febrero et al. (2015), the ratio of alcaline oxides content (CaO, Fe_2O_3, MgO, Na_2O, K_2O) and acidic oxides content (SiO2, Al2O3, TiO2) can be used to judge the ash fusibility and slagging property of energy material, and was calculated using equation 6.1. The equation 6.2 proposed by Pronobis (2005) seems to be most compatible with the biomass composition since it considers the influence of several ash constituents, and therefore, was used in this study.

$$B/A = \frac{\left(Fe_2O_3 + CaO + MgO + Na_2O + K_2O\right)}{\left(SiO_2 + Al_2O_3 + TiO_2\right)} \tag{6.1}$$

$$B/A_{+P} = \frac{\left(Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5\right)}{\left(SiO_2 + Al_2O_3 + TiO_2\right)} \tag{6.2}$$

The **fouling index (F_u)** of a solid fuel gives the indication of fouling tendency and was measured using equation 6.3 (Teixeira et al., 2012). **The slag viscosity index (S_R)** can be used to predict the slagging tendency which leads to a better understanding of the structure of slag, and was calculated by equation 6.4 (Yin et al, 2005; Pronobis, 2013).

$$F_u = (B/A)(Na_2O + K_2O) \tag{6.3}$$

$$S_R = \frac{(SiO_2)}{(SiO_2 + Fe_2O_3 + CaO + MgO)} \cdot 100 \tag{6.4}$$

6.2.1.3 Annual productions and energy potential

The annual productions of agroindustrial residues (from soybean, corn, sugarcane, bean, rice, wheat, coffee, banana, orange, and coconut crops) in 2016 were obtained from the Brazilian Institute of Geography and Statistics (IBGE, 2017), and were presented in table 1. To measure the amount of waste considering different types of crops, crop production-to-residue ratio should be taken into account. Therefore, an evaluation made on the total amount of residues that originates from agro-industrial activities in Brazil shows that over 679.5 million tones of agricultural residues were generated in 2016.

To estimate the energy potential of crop residues, the procedure documented Singh et al., 2008 was considered, and the energy potential of agro-industrial residues was calculated using Equation (6.5);

$$EP_i = \sum_{i=1}^{n} (P_i \cdot Y_i \cdot LHV_i) \tag{6.5}$$

where, EP is the annual gross energy potential of agricultural residues at 100% efficiency, P is the annual production of crop. Factor, n is the total number of residue categories, and LHV is the lower heating value of a given crop. The variable Yi is the residue-to-product ratio of crop i, residue, given by reside-to-product ratio (RPR) method, and were obtained from the available literature (IBÁ, 2017). For bamboo, elephant grass, eucalyptus and pinus, the energy potential = productivity x LHV.

6.2.2 Carbon sequestration potential

The biomass data were used to calculate the carbon stock and carbon sequestration potential of the biomass in renewable energy practices by the thermochemical conversion. Five scenarios have been compared for their carbon release or carbon sequestration potentials; (I) conversion of biomass to bioethanol as an alternative sustainable source to replace gasoline, (II) biogas production from biomass by anaerobic digestion, (III) direct combustion of biomass residue for power generation as an alternative source to replace coal, (IV) conversion of biomass to gases as renewable alternative to replace natural gas, and (V) bio-oleo production from fast pyrolysis as substitutes for fuel oil. The Figure 1 shows the development of five scenarios for biomass residue utilization and their environmental impacts. The established scenarios are aimed at harvesting the inherent energy of the residual biomass, while simultaneously sequestering the CO_2 emissions by diminishing the fossil fuel utilization.

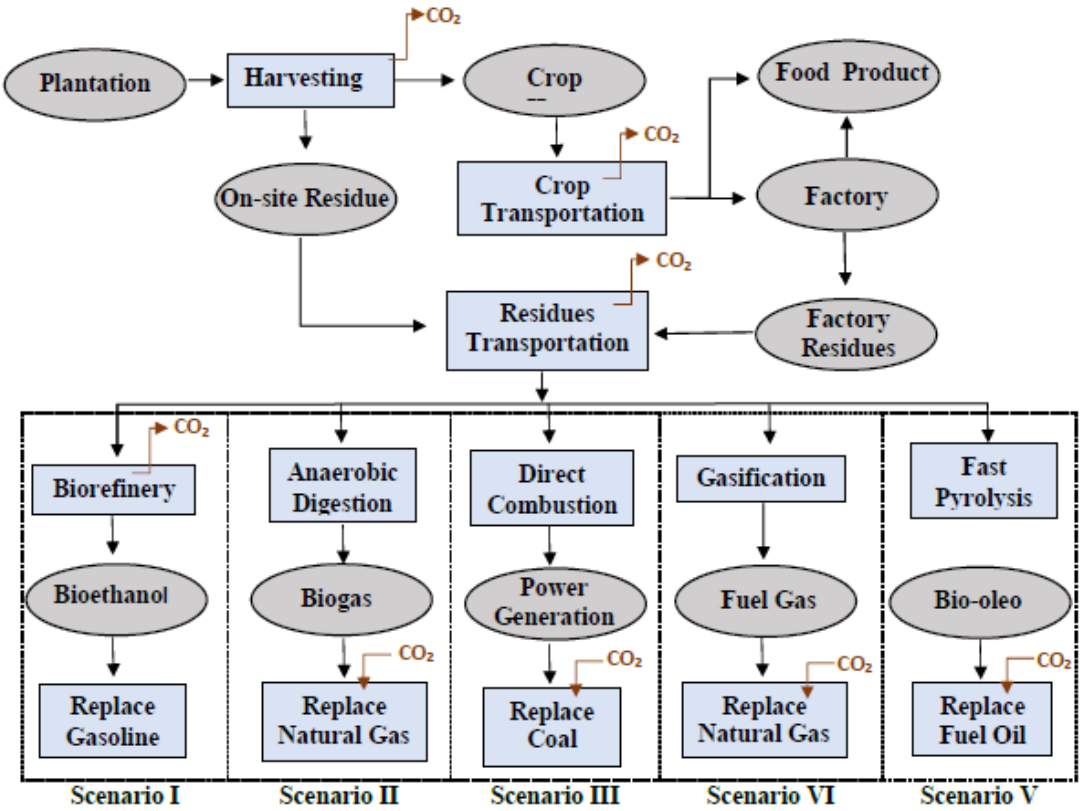

Figure 1. Scenario development for biomass utilization

For calculate the carbon sequestration potential by each scenario, the methodology described by EPA (2016)(EPA - United States Environmental Protection Agency, 2016) was applied, and equation 7 was used:

$$TC_{scenario} = C_{renewble\ fuel}^{fossil\ fuel} \cdot \sum_{i=1}^{n} y_i \cdot P_i \cdot Y_i \quad (7)$$

where $TC_{scenario}$ is the total carbon sequestration potential; y_i is the yield of renewable fuel production from associated biomass in a specific scenario; and $C_{renewble\ fuel}^{fossil\ fuel}$ is the carbon sequestration potential ration of the renewable fuel to fossil fuel.

6.3 Resultas and Discussion

6.3.1 Analysis of Brazilian Biomass Focusing on Thermochemical Conversion processes

6.3.1.1 Biomass characteristics

The properties of the biomasses evaluated were presented in the sequence, including proximate and ultimate composition, energy content, composition and fusibility trends of the ashes. Table 2, 3 and 4 shows the properties of the solid fuel studied from the scientific literature. Also, the ash fusibility trends of biomasses were presented in Table 3.

The actual amount for energy recovered will depend on the efficiency and necessities of the specific conversion technology. However, lower heating value expresses the maximum amount of energy that can be potentially recovered from a biomass source, and can be considered as one of the important parameters for energy evaluating and modeling in thermochemical conversion processes (Tanger et al., 2013). Among the evaluated biomasses, the lower heating value (LHV) ranged from 14 MJ/kg to 19.4 MJ/kg on a dry and ash free basis, wherein the highest values found were from the forest and fast-growing biomasses. Thus, the lower heating values of biomasses higher than 14.0 MJ/kg indicated that all types of samples were suitable for thermochemical conversion processes (Arena, 2012; Tsai et al., 2006).

Table 1. Heating value, proximate and ultimate analysis of evaluated biomasses.

		Proximate analysis (% mass)				Ultmate analysisb (% mass)					LHV	HHV
Resource	Residue	M	V	FC	Ash	C	H	O	N	S	MJ/kg	MJ/kg
Agro-industrial cereal residues												
Soybean [b]	Stalk	8	74.2	17.8	9.9	40.8	6.2	45.3	0.6	0.6	17.2	17.5
	Straw	1.8	75.5	19.8	4.7	47.8	6.9	44.3	1	0.1	16.9	15.5
	Husk	6.3	74.3	20.3	5.4	45.4	6.7	46.9	0.9	0.1	14	14.1
Rice [c]	Straw	8.3	72.2	14.4	13.4	45.4	6.3	47.1	1	0.2	16.9	17.1
	Husk	7.4	73.7	20.0	13.0	39.5	5	55.2	0.3	0	14.4	16.4
Wheat [d]	Straw	9.5	85.7	8.0	6.3	42.6	5.7	36.5	0	a	14.6	15.1
Agro-industrial fruit residues												
Corn [e]	Straw	4.4	76.0	16.9	7.0	44.1	5.9	48.8	0.9	0.3	16.9	20.4
	Cob	6.4	6.4	81.3	18.3	45.5	6.7	47	0.5	0.3	17.6	19.3
Coffee [f]	Husk	10.1	10.1	79.3	18.5	46.4	5.8	45	1.5	0.1	16.9	18.2
Banana [g]	leaves j	7.8	78.2	15.6	6.2	43.5	6.2	42.3	0.9	1.0	15.6	17.1
	Stem	12.6	91.9	11.4	9.2	39	5.4	54.8	0.8	a	14.5	16.1
Orange [h]	Bagasse	74.8	79.6	14.1	4.7	42.3	5.7	49.6	1.3	0.2	15.5	15.8
Coconut [i]	Husk	10.2	92.8	5.9	1.3	53.1	5.7	40.1	0.2	0	18.2	19.9
	Shell	4.4	73.7	23.0	3.2	51.2	5.6	43.1	0	0.1	15.8	15.9
Sugarcane [j]	Straw	-	78.6	17.5	4.3	44.6	6.6	48.1	0.3	0.4	16.4	18.1
	Bagasse	11	93.5	6.0	7.4	46.9	6.1	42.9	0.6	0.5	16.1	18.4
Forestry biomass												
Eucalyptus [k]	Wood	10.9	86.3	13.1	0.2	49.2	5.9	44.8	0.1	1.0	18.2	18.5
Pinus [k]	Wood	-	78.0	20.0	2.1	47.4	5.4	44.7	0.7	1.0	18.5	18.7
Fast growing biomass												
Bamboo [k]		9.09	78.0	19.8	2.2	78.0	5.92	41.47	0.09	0.05	19.39	19.60
Elephat grass [k]		10.18	77.0	18.0	5.0	77.0	5.77	42.23	0.53	0.08	18.37	18.60

M − moisture; V − volatiles; FC − fixed carbon; LHV – Lower heating value; HHV – higher heating value; a Below instrument detection limit (<1%); data from b, c (Rambo et al., 2015; Shie et al., 2011, Virmond et al., 2012), d (Werther et al., 2000), f (Rambo et al., 2015; Wilson et al., 2011), g (Rambo et al., 2015), h (Lopez-Velazquez et al., 2013, Lorena Coelho Benevides, 2015), i (Rocha et al., 2015; Werther et al., 2000), k (Rocha et al., 2015; Werther et al., 2000); j pre-dried.

Moisture content can affect the overall energy conversion as it influences the heating values of solid fuel because a wet fuel requires extra energy for heating and evaporating the water present before thermochemical conversion can take place in conventional technologies (Demirbas, 2004; Swaaij et al., 2015). As a result of higher moisture content in biomass, the energy generation cost is higher and the storage system (space) for the feedstock has to be larger (Demirbas, 2009; Tanger et al., 2013). However, as can be observed in table 2 that most biomasses have a quite suitable content of moisture (<11 %), except for orange bagasse and banana stem that having the highest moisture contents, 74.8 and 12.6 %, respectively. However, the energy value of orange bagasse and banana stem should not be underestimated, since orange bagasse and banana stem materials are agro-industrial waste and the management. Furthermore, the sustainable ways to convert thermochemical wet biomass are hydrothermal carbonization and hydrothermal liquefaction (Demirbas, 2009; Sermyagina et al., 2015; Swaaij et al., 2015).

Table 2. Chemical Composition (% dry mass) of evaluated biomasses.

Resource	Type of residue	Extractive (%)	Lignin (%)	Cellulose (%)	Hemicelluloses (%)
Soybean b	Straw	16.9 [a]	16.9	34.5	11
	Husk	6.8 [a]	7.6	35	22.8
Rice c	Straw	16.7	14.1	38.1	19.9
	Husk	4.1 [a]	23.9	36.2	19.8
Wheat d	Straw	5	21.5	37.9	22.8
Agroindustrial fruit residues					
Corn e	Straw	11.3	13.9	35.5	18.6
	Cob	19	18.4	32.2	29
Coffee f	Husk	4.2 [a]	24.5	35.3	27.2
Banana g	Leaves	9.84	24.8	25.6	17
	Stem	25.1 [a]	8.4	36.3	12.2
Orange h	Bagasse	8	2.8	13	22.4
Coconut i	Husk	1.41	34.5	33.7	17.6
	Shell	ND	25.4	16.5	32.5
Sugarcane j	Straw	9.2	13.9	36.3	28.4
	Bagasse	18.2	21.4	41.8	28.9
Forestry biomass					
Eucalyptus k	wood	3.4	30.1	49.0	14.7
Pinus l	wood	1.9	31.2	41.5	21.4

Fast growing biomass				
Bamboo m	7.8	22.6	46.3	15.4
Elephant grass n	14.8	19.8	37.5	18.4

A Ethanol extractive; ND not determined; data from b (Werther et al., 2000; Zhou et al., 2015), c (Miles et al., 1995; Vassilev et al., 2017; Virmond et al., 2012; Wu et al., 2017), d (Wu et al., 2017), e (Yu et al., 2014), f (Werther et al., 2000); g (Kanning et al., 2014; Yu et al., 2014, 2014); h, i (Nimityongskul and U. Daladar, 1995, P.B Madakson et al., 2012, Werther et al., 2000), j (Szczerbowski et al., 2014; Virmond et al., 2012); k (Rocha et al., 2015); l (Berrocal et al., 2004), m (Rambo et al., 2015; Rocha et al., 2015), n (Rambo et al., 2015; Rocha et al., 2015).

Table 3. Ash composition and ash fusibility trends of evaluated biomasses.

		Ash composition									Ash fusibility trends			
Resource	**Residue**	**F_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**SiO_2**	**Al_2O_3**	**TiO_2**	**P_2O_5**	**B/A**	**B/A+P**	**Fu**	**SR**
Agroindustrial cereals residues														
Soybean a	Stalk	0.8	31.1	9.2	0.9	17.6	28.5	2	0.1	2.5	1.9	2.0	35.9	41.0
	Husk	2.5	21.4	7.1	5.3	30.5	1.7	7.4	0.2	4.9	7.2	7.7	257.1	5.2
Rice b	Straw	2	3.7	2	2.4	10.7	68.2	1.9	0.1	2.8	0.3	0.3	3.9	89.9
	Husk	0.2	0.8	0.4	0.2	1.7	94.6	0.5	0	0.9	0.0	0.0	0.1	98.5
Wheat c	Straw	6.3	8.1	3	9.2	17.4	36.9	8	0.4	2	1.0	1.0	25.7	68.0
Agroindustrial fruit residues														
Corn d	Straw	1.4	15.8	10	0.8	23.6	32.6	2.8	NA	NA	1.5	-	35.8	54.5
	Cob	4.4	11.6	2	0.4	4.9	66.33	7.5	NA	NA	0.3	-	1.7	78.7
Coffee e	Husk	0.2	9.2	2.2	0.6	43.8	3.8	7.5	0.2	4.1	4.9	5.2	216.2	24.7
Banana f	Leaves	2.2	20	7.8	3.5	19.5	26	2.6	0.2	7.3	1.8	2.1	42.6	46.4
	Stem	0.4	4.4	0.7	0.2	64.8	11.6	0.6	NA	NA	5.8	-	376.4	67.8
Orange g	Bagasse	2.9	22.2	6.3	6.8	31.6	3.2	2.5	0.2	10.7	11.8	13.6	454.3	9.2
Coconut h	Husk	2.7	4.1	5.4	8.4	31.2	25.7	1.7	0	0	1.9	1.9	74.8	68.0
	Shell	9.4	1.5	8.9	2.6	4.7	57.2	8.8	0	1.6	0.4	0.4	3.0	74.2
Sugarcane i	Straw	0.1	15.6	4.9	0.2	6.7	54.4	NA	2	2.2	0.5	0.5	3.4	72.6
	Bagasse	0.5	6.2	8	0.5	23.4	48.7	2.4	0.2	6.9	0.8	0.9	17.9	76.9
Forestry biomass														
Eucalyptus j		1.3	30.6	2.4	1.7	19.0	2.2	0.3	0.1	3.1	21.2	22.3	437.9	6.0
Pinus k		4.1	36.0	6.3	0.7	9.7	25.1	6.5	0.5	0.8	1.8	1.8	18.5	35.1
Fast growing biomass														
Bamboo l		0.7	4.1	4.7	0.5	39.3	32.1	1.0	0.0	20.3	1.5	2.1	59.2	77.2
Elephant grass m		0.7	7.5	10.7	0.5	15.1	NA	1.3	51.8	7.0	0.6	0.8	10.1	-

NA - not available; data from a (Werther et al., 2000; Zhou et al., 2015); b(Miles et al., 1995; Vassilev et al., 2017; Virmond et al., 2012; Wu et al., 2017), c(Wu et al., 2017), d(Adesanya and Raheem, 2010; Yu et al., 2014); e(Werther et al., 2000); f(Kanning et al., 2014; Wang and Stiegel, 2016; Yu et al., 2014); g(Astride Del S. Altamar Consuegra, 2013) ; h(Nimityongskul and U. Daladar, 1995, P.B Madakson et al., 2012; Werther et al., 2000), i(Szczerbowski et al., 2014; Virmond et al., 2012); j(Saddawi et al., 2012), k(Rizvi et al., 2015; Vamvuka et al., 2008; Yu et al., 2014), l (Scurlock et al., 2000; Yu et al., 2014), and m (Erika Y. Nakanishi<sup>* et al., 2014; Silva, A. M. F. D. et al., 2012).

Volatile matter comprises components of a solid fuel, with the exception of moisture, which are driven off agases at a high temperature in the absence of oxidative agent. Knowledge on volatile matter content simulates the practical aspect of combustion of the biomass in the boiler and the potential for liquid and char generation in pyrolysis (Rocha et al., 2015; Tanger et al., 2013). The highest values were found for most agroindustrial fruit residues, sugarcane residues, wheat straw and forest biomass (74-94%). Thus, higher volatile matter indicates that the biomass can be easily ignited, and subsequently converted into products.

The ultimate analysis provides an indication of the presence of C, H, N, O and S in biomass. High O content in corn straw, banana stem and leaves, rice husk and straw, sugarcane straw and orange bagasse biomasses (47.1-55.2 %) are not desirable for fuel as it contributes to a lower heating value of thermal conversion products. Thus, high oxygen content can promote high oxygen content in the bio-oil from fast-pyrolysis and poor stability (Bridgwater, 2012). As for the content of carbon, the highest values were observed in the soybean straw, coconut residues, forest and fast-growing biomasses (47.4-53.1 %), and the lowest values in the banana steam (39.0%) and rice husk (39.5%). Thus, N and S contents can provide the amount of undesirable emissions, i.e., NOx and SOx. According to Obernberger et al., (2006), emission problems (exceeding of emission limits) related to solid biofuels can be expected at fuel S concentrations above 0.2% and at fuel N concentrations above 0.6 w %. This can occur during the combustion of the some of the agroindustrial biomasses evaluated. The N content found in biomasses coffee husk (1.5%), banana leaves (0.9%), soybean husk (0.9%) and corn straw (0.9%) were the highest amongst the biomass samples studied. For S content, the most biomass showed small values which the highest values were found for soybean stalk and sugarcane straw and bagasse (0.2 – 0.6%). Therefore, elemental composition of some evaluated biomasses can affect their thermal utilization thus improve emissions control practices (as flue gas cleaning technologies), and a good control of the process variables are necessary.

The chemical composition of all residues studied is summarized in Table 3, revealing that extractives, cellulose, hemicelluloses, and lignin content vary significantly from one biomass to another. Extractives are in the range of 1.41−25.1%. Cellulose is in the range of

13% (orange bagasse) to 41.8% (sugarcane bagasse), whereas, hemicelluloses, 12.7% (banana stem) to 32.5% (Coconut shell). The maximum lignin is in coconut husk (34.5%) and the minimum in orange bagasse (2.8%). Thus, the fast pyrolysis of biomass with a high percentage of lignin, as in coconut husk and shell, can produce bio-oil with lower oxygen content and therefore a higher energy density (Bridgwater, 2012). Accordingly, the corn straw, banana residues, rice residues and orange bagasse biomasses are least suitable for the fast pyrolysis of the evaluated biomass. However, the agro-industrial residues is a widely dispersed resource that has to be transported to the conversion facility. The low bulk density of waste, which can be as low as 131 kg/m^3 for sugarcane bagasse (Rocha et al., 2015) means that transport costs are high and the number of vehicle movements for transportation to a large-scale processing facility are also very high. Conversion of residue to an energy liquid by fast pyrolysis at or near the biomass source can reduce transport costs and reduce environmental concerns as the liquid has a density of 1.2 kg/m^3.

In another way, a potetial biomass for bioethanol production should have a higher amount of cellulose and hemiceluloses content than lignin and ash content. The highest content of sugars present in corn cob, sugarcane bagasse and straw, wheat straw and coffee husk (60.7-70.7 %) makes them a material of choice for bioethanol production.

For biomass combustion, the ash consists of mainly inorganic elemental oxides residue remaining after combustion. For energy application, a good solid fuel characteristic is that, upon combustion, the material does not leave too much of residue, and if the ash should contain desirable elements for utilization in other areas (as soil application), this would make the ash a valuable source of the elements. Because of the temperature of gasification process, generally the gasification requires a feedstock with less than 5% ash content, preferably less the 2%, in order to prevent the formation of clinkers (Rocha et al., 2015; Swaaij et al., 2015). The biomasses with ash contente below 2% are coconut husk and corn cob, between 2 and 5 % are soybean straw, surgar cane straw, coffee husk, orange bagasse and coconut shell, and values greater than 5% are soybean stalk and husk, corn straw, sugarcane bagasse, rice straw and husk, banana leaves and stalk and wheat straw.

Table 2 shows the composition of the ash samples obtained from literature, base-to-acid ratio (B/A), slagging index (S_R) and fouling index (F_u) of biomass ash. It can be observed

that there is a wide variation in the ash composition of the different biomasses. Rice residues, sugarcane residues, corn cob and coconut shell are high in silica content at 48.7% to 94.6%. The alumina and iron oxide content of all the residues is considerably low (0.3-8.8% and 0.06-9.4%, respectively). According to Pronobis (2005) , the slagging was low when B/A < 0.75, it increased when B/A = 0.75–2.0 and when B/A ≥ 2 the dependence was not noticeable. The results of coconut shell, rice straw, rice husk, sugarcane straw and sugarcane bagasse residues were not found to be over 0.75, meaning that they have lower medium slagging potential. While the values of some residues were over 0.75, implying that they may greatly increase the deposition tendency in combustion temperature. The slagging index (RS) value showed the similar trend with B/A ratio, expect for residue with Rs value was low (RS<0,6) that suggest low slagging inclination. High S_R (>72) value corresponds to high viscosity and therefore to low slagging inclination, and S_R values greater than 72 were observed for sugarcane straw, sugarcane bagasse, rice straw, rice bagasse, coconut shell and bamboo. S_R value for wheat straw, banana steam and coconut husk were at 65 to 72 that indicate medium slagging inclination (Pronobis, 2005). For soybean residues, corn straw, coffee husk, banana leaves value were less than 65 that corresponds to high slagging trend. Most biomasses evaluated high tendency to sintering of deposits, except for the sample of rice husk that presented low fouling inclination (Fu<0.6)(Febrero et al., 2015). It's important to highlight that co-processing of biomass with conventional fuels is potentially a very attractive option that enables full economies of scale to be realized as well as reducing the problems of product quality and clean up. Most current co-firing applications are those where the biomass fuels are added to the coal feed and this is widely practiced at up to 5% of the energy demand of the power station (Bridgwater, 2012).

6.3.1.2 Energy potential from residual biomasses in Brazil

The energy potential of from main crops produced in Brazil, namely rice, sugar cane, soybean, wheat, coffee, banana, orange and coconut were presented were presented in Table 4.

Table 4. Energy potential from main Brazilian biomasses.

Crop produced	Annual crop production (kton) b	Type of residue	Residue to product ratio (RPR) [c]	Quantity of residue (kton)	Energy potential (PJ/yr)
Agroindustrial cereals residues					
Soybean	96296.7	Stalk and straw	2.0	193556.4	3319.5
		Husk	0.1	7703.7	109.0
Rice	10622.2	Straw	1.5	16358.2	280.4
		Husk	0.3	2761.8	45.4
Wheat	6834.4	Straw	1.6	10593.4	160.0
Agroindustrial fruit residues					
Corn	39680.4	Straw	0.2	8332.9	186.9
		Cob	0.2	5952.1	115.0
Coffee	3019.1	Husk	0.3	996.3	18.1
Banana	6764.6	Leaves	0.5	3247.0	52.4
		Stem	3.0	20293.8	319.2
Orange	17251.3	Bagasse	0.5	8625.6	136.4
Coconut a	1589.5	Husk	0.7	1144.5	22.8
		Shell	0.1	206.6	3.3
Sugarcane	768678.4	Straw	0.3	199856.4	3611.4
		Bagasse	0.3	199856.4	3677.4
Forestry biomass					
	Planted area (ha)	Productivity (ton /ha yr)			Energy potential (PJ/yr)
Eucalyptus	5673784.0	30.0			3098.2
Pinus	1584333.0	25.0			731.6
Fast growing biomass					
	Plante area (ha)	Productivity (ton /há yr)			
Bamboo	300000.0[d]	40.0			232.7
Elephant grass	300000.0[d]	32.0			176.4

a Considering a production of 1766164 thousand fruits (IBGE - Fundação Instituto Brasileiro de Geografia e Estatística, 2017).
b Based on (IBGE - Fundação Instituto Brasileiro de Geografia e Estatística, 2017).
c Based on average Residue to product ratio (RPR) from (A T Matos, 2005; "ABIB Inventário Residual Brasil - Wood Pellets - Briquete - Energia," n.d.; Fernandes et al., 2013; Ferreira-Leitão et al., 2010; George et al., 2010; Portugal-Pereira et al., 2015; Wilkins et al., 2007; Zhang et al., 2012)
d Considering the big plantations in Brazil.

As shown in table 1, over 679.5 million tones of agricultural residues were generated in 2016 which means an energy potential of 1257.0 PJ, with high potential from sugarcane, soybean and banana crop residues (7288.8, 3428.5 and 371.6 PJ/yr respectively). In 2016, eucalyptus and pine plantations covered 5.6 and 1.6 million hectares of the area of planted

trees in the country, respectively (IBÁ - Brazilian tree industry, 2017). The total energy potential from the eucalyptus and pine plantations was estimated to be about 3829 PJ. Additionally, for bamboo and elephant grass, the energy potential was estimated to be 220.4 and 134.4 PJ/yr for each three thousand hectares planted, respectively.

6.3.2 Carbon sequestration analysis.

Based on the available technologies and quantity of crop residues in Brazil, the carbon contents associated with these residues were calculated for each scenario. According to the average moisture and carbon percentages of the biomasses, as shown in table 4, the carbon contents of these residues have been calculated to be 84.8, 6.0, 163.7, 7.8, 4.1, 0.4, 8.3, 0.9 and 0.6 Tg for soybean, corn, sugarcane, rice, wheat, coffee, banana, orange and coconut, respectively. For eucalyptus, pinus, bamboo and elephant grass, the carbon contents have been calculated to be 151.1, 35.6, 10.9, 10.8 Tg/yr, respectively. The overall carbon content from agroindustrial residues is approximately 276 Tg, which has the potential to generate approximately 1014.2 Tg carbon dioxide by uncontrolled burning of residues, which often happens with the aim of reducing the volume of this so-called “undesirable” biomass. According to the report by ICPP working Group (Solomon, S et al., 2007), open burning can also release high amounts of NOx that is a noxious substance that will have drastic environmental impacts if not treated before entering the ecosystem. Furthermore, the global warming effect of N_2O is almost 300 times that of the CO_2, implying that the release of trace amounts of N_2O will bring about uncompensable environmental outcomes. Another important issue is that the most of these wastes remain in the cultivation area until their decomposition by microorganisms producing greenhouse gases (as methane gas). In this since, the use of such residues for energy production, in addition to reducing environmental pollution by their removal from the field, provides added value to wastes.

Table 5. Carbon sequestration analysis.

	Crop produced									Planted biomass			
	Soybean	**Corn**	**Sugarcane**	**rice**	**wheat**	**coffee**	**banana**	**Orange**	**Coconut**	**Eucalyptus**	**Pinus**	**Bamboo**	**Elephant grass**
Carbon content (Tg)	84.8	6.0	163.7	7.8	4.1	0.4	8.3	0.9	0.6	74.3	16.9	5.7	5.5
Carbon sequestration (Tg-CO2)	310.9	22.2	599.8	28.7	15.0	1.5	30.4	3.4	2.4	272.3	61.9	21.0	20.3
Scenario I -Bioethanol production													
Biothanol potential (v/w%)	22.3	24.1	28.2	24.4	25.8	26.0	19.3	13.6	20.3	28.4	27.0	27.4	24.1
Ethanol (GL)	42.7	3.3	101.1	4.3	2.5	0.2	4.1	0.3	0.2	43.1	9.6	3.0	2.6
Equivalent gasoline (GL)	30.7	2.4	72.7	3.1	1.8	0.2	3.0	0.2	0.2	30.9	6.9	2.1	1.9
CO2 emission from biethanol production	4.3	0.3	10.1	0.4	0.2	0.0	0.4	0.0	0.0	4.3	0.96	0.3	0.3
Carbon sequestration (Tg-CO2)	65.1	5.0	154.1	6.5	3.8	0.4	6.3	0.5	0.4	65.5	14.7	4.5	4.0
Scenario II-biogas production													
Biogas potential (Gm3)	105.2	7.6	226.4	9.0	5.8	0.6	12.4	4.8	0.8	91.6	21.6	6.0	5.8
Equivalent energy (PJ)	2240.0	162.5	4821.9	191.9	122.6	11.8	264.3	102.3	18.0	1952.0	460.3	126.9	123.8
Carbon sequestration (Tg CO2e)	136.6	9.9	294.1	11.7	7.5	0.7	16.1	6.2	1.1	119.1	28.1	7.7	7.6
Scenario III - Combustion													
Heat value (MJ/kg)	16.9	17.2	16.3	16.6	14.6	16.9	15.5	15.5	17.8	17.8	17.8	17.8	17.8
Havested Energy (PJ)	3230.5	232.3	5814.9	290.7	140.0	15.1	333.8	33.6	21.8	2694.4	635.6	194.5	192.2
Equivalent Coal (Tg)	125.7	9.0	226.3	11.3	5.4	0.6	13.0	1.3	0.8	104.8	24.7	7.6	7.5
Carbon sequestration (Tg CO2)	289.1	20.8	520.4	26.0	12.5	1.4	29.9	3.0	2.0	241.1	56.9	17.4	17.2
ScenarioI IV - Gasefication (ar)													
Heat value of gas (MJ/Nm3)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Havested Energy (PJ)	2295.9	162.5	4294.1	210.8	115.0	10.8	257.7	26.1	14.7	1813.3	427.8	130.9	129.3
Equivalent Natural gas (Nm3)	62.1	4.4	116.1	5.7	3.1	0.3	7.0	0.7	0.4	49.0	11.6	3.5	3.5
Carbon sequestration (Tg)	133.4	9.4	249.5	12.2	6.7	0.6	15.0	1.5	0.9	105.4	24.9	7.6	7.5
Senario V - fast-pyrolysis (substitutes for fuel oil)													
Heat value of bio-oleo (MJ/kg)	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Havested Energy (PJ)	1913.3	135.4	3578.4	175.6	95.9	9.0	214.7	21.7	12.2	1511.1	356.5	109.1	107.8

Equivalent fuel oil (Tg)	44.5	3.1	83.2	4.1	2.2	0.2	5.0	0.5	0.3	35.1	8.3	2.5	2.5
Carbon sequestration (Tg) (fuel oil)	133.4	9.4	249.4	12.2	6.7	0.6	15.0	1.5	0.9	105.3	24.8	7.6	7.5

In the first scenario, **conversion of biomass to bioethanol as an alternative sustainable source to replace gasoline**, the following considerations have been established. As described by Zhu and Zhuang (2012), the bioethanol production yield is closely related to the type of the biomass in addition to the type of the process and process variables, such as enzyme loading and acidity of the medium. However, the theoretical bioethanol yield based on sugars of feedstock was estimate as described by Im et al. (2016). Furthermore, it was considered that the CO_2 emission for the production of 1 GL bioethanol is around 0.1 Tg as described by Hudiburg et al. (2016), and the volumetric energy density of ethanol was assumed to be approximately 71.9% than the gasoline. Therefore, as shown in table 4, the CO_2e emission estimated in the conversion of biomass to bioethanol from the biomass residue was approximately 63.6 Tg, and the carbon sequestration potential of the produced bioethanol was determined as 65.1, 5.0, 154.1, 6.5, 3.8, 0.4, 6.3, 0.5, 0.4 Tg/yr for soybean, corn, sugarcane, rice, wheat coffee, banana, orange and coconut biomasses, respectively. For planted biomass, the carbon sequestration potential was determined to be approximately 88.7 Tg/yr.

In the second scenario, CO2 sequestration by biogas production from biomass by anaerobic digestion, for the average pure biogas production yield, 0.7 m^3 from each kg of volatile solids as found by Rana et al. (2016) was considered for several feedstocks, and for the biogas low heating value, (LHV) to be 21.3 MJ/ m^3(IPEA Instituto de pesquisa econômica aplicada, 2012) was considered. That values were combined with the volatile content of biomasses to determine the amount of biogas and the energy production from the biomass. Accordingly, the amount of the biogas production from the main biomass residue in Brazil can be evaluated to be around 67.0 Gm^3 biogas (see Table 4), and the potential energy production from agroindustrial residues and planted biomass in scenario II can be determined as and 7935.3 PJ/yr and 2663.1 PJ /yr, respectively. To estimate the total carbon sequestration potential of biogas production from biomass residues, the emission rate for natural gas to be 61. gCO_2e for each MJ (EPA, 2016; Rana et al., 2016) was considered. As can be see in table 4, the total carbon sequestration (CO_2e) the potential of biogas production from biomass residues has been calculated to be approximately 484.0 Tg/yr, and for planted biomass to be approximately 162.4 Tg/yr.

In the world, coal is the biggest source of energy for electricity production and its share is growing, particularly for power generation, and provide over 42% of global electricity supply. At the same time, these Coal-fired power plants account for over 28% of global carbon dioxide (CO_2) emissions (Tanaka N, 2010). The biomass co-firing operations can be implemented to reduce cost and greenhouse gas emissions. Thus, Biomass co-firing is one technology that can be implemented immediately in nearly all coal-fired power plants in a relatively short period of time and without the need for huge investments (Basu et al., 2011). As described before, the biomasses avalieted can generate total energy as high as 16241.6 PJ. It was assumed that each kg coal can generate 25.7 MJ (Tanaka, 2010) energy on average and leads to the emission of 2.3 kg CO_2 (90.5 gCO2/MJ (2017)). Using these value, it was calculated for scenario III that the equivalent total amount of CO_2 sequestration from the biomass in Brazil for co-combustion with coal in power plants can be determined to be approximately 1237.7 Tg/yr.

In scenario IV was evaluated the CO_2 sequestration by conversion of biomass to gases by gasification as renewable alternative to replace natural gas**.** Gasification of biomass has a long history and has been considered as one of the most attractive options for converting into mechanical energy and electricity in modern technology or to produce high-quality synthetic liquid and gaseous fuels (Swaaij et al., 2015). For biomass gasification, a variety of technologies are available which air normally is used as gasification agent. This use of air means that all the nitrogen in the air fed to the system ends up in the product gas (usually in volume fractions of 40%-60%) (Swaaij et al., 2015). If the gas low heating value (LHV) is considered to be approximately 6 MJ/m^3 (found in range from 5-7 MJ/m^3 (Swaaij et al., 2015) and the gas production capacity is around 2 Nm^3 for each biomass kg, the potential energy production from agroindustrial residues and planted biomasses can be determined as around 7387.5 and 2501.2 PJ respectively. If it is assumed that each Nm^3 natural gas generates 37.0 MJ energy on average (World Nuclear Association, 2008), and leads to the emission of 1.86 kg CO_2 (The mission factors by natural gas was found to be equal 53.06 gCO_2/MJ (EPA , 2016)), the total carbon sequestration potential of conversion of biomass to gases by gasification as renewable alternative to replace natural gas has been estimated to be approximately 574.6 Tg CO_2e.

Together with gasification, pyrolysis is one of the most researched processes for thermochemical biomass conversion. Pyrolysis provides a liquid fuel yields that can substitute fuel oil in any static heating or electricity generation application (Dhyani and Bhaskar, 2017). Many researchers calculated the energy production yield of bio-oleo for several feedstocks and concluded that the average bio-oleo production yield is in the range 26.3 to 75% (Bridgwater, 2012; Kersten and Garcia-Perez, 2013; Mesa-Pérez et al., 2013). Given these values and the volatile solid contents of the agricultural residues, the amount of bio-oleo production from the main Brazilian biomass can be evaluated to be around 191.6 Tg bio-oleo in scenario V. If bio-oleo low heating value (LHV) and density value are considered to be approximately 20 MJ/m^3 (Low heat value of bio-oleo can range from 16–22.95 MJ/kg (Bridgwater, 2012; Kersten and Garcia-Perez, 2013; Swaaij et al., 2015), the harvested energy from soybean, corn, sugarcane, rice, wheat coffee, banana, orange and coconut, eucalyptus, pinus, bamboo and elephant grass biomasses can be determined as around 1913.3, 135.4, 3578.4, 175.6, 95.9, 9.0, 214.7, 21.7, 12.2, 1511.1, 356.5, 109.1 and 107.8PJ respectively. According to EPA (2016), the emission factor for fuel-oil combustion is about 69.7 g CO_2e per MJ. Thus, given the average energy contents of 43 MJ/kg for fuel-oil (World Nuclear Association, 2008), the total carbon sequestration potential of bio-oleo production from fast pyrolysis as substitutes for fuel oil has been estimated to be approximately 574.4 Tg CO2e.

Accordingly, the CO_2 sequestration value for use of biomass in replacing coal in power plants saves the atmosphere from the noxious effects of CO_2 to a larger extent than its utilization for bioenergy production in other scenarios. And this can be mainly associated to the high potential of CO_2 emission from coal burning (2.3 kg/kg) and the fact that all dry weight of the biomass can be directly used for co-combustion with no chemical or biological treatment applied. Further, beyond the description of the potential of biomass in CO_2 balanced sequestration from the sceneries selected, the emission of CO_2 during the transportation of biomass was examined. Since the transportation data for the residues of waste for conversion units were not available, this average transportation distance was assumed for cases in this study. However, in some situations, the residues are generated within the potential unit of conversion as with sugarcane bagasse from bioethanol industry. If a generic rural truck (capacity of about 15 ton) powered by a diesel consumption

rate of 0.30 L/km is considered for biomass transportation, in the case of least efficient packing density, with an average transport distance of 23 km (Macedo et al., 2008), the total fuel consumption for the transportation of the whole residues will be approximately 0.4 GL. For the CO_2 release factor of diesel igual 2.7 kg CO_2 per each liter of diesel (EPA , 2016), the total CO_2 release was determined to be 1.1 Tg CO_2 for the transport of biomasses.

6.4 Conclusion

Brazil is one of the World's major agricultural producers and generates significant amounts of biomass residues in activities arising from harvesting and processing of agricultural products, of which the main ones are soybean, corn, sugarcane, bean, rice, wheat, coffee, banana, orange, and coconut. An evaluation made on the total amount of residues that originates from agro-industrial activities in Brazil shows that over 679.5 million tones of agricultural residues were generated in 2016 which means an energy potential of 1257.0 PJ, with high potential from sugarcane, soybean and banana crop residues (7288.8, 3428.5 and 371.6 PJ/yr respectively). Another's potential renewable energy feedstocks are eucalyptus, pinus, elephant grass and bamboo.

From the four main parameters evaluated were chemical composition, heating value, proximate and ultimate compositions of biomasses: forest biomass and sugar cane residues exhibited higher total sugar content (63.7 -70.7%); the highest lignin contents were observed in forest biomasses (27.1-30.1) and coconut residues (25.4-34.5%) and the minimum in orange bagasse (2.8%); the lower heating value of the biomasses ranged from 14.0 MJ kg-1 to 19.4 MJ kg^{-1}, on a dry and ash free basis that indicated that all types of samples were suitable for thermochemical conversion processes (Arena, 2012; Tsai et al., 2006), and most biomasses have a quite suitable content of moisture (<11 %), except for orange bagasse and banana stem; and the low ash contents were found in forest biomass (0.2-2.1%), corn cob (1.2) and coconut husk (1.3%). Therefore, the ash properties and elemental composition of the some evaluated biomasses can affect their thermal utilization thus improve practices for control the emissions (as flue gas cleaning technologies) and good control of the process variables are necessary.

From the scenarios developed to determine the CO_2 release/sequestration from biomass residues, the overall carbon content from agroindustrial residues is approximately 276 Tg, which has the potential to generate approximately 1014.2 Tg carbon dioxide by uncontrolled burning of residues, which often happens with the aim of reducing the volume of this so-called "undesirable" biomass. For eucalyptus, pinus, bamboo and elephant grass, the carbon contents have been calculated to be 151.1, 35.6, 10.9, 10.8 Tg/yr, respectively. The potential for application of the main Brazilian biomasses studied as alternative energy sources in thermochemical processes has been identified, especially concerning the potential of agro-industrial residues to provide considerable carbon credits for sustainable agricultural development

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CHAPTER 7

7. 1 Conclusions

This chapter provides the main conclusions of this work.

- The understanding of the biomass thermal behavior, properties and their environmental impact in the long-term represents an important factor for the development of renewable energy applications. Therefore, comprehensive knowledge of the chemical structure of the biomass is a critical factor for the optimal selection of the most suitable conversion technology. The results of thermogravimetric analysis in **Chapter 2 and 3** indicated strong correlation between cellulose and hemicellulose contents and pyrolysis behavior: a higher percentage in the original material intensified thermal degradation. The research confirms that other constituents, such as mineral matter, modify the thermal behavior of the main components. Potassium catalyzed pyrolysis resulted in increased char yields and reduced degradation temperatures. The result of proximate analysis on samples can be used to predict the product yield produced during pyrolysis. Furthermore, the data in this thesis demonstrate significant diversity in composition amongst studied species that will be important in selecting candidates for the development of feedstocks for thermal conversion processes.

- Decomposition of lignocellulosic biomass during thermal conversion is significantly influenced by the reaction parameters. In this sense, the stability of kinetic parameters obtained in **chapter 2** shows that the pyrolysis model describes the thermal degradation of biomass quite adequately for the samples studied. The same activation energies were obtained for all species at the end of the optimization of kinetic parameters and the decomposition of the pseudo-components resulted in relatively similar values of activation energies for all biomass, such tendencies proves the similarities in the kinetic behavior of the samples. The kinetic parameters estimated with the model were comparable with

those reported in the literature, and were used to simulate decomposition curves of pseudo-components at different heating rates. Through the methodology used, kinetic parameters were obtained that may provide useful data for effective design and improvement of thermochemical conversion units.

- In **chapter 4**, an extensive characterization of residual biomasses from the coffee production chain for energy purposes was presented, increasing knowledge about the alternatives applicable to the energy matrix of countries where the coffee industry is a major agricultural activity, through physical and chemical analyzes that identify the most important quality indices, the interactions between them, as well as the quantification of its importance. Results showed that moisture content ranged 8.69 to 18.46%, carrying an average higher heating value of 18.3–19.45 MJ/kg, and volatile matter content of 74.07-83.70 %. The silica (0–0.4 %) contents are quite small for all biomass samples. Glucans is the dominant component in the carbohydrate fraction of all studied samples (17.90-33.25%). Additionally, The high contents of extractives (10.57 -24.72%) and lignin (26.59-43.17%) of the samples found in this study can be associated with the advanced age of the coffee shrub. The characterization of the samples shows that the thermochemical conversion is an environmentally friendly alternative contributing to upgrading the large quantity of waste generated by the coffee industry into energetic valued residues and the improvement of their management.
- In **Chapter 5**, the pyrolytic behavior of woods were investigated under inert and oxidative conditions at the heating rates of 10, 25 and 50 ^{o}C/min by thermogravimetric analyzes. The thermal decomposition of samples presented three stages in the two atmospheres analyzed. In nitrogen, there were drying, active pyrolysis (devolatilization), and passive pyrolysis (carbonization). In oxidative atmosphere, there were drying, active oxidative pyrolysis (devolatilization), and char combustion. In oxidative atmosphere the different decomposition stages have occurred at lower temperatures and a higher rate of decomposition than decomposition in nitrogen atmosphere that were more pronounced for the eucalyptus residues. Moreover, the pyrolysis of eucalyptus wood and coffee shrub in the pilot-scale plant (feed rate capacity of about 20 kg/h) was successfully carried out. Thus, the characterization of Brazilian residues and products from oxidative fast pyrolysis ensures that these biomasses are potential

candidates for bioenergy production by fast pyrolysis. Therefore, Brazilian residues have the potential to favorably compete with other conventional biomass sources such as sugar cane straw, pine wood and banana leaves, as well as in thermochemical conversion technologies.

- **In Chapter 6** was estimated the potential of main Brazilian biomasses for generating renewable energy in Brazil such as sugarcane straw, sugarcane bagasse, coffee husks, banana leaves, banana stalk, coconut husk, coconut shell, soybean straw, soybean husk, corn straw, corn cob, rice straw, rice husk, orange bagasse, bamboo, elephant grass, eucalyptus and pinus. In agro-industrial activities in Brazil, over 679.5 million tones of agricultural residues were generated in 2016 which means an energy potential of 12.1 million PJ. The total energy potential from the eucalyptus and pine plantations was estimated been about 3829 PJ. Additionally, for bamboo and elephant grass, the energy potential was estimated to be 220.4 and 134.4 PJ/yr for each three thousand hectares planted, respectively. From the four main parameters evaluated were chemical composition, heating value, proximate and ultimate compositions of biomasses: forest biomass and sugar cane residues exhibited higher total sugar content (63.7 -70.7%); the highest lignin contents were observed in forest biomasses (27.1-30.1) and coconut residues (25.4-34.5%) and the minimum in orange bagasse (2.8%); the lower heating value of the biomasses ranged from 14.0 MJ kg-1 to 19.4 MJ kg-1, on a dry and ash free basis, and most biomasses have a quite suitable content of moisture (<11 %), except for orange bagasse and banana stem; and the low ash contents were found in forest biomass (0.2-2.1%), corn cob (1.2) and coconut husk (1.3%). Therefore, the ash properties and elemental composition of the some evaluated biomasses can affect their thermal utilization thus improve practices for control the emissions (as flue gas cleaning technologies) and good control of the process variables are necessary. From the scenarios developed to determine the CO2 release/sequestration from biomass residues, the overall carbon content from agro-industrial residues is approximately 276 Tg, which has the potential to generate approximately 1014.2 Tg carbon dioxide by uncontrolled burning of residues. For eucalyptus, pinus, bamboo and elephant grass, the carbon contents have been calculated to be 151.1, 35.6, 10.9, 10.8 Tg/yr, respectively. The potential for application of the main Brazilian biomasses studied as

alternative energy sources in thermochemical processes has been identified, especially concerning for potential of agro-industrial residues to provide considerable carbon credits for sustainable agricultural development.