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Keywords:
Biochar
Biomass
Carbon immobilization
Soil conditioner
Charcoal

ABSTRACT: The use of biomass for biochar production is already a reality. However, little is known about its structure and composition, mainly due to the changes occurred during the heat treatment. This information is crucial since it will have an immediate impact on the quality and applicability of the material produced. Therefore, this study aimed to analyze different biomasses, characterizing their potential for biochar production. Woods from *Eucalyptus urophylla* and *Corymbia citriodora* and coffee husk were assessed. The biomass was ground and sieved, and then stored under controlled conditions of temperature and humidity. Subsequently, the material characterizations were performed through proximate analysis, elemental analysis, thermogravimetric analysis and Fourier transform infrared spectroscopy (FTIR). In general, all biomasses presented potential to be used in the production of biochar, where low H/C and O/C ratios were found. The coffee husk has higher lignin, extractives, ash and fixed carbon contents, which certainly contributed to its greater thermal stability. The FTIR analysis showed the presence of bands related to recalcitrant chemical groups such as carboxylics and phenolics in the spectra of all biomasses. The thermogram profiles of the *C. citriodora* and *E. urophylla* wood were similar to each other, and different from that of the coffee husk, which showed higher thermal stability.

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CARACTERIZAÇÃO DE DIFERENTES BIOMASSAS VEGETAIS PARA PRODUÇÃO DE BIOCARVÕES

Palavras chave:
Biochar
Biomassa vegetal
Imobilização de carbono
Condicionador de solo
Carvão vegetal

RESUMO: A utilização da biomassa para produção de biocarvões já é uma realidade. Porém, pouco se sabe sobre a sua estrutura e composição, principalmente, mediante as transformações ocorridas durante o tratamento térmico. Estas informações são fundamentais, uma vez que terão impacto imediato na qualidade e aplicabilidade do material produzido. Portanto este trabalho objetivou analisar diferentes biomassas, caracterizando-as como potenciais para produção de biocarvões. Foram utilizadas madeiras de *Eucalyptus urophylla* e *Corymbia citriodora* e cascas de café. As biomassas foram moídas e peneiradas e, em seguida, armazenadas sob condições de temperatura e umidade controlada. Posteriormente realizou-se a caracterização dos materiais, por meio de análise química, química imediata, elementar (CHNS-O), térmica (TGA e DTA) e de espectroscopia vibracional na região do infravermelho (FTIR). De forma geral, todas as biomassas apresentaram potencial para serem utilizadas na produção de biocarvão, no entanto, a casca de café apresentou maiores teores de lignina, extrativos, cinzas e carbono fixo, o que, certamente, contribuiu para que a mesma apresentasse maior potencial de utilização como condicionador de solos. Com relação à análise de FTIR, observou-se a presença de bandas referentes aos grupos químicos recalcitrantes, como os carboxílicos e fenólicos nos espectros de todas as biomassas. O perfil dos termogramas de *C. citriodora* e de *E. urophylla* foram semelhantes entre si e diferentes da casca de café, que apresentou maior estabilidade térmica.

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INTRODUCTION

Brazil has huge forests and is a massive agricultural producer and, consequently, a large amount of raw material and waste is produced each year in all regions of the country. Although some producers have plans for environmental management and integrated use of its by-products, waste is still improperly discarded, causing serious damage to the environment, such as soil and water contamination.

Among agricultural waste, coffee husks obtained from the bean processing can be highlighted as an interesting potential raw material, since it is produced on a large scale in Brazil. Brazil is the world's largest coffee producer and, in 2015, approximately 43.23 million bags (60 kilograms) of processed coffee (CONAB, 2016) were harvested. On the other hand, the waste content produced in this process can reach 50% of the harvest volume (ROCHA et al., 2006).

The Brazilian forest sector occupies 7.74 million hectares, which correspond to 0.9% of the national territory, accounting for up to 91% of wood production for industrial purposes. From this total of forest crops, around 71.9% correspond to *Eucalyptus spp.*, mainly located in the states of Minas Gerais (25.2%), São Paulo (17.6%) and Mato Grosso do Sul (14.5%) (INDÚSTRIA BRASILEIRA DE ÁRVORES - IBÁ, 2015). There are many products that can be obtained from forest plantations, like: pulp and paper, lumber, panels and charcoal. However, many researchers seek the development of innovative bioproducts, which may contribute to environmental and energy issues, as well as for the future demand for food, soil and water.

New technologies have been developed aiming to transform biomass and waste materials into higher value-added products. Research has shown that, with adequate treatment, different biomass and wastes may be used to retain nutrients in the soil (GLASER; LEHMANN; ZECH, 2002). Another strategy is the thermal treatment process optimization in procedures by which the biomass is transformed into biochar, such as in boilers and industrial furnaces, reducing gas emission and generating specific biochar structures with desirable properties to be used in poor soils.

The motivation for the transformation of biomass into biochar is based on soils from the Amazon region, called "Terras Pretas de Índio" or Indian Dark Earth. These soils presents high fertility and stable carbon in their organic fraction, which contrast very strongly with adjacent soils, which are characterized by having low fertility and limited agricultural use (GLASER et al., 2001).

Some investigation was performed (CHEN et al., 2015; ZENG et al., 2015; ZHAO et al., 2013) aiming to reproduce carbonaceous material similar to that found in Terras Pretas de Índio. Previously, it is important to perform a precursor selection, since each biomass has different composition, reacting differently when carbonized; hence essential to characterize their structure and applicability in different soil conditions.

Eucalyptus wood, whether or not originating from waste, as well as coffee husk, has been shown to have potential for use as a biochar. However, to optimize the use of such materials, it is essential to investigate their properties, as well as their behavior in soil. Thus, this study aimed to characterize *Eucalyptus* wood and coffee husk biomass or feedstock, evaluating their potential for biochar production.

MATERIAL AND METHODS

Material

The coffee husks (shell + pulp + parchment) of *Coffea Arabica* obtained through the pulping process (dry coffee beans) and *Eucalyptus urophylla* and *Corymbia citrodora* wood from the DAP region (7-years-old) were used in this study. Three trees were used per eucalipto species, while for the coffee, the samples were taken from the same batch. The samples of the different biomasses were obtained according to Table 1.

TABLE 1 Information on the biomasses.

Material	Specie	Company	Town
Coffee husk	*Coffea Arabica*	Limeira farm	Nepomuceno/MG/ Brazil
Wood	*Corymbia citriodora*	Vallourec Florestal Ltda.	Paraopeba/MG/ Brazil
Wood	*Eucalyptus urophylla*	Vallourec Florestal Ltda.	Paraopeba/MG/ Brazil

Statistical analysis

Three replicates were used per material for all analyzes, totaling 9 samples. For wood species, three individuals were used per species, while for the coffee tree the three replications were taken from the same batch. The results were submitted to variance analysis (ANOVA). In case of significant differences, average comparisons were performed by the Tukey test (α=5%).

Extractive content

Extractive content was quantified using the biomass fraction retained between 40-60 mesh sieves, according to NBR 14853 (ASSOCIAÇÃO BRASILEIRA

DE NORMAS TÉCNICAS - ABNT, 2010). A soxhlet extractor was used and samples were submitted to extraction sequence with toluene-ethanol in the ratio 2:1 (5 hours), ethanol (4 hours) and hot water (2 hours).

Lignin content

The insoluble lignin content was quantified according to the procedure described in NBR 7989 (ABNT, 2010). Samples of approximately 2 g, absolutely dry and without extractives, were used. The solvent was sulfuric acid (72%) maintained cold at 10 – 15ºC.

The soluble lignin (SL) content was determined by spectrophotometry using the equation described by Goldschimid (1971), according to Equation 1. The total lignin content was the sum of soluble and insoluble lignin.

$$\%SL = \left(\left(4.538 * absorbance(215nm)\right) - absorbance(280)\right) * 1.11 \quad [1]$$

Holocellulose content

The holocellulose content was obtained by the difference in relation to other chemical and mineral constituents.

Proximate analysis and nutrient content

Moisture, volatile materials, ash and fixed carbon content were quantified by proximate analysis according to NBR 8112 (ABNT, 1986). Fixed carbon content was quantified by mass difference. Biomass fractions retained between 40-60 *mesh* after sieving were used for analysis.

The nutrient content analysis was performed according to the nitroperchloric digestion methodology proposed by Malavolta, Vitti and Oliveira (1997), using the atomic absorption spectrometry technique, UV-visible spectrometer at 420 nm and flame photometer.

Elemental analysis

Carbon, nitrogen, hydrogen, sulfur and oxygen were quantified in elemental analysis. The oxygen content was quantified by difference. The analyses were carried out in an universal analyzer (Elemental, model Vario Micro Club) using samples with sizes between 200-260 *mesh* . The analyzer uses helium and oxygen as input gas and ignition gases, respectively. The 2 mg samples were packed in tin capsules and completely incinerated at 1,200°C.

Thermogravimetric analysis -TGA

The biomass thermal behavior and stability were investigated by TGA in a Shimadzu-DTG 60 H analyzer. This analysis was carried out from 25 to 900°C, with heating rate of 10°C·min^{-1} under N_2 atmosphere and flow of 50 mL·min^{-1}.

Fourier transformed infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy was performed in the infrared region aiming to identify surface functional groups. Spectra were obtained in a Digilab-Excalibur spectrophotometer, using KBr tablets (4 cm^{-1} resolution and 8 accumulations). Approximately 3 mg of each sample and 97 mg of KBr were used for FTIR analysis.

RESULTS AND DISCUSSION

Biomass chemical characterization

A comparison of the chemical and physical properties among biomasses was performed aiming to better understand the behavior of each biomass. According to Table 2, there are significant differences in chemical composition of the biomasses, with the coffee husk showing higher extractive, lignin and ash contents. These results are similar to the findings of Protásio et al. (2012), since agricultural wastes, such as corn, coffee, rice and cane wastes tend to have higher levels of lignin and extractives, while forest biomass tends to have lesser ash amount.

TABLE 2 Means of the main chemical components of coffee husk, Corymbia citriodora and Eucalyptus urophylla wood.

Chemical analysis	Biomass (%)			
	Coffee husk	*Corymbia citriodora*	*Eucalyptus urophylla*	Experimental coefficient of variation
Extractives	47.38 C $^{(0.08)*}$	14.09 B $^{(0.31)}$	12.30 A $^{(0.06)}$	0.76
Total lignin	29.55 C $^{(0.40)}$	24.10 A $^{(0.31)}$	27.48 B $^{(0.69)}$	1.82
Holocellulose	15.32 A $^{(0.37)}$	61.63 C $^{(0.21)}$	59.81 B $^{(0.61)}$	0.94
Ashes	7.75 C $^{(0.05)}$	0.19 A $^{(0.01)}$	0.41 B $^{(0.02)}$	1.05

Values followed by the same letter in the same line do not differ from each other by the Tukey test (α=0.05); *Sample standard deviation.

Coffee husk has extractive content approximately three times higher (47.38%) than *Corymbia citriodora* (14.09%) and *Eucalyptus urophylla* (12.30%) wood. Biomass extractive content, as well as the persistence of its oxygen-functional groups during the thermal conversion process, contributes to higher cation exchange capacity of biochar (AMONETTE; JOSEPH, 2009). Thus, this impacts the capacity to retain nutrients in the cation form available to plants, which is directly reflected in its potential use as a soil conditioner.

Coffee husk shows low holocellulose content (15.32%), followed by *Eucalyptus urophylla* (59.81%) and *Corymbia citriodora* (61.63%) (Table 2). Holocellulose is composed of hemicellulose and cellulose and according to Raveendran, Ganesh and Khilar (1996), cellulose produces about 24% charcoal (wood base) while hemicellulose produces 12% charcoal and volatile materials. Therefore, for charcoal yield, lignin is the main component. Due to its high thermal stability, it is responsible for up to 55% of charcoal production.

Couto et al. (2015), studying anatomical, physical and chemical properties of *Corymbia citriodora* and *Eucalyptus urophylla,* reported total lignin values ranging from 24.87 to 27.08% for *Corymbia citriodora* and from 28.51 to 34.45% for *Eucalyptus urophylla*, corroborating results found in this study. Protásio et al. (2012), studying the waste from coffee processing, reported lignin content of 31.03%, similar to the content presented in Table 2.

Generally, biomass which present higher amounts of lignin and nutrients in its composition result in biochar with higher ash, nutrient content, electric conductivity and thermal stability, thus consequently higher potential for use as a soil conditioner (KLOSS et al., 2012). Analyzing wood ash content of *Corymbia citriodora* (0.19%), *Eucalyptus urophylla* (0.41%) and coffee husk (7.75%) (Table 2), the agricultural biomass showed an ash content seven times higher than the others. According to Nanda et al. (2012), the ash chemical composition is an important feature to be observed during the conversion of biomass into biochar, since it may contribute to increase soil fertility.

The mean content obtained by biomass elemental analyses is shown in Table 3. *C. citriodora* and *E. urophylla* wood showed higher carbon content when compared to coffee husk. *Eucalyptus urophylla* had higher carbon content. The oxygen content of *C. citriodora* and *E. urophylla* is close to that of the coffee husk. The hydrogen content was statistically the same for all evaluated biomasses. *C. citriodora* and *E. urophylla* showed less nitrogen and sulfur content.

Elemental analyses presented in Table 3 are in accordance with the values found in other studies (BRUM, 2007; PAULA et al., 2011; SEYE; CORTEZ; GÓMEZ, 2003; SANTOS et al., 2012; COUTO et al., 2013). Observing these values, all materials show high H/C and O/C ratios, which indicates presence of aromatic structures (Zheng et al., 2013). Some authors (ANGIN, 2013; LEE et al., 2013; ZHENG et al., 2013) affirm that when biomass undergoes heat treatment, it tends to be more carbonaceous and, as a consequence of hemicellulose thermal degradation, part of the oxygen and aromatic components are lost. Thus, the H/C and O/C ratios tend to decrease with the increase of the temperature during pyrolysis, giving origin to a material that is more resistant to degradation.

TABLE 3 Mean values of elemental analysis of coffee husk, *Corymbia citridora* and *Eucalyptus urophylla* woods.

Elemental analysis	Biomass (%)		
	Coffee husk	*Corymbia citriodora*	*Eucalyptus urophylla*
Carbon	43.79 A (1.66)*	46.59 B (2.50)	49.17 C (1.34)
Hydrogen	5.64 A (1.72)	5.67 A (3.65)	5.97 A (1.38)
Nitrogen	2.74 B (0.21)	0.48 A (5.60)	0.66 A (4.65)
Sulfur	0.14 B (4.75)	0.02 A (27.45)	0.01 A (48.31)
Oxygen	47.69 B (1.72)	47.24 B (3.00)	44.20 A (1.32)
H/C	1.54 B (0.69)	1.45 A (1.90)	1.45 A (2.68)
O/C	0.81 B (3.35)	0.76 B (5.56)	0.67 A (2.64)

C: carbon; H: hydrogen; O: oxygen; Values followed by the same letter in the same line do not differ from each other by Tukey test (α=0.05); *Values of sample variation content (%).

The humic substances found in "Terras Pretas de Índio" are references for biochar production, showing high aromaticity, providing high soil stability and high reactivity, mainly due to the carboxyl groups that occur in these molecules (CUNHA et al., 2007). These properties are strongly desirable when biochar is intended to produce an organic conditioner for use in tropical soils, resulting in good persistence and high cation-exchange capacity.

The mean values of volatile materials, ash and fixed carbon of biomasses, as well as the percentage of nutrients are showed in Table 4. The coffee husk presented much higher nitrogen, phosphorus, potassium, calcium, magnesium and sulfur values than the woods of *C. citriodora* and *E. urophylla*, which will certainly contribute to the formation of biochar with better physical and chemical characteristics, and consequently, greater use potential.

Generally, coffee husk showed higher ash and fixed carbon content, followed by *Corymbia citriodora* and *Eucalyptus urophylla* wood (Table 4). Possibly, the high level of minerals in coffee husk (Table 4) contributed to increase ash content. In the literature the ash content is reported to vary from 9 to 13.86% for coffee husk, and from 0.17 to 0.34% in *Eucalyptus* wood (ARANTES

TABLE 4 Mean values of proximate analysis and the percentage of nutrients of the biomass used in biochar production.

Composition	Biomass (%)		
	Coffee husk	*Corymbia citriodora*	*Eucalyptus urophylla*
Volatile materials	70.02 A	80.10 B	83.35 C
Fixed carbon	22.12 C	19.51 A	16.46 B
Ash	7.86 C	0.19 A	0.39 B
Nitrogen	1.71	0.21	0.11
Phosphorous	0.14	0.00	0.00
Potassium	2.00	0.06	0.04
Calcium	0.71	0.39	0.28
Magnesium	0.15	0.04	0.01
Sulfur	0.05	0.00	0.00

* Values followed by the same letter do not differ from each other by the Tukey test (α=0.05).

et al., 2008; PROTÁSIO et al., 2012; TRUGILHO; LIMA; MORI, 2003; VALE et al., 2007), agreeing with the values found in this study.

Fixed carbon is an important information of biomass quality since it is the most resistant portion that remains in biochar after pyrolysis. It is organized in aromatic chains (AMONETTE; JOSEPH, 2009) and is inversely related to volatile materials and ash content, which explains its higher content in coffee husks (Table 4). Fixed carbon and lignin content are the most important components for thermal stability, directly reflecting in biochar permanence in soil.

Vale et al. (2007), studying the energy potential of coffee husks, reported volatile materials similar to those found in this study (75.73%), and lower fixed carbon content (10.31%). Paula et al. (2011) studied coffee parchment and *Eucalyptus* sp. wood sawdust and reported fixed carbon content of 19.90 and 21.03%, respectively, and volatile materials content of 79.14 and 78.89%, respectively.

Fourier transformed infrared spectroscopy (FTIR)

The spectra acquired by Fourier Transformed Infrared Spectroscopy showed information about chemical groups present in the biomass structure (Figure 1).

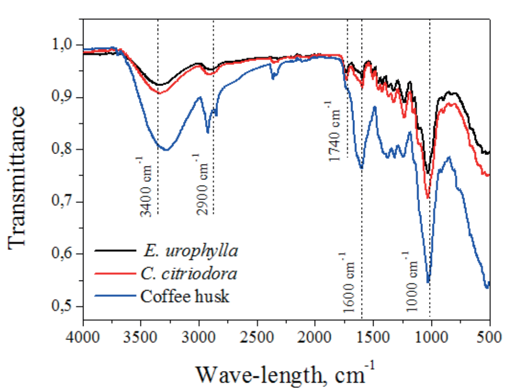

FIGURE 1 FTIR spectra of coffee husk, *Eucalyptus urophylla*, and *Corymbia citriodora* wood.

The Figure 1 shows a large band at 3400 cm^{-1}, which corresponds to the presence of hydroxyl groups. The 2900 cm^{-1} band, in both spectra, is related to the C-H stretching of cellulose and hemicellulose vibration (CASTRO, 2003).

The 1740 cm^{-1} band in *C. citriodora* and *E. urophylla* spectra corresponds to the C=O axial stretching (carbonyl group) (IBRAHIM et al., 2010). In the coffee husk spectrum, the 1600 cm^{-1} band seems to have higher intensity and may be related to the C=C bond of aromatic groups (COUTO et al., 2012). This fact corroborates with the results presented in Table 2, where a high lignin level was reported for coffee husks, affecting this band intensity.

According to Hergert (1971), the 1512 and 1431 cm^{-1} bands (Figure 1) are related to the lignin aromatic ring vibration and is specific to the guaiacyl type. The 1320 and 1330 cm^{-1} signals refer to vibrations of the guaiacyl-syringyl ring and the band between 1250 and 1270 cm^{-1} of guaiacyl rings (ABREU; OERTEL, 1999). In the *C. citriodora* and *E. urophylla* spectra, the bands between 1500-1250 cm^{-1} were not well defined, because this band region overlays with different groups.

Near the 900 cm^{-1} band, in both *C. citriodora* and *E. urophylla* spectra (Figure 1), there is a band with low intensity that is related to cellulose. Generally, the bands observed below 1000 cm^{-1} are associated with cellulose hydroxyl groups (CASTRO, 2003).

Thermogravimetric analysis

According to Gani and Naruse (2007), biomass volatilization and thermal degradation are intimately related to the chemical composition, especially cellulose and lignin content. Thermograms provide information about thermal stability and biomass composition (Figure 2).

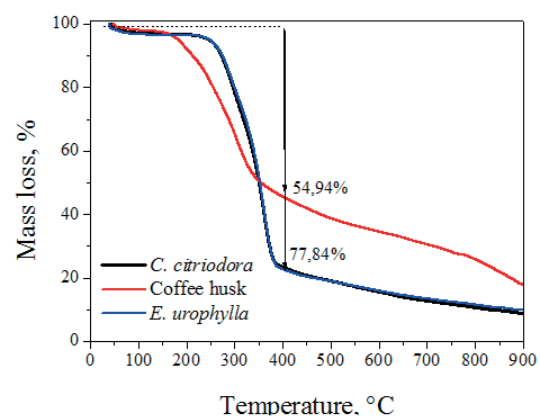

FIGURE 2 Mass loss with temperature raise in coffee husk, *Corymbia Corymbia*, and *Eucalyptus urophylla* woods.

All biomass showed three mass loss zones. The first, and presenting lower mass loss at temperatures around 100°C, is generally attributed to water loss. The second zone between 250 and 350°C refers to the hemicellulose degradation and also the degradation of a small amount of cellulose. The third zone between 350 and 500°C refers to cellulose and lignin degradation as reported by Ouajai e Shanks (2005).

The thermograms of *C. citriodora* and *E. urophylla* wood showed similar thermal stability, while coffee husk shows higher thermal stability. Coffee husk showed

54.94% mass loss at 400ºC, while *C. citriodora* and *E. urophylla* showed 77.84%. This result can be attributed to the higher lignin and fixed carbon contents in coffee husk (Tables 1 and 3). According to Shafizadeh (1985), lignin is the highest molecular mass and thermal stability component due to the carbon-carbon bonds between phenyl-propane monomeric units.

According to Figure 2, *Eucalyptus urophylla* and *Corymbia citriodora* showed higher mass loss between 250 and 350ºC, which is attributed to the holocellulose content in these materials. Similar results were found by Protásio et al. (2013), evaluating the thermal degradation of briquettes produced from *Eucalyptus* and coffee wastes. The authors observed that coffee husk showed higher fixed carbon, lignin content and better thermal stability.

As presented in Figure 2, *C. citriodora* and *E. urophylla* wood showed a peak of higher intensity between 180 and 400ºC, evidencing higher mass loss at this temperature, which may be related to hemicellulose and cellulose loss (Figure 3) (CONZ, 2015).

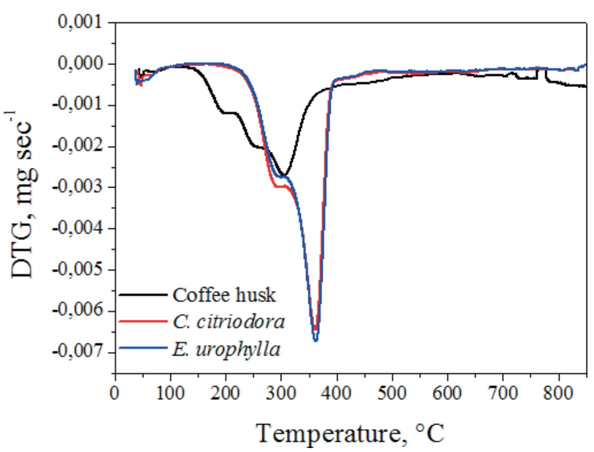

FIGURE 3 DTG of coffee husk and *Corymbia citriodora* and *Eucalyptus urophylla* wood.

CONCLUSIONS

The Coffee husk, *Corymbia citriodora,* and *Eucalyptus urophylla* wood spectra confirmed the presence of carboxylic and phenolic chemical groups. Coffee husk showed higher fixed carbon and nutrient contents, which is directly related to higher lignin and extractives content found in its composition.

Thermograms of *C. citriodora* and *E. urophylla* woods are similar, and different from that of coffee husk, which showed higher thermal stability, due to higher lignin content.

Generally, coffee husk, *C. citriodora,* and *E. urophylla* wood are potential biomasses to be used as precursors for biochar production. However, the coffee husk use for biochar production is specially promising because of its physical, chemical and thermal characteristics.

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REFERENCES

ABREU, H. S.; OERTEL, A. C. Estudo químico da lignina de Paullinia rubiginosa. **Cerne**, Lavras, MG, v. 5, n. 1, p. 52-60, 1999.

AMONETTE, J. E.; JOSEPH, S. Characteristics of *biochar*: microchemical properties. In: LEHMANN, J.; JOSEPH, S. (Ed.). ***Biochar* for environmental management science and technology**. London: Earthscan, 2009. p. 34-51.

ANGIN, D. Effect of pyrolysis temperature and heating rate on *biochar* obtained frompyrolysis of safflower seed press cake. **Bioresource Technology**, Oxford, v. 128, p. 593-587, Jan. 2013.

ARANTES, M. D. C.; MENDES, L. M.; RABELO, G. F.; SILVA, J. R.M.; MORI, F. A. BARBOSA, A. M. Gaseificação de materiais lignocelulósicos para geração de energia elétrica. **Ciencia Florestal**, Santa Maria, v. 18, n. 4, p. 525-533, 2008.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 8112:** carvão vegetal: análise imediata. Rio de Janeiro, 1986. 5 p.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 14853:** madeira: determinação do material solúvel em etanol-tolueno e em diclorometano e em acetona. Rio de Janeiro, 2010. 3 p.

BRITO, J. O.; BARRICHELO, L. E. G. Correlações entre características físicas e químicas da madeira e a produção de carvão vegetal: I., densidade e teor de lignina da madeira. **IPEF**, Piracicaba, v. 14, n. 14, p. 9-20, 1977.

BRAND, M. A. **Energia de biomassa florestal**. Rio de Janeiro: Interciência, 2010. 131 p.

BRUM, S. S. **Caracterização e modificação química de resíduos sólidos do beneficiamento do café para produção de novos materiais**. 2007. 138 p. Dissertação (Mestrado em Agroquímica)-Universidade Federal de Lavras, Lavras, 2007.

CARRIER, M.; HUGO, T.; GORGENS, J.; KNOETZE, H. Comparison of slow and vacuum pyrolysis of sugar cane bagasse. **Journal of Analytical and Applied Pyrolysis**, Amsterdam, v. 90, n. 1, p. 18-26, 2011.

CASTRO, G. R. **Síntese, caracterização e aplicação de celulose funcionalizada com ligante p-Aminobenzoico em pré-concentração de íons metálicos**. 2003. 57 p. Dissertação (Mestrado em Química Analítica)-Universidade de São Paulo, São Paulo, 2003.

CHEN, D. et al. Bamboo pyrolysis using TG-FTIR and a lab-scale reactor: analysis of pyrolysis behavior, product properties, and carbon and energy yields. **Fuel**, London, v. 148, p. 79-86, May 2015.

CIMO, G.; KUCERIK, J.; BERNS, A. E.; SCHAUMANN, G. E. ALONZO, G.; CONTE, P. Effect of heating time and temperature on the chemical characteristics of biochar from poultry manure. **Environmental Science & Technology**, Washington, v. 62, n. 8, p. 1912-1918, 2014.

COMPANHIA NACIONAL DE ABASTECIMENTO. **Indicador agropecuário:** fechamento de edição. Brasília, 2016. 100 p.

CONZ, R. F. **Caracterização de matérias-primas e *biochars* para aplicação na agricultura**. 2015. 132 p. Dissertação (Mestrado em Solos e Nutrição de Plantas)-Escola Superior de Agricultura "Luiz de Queiroz", Piracicaba, 2015.

COUTO, A. M.; TRUGILHO, P. F.; NAPOLI, A. LIMA, J. T.; SILVA, J. R. M.; PROTÁSIO, T. P. Qualidade do carvão vegetal de *Eucalyptus* e *Corymbia* produzido em diferentes temperaturas finais de carbonização. **Scientia Forestalis**, v. 43, n. 108, p. 817–831, 2015.

COUTO, A. M.; Protásio, T. P.; Trugilho, P. F.; Neves, T. A.; Sá, V. A. Multivariate analysis applied to evaluation of *Eucalyptus* clones for bioenergy production. **Cerne**, Lavras, v. 19, n. 4, p. 525-533, 2013.

COUTO, G. M.; DESSIMONI, A.L.A.; BIANCHI, M. L.; PERÍGOLO, D.M.; TRUGILHO, P. F. Use of sawdust *Eucalyptus* sp. in the preparation of activated carbons. **Ciência e Agrotecnologia**, Lavras, v. 36, n. 1, p. 69-77, jan./fev. 2012.

GANI, A.; NARUSE, I. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. **Renewable Energy**, Oxford, v. 32, n. 4, p. 649-661, 2007.

GLASER, B.; HAUMAIER, L.; GUGGENBERGER, G.; ZECH, W. The "Terra Preta" phenomenon: a model for sustainable agriculture in the humid tropics. **Naturwissenschaften**, Berlin, v. 88, n. 1, p. 37-41, 2001.

GLASER, B.; LEHMANN, J.; ZECH, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal: a review. **Biology and Fertility of Soils**, Berlin, v. 35, n. 4, p. 219-230, 2002.

GOLDSCHIMID, O. Ultraviolet spectra. In: SARKANEN, K. V.; LUDWIG, C. H. (Ed.). **Lignins:** occurrence, formation, structure and reactions. New York: J. Wiley Interprice, 1971. p. 241-298.

HERGERT, H. L. **Lignins:** occurrence, formation, structure and reactions. New York: J. Wiley, 1971. 297 p.

IBRAHIM, N. A.; HADITHON, K. A.; ABDAN, K Effect of fiber treatment on mechanical properties of kenaf fiber-ecoflex composites. **Journal of Reinforced Plastics and Composites**, Westport, v. 29, n. 14, p. 2192-2198, 2010.

INDÚSTRIA BRASILEIRA DE ÁRVORES. **Anuário estatístico da IBÁ:** ano base 2015. Brasília, DF, 2015. 80 p.

KIM, H. S.; KIM, S.; KIM, H. J.; YANG, H. S. Thermal properties of bio-flour-filled polyolefin composites with different compatibilizing agent type and content. **Thermochimica Acta**, Amsterdam, v. 451, n. 1/2, p. 181-188, 2006.

KLOSS, S.; ZEHETNER, F., DELLANTONIO, A., HAMID, R., OTTNER, F, LIEDTKE, V., SCHWANNINGER, M., GERZABEK, M.H., SOJA, G. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on *biochar* properties. **Journal of Environmental Quality**, Madison, v. 41, n. 4, p. 990-1000, 2012.

LEE, Y, PARK, J, RYU, C, GANG, KS, YANG, W, PARK, YK, JUNG, J, HYUN S. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C. **Bioresource Technology**, Oxford, v. 148, p. 196-201, 2013.

MALAVOLTA, E.; VITTI, G. C.; OLIVEIRA, S. A. **Avaliação do estado nutricional das plantas: princípios e aplicações.** 2. ed. Piracicaba: Associação Brasileira para Pesquisa da Potassa e do Fosfato, 1997. 319 p.

NANDA, S.. MOHANTY, P.; PANT, K. K.; NAIK, S. KOZINSKI, J. A. DALAI, A. K. Characterization of North American lignocellulosic biomass and *biochars* in terms of their candidacy for alternate renewable fuels. **BioEnergy Research**, New York, v. 6, n. 2, p. 663- 677, 2012.

PAULA, L. E. R. E.; TRUGILHO, P. F.; NAPOLI, A.; BIANCHI, M. L. Characterization of residues from plant biomass for use in energy generation. **Cerne**, Lavras, v. 17, n. 2, p. 237-246, 2011.

PROTÁSIO, T. P.; TONOLI, G. H. D.; GUIMARÃES JÚNIOR, M.; BUFALINO, L. COUTO, A. M. TRUGILHO, P. F. Correlações canônicas entre as características químicas e energéticas de resíduos lignocelulósicos. **Cerne**, Lavras, v. 18, n. 3, p. 433-439, 2012.

PROTÁSIO, T. D. P.; MELO, I. C. N. A.; GUIMARÃES JUNIOR, M.; MENDES, R. F.; TRUGILHO, P. FThermal decomposition of torrefied and carbonized briquettes of residues from coffee grain processing. **Ciência e Agrotecnologia**, Lavras, v. 37, n. 3, p. 221-228, 2013.

OUAJAI, S.; SHANKS, R. A. Composition, structure and thermal degradation of hemp cellulose after chemical treatments. **Polymer Degradation and Stability**, Essex, v. 89, n. 2, p. 327-335, Aug. 2005.

ROCHA, F. C.; GARCIA, R. FREITAS, A. W.; SOUZA, A. L.; GOBBI, K. F.; VALADARES FILHO, S. C.; TONUCCI, R. G.; ROCHA, G. C. Casca de café em dietas para vacas em lactação: consumo, digestibilidade, produção e composição de leite. **Revista Brasileira de Zootecnia**, Viçosa, MG, v. 35, p. 2163-2171, 2006.

RAVEENDRAN, K.; GANESH, A.; KHILAR, K. C. Pyrolysis characteristics of biomass and biomass componentes. **Fuel**, London, v. 75, n. 8, p. 987-998, Jan. 1996.

SANTOS, L. C.; CARVALHO, A. M. M. L.; PEREIRA, B. L. C.; OLIVEIRA, A. C; CARNEIRO, A. C. O.; TRUGILHO, P. F. Propriedades da madeira e estimativas de massa, carbono e energia de clones de *Eucalyptus* plantados em diferentes locais. **Revista Árvore**, Viçosa, MG, v. 36, n. 5, p. 971-980, 2012.

SHAFIZADEH, F. Pyrolytic reactions and products of biomass. In: **Fundamentals of Biomass thermochemical conversion**. London: Elsevier, 1985. p. 183-217.

SEYE, O.; CORTEZ, L. A. B.; GÓMEZ, E. O. Estudo cinético da biomassa a partir de resultados termogravimétricos. **Energia no Meio Rural**, Campinas, ano 3, 2003. Disponível em: <http://www.proceedings.scielo.br/scielo.php?pid=MSC0000000022000000200022&script=sci_arttext>. Acesso em: 19 out. 2009.

TRUGILHO, P. F.; LIMA, J. T.; MORI, F. A. Correlação canônica das características químicas e físicas da madeira de clones de *Eucalyptus grandis* e *Eucalyptus saligna*. **Cerne**, Lavras, v. 9, n. 1, p. 81-91, 2003.

VALE, A. T.; GENTIL, L. V.; GONÇALEZ, J. C.; COSTA, A. F. Charactherization of biomass energy and carbonization of coffee grains (*Coffea arabica*, L) and (*Cedrelinga catenaeformis*), duke wood residues. **Cerne**, Lavras, v. 13, p. 416-420, 2007.

ZENG, K.; MINH; D.P.; GAUTHIER, D.; WEISS-HORTALA, E.; NZIHOU, A., FLAMANT G. The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood. **Bioresource Technology**, Essex, v. 182, p. 114-119, Feb. 2015.

ZHAO, L.; CAO, X.; MAŠEK, O.; ZIMMERMAN, A. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. **Journal of Hazardous Materials**, Amsterdam, v. 256/257, p. 1-9, July 2013.

ZHENG, H.; WANG, Z.; DENG, X.; ZHAO, J.; LUO, Y.; NOVAK, J. HERBERT, S. XING, B. Characteristics and nutrient values of biochars produced from giant reed at different temperatures. **Bioresource Technology**, Essex, v. 130, p. 463-471, 2013.