ENERGETIC VALORIZATION OF SAWMILL WASTE THROUGH SLOW PYROLISIS

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Abstract

Brazil is a large producer of sawmill waste, which is commonly used to supply boilers and produce energy. In order to reduce unwanted characteristics of this material, thermochemical conversions through pyrolysis are an alternative. Thus, the aim of this study was to characterize the energetic proprieties of raw and pyrolyzed sawmill waste of *Eucalyptus* sp. and *Pinus* sp. In order to analyze the environmental impact of the emission of pyrolysis gases, the behavior of these gases during pyrolysis was determined. Slow pyrolysis was performed in an electric oven, whose gases were conducted through a condensation system of bio-oil, and later in a gas analyzer. The yields of charcoal, bio-oil and gases were obtained by gravimetry. The chemical composition of wood and charcoal was evaluated, as well as the high heating value, equilibrium moisture and basic density. Charcoal from hardwood and softwood presented several differences, especially regarding yields due to quantity and types of lignin. The main gases from the pyrolysis were CO_2, CO, CH_4, and H_2. Hardwood had a higher production of carbon dioxide and, in minority, methane and carbon monoxide, mainly due to the composition of the wood. The emission of gases produced during the pyrolysis increases the environmental impact of industry and is a waste of energy, which could be harnessed more efficiently. Pyrolysis is an alternative to obtain better energetic characteristics of sawmill waste. However, forms to mitigate the emission of gases in operational scale should be evaluated.

Keywords: Charcoal, greenhouse gases, thermal degradation.

Resumo

Valorização energética de resíduos de serraria pelo processo de pirólise lenta. O Brasil é um grande produtor de resíduos de serraria, comumente utilizados para abastecer caldeiras para a geração de vapor e energia. Para reduzir características indesejadas do material, a conversão térmica através da pirólise se torna uma alternativa interessante. O objetivo deste estudo foi caracterizar as propriedades energéticas de resíduos de *Eucalyptus* sp. e *Pinus* sp. *in natura* e carbonizados. A emissão dos gases durante a pirólise foi determinada visando analisar o impacto ambiental deste processo. A pirólise lenta desses resíduos foi realizada em um forno elétrico tipo mufla, cujos gases foram conduzidos através de um sistema de condensação do bio-óleo, e posteriormente em um analisador de gases. Os rendimentos de carvão, bio-óleo e gases foram obtidos por meio da gravimetria. Foi avaliada a composição química da madeira e do carvão vegetal, além do poder calorífico superior, umidade de equilíbrio e densidade básica. Os carvões de folhosas e coníferas apresentaram diferenças nos rendimentos, devido, principalmente, à quantidade e tipo de lignina. Os principais gases resultantes da pirólise foram CO_2, CO, CH_4 e H_2. As folhosas apresentaram uma maior produção de dióxido de carbono e, minoritariamente, metano e monóxido de carbono. A liberação dos gases produzidos durante a pirólise aumenta o impacto ambiental da indústria e é um desperdício de energia, que pode ser aproveitada de forma mais eficiente. A pirólise melhorou as características energéticas dos resíduos. No entanto, apesar das vantagens da carbonização, formas de mitigar a emissão de gases em escala operacional devem ser avaliadas.

Palavras chave: Carvão vegetal, gases de efeito estufa, degradação térmica.

INTRODUCTION

Brazil is the fifth largest producer of sawn wood in the world, having produced about 8.6 million m^3 in 2016. Compared to 2015, the sector has increased exports of sawn wood by 39% (IBA, 2017). New sawing techniques, quality of the raw material and characteristics of the equipment have provided a yield of up to 60% and good quality of the lumber (CUNHA *et al.*, 2015). However, the raise on its production increases the generation of waste. The volume of wood lost during primary and secondary processing of the material corresponds to 20 to 40% (FINOTTI *et al.*, 2006).

Sawmill waste in Brazil is commonly used to supply boilers that produce energy. This material is characteristically heterogeneous, with high moisture content, low calorific value and low grindability (BACH *et al*., 2016). In order to reduce these characteristics, thermochemical conversion of biomass is a viable alternative. For instance, slow pyrolysis is a process in which heat is applied to a material under an inert atmosphere, having a final temperature between 300 and 500 °C. This process has the charcoal, a solid material rich in carbon, as its main product. In addition, a volatile portion constituted of bio-oil and gases is produced (PEREIRA *et al*., 2013).

Thus, charcoal from sawmill waste can be used to supply boilers more efficiently than the raw material. Using this charcoal in co-firing systems, i.e., the blending and combustion of biomass with another fuel in a boiler, is another alternative. Co-firing biomass has been endorsed due to its advantage as a renewable energy source and carbon neutral. Additionally, when a boiler operates with a significant amount of biomass, CO_2 emission may decrease due to the reduction in consumption of fossil fuel. Biomass is currently applied in about 5 to 10% of co-firing systems, although it has the potential to replace more than 50% of the fuel used (RONI *et al*., 2017).

In the current global energy context that depends on fossil fuels, biomass utilization offers companies the opportunity to be more environmentally sustainable. Therefore, the objectives of this study were: 1) to characterize and evaluate the energetic proprieties of raw biomass and pyrolyzed biomass of sawmill waste in order to propose alternatives for non-desirable energetic proprieties of the raw material in the future and 2) to analyze the environmental impact of greenhouse gases emission by pyrolysis.

MATERIAL AND METHODS

Waste

The present study used waste of *Eucalyptus* sp. and *Pinus* sp., such as slabs and shavings, which were supplied by the sawmill of the Federal University of Viçosa (state of Minas Gerais, Brazil).

Pyrolysis

Slow pyrolysis was performed to produce charcoal of *Eucalyptus* sp. and *Pinus* sp. in an electric laboratory kiln, using about 350 g of oven-dry waste. Wood was dried since the moisture content can influence the charcoal and its properties. The samples were placed in a metallic cylindrical container with 0.003 m^3 of volume. The initial temperature of pyrolysis was 100 °C, and the final temperature was 350 °C. The heating control was conducted manually in increments of 50 °C every 30 minutes, which resulted in a heating rate of 1,67 $° \text{ min}^{-1}$.

Gas products were conducted in the electric laboratory kiln exit through a condensable gas recovery system. This system is constituted by a water cooled tubular condenser coupled to a collection vessel. The gases were conducted to an online gas analyzer (Gasboard 3100 Wuhan CUBIC Optoeletronics Co., LTDA.) in a flow rate of 1 liter per minute. The gas analyzer measures instantly CO, CO_2 and CH_4 by using a thermal conductivity detector and H_2 by using an electron capture detector. Figure 1 and 2 shows the schematic diagram of the pyrolysis reactor and the gas analyzer, respectively.

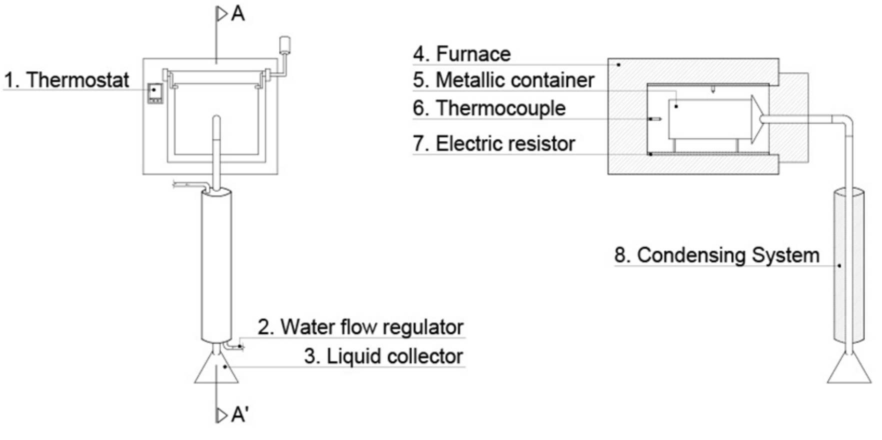

Figure 1. Schematic diagram of the pyrolysis reactor.
Figura 1. Diagrama esquemático do reator de pirólise.

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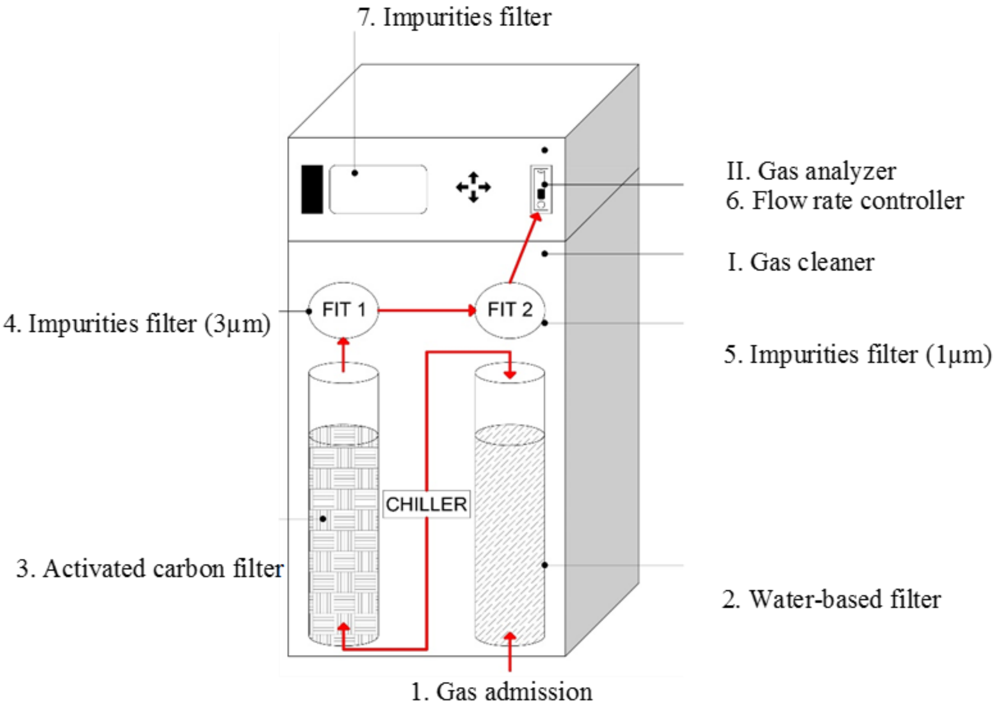

Figure 2. Schematic diagram of the gas analyzer.
Figura 2. Diagrama esquemático do analisador de gases.

Wood and charcoal properties

Extractive contents of wood were determined in duplicates according to TAPPI 204 om-88 (TAPPI, 1996), using the total extractive method. Lignin contents were determined according to ASTM D1106 – 96 (2013), and total lignin content was obtained by summing the values of soluble and insoluble lignin. Carbohydrate composition was determined according to Wallis *et al.* (1996). Cellulose content was determined by considering the glucose percentage, excluding the content of mannose.

The proximate analysis of raw material and charcoal was done according to ASTM D3174-04 (2010) for ash analysis and ASTM D3175-89a (1997) for volatile matter. Equilibrium moisture content was determined according to the procedures established by DIN EN 14774-1. The high heating value (HHV) was calculated according to ASTM D240-02 (2002), using an adiabatic calorimeter IKA300. Basic density was calculated by the hydrostatic method, immersed in mercury.

RESULTS

Table 1 shows the chemical component analysis of *Eucalyptus sp.* and *Pinus sp*. Usually, depending on the taxonomic group, the chemical compositions of hardwood and softwood species are different. Hardwood hemicelluloses contain mainly xylan, while the major component of softwood hemicelluloses is glucomannan, followed by xylan. The lignin content in hardwood is lower than in softwoods. Furthermore, hardwood lignins consist in units of guaiacyl and syringyl, whereas softwood lignins are composed almost exclusively of units of guaiacyl (4-hydroxy-3-methoxyphenyl) (LIN *et al*., 2012).

Table 1. Chemical components in wood samples.
Tabela 1. Componentes químicos nas amostras de madeira.

Chemical compositions (dry %)	*Eucalyptus sp.*	*Pinus sp.*
Glucan	39.8 ± 0.8	36.8 ± 0.6
Xylan	11.6 ± 0.3	6.1 ± 0.1
Arabinan	0.4 ± 0.2	1.2 ± 0.3
Galactan	0.5 ± 0.1	2.4 ± 0.2
Glucomannan	0.4 ± 0.1	10.4 ± 0.1
Lignin	30.1 ± 0.5	33.1 ± 0.6
Extractives	4.5 ± 0.3	2.5 ± 0.1
Ash	0.2 ± 0.01	0.6 ± 0.02

The yield of products from slow pyrolysis is shown in Table 2. In wood pyrolysis, with the aim at producing charcoal, it is desirable to obtain a high yield of charcoal. This parameter is a result of the better use of wood in the pyrolysis oven and, consequently, higher energy yield, among other factors.

Table 2. Yield of charcoal, bio-oil and gas for *Eucalyptus* sp. and *Pinus* sp.
Tabela 2. Rendimento do carvão vegetal, bio-óleo e gases para *Eucalyptus* sp. e *Pinus* sp.

Pyrolysis products yield %	*Eucalyptus* sp.	*Pinus* sp.
Charcoal	39 ± 1.2	44 ± 1.2
Bio-oil	47 ± 0.8	41 ± 0.6
Gas	14 ± 0.6	15 ± 0.5

Proximate analysis, equilibrium moisture, high heating value (HHV) and basic density of the raw material and charcoal are shown in Table 3.

Table 3. Proximate analysis, high heating value, equilibrium moisture and basic density of the raw material and charcoal for *Eucalyptus* sp. and *Pinus* sp.
Tabela 3. Composição centesimal, poder calorífico superior, umidade de equilíbrio e densidade básica *in natura* e em carvão vegetal para *Eucalyptus* sp. e *Pinus* sp.

	Raw material		Charcoal	
	***Eucalyptus* sp.**	***Pinus* sp.**	***Eucalyptus* sp.**	***Pinus* sp.**
Proximate analysis (dry. %)				
Volatile matter	83.7 ± 0.3	85.6 ± 0.5	37.4 ± 0.4	37.9 ± 0.6
Fixed carbon	16.1 ± 0.4	18.2 ± 0.7	62.2 ± 0.5	60.8 ± 0.7
Ash	0.20 ± 0.01	0.60 ± 0.02	0.40 ± 0.03	1.30 ± 0.04
HHV (MJ.kg $^{-1}$)	20.4 ± 1.5	19.9 ± 0.7	29.3 ± 1.0	29.3 ± 0.8
Equilibrium moisture (%)	13.8 ± 0.8	10.9 ± 0.8	7.40 ± 0.7	5.40 ± 0.6
Basic density (kg/m^3)	560.0 ± 0.5	430.0 ± 20.6	380.0 ± 12.5	210.0 ± 33.7

The emission of greenhouse gases in kg of gases per tones of wood for waste of *Eucalyptus* sp. and *Pinus* sp. is show in Figure 3.

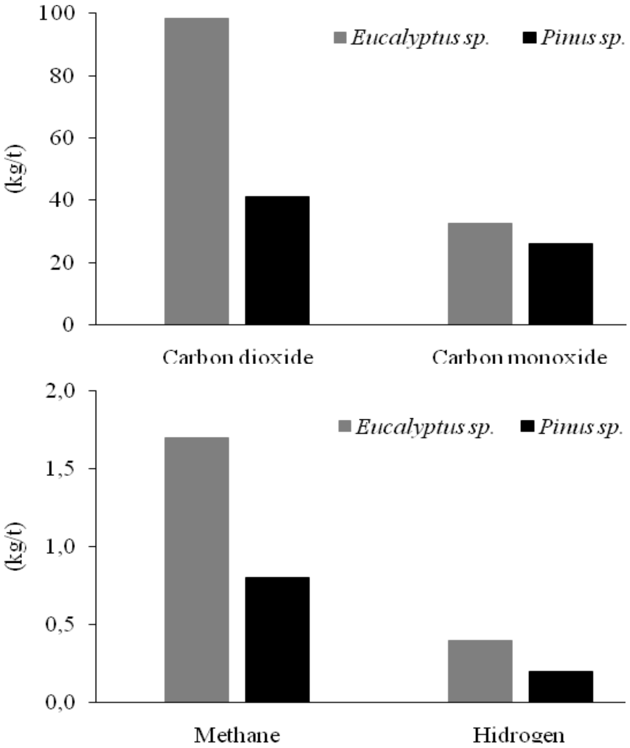

Figure 3. Emission of greenhouse gases in the pyrolysis process.
Figura 3. Emissão de gases de efeito estufa no processo de pirólise.

The behavior of the high heating value of gases from pyrolysis is shown in Figure 4. The growing worldwide concern on the emission of greenhouse gases in the atmosphere has induced the creation of laws and regulations controlling industries regarding the emission of such gases.

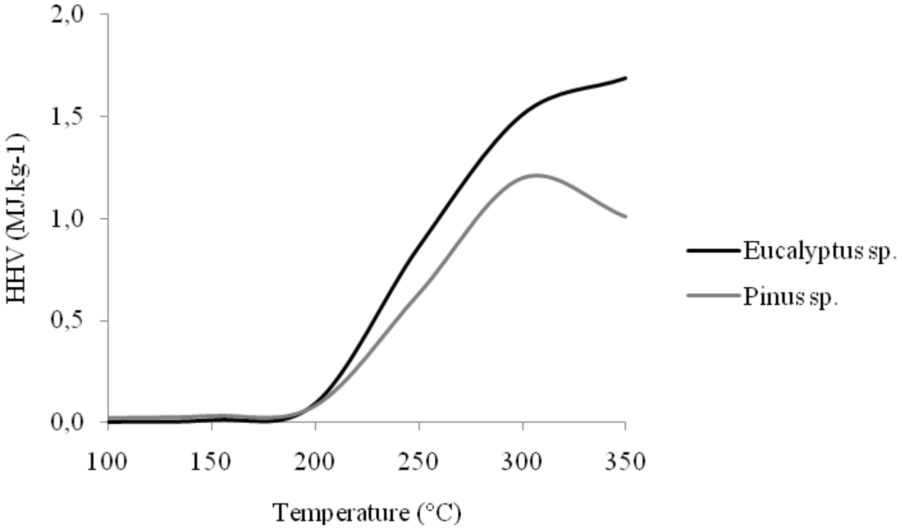

Figure 4. High heating value (HHV) of gases from the pyrolysis process.
Figura 4. Poder calorífico superior de gases provenientes do processo de pirólise.

DISCUSSION

Cellulose and hemicellulose have low resistance to thermal degradation, presenting maximum peaks of mass lost in the pyrolysis process of approximately 275 ºC and 350 ºC, respectively (YANG *et al*. 2007). Compared to these components, Lignin has high resistance to thermal degradation. During the thermal degradation process of a wood material, a portion of it is removed as volatile material from degradation reactions of the hemicelluloses, cellulose and part of the extractives. This process results in the concentration of fixed carbon and ash in the final product (KOPPEJAN *et al*., 2012).

The value of equilibrium moisture for charcoal decreases when compared to wood. In the process of thermal degradation, hemicellulose is the primary component due to its structural constitution with higher numbers of hydroxyl groups. These groups are available for water adsorption (ACHARJEE *et al*., 2011). Meanwhile, the high heating value for charcoal is greater than for wood due to the degradation of most stable components during the pyrolysis process, favoring the concentration of lignin compounds. Lignins have fundamental units linked by ether and carbon-carbon bonds, being the energy in C-C higher than in C-O and C-H bonds (PHANPHANICH, MANI, 2011). Therefore, the increase in the content of carbon during the thermal process of degradation results in high calorific value.

Lignin also has high level of aromaticity and size when comparted to other wood components (HAYKIRI-ACMA *et al*., 2010). The presence of extractives may increase or decrease the gravimetric yield of charcoal, depending on its chemical composition (CARNEIRO *et al.*, 2017). High levels of cellulose and hemicelluloses and some extractives contribute to a higher production of gas and bio-oil.

Final temperature, heating rates, pressure and reaction time of slow pyrolysis are the factors that most influence the yield of charcoal. Furthermore, parameters related to the raw material used, such as the type of biomass, may influence it. The sawmill waste of *Eucalyptus* sp. and *Pinus* sp. presents differences between its yields of pyrolysis products. The chemical composition of waste affected the yield of charcoal mainly due to the presence and high amount of different types of lignin. Hardwood lignin consists of two units: guaiacyl (4-hydroxy-3-methoxyphenyl) and syringyl (3,5-dimethoxy-4-hydroxyphenyl), whereas softwood lignin consists almost exclusively of units of guaiacyl (ASMAD *et al*., 2017; PEREIRA *et al*., 2013; YANG *et al*., 2007).

The emission of greenhouse gases in the slow pyrolysis also shows a difference between hardwood and softwood. The carbon dioxide is the main element that differs these two taxonomic groups. Hardwoods produce a higher amount of acetic acid in slow pyrolysis, which is converted mainly into carbon dioxide, and a minor extent of it is converted into methane and carbon monoxide (ASMADI, 2014). The pyrolysis of wood is described by a series of models based on the reactions that occur parallelly, consecutively and competitively (TURNER *et al*., 2010). The behavior of non-condensable gases of slow pyrolysis is related to these reactions and to the component analysis of the material.

At temperatures between 100 °C and 200 °C, no gas was released. From 200 °C on, a progressive increase of gas emissions occurred. The major emission participants for this temperature were carbon monoxide and carbon dioxide. The decarboxylation reactions and secondary carbon reactions, for example, are responsible for the formation of these gases. Moreover, hemicellulose is the wood component that contributes the most to the emission of these gases (YANG *et al*., 2007).

The formation of methane at temperatures below 500 °C is attributed to the breaking of $O\text{-}CH_3$ and methylene groups. At elevated temperatures, methane emission occurs due to the rupture of the aromatic rings of lignin molecules and reactions among the components of the gas phase. Lignin is the component that contributes the most to the emission of methane due to the high content of methoxyl groups. Hydrogen gas is the result of tar cracking (YANG *et al.*, 2007). In general, the reactions for gas formation are secondary cracking and water-gas substitution reaction (VELDEN *et al.*, 2010).

The main gases from slow pyrolysis of wood are CO_2, CO, CH_4, and H_2. Some of these gases are inert, such as CO_2, and some of them have a chemical energy, like CO, CH_4, and H_2. The emission of these gases to the atmosphere together with the increasing environmental impact caused by industry are still a waste of energy that could be harnessed more efficiently. These gases could be processed in burners or furnace, and the thermal energy generated by it could be used for the production of electric energy (PEREIRA, 2017). Studies regarding the energy potential of gases can subsidize the installation of structures for the use of gases as energy, as well as improve the sustainability of the charcoal industry.

CONCLUSION

- Pyrolysis increased the energetic characteristics of sawmill waste and is a promising alternative to better local use of energy.
- Despite the advantages of pyrolysis, forms to mitigate the emission of gases in operational scale should be evaluated.

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