ORIGINAL ARTICLE

Valorization of agroforestry biomass residue via slow pyrolysis

Valorização de resíduos de biomassa agroflorestal por pirólise lenta

Clarissa Gusmão Figueiró¹ , Angélica de Cássia Oliveira Carneiro¹ , Lucas de Freitas Fialho¹ ,
Leticia Costa Peres¹ , Paula Gabriella Surdi¹ , Vinicius Resende de Castro¹

¹Universidade Federal de Viçosa – UFV, Viçosa, MG, Brasil

How to cite: Figueiró, C. G., Carneiro, A. C. O., Fialho, L. F., Peres, L. C., Surdi, P. G., & Castro, V. R. (2021). Valorization of agroforestry biomass residue via slow pyrolysis. *Scientia Forestalis*, 49(131), e3518. <https://doi.org/10.18671/scifor.v49n131.03>

Abstract

Biomass residues play a fundamental role in the transition process for a renewable energetic matrix. Biomass thermal treatment processes, e.g. slow pyrolysis, could supply products with a high energetic density and increased value. The aim of this study was to evaluate the pyrolysis products of three biomass residues obtained from agriculture (sugarcane bagasse and bean straw) and forestry cultures (eucalypts). The focus of this study was to qualify and quantify the gaseous non-condensable fractions, according to the final pyrolysis temperature (400, 550 and 700 °C). The thermogravimetric (TG) analysis was performed. The pyrolysis process was conducted in a laboratory electric oven. The pyrolysis byproducts, after having passed through the bio-oil recovery system, were directed to an on-line gas analyzer. It was verified that the biomass composition can directly influence its thermal degradation, thus affecting the characteristics of the produced gases. An increase in the final pyrolysis temperature from 400 °C to 700 °C caused a decrease in the charcoal yield and an increase in total non-condensable gas production. For all biomasses, with the exception of CH₄ produced from bean straw, which presented as a logistic behavior, the CO₂, CO, and CH₄ emissions increased as the final pyrolysis temperature increased and presented as a natural logarithmic behavior.

Keywords: Carbonization; Heat action on wood; Methane; Thermal effect.

Resumo

Os resíduos de biomassa desempenham papel fundamental no processo de transição para uma matriz energética renovável. Processos de tratamento térmico de biomassa, assim como a pirólise lenta, poderiam fornecer produtos com alta densidade energética e maior valor. O objetivo deste estudo foi avaliar os produtos de pirólise de três resíduos de biomassa obtidos da agricultura (bagaço de cana e palha de feijão) e culturas florestais (eucalipto). O foco deste estudo foi qualificar e quantificar as frações gasosas não condensáveis, de acordo com a temperatura final da pirólise (400, 550 e 700 °C). A análise termogravimétrica foi realizada. O processo de pirólise foi conduzido em mufla. Os subprodutos da pirólise, após passarem pelo processo de recuperação do bio-óleo, foram direcionados para o analisador de gases. Verificou-se que a composição da biomassa pode influenciar diretamente sua degradação térmica, afetando as características dos gases produzidos. O aumento na temperatura final de pirólise de 400 °C para 700 °C causou diminuição no rendimento de carvão e aumento na produção total de gás não condensável. Para todas as biomassas, com exceção do CH₄ produzido a partir da palha de feijão, que apresentou comportamento logístico, as emissões de CO₂, CO e CH₄ aumentaram à medida que a temperatura final da pirólise aumentou e apresentou comportamento logarítmico natural.

Palavras-chave: Carbonização; Ação térmica na madeira; Metano; Efeito térmico.

Financial support: Nothing to declare.

Conflict of interest: Nothing to declare.

Corresponding author: clarissagfigueiro@gmail.com

Received: 19 November 2019.

Accepted: 23 November 2020.

Editor: Paulo Henrique Müller Silva.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

The world's energy sources are related to the use of fossil fuels, which are associated with the social and environmental impacts as a result of global energy demands (Bajwa et al., 2018). In order to reduce non-renewable energy sources, diversification of the energy matrix is a viable alternative to traditional energy sources. Favoring green alternatives for the sustainable development of nations, such as the use of biomass residues (Vadenbo et al., 2018; Fialho et al., 2019) should be an important objective. However, knowledge of the chemistry and thermal behavior of biomass is essential for sustainable energy generation in regional enterprises (Kelty, 2006; Amazonas et al., 2018).

The biomasses chosen for this study have potentials for different reasons. Sugarcane bagasse is produced on a large scale in Brazil, since the country is the largest producer of sugarcane in the world. Bean straw is a residue from legumes, which represents one of the food bases of the country, being the third largest producer in the world of beans (Food and Agriculture Organization of The United Nations, 2017). In addition, legumes are also related to sustainable development due to their usage in crop rotation and in biological nitrogen fixation (Aschi et al., 2017). Eucalypts are the main tree culture planted in Brazil, reducing pressure on natural forest areas and supplying material with best characteristics for many uses (Indústria Brasileira de Árvores, 2017).

The use of biomass residues as a fuel presents limitations, such as high heterogeneity, high moisture content, low calorific value, and low grindability. These characteristics harm its potential use for energy production. In order to turn the biomass residue into a more competitive fuel source, the utilization of an energetic valorization process could be of potential value (Bach & Skreiberg, 2016; Figueiró et al., 2019). Slow pyrolysis is a thermochemical conversion that contributes to the improvement of combustible energy properties. In this thermal degradation process, the biomass is submitted to a slow heating rate in a non-oxidizing atmosphere. The pyrolysis products are charcoal, condensable gas, and non-condensable gas (Pereira et al., 2013).

Slow pyrolysis for the valorization of biomass residue is not a consolidated large-scale technique in agricultural countries such as Brazil. In Brazil, residue production techniques are applied, but these resources are not fully utilized. Approximately 10% of crop residues are reutilized in Brazil for agricultural purposes. It is expected that by 2050, 40% of all crop residues will be harvested through technological advances (Foster-Carneiro et al., 2013; Welfle, 2017). However, an alternative to biomass residue treatment is the processing of all products generated during the slow pyrolysis process; especially its lesser utilized products, e.g., pyrolysis' non-condensable gases.

The pyrolysis gases can be classified as combustibles (carbon monoxide, methane, and hydrogen) and as inert gases (carbon dioxide and oxygen). The combustible fraction, which is rich in carbon and hydrogen, can chemically react with oxygen under appropriate temperature and pressure conditions. This reaction releases thermal energy that could be used for heat and electricity production (Pereira et al., 2017).

The pyrolysis gases are influenced by the pyrolysis conditions (final temperature, time, pressure, and heating rate) and the characteristics of the raw material (species, moisture content, chemical composition, etc.). In this sense, it was important to determine the effects of these factors, in order to create an optimized conversion process for biomass residue (Figueiró et al., 2019). In addition, the qualification and quantification of the combustible gases and inert gases is another fundamental factor for optimizing the conversion process.

The integrated use of slow pyrolysis products could guarantee a supply of high energetic fuel, with a high aggregated value. In this sense, the aim of this study was to evaluate the pyrolysis products of three biomass residues obtained from agriculture (sugarcane bagasse and bean straw) and forestry cultures (eucalypts). The focus of this study was to qualify and quantify the gaseous non-condensable fractions, according to the final pyrolysis temperature.

MATERIAL AND METHODS

Sugarcane (*Saccharum* sp.) bagasse and bean (*Phaseolus vulgaris*) straw (leaves, roots and pods) agricultural residues were used as biomass. The sugarcane was harvested a year-and-half after planting, and the bean straw was harvested with 3 months from a bean plantation. The *Eucalyptus urophylla* wood was harvested from a clonal test, cultivated in 3 meters x 3 meters spacing, with 84 months of age.

The thermogravimetric (TG) analysis was performed in previously ground, sifted, and dried samples according to American Society for Testing and Materials (2007), using a DTG-60H simultaneous measuring instrument (Shimadzu, Kyoto, Japan), under a nitrogen atmosphere. The samples composed of 2 g of material were degraded, with an initial temperature of 100 °C and a final temperature of 700 °C, with a 10 °C/min⁻¹ heating rate. The additional analysis used to further characterize the raw materials are presented in Table 1.

Table 1. Raw Biomass Properties

Ultimate Analysis (dry wt.%) ^a	Eucalypts	Bean Straw	Sugarcane Bagasse
C	47.84	39.30	42.48
H	6.27	5.10	5.16
N	0.61	1.27	0.76
S	0.00	0.22	0.04
O	44.77	47.30	46.47
H/C molar ratio	1.57	1.56	1.46
O/C molar ratio	0.70	0.90	0.82
Component Analysis (dry wt.%)			
Extractives ^b	6.70	21.10	19.68
Lignin ^c	31.70	15.38	22.07
Holocellulose	61.10	56.70	58.25
Ash ^d	0.50	6.82	5.10
HHV, MJ kg ⁻¹ ^e	19.16	17.87	18.27

Analysis procedures used following sources; ^a DIN EN 15104 (German Institute for Standardization, 2011); ^b TAPPI (Technical Association of the Pulp and Paper Industry, 1988); ^c Gomide & Demuner (1986); ^d ABNT NBR 8112 (Associação Brasileira de Normas Técnicas, 1986a); ^e ABNT NBR 8633 (Associação Brasileira de Normas Técnicas, 1986b).

The pyrolysis process was conducted in a laboratory electric oven using a metal container approximately 0.003 m³ in volume. The temperature was managed manually, increasing by 50 °C every 30 min, which corresponded to a heating rate of 1.67 °C/min⁻¹. Three final pyrolysis temperatures were analyzed, 400 °C, 550 °C, and 700 °C.

To determine the amount of condensable gases produced during the pyrolysis process, the gases were conducted at the outlet of the oven into a bio-oil recovery system developed in the Panels and Wood Energy Laboratory from Federal University of Viçosa (LAPEM/UFV) (Fialho et al., 2019). This system consisted of a water cooler tubular condenser coupled to a collecting vessel. The condensable gases was collected in this recovery system and weighed to obtain the total yield. At the end of the collection process, the charcoal and the condensable gases produced were weighed to determine the gravimetric yield of the charcoal, condensable gas, and non-condensable gas *via* gravimetry. To perform the non-condensable gas characterization, the pyrolysis byproducts, after having passed through the bio-oil recovery system, were directed to an on-line gas analyzer (Gasboard 3100 Wuhan CUBIC Optoelectronics Co. Ltd., Wuhan, China). The amount of CO, CO₂, and CH₄ produced throughout the process was measured.

To explain the effect of final pyrolysis temperatures on greenhouse emissions, several regression models were adjusted using R (R Core Team, R Version 3.5.2, Vienna, Austria). The

best adjusted models were selected based on significance of the parameter estimates and the precision measurements of the equations for each biomass, e.g., the adjusted determination coefficient ($\bar{R}^2$), the residual standard error ($Sy.x$) and residues distribution. The graphics of residual dispersion for each biomass and greenhouse gas were plotted using the best fitted model.

RESULTS AND DISCUSSION

The thermogravimetric (TG) analysis of the biomasses are presented in Figure 1. The low thermal degradation of the materials at temperatures between 100 °C and 200 °C was verified, with mass loss rates varying between 0.13% and 0.91%, with an average loss of 0.4%. This temperature range is called the zone of thermal stability, due to the limited degradation of the main constituents in the wood, and only water and some volatile organic compounds are released (van der Stelt et al., 2011).

Figure 1. Thermogravimetric curves (TGA and DTG) of A) eucalypts; B) bean straw; and C) sugarcane bagasse

The mass of the samples significantly decreased between 200 °C and 450 °C, which was the temperature range in which the thermal decomposition of cellulose and hemicellulose occurs (Yang et al., 2007; Kim et al., 2010), whereas the decomposition of lignin occurred in a wider temperature range, which ranged from 225 °C to 900 °C (Pereira et al., 2013). Thus, the abrupt mass variation along the temperature increase was caused by the difference in cellulose or hemicelluloses content between the biomasses. Hemicelluloses form a

heterogeneous group and are generally less stable to thermal degradation, with mass loss occurring over a wide temperature range from 100 °C to 250 °C. Cellulose is a homogeneous and relatively more stable compound, with the largest concentrated mass loss approaching 350 °C (van der Stelt et al., 2011).

Although lignin degradation occurs over a wider temperature range, its total mass loss is lower when compared to cellulose and hemicellulose (Raad et al., 2006; Burhenne et al., 2013). It should be noted that with increasing temperature, hemicellulose and cellulose undergo complex degradation and devolatilization reactions (Khan et al., 2009). Part of the branched chain of the cellulose, as well as the microcrystalline regions, presented extensive depolymerization, thus increasing the proportional content of lignin (Zheng et al., 2017). Part of the lignin content, and a small amount of the cellulose content were decomposed and converted into charcoal. The mass yields of the different pyrolysis products (charcoal, water and condensable gas, and non-condensable gas) are shown in Table 2.

Table 2. Products Yield

Products (%)	Eucalypts			Bean Straw			Sugarcane Bagasse		
	Temperature (°C)								
	400	550	700	400	550	700	400	550	700
Charcoal	38.00	31.65	28.64	41.97	30.22	29.84	40.94	36.21	33.11
Condensable gas	43.50	45.01	45.08	28.84	30.52	27.22	36.06	38.33	38.54
Non-condensable gas	18.50	23.34	26.28	29.19	39.26	42.94	23.00	25.46	28.35

The pyrolysis temperature has a strong influence on the yield of the products. The kinetics of the pyrolysis reactions showed that the primary pyrolysis reactions occurred in the temperature range of 200 °C to 400 °C, which resulted in the formation of the solid product charcoal. At temperatures above 400 °C, the solid residue slowly undergoes chemical and physical transformations that lead to the formation of liquid and gaseous products. Pyrolysis temperatures of up to 600 °C maximize condensable gas production and temperatures above 700 °C maximize gaseous products, while minimizing solid carbon formation (Pütün et al., 2004).

The highest charcoal yield was observed in bean straw at 400 °C (Table 3) and can be explained by the degradation of the organic components, and the preservation of the inorganic components (Phanphanich and Mani 2011). Bean straw had the highest ash content (Table 1) which possibly resulted in a higher charcoal yield, but with a low energy potential, limiting its energetic use. Therefore, the use of charcoal as a soil conditioner, *i.e.* bio-char, is a possible use for this material, while the gas still works as a source of energy.

The charcoal yields of the three biomasses decreased as the temperature increased. The charcoal gravimetric yield depended on both the variables inherent to the biomass itself and the conditions of the pyrolysis process (Carneiro et al., 2016). The variations in the holocellulose (polysaccharide) content and the lignin content directly influenced the gravimetric yield of charcoal. The holocellulose fraction contributed less to the charcoal yield, whereas the lignin fraction contributed the most in the formation of products with high thermal stability and a high carbon content (Haykiri-Acma et al., 2010; Pereira et al., 2013). This characteristic of lignin can be attributed to the phenylpropane units that form strong bonds between them, which give rise to a condensed molecule that has strong resistance properties against thermal degradation (Yang et al., 2007).

The total yield of condensable gas increased as the pyrolysis temperature was increased, with the greatest increase from 400 °C to 550 °C (3.47% in eucalypts, 5.83% in bean straw, 6.30% in sugarcane bagasse). The pyrolysis of the eucalypts biomass led to a higher condensable gases production at 700 °C, with a maximum value of 45.08% (Table 3). At higher reaction temperatures, the proportional condensable gas yield decreased for bean straw and the non-condensable gas yield increased for the three analyzed biomasses. These results were due to the conversion of pyrolysis vapors into gas *via* secondary cracking at high reaction temperatures (Jung et al., 2008).

Eucalypt charcoal is well known for its energetic properties, and therefore the non-condensable gas produced can be used as a secondary byproduct and an additional energy source (Carneiro et al., 2017). For this the most profitable final temperature of the pyrolysis process was 400 °C, in order to generate a higher charcoal yield. When considering the sugarcane bagasse and the bean straw, however, the ash content was so high that the use of this charcoal as an energy source can become unprofitable, since it has low energy density and can cause damage to equipment (Pereira et al., 2013). In this scenario, a higher final pyrolysis temperature can promote a higher yield of advantageous products.

Biochar is a form of charcoal used as a soil conditioner and can be an alternative use of the biomasses presented with a high ash content, since using the solid fraction for energy is unsustainable. Biochar is known as a fertilizer, which can reduce N leaching, increase microbial biomass and diversity in the soil, improve the physical properties of the soil, and can have an acid-neutralizing capacity, dependent on the origin material and the final pyrolysis temperature (van Zwieten et al., 2015; Omondi et al., 2016; Xu et al., 2016).

In this instance, the higher temperatures increased the non-condensable gas yield, which was designated as a fuel source, and the solid fraction was applied to the soil. However, it was important to study the optimal final temperature, since it highly influences the yield and the characteristics of the byproducts, and find the most profitable one, which permits the use of the non-condensable gas as an energy source.

The models that best fit the data dispersion, and the adjustment statistics of these models are presented in Table 3. In general, the equations presented an adequate adjustment to the data for the emission of gases for the three biomasses used.

Table 3. Model Adjustment for the Greenhouse Gas Emissions, Significance of the Parameter Estimates, and Precise Equation Measurements for Each Biomass

Biomass	Greenhouse Gas	Model	Parameters	Estimation of Parameters	p-value	R ²	Sy.x
Eucalypt Wood	Carbon dioxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-242.56	< 0.01	95.4	2.9
			β_1	59.14	< 0.01		
	Carbon monoxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-105.39	< 0.01	94.3	3.35
			β_1	29.29	< 0.01		
	Hydrogen	$X = 1/(\beta_0 + \beta_1 \ln(X))$	β_0	6.10	< 0.01	96.5	0.07
			β_1	-3.86	< 0.01		
	Methane	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-223.82	< 0.01	99.5	0.63
			β_1	38.60	< 0.01		
Bean Straw	Carbon dioxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-877.33	< 0.01	95.8	11.3
			β_1	182.40	< 0.01		
	Carbon monoxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-133.23	< 0.01	98.2	5.2
			β_1	34.52	< 0.01		
	Hydrogen	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-9.93	< 0.01	97.4	0.11
			β_1	1.75	< 0.01		
	Methane	$X = \beta_0/(1 + (X/\beta_1)^{\beta_2})$	β_0	20.07	< 0.01	96.5	1.35
			β_2	429.44	< 0.01		
Sugarcane Bagasse	Carbon dioxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	-13.74	< 0.01	94.05	6.56
			β_1	-380.08	< 0.01		
	Carbon monoxide	$X = \beta_0 + \beta_1 \ln(X)$	β_0	94.06	< 0.01	95.98	1.52
			β_1	-112.06	< 0.01		
	Hydrogen	$X = \beta_0 + \beta_1 \ln(X)$	β_0	33.22	< 0.01	96.40	0.08
			β_1	-6.93	< 0.01		
	Methane	$X = \beta_0 + \beta_1 \ln(X)$	β_0	1.27	< 0.01	99.1	0.98
			β_1	-270.87	< 0.01		

For all the gases, the effects of the final pyrolysis temperature and the biomass used were observed. Most of the gases presented a natural logarithmic behavior; however, for the methane emission of bean straw, a logistic behavior was observed. The emission of gases during the pyrolysis process was dependent on the chemical composition of the biomass and the process variables, such as final temperature, heating rate, pressure, type of reactor, *etc.* (Hu & Gholizadeh, 2019).

During pyrolysis, some hemicelluloses and extractives are the first components to degrade, which are responsible for the first release of CO₂, CO, and CH₄ gases. As the pyrolysis temperature was increased, up to approximately 380 °C, the degradation of cellulose began to occur, which led to a second gas release peak (Loredo Medrano et al., 2016). A majority of the degradation of the biomass components occurred as the pyrolysis process reached the final temperature of approximately 400 °C, which accounted for most of the non-condensable gas emissions.

As temperatures reached 500 °C, a second greenhouse gas release peak occurred, which was characterized by the degradation of the remainder of the hemicelluloses content, as well as some possible high molecular weight extractive. At temperatures above 600 °C, the secondary pyrolysis reactions began to occur, in addition to the intensification of lignin degradation. During this stage a new release peak of CO₂, CO, and CH₄ was observed (Figure 2) (Toro-Trochez et al., 2019).

Figure 2. The dispersion of data and the model adjustment of greenhouse gas emissions for each biomass. Legend: Carbon D. = Carbon dioxide; Carbon M. = Carbon monoxide; EW = Eucalypt wood; BS = Bean straw; SC = Sugarcane bagasse.

The cracking and reformation of the COOH groups and the carboxyl groups were primarily responsible for the release of CO₂ (Yang et al., 2007). The highest release rate of CO₂ was observed in bean straw, with less released from sugarcane bagasse, and even less from eucalypts wood. This result showed that higher cellulose, hemicelluloses, and lignin content was found in the structural components of the bean straw, compared to the other biomasses used.

The primary CO emissions were from the cracking of carbonyl (C-O-C) and carboxyl (CO) groups. At temperatures below 600 °C, the primary cause of the emission of CO was from the degradation of hemicelluloses, as lignin only contributed to CO emissions at temperatures above 760 °C (Parascanu et al., 2017). The gradual degradation of the wood components as related to the increase of the final pyrolysis temperature was demonstrated by the natural logarithmic behavior observed during the pyrolysis process. However, for the methane emission during the bean straw pyrolysis process, a different behavior was observed.

Methane emission was caused by the cracking of the methoxyl-O-CH₃ groups (Yang et al., 2007). Methoxyl-O-CH₃ groups are found in the three main components of wood; cellulose, hemicelluloses, and lignin, with lignin being primarily responsible for the emission of methane at high temperatures. Bean straw had a low lignin content (Table 1), and at high temperatures, there was a reduction in methane emissions due to the low amount of lignin to be degraded. This low lignin content explained the logistic behavior of the methane emission for the bean straw.

The non-condensable gas emitted during pyrolysis are considered a residue. However, these gases have a potential to be used as a by-product of this process, as methane and carbon monoxide have a high calorific value of 55.4 MJ/Kg and 10.0 MJ/Kg, respectively. Therefore, these gases can be burned to produce thermal energy and this energy can be used as a by-product for the generation of electricity, biomass drying, etc.

The use of pyrolysis products is an alternative to add value to the residues produced as byproducts, which can contribute to the optimized usage of resources. Such products can be utilized to; produce thermic and electric energy (charcoal, non-condensable gases, and condensable gases), as a soil conditioner (bio-char), and in the production of chemical products (bio-oil). The incorporation of valorization routes for biomass residues can contribute to the sustainability of the enterprise, diminishing costs with electricity, fertilizers, and even increase profits from the sale and processing of bio-oil. In addition, the environmental impact is lessened, since these waste products will no longer be considered an environmental liability.

The route of exploitation for biomass residues will be dependant on the attributes of each company. Certain factors should be taken into consideration for the usage of residues, such as; the type of crop and its energetic proprieties, the infrastructure of the company, the amount of capital available for investment, and the availability and characteristics of the consumer market. The pyrolysis process has strong potential for valorization, due to the potential of producing various products that can be destined for multiple uses.

CONCLUSIONS

1. The increase of the final temperature of pyrolysis from 400 °C to 700 °C caused a decrease in the yield of charcoal and an increase in the production of non-condensable gases.
2. For all biomasses, with the exception of CH₄ produced from bean straw, which presented as a logistic behavior, the CO₂, CO, and CH₄ emissions increased as the final pyrolysis temperature increased and presented a natural logarithmic behavior.

ACKNOWLEDGEMENTS

The authors would like to thank the Brazilian agencies "Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES/PELD), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), and Programa Cooperativo sobre Proteção Florestal (PROTEF) do Instituto de Pesquisas e Estudos Florestais (IPEF)" for the scholarships and financial support.

REFERENCES

- Amazonas, N. T., Forrester, D. I., Silva, C. C., Almeida, D. R. A., Rodrigues, R. R., & Brancalion, P. H. S. (2018). High diversity mixed plantations of Eucalyptus and native trees: an interface between production and restoration for the tropics. *Forest Ecology and Management*, 417, 247-256.

- American Society for Testing and Materials – ASTM. (2007). *ASTM D240-02: standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter*. West Conshohocken: ASTM International.
- Aschi, A., Aubert, M., Riah-Anglet, W., Nélieu, S., Dubois, C., Akpa-Vinceslas, M., & Trinsoutrot-Gattin, I. (2017). Introduction of Faba bean in crop rotation: impacts on soil chemical and biological characteristics. *Applied Soil Ecology*, 120, 219-228.
- Associação Brasileira de Normas Técnicas – ABNT. (1986a). *ABNT NBR 8112 : carvão vegetal: análise imediata*. Rio de Janeiro: ABNT.
- Associação Brasileira de Normas Técnicas – ABNT. (1986b). *ABNT NBR 8633: carvão vegetal: determinação do poder calorífico: método de ensaio*. Rio de Janeiro: ABNT.
- Bach, Q. V., & Skreiberg, O. (2016). Upgrading biomass fuels via wet torrefaction: a review and comparison with dry torrefaction. *Renewable & Sustainable Energy Reviews*, 54, 665-677.
- Bajwa, D. S., Peterson, T., Sharma, N., Shojaeiarani, J., & Bajwa, S. G. (2018). A review of densified solid biomass for energy production. *Renewable & Sustainable Energy Reviews*, 96, 296-305.
- Burhenne, L., Messmer, J., Aicher, T., & Laborie, M. P. (2013). The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 101, 177-184.
- Carneiro, A. C. O., Vital, B. R., Frederico, P. G. U., Figueiró, C. G., Fialho, L. F., & Silva, C. M. S. (2017). Energetic characterization of the wood from Eucalyptus clones grown in different localities. *Brazilian Journal of Wood Science*, 8(3), 127-135.
- Carneiro, A. D. C. O., Vital, B. R., Frederico, P. G. U., Fialho, L. D. F., Figueiró, C. G., & Silva, C. M. S. (2016). Effect of genetic materials and the site in charcoal quality of short rotation wood. *Floresta*, 46(4), 473-480.
- Fialho, L. F., Carneiro, A. C. O., Carvalho, A. M. M. L., Figueiró, C. G., Da Silva, C. M. S., Magalhães, M. A., & Peres, L. C. (2019). Bio-coal production with agroforestry biomass in Brazil. *Maderas. Ciencia y Tecnología*, 21(3), 1-20.
- Figueiró, C. G., Vital, B. R., Carneiro, A. C. O., Silva, C. M. S., Magalhães, M. A., & Fialho, L. F. (2019). Energy valorization of woody biomass by torrefaction treatment: a Brazilian experimental study. *Maderas Ciencia y Tecnología*, 21(3), 1-16.
- Food and Agriculture Organization of The United Nations – FAO. (2017). *Statistics Division – FAOSTAT*. Retrieved in 2019, November 19, from <http://www.fao.org/faostat/en/#data/QC>
- Foster-Carneiro, T., Berni, M. D., Dorileo, I. L., & Rostagno, M. A. (2013). Biorefinery study of availability of agriculture residues & wastes for integrated biorefineries in Brazil. *Resources, Conservation and Recycling*, 77, 78-88.
- German Institute for Standardization. (2011). *DIN EN 15104: solid biofuels: determination of total content of carbon, hydrogen and nitrogen: instrumental methods*. Berlin.
- Gomide, J. L., & Demuner, B. J. (1986). Determinação do teor de lignina em material lenhoso: método Klason modificado. *O Papel*, 47(8), 36-38.
- Haykiri-Acma, H., Yaman, S., & Kucukbayrak, S. (2010). Comparison of the thermal reactivities of isolated lignin and holocelulose during pyrolysis. *Fuel Processing Technology*, 91(7), 759-764.
- Hu, X., & Gholizadeh, M. (2019). Biomass pyrolysis: a review of the process development and challenges from initial researches up to the commercialization stage. *Journal of Energy Chemistry*, 39, 109-143.
- Indústria Brasileira de Árvores – IBÁ. (2017). *Relatório anual 2017* (77 p.) Brasília.
- Jung, S.-H., Kang, B. S., & Kim, J. S. (2008). Production of bio-oil from rice straw and bamboo sawdust under various reaction conditions in a fast pyrolysis plant equipped with a fluidized bed and a char separation system. *Journal of Analytical and Applied Pyrolysis*, 82(2), 240-247.
- Kelty, M. J. (2006). The role of species mixtures in plantation forestry. *Forest Ecology and Management*, 233(2-3), 195-204.
- Khan, A. A., De Jong, W., Jansens, P. J., & Spliethoff, H. (2009). Biomass combustion in fluidized bed boilers: potential problems and remedies. *Fuel Processing Technology*, 90(1), 21-50.
- Kim, S. J., Jung, S. H., & Kim, J. S. (2010). Fast pyrolysis of palm kernel shells: influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresource Technology*, 101(23), 9294-9300.

- Loredo Medrano, J. A., Bustos Martínez, D., Rivera De la Rosa, J., Carrillo Pedraza, E. S., Flores-Escamilla, G. A., & Ciuta, S. (2016). Particle pyrolysis modeling and thermal characterization of pecan nutshell. *Journal of Thermal Analysis and Calorimetry*, 126(2), 969-979.
- Omondi, M. O., Xia, X., Nahayo, A., Liu, X., Korai, P. K., & Pan, G. (2016). Quantification of biochar effects on soil hydrological properties using meta-analysis of literature data. *Geoderma*, 274, 28-34.
- Parascanu, M. M., Sandoval-Salas, F., Soreanu, G., Valverde, J. L., & Sanchez-Silva, L. (2017). Valorization of Mexican biomasses through pyrolysis, combustion and gasification processes. *Renewable & Sustainable Energy Reviews*, 71, 509-522.
- Pereira, B. L. C., Carneiro, A. C. O., Carvalho, A. M. M. L., Colodette, J. L., Oliveira, A. C., & Fontes, M. P. F. (2013). Influence of chemical composition of eucalyptus wood on gravimetric yield and charcoal properties. *BioResources*, 8(3), 4574-4592.
- Pereira, E. G., Martins, M. A., Pecenka, R., & Carneiro, A. C. O. (2017). Pyrolysis gases burners: sustainability for integrated production of charcoal, heat and electricity. *Renewable & Sustainable Energy Reviews*, 75, 592-600.
- Phanphanich, M., & Mani, S. (2011). Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource Technology*, 102(2), 1246-1253.
- Pütün, A. E., Apaydin, E., & Pütün, E. (2004). Rice straw as a bio-oil source via pyrolysis and steam pyrolysis. *Energy*, 29(12-15), 2171-2180.
- Raad, T. J., Pinheiro, P. C. C., & Yoshida, M. I. (2006). General equations of carbonization of *Eucalyptus* spp. kinetic mechanisms. *Cerne*, 12(2), 93-106.
- Technical Association of the Pulp and Paper Industry – TAPPI. (1988). *TAPPI T204 om-88: solvent extractives of wood and pulp*. Atlanta: TAPPI Press.
- Toro-Trochez, J. L., Carrillo-Pedraza, E. S., Bustos-Martínez, D., García-Mateo, F. J., Ruiz-Rosas, R. R., Rodríguez-Mirasol, J., & Cordero, T. (2019). Thermogravimetric characterization and pyrolysis of soybean hulls. *Bioresource Technology Report*, 6, 183-189.
- Vadenbo, C., Tonini, D., Burg, V., Astrup, F., Thees, O., & Hellweg, S. (2018). Environmental optimization of biomass use for energy under alternative future energy scenarios for Switzerland. *Biomass and Bioenergy*, 119, 462-472.
- van der Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., & Ptasinski, K. J. (2011). Biomass upgrading by torrefaction for the production of biofuels: a review. *Biomass and Bioenergy*, 35(9), 3748-3762.
- van Zwieten, L., Rose, T., Herridge, D., Kimber, S., Rust, J., Cowie, A., & Morris, S. (2015). Enhanced biological N₂ fixation and yield of faba bean (*Vicia faba* L.) in an acid soil following biochar addition: dissection of causal mechanisms. *Plant and Soil*, 395(1-2), 7-20.
- Welfle, A. (2017). Balancing growing global bioenergy resource demands - Brazil's biomass potential and the availability of resource for trade. *Biomass and Bioenergy*, 105, 83-95.
- Xu, N., Tan, G., Wang, H., & Gai, X. (2016). Effect of biochar additions to soil on nitrogen leaching, microbial biomass and bacterial community structure. *European Journal of Soil Biology*, 74, 1-8.
- Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 86(12-13), 1781-1788.
- Zheng, Y., Tao, L., Yang, X., Huang, Y., Liu, C., Gu, J., & Zheng, Z. (2017). Effect of the torrefaction temperature on the structural properties and pyrolysis behavior of biomass. *BioResources*, 12(2), 3425-3447.

Authors' contributions: CGF, LFF and ACOC: conceptualization, supervision, data curation, writing - original draft; LCP, PGS and VRC: methodology, writing - review & editing.