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CARACTERIZAÇÃO E CONVERSÃO TERMOQUÍMICA E MECÂNICA DA BIOMASSA RESIDUAL DO CAFÉ (*COFFEA ARÁBICA* L.) PARA ENERGIA

Dissertação de mestrado apresentada ao programa de Pós-Graduação em Engenharia Química da Universidade Federal de Minas Gerais

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Dissertação submetida à Banca Examinadora designada pelo Colegiado do Programa de Pós-graduação em Engenharia Química da Escola de Engenharia da Universidade Federal de Minas Gerais, como parte dos requisitos à obtenção do título de **MESTRE EM ENGENHARIA QUÍMICA**.

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Dedico

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RESUMO

O café é uma das culturas agrícolas mais importantes no mundo. Durante seu processamento, é gerada uma quantidade significativa de resíduos, que sem tratamento podem representar sérios problemas ambientais. Este estudo foi realizado com o objetivo de avaliar a qualidade e o potencial energético de resíduos gerados na cadeia produtiva de café, propondo uma alternativa que possa ser aplicada na matriz energética de países que envolvam a indústria do café em suas atividades agrícolas. No Artigo I foram avaliadas as propriedades do (I) pergaminho do fruto de café, (II) folhas e (III) madeira, diferenciando as partes madeireiras do arbusto de café. Determinaram-se propriedades físicas e químicas das diferentes biomassas. Dentre as biomassas, destacam-se o caule, galho primário e galho secundário do arbusto de café, devido ao maior poder calorifico útil (16,10 $MJ.kg^{-1}$-15,92 $MJ.kg^{-1}$) e menor teor de cinzas (1,67%-3,45%), propriedades favoráveis para a produção de energia por métodos termoquímicos como pirolise lenta, gaseificação e combustão, e métodos físicos como peletização e briquetagem. O Artigo II objetivou estudar a viabilidade de aproveitar os resíduos gerados no cultivo café juntamente com finos de madeira de pinus na fabricação de briquetes para geração de energia. A madeira de pinus foi misturada em proporções de 0%, 25%, 50%, 75% e 100% com os resíduos do cultivo café. Determinaram-se propriedades físicas, mecânicas e químicas dos briquetes produzidos. A maior presença de Pinus nos tratamentos contribuiu para a melhoria das propriedades de resistência a compressão diametral, densidade aparente e densidade energética, entretanto foi afetada a taxa de compactação dos briquetes, parâmetro importante para avaliar a estabilidade do briquete quando submetidos às condições de transporte e armazenamento. O Artigo III teve como objetivo analisar o processo de pirolise oxidativa rápida em um reator de leito fluidizado, alimentado com madeira de eucalipto da indústria de celulose e madeira do arbusto de café. Determinaram-se as características físicas e químicas das biomassas, do bio-oleo e do bio-char obtido no processo. Os bio-óleos apresentaram uma maior densidade energética do que as biomassas *in natura* (6,31 vezes maior para madeira de eucalipto e 4,26 vezes maior para madeira do arbusto de café). O bio-char apresentou o maior valor de aquecimento (21,19 MJ kg^{-1} para madeira do arbusto de café e 22,08 MJ kg^{-1} para madeira de eucalipto), permitindo a sua utilização como combustível. Em geral, os resultados indicam que os resíduos utilizados são potenciais candidatos na produção de bioenergia por pirólise rápida. Concluiu-se que a utilização de biomassas residuais obtidas da cadeia produtiva do café são matérias primais viáveis para serem utilizadas na produção de energia implementando processos como briquetagem e pirolises rápida.

Palavras-chave: Energia da biomassa, densidade energética, briquetes, pirolises rápida, Caracterização físico-química.

ABSTRACT

Coffee is one of the most important agricultural crops in the world. During its processing, a significant amount of residues are generated, which without treatment can represent serious environmental problems. This study was carried out with the objective of evaluating the quality and energy potential of residues obtained in the coffee production chain, proposing an alternative that can be applied in the energy matrix of countries that involve the coffee industry in its agricultural activities. In Article I the properties of the (I) parchment of the coffee cherry, (II) leaves and (III) wood, highlighting the woody parts of the coffee shrub, were evaluated. Physical-chemical properties of the different biomasses were determined. Among the biomasses, the stem, primary branch and secondary branch of the coffee shrub stood out due to the greater net heating value (16.10 MJ.kg-1-15.92 MJ.kg-1) and lower ash content (1.67%-3.45%), favorable properties for the production of energy by thermochemical methods such as slow pyrolysis, gasification and combustion, and physical methods such as pelletizing and briquetting. Article II aimed to study the feasibility of use residues generated in coffee cultivation and pine wood fines in the manufacture of briquettes for energy generation. The pine wood was mixed in proportions of 0%, 25%, 50%, 75% and 100% with residues from the coffee crop. Physical, mechanical and chemical properties of the briquettes produced were determined. The higher presence of pine in the treatments contributed to the improvement of the properties of resistance to diametrical compression, apparent density and energetic density. However, the compaction rate of the briquettes was affected, an important parameter to evaluate the stability of the briquettes when submitted to transport and storage conditions. Article III had the objective of analyzing the fast oxidative pyrolysis process in a fluidized bed reactor, fed with eucalyptus wood from the pulp industry and wood of the coffee shrub. The physical and chemical characteristics of the biomass, the bio-oil and the bio-char obtained in the process were determined. Bio-oils had a higher energy density than *in natural* biomasses (6.31 times higher for eucalyptus wood and 4.26 higher for wood of the coffee shrub). The bio-char presented the highest heating value (21.19 MJ kg^{-1} for wood of the coffee shrub and 22.08 MJ kg^{-1} for eucalyptus wood), allowing its use as fuel. In general, the results indicate that the residues used are potential candidates in the production of bioenergy by fast pyrolysis. It was concluded that the use of residual biomasses obtained from the coffee production chain are viable raw materials to be used in the production of energy by implementing processes such as briquetting and fast pyrolysis.

Keywords: Biomass energy, Energy density, Briquettes, Fast pyrolysis, Physical-chemical characterization.

INTRODUÇAO GERAL

O interesse na utilização da bioenergia a partir de biomassa como fonte energética alternativa vem aumentando nas últimas décadas em virtude da crescente demanda mundial por energia (Rosillo-Calle, 2016). Além disso, a sua utilização em processos industriais para geração de calor e eletricidade é atrativa por ser de baixo custo de obtenção e atender a maioria dos preceitos socioambientais envolvidos. O Brasil é um dos países com maior potencial nesse cenário energético devido à sua grande disponibilidade de biomassa lignocelulósica residual, decorrente da alta produtividade dos setores agrícola e florestal do país (Bevilacqua, 2016). De acordo com The Global Energy Network Institute, o potencial energético por meio da utilização de toda biomassa no Brasil encontra-se entre 250-500 EJ (Meisen e Hubert, 2010). No entanto, estudos mais conservadores referem-se a um potencial para bioenergia em torno de 11690-13930 PJ, considerando a produtividade média no Brasil entre 20 -80 toneladas de cultura agrícola por hectare (Meisen e Hubert, 2010). Resíduos provenientes do cultivo e produção de café, cacau, cana de açúcar e milho são algumas das biomassas disponíveis que apresentam grande potencial de utilização no cenário energético sustentável brasileiro.

O café se destaca por ser um dos produtos de maior comercialização no mercado mundial, sendo reconhecida por ser a bebida mais consumida e uma das culturas agrícolas mais importantes do mundo. O cultivo, industrialização e comercialização deste produto do agronegócio representa grande importância para o desenvolvimento de países como Brasil e Colômbia, sendo que gera grande número de empregos e divisas. Em 2016, a produção mundial de café atingiu 155,7 milhões de sacas de 60kg, sendo o Brasil o maior produtor (29,9%), seguido por Vietnam (19%) e Colômbia (9,3%) (Ico, 2016; Usda, 2016). No entanto, a alta produção industrial, é responsável pela formação de grande quantidade de resíduos. Estima-se que anualmente são geradas 225 milhões de toneladas de resíduos líquidos e 9,9 milhões de toneladas de resíduos sólidos em nível mundial em relação a produção anual mundial de café (Schwan *et al.*, 2014). Estes podem representar sérios problemas ambientais, dado que a maioria dos resíduos são vertidos a campo aberto sem tratamento, causando o empobrecimento dos solos e aumento da necessidade de fertilizantes artificiais. Todavia, os resíduos sólidos provenientes do processamento de café frequentemente não são utilizados como matéria prima para a produção de energia, porque apresentam características indesejáveis quando é utilizada na condição *in natura*, como baixo poder calorífico, alta umidade, formato irregular e heterogeneidade elevada. Assim, torna-se necessário desenvolver e avaliar tecnologias e pré tratamentos, podendo-se citar, a geração de energia pela queima direita, produção de combustíveis sólidos (briquetes, pellets, carvão vegetal), líquidos como bio-óleo, biogás, além de diversos produtos químicos, que possam amenizar essas características indesejáveis da biomassa, tornando-a um combustível mais atrativo e competitivo dentro do mercado de energia.

Tecnologias de conversão das biomassas incluem processos termoquímicos, biológicos e mecânicos ou físicos, gerando muitas vezes produtos múltiplos e complexos que fornecem um custo eficaz e sustentável de energia. Processos biológicos estão essencialmente compostos pelos métodos de digestão microbiana e fermentação, tecnologias caracterizadas por fornecer baixas quantidades de produtos com altos rendimentos. Processos de conversão físicos como a briquetagem e a peletização produzem combustíveis sólidos de formato regular com alta densidade energética e resistência e baixa umidade, características que propiciam maiores eficiências operacionais e energéticas nos sistemas de queima apropriados. Métodos termoquímicos como pirólise, combustão e gaseificação normalmente transformam toda a biomassa para produzir hidrocarbonetos de valor agregado, potência ou calor (Bridgwater, 2012), na forma de gás combustível, líquido e sólido, em proporções variadas devido a influência dos parâmetros dos processos. Temperaturas de processo mais baixas e tempos de residência mais prolongados favorecem a produção de char, "carvão" (pirólise lenta ou torrefação). Temperaturas elevadas e tempos de residência mais longos aumentam a conversão de biomassa em gás (gaseificação), e temperaturas moderadas e tempo de residência curto de vapor são ótimos para a produção de líquidos (pirólise rápida). A liquefação hidrotérmica (HTL) e a carbonização hidrotérmica (HTC) também são processos termoquímicos promissores para a valorização da biomassa, especialmente da biomassa de alta umidade. A biomassa com alto teor de água pode ser transformada em bio-óleo e em produtos químicos de plataforma por meio do processo de liquefação hidrotérmica (Singh *et al.*, 2016), ou transformada em carvão com alta eficiência de retenção energética por meio do processo de carbonização hidrotérmica (Kim *et al.*, 2016).

Diante o exposto, o objetivo deste trabalho é apresentar uma caracterização de biomassas residuais obtidas na cadeia produtiva do cultivo de café para fins energéticos, mediante o comportamento das propriedades físicas e químicas que identificam os índices de qualidade mais importantes, as interações entre eles, além do estudo e quantificação dos processos de conversão termoquímico, através da implementação do processo de pirólise rápida, e conversão física através do processo de briquetagem.

Para alcançar o objetivo do trabalho forma elaborados três artigos, conforme a seguir:

-Artigo I: Caracterização de biomassas residuais provenientes da cadeia produtiva de café para fins energéticos.

-Artigo II: Caracterização de briquetes produzidos com misturas de madeira de Pinus e biomassa residual da cadeia produtiva de café.

-Artigo III: Pirolise oxidativa rápida como forma sustentável para conversão de resíduos da indústria de polpa celulósica e plantação de café para um combustível renovável.

A versão final desta dissertação contém os artigos I e III submetidos em revista. O artigo II vai sofrer modificações antes de ser submetido. Caso os artigos sejam aceitos, provavelmente terão modificações de acordo com as correções dos revisores.

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ARTIGO I

CHARACTERIZATION OF RESIDUAL BIOMASSES FROM THE COFFEE PRODUCTION CHAIN FOR ENERGY PURPOSES

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 agroindustrial solid residues from coffee crops – parchment and coffee bush, i.e., stem, primary branch, secondary branch and leaves – 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 18.3–19.45 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 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.

Keywords: Bioenergy; Chemical characterization; Coffee shrub; Thermochemical conversion.

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 e Nuti, 2017). These residues represent a serious source of environmental contamination (Silva, 2008), 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 25.58 sc/ha; *Coffea Arábica* L. and *Coffea Robusta* production was 81.09% and 18.91%, respectively (Abastecimiento, 2016).

The coffee shrub is a perennial plant and evergreen *in nature*. As can be observe in Fig. 1, it has a prominent vertical stem with shallow root system, feeder roots of arábica coffee penetrate relatively deeper into the soil whereas robusta has feeder roots concentrated very close to the soil surface. Coffee leaves appear shiny, wavy, and dark green in color with conspicuous veins and coffee leaves are opposite decussate on suckers. Coffee cherries are the raw fruit of the coffee plant, which are composed of two coffee beans covered by a thin parchment to like hull and further surrounded by pulp (Murthy e Naidu, 2012).

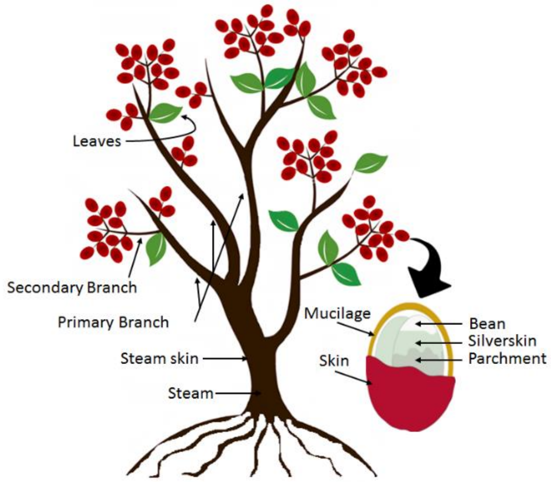

Fig. 1. Parts of coffee shrub and cross-section of coffee cherry

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, Carneiro, *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. In this sense, agroindustrial 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 acetyl 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.

2. MATERIALS AND METHODS

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 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.

The measurement for Basic density of wood sample (stem) was determined according to SCAN CM 43:95 standard procedures (Scan, 1995) 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 -24°C) and relative moisture (60-70% U) control. The mass loss of the samples was monitored by periodic weightings until reaching anhydrous mass.

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 (Din, 2011). The molar ratios of oxygen and hydrogen to carbon were determined.

The proximate analysis aims to quantify the moisture, volatiles (condensable and non-condensable), fixed carbon and ash biomass content. The equilibrium hygroscopic moisture content (EHM) was determined by the mass difference according to DIN EN 14774-1 standard procedure (Din, 2010a). The volatile matter analysis was performed according to methodology DIN EN 15148 standard procedure (Din, 2010c). Ash content was determinate according to DIN EN 14775 standard procedure(Din, 2009). Fixed carbon was calculated of the difference between 100 and the sum of volatiles and ash biomass content. The analyses of ash with respect to silica, sodium, iron, copper, manganese, potassium, calcium and magnesium content were carried out directly on the raw sawdust, according to TAPPI T266 om-2 standard procedure (Tappi, 2006).

The higher heating value (HHV) has determined according to DIN EN 14918 standard procedure (Din, 2010b), in duplicate, using a bomb calorimeter adiabatic IKA300. The Net heating value (NHV) was determined according to equation 1 of the annex E of the DIN EN 14918 standard procedure (Din, 2010b) standard procedure.

$$\text{NHV} (\text{J.g}^{-1}) = (\text{HHV} (\text{J.g}^{-1}) - 212.2 * \text{Hydrogen content} (\%) - 0.8 * (\text{Oxygen content} (\%) + \text{Nitrogen content} (\%)) * (1 - 0.01 * \text{EHM} (\%)) - (24.43 * \text{EHM} (\%)) \qquad (1)$$

The chemical composition of studied biomass samples was evaluated within the following procedure. Total extractives contents were determined in ethanol/toluene (1:2) → ethanol → hot water solvent series according TAPPI T204 cm-97 (Tappi, 1997) standard procedure. 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 contents of uronic acids, acetyl groups and sugars (Glucans, Mannans, Galactans, Xylans and Arabinans) in the extractive-free biomass were determined according to (Scott, 1979), (Solar *et al.*, 1987) and SCAN-CM 71:09 (Scan, 2009) standard procedure, respectively . On the same extractives-free biomass, the acid insoluble lignin and acid soluble lignin were determined according to TAPPI T 222 om-11 (Tappi, 2011) standard procedure and (Goldschinid, 1971), respectively.

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), at heating rates of 10 ºC/min with final temperature at 1000 ºC.

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.

The results were submitted to analysis of variance (ANOVA) at 5% of significance and when significant differences were established, the treatments were compared by Tukey test at a 5% probability level.

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

3. RESULTS AND DISCUSSION

3.1 Stock estimation of the coffee shrub woods parts

Table 1 shows stock estimation of the biomass (stem, primary branch and secondary branch) in the coffee shrub.

Table 1. Stock estimation of the woods parts (stem, primary branch and secondary branch) in the coffee shrub.

Estimation	Wood Parts of coffee shrub			Total
	Stem	Primary Branch	Secondary Branch	
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

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 Arabica coffee shrub is slow during the dry, cool season, and rapid in the rainy, warm season (Barros, 1974; Da Matta *et al.*, 1999). The growth of the shrub is also influenced by age, planting density, cultural practices and weed competitions (Damatta *et al.*, 2007).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 stereo mass than the branches, as a result of the significant difference between the densities.

3.2 Chemical analysis of residual biomasses from the coffee production chain

Table 2 shows a chemical analysis of the residual biomasses from the coffee production chain.

Table 2. Chemical analysis of residual biomasses from the coffee production chain

Components	Biomasses					
	Leaves	Primary branch	Secondary branch	Stem 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 %)						
EHM	16.35 b	8.70 d	9.28 d	18.11 a	10.96 c	11.09 c
VM[a]	74.71 c	80.62 b	75.31 c	75.63 c	83.70 a	74.07 c
FC[a]	18.12 bc	16.95 cd	21.23 a	20.03 ab	14.62 d	20.09 ab
AC[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
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
NHV	14.68 c	16.10 a	15.92 a	14.11 d	15.44 b	14.81 c
Structural 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
Glucans[b]	19.65 c	33.25 a	29.05 b	17.90 c	31.65 ab	29.60 ab
Xylans[b]	5.30 e	11.85 b	10.30 c	6.25 d	12.20 b	14.55 a
Galactans[b]	2.50 a	1.15 cd	1.45 bc	1.20 cd	0.90 d	1.65 b
Mannans[b]	1.10 d	2.55 b	1.70 c	0.90 d	3.30 a	1.00 d
Arabinans[b]	4.50 a	1.55 d	2.90 c	4.25 a	1.35 d	3.45 b
Total sugars[b]	33.05 b	50.35 a	45.40 a	30.50 b	49.40 a	50.25 a
Uronicacids[b]	4.80 b	3.80 c	4.70 b	5.20 a	3.30 c	5.50 a
Acetyl group[b]	1.00 c	1.8 b	1.8 b	1.00 c	2.80 a	2.85 a
Others[b]	22.04	14.20	15.85	20.13	14.93	14.81

[a]dry basis. [b]dry ash free basis. *nd*-not determined. EHM-Equilibrium Hygroscopic Moisture. V-Volatile matter. FC-Fixed Carbon. AC-Ash content. HHV-Higher Heating Value. NHV-Net Heating Value.

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

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, reason being that higher wood density is preferred, resulting in higher mass production for a given volume of wood. In addition, the charcoal apparent density will be higher, obtaining 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 (Botrel *et al.*, 2007). 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 e Zani Filho, 1993).

Heating value, proximate and ultimate analysis of residual biomasses

For the ultimate analysis the proportional values of carbon (C), hydrogen (H), Oxygen (O), nitrogen (N) and sulfur (S) in dry ash free basis were determined, verifying that the biomasses collected are basically composed of C (50.26 – 54.41%, dry basis), H (6.13 - 6.59%, dry basis) and O (35.52 - 42.29%, dry basis). For energy production, it is desirable that the biomass present high values of carbon and hydrogen and low values of nitrogen and sulfur, considering the relationship with the heating value. 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. The content of S observed in the elemental composition were 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 N requirements increases with shrub age especially at the beginning of grain production (Catani e De, 1958). If there are not limiting factor, the N 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 (Carelli *et al.*, 2006), that's the reason of the highest levels of nitrogen in leaves with significant difference between the other biomasses. The N content in biomasses varies in the interval of 0.10 – 12% (Manyà e Arauzo, 2008; Vassilev *et al.*, 2010). Then, the values of N and S found in this study do not compromise the energy use of the samples.

The molar ratios of oxygen and hydrogen to carbon for the residues studied are shown in Fig 2. The samples with a relatively low O/C ratio 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 ratio O/C. 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.

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 2 shows mean values between 18.30-19.45 $MJ.kg^{-1}$, similar sighted in literature (18.60 -19.02 $MJ.kg^{-1}$) (Paula, 2010) for residues from coffee production chain and analogous to biomasses commonly used in energy generation (19.50 – 21.00 $MJ.kg^{-1}$) (De Oliveira *et al.*, 2013; Keipi *et al.*, 2014; Doumer *et al.*, 2015). NHV shows mean values between 14.11-16.10 $MJ.kg^{-1}$. Primary branch has the higher value of NHV 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) (Table 2).

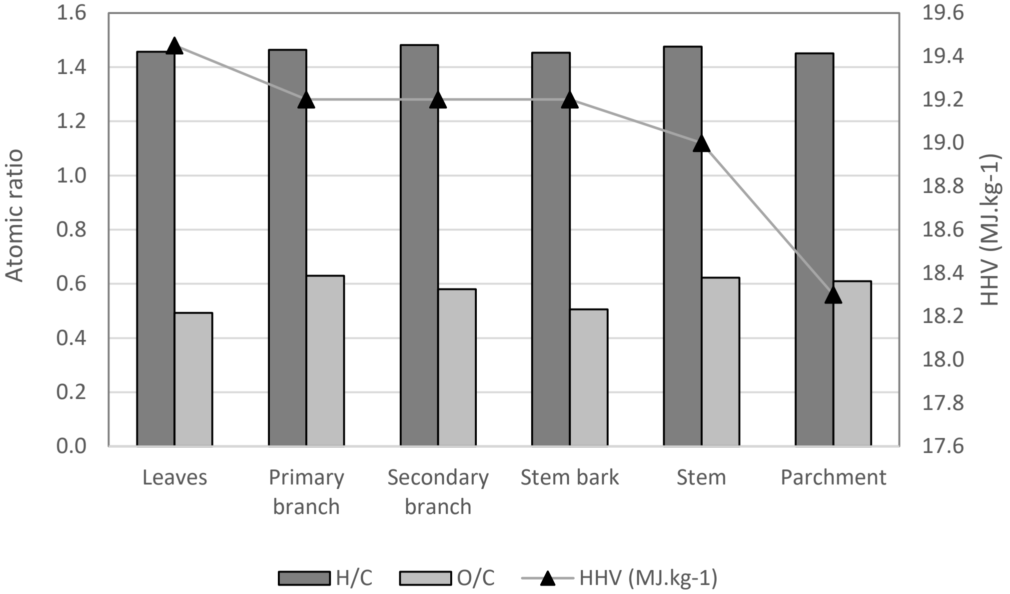

Fig. 2. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain

For proximate analysis, 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 stem 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 (Demirbaş, 2003; De Souza-Santos, 2010). For volatile matter (VM), 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 %) (Parikh *et al.*, 2007; Donahue e Rais, 2009). 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 (Lora e Nogueira, 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 2) 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 (Basu, 2010; 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).

Chemical composition

Another important characteristic of biomass is the composition in terms of the 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 glucans joined linearly. It also contains 15 to 30% of hemicelluloses, which is a polymer with heterogeneous branched chains composed mainly of Glucans, Xylans, Galactans, Mannans and Arabinans. The lignin is 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 (Mckendry, 2002; Basu, 2010; Sjostrom, 2013).Lignin generally constitutes 4%-35% of biomass (Basu, 2010; Sjostrom, 2013). Extractives are the organic materials of plants that may be separated from the insoluble cell wall using their solubility in water or neutral organic solvents. However, residues from coffee production chain are constituted by several other components, including lipids, tannin, polyphenols, fiber and nitrogenous compounds (Oestreich-Janzen, 2010; Mussatto, Machado, *et al.*, 2011; Farah, 2012; Murthy e Naidu, 2012), these latter components were not evaluated in this study. Obtained data of chemical composition are presented in Table 2.

Glucans are the dominant component in the carbohydrate fraction of all studied samples (17.90% - 33.25%). For lignin, higher contents in biomass are more sustainable for energy production as lignin is the chemical component that has a greater thermal stability due to the C-C ligations between monomeric units of phenyl-propane, and consequently has more stability in its aromatic matrix contributing for coal and products like methanol and bio-oleo formation. The total extractive content ranged from 10.57% to 24.72%, the extractive content of parchment was higher than values described in the literature (7%-15%) (Brum *et al.*, 2006; Mussatto, Machado, *et al.*, 2011). The high contents of extractives and lignin of the samples can be associated with the age of the coffee shrub. Thus, Silva *et al.* (2005) concluded that the extractive and lignin contents increased with age, with greater concentrations near the base of the shrub; the holocellulose content also decreased with age with greater concentrations in the upper parts of the stem. For lignin total values founded in this study (26.81% -39.06%) were higher than those reported in the literature. (Mussatto, Machado, *et al.*, 2011)found values of 9±6% for parchment, and Silva et al. (2014) found values from 30.04% to 34.04% for coffea wood.

Thermogravimetric analysis

Fig. 3 shows the thermal behavior of the residual biomasses of the coffee production chain by Thermogravimetric analysis (TGA) and Differential thermogravimetric analysis (DTA).

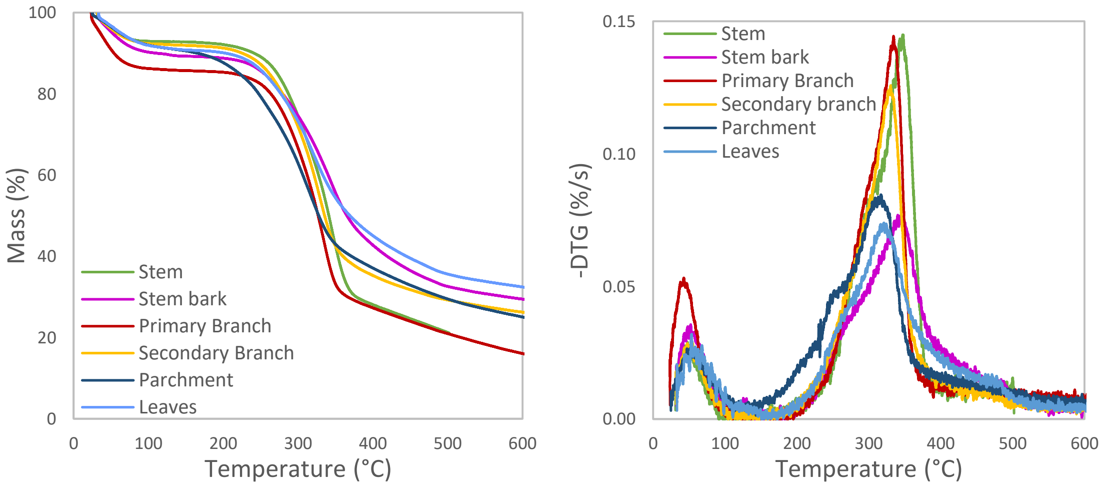

Fig. 3. TGA and DTG of the residual biomasses of the coffee production chain.

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 curves 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 (Yang *et al.*, 2007; Santos *et al.*, 2013). The Table 3 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 3. 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
Stem 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

The mass lost in the first stage, ranging from 7.04 to 13.76 %, occurs from dehydration by evaporation. It was found that the loss of mass in the temperature range from 100°C to 200°C was minimal. According to Santos *et al.* (2013) this is called the thermal stability zone, which is limited by the initial temperature of thermal degradation temperature of the main components of the biomasses. In the range of 200°C to 400°C the greatest mass loss occurs, the majority is attributed to the degradation of hemiceluloses and cellulose. The stem and primary branch of the coffee shrub presents higher mass losses in the range of 200°C to 400°C, 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. 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–19.45 MJ/kg, 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.

Glucans is the dominant component in the carbohydrate fraction of all studied samples (17.90%-33.25%). 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.

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.

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ARTIGO II

CHARACTERIZATION OF BRIQUETTES PRODUCED WITH MIXTURES OF PINE WOOD AND RESIDUAL BIOMASS OF COFFEE PRODUCTION CHAIN

ABSTRACT – In Brazil, the biomass residues come mainly from agricultural and agro-industrial activities and forest byproducts. This work aimed to produce and characterize briquettes made from coffee and pine residues to evaluate their physical, chemical and mechanical properties. Particles with granulometry less than 2 mm and a moisture content of 8 ± 0.5% were used. The briquettes were produced in a piston-press-type, laboratory-scale briquetting machine from Lippel®, model LB 32. The temperature of compressing was 120 °C and pressure equal to 8.27 Mpa, during 4 min, with a cooling time of 8 minutes. Pine was mixed in ratios of 0%, 25%, 50%, 75% and 100% with stem, primary branch, secondary branch, mixture of wood parts (stem, primary branch and secondary branch) of coffee shrub and parchment of coffee cherry, totaling a mass of 20 g of residue of each composition of raw material used for briquette production. For understand the energy behavior of briquettes, the ash content, the volatile materials, the fixed carbon and calorimetric analysis of biomasses were assessed. Besides these features, apparent density, energy density, compressive strength and hygroscopic equilibrium moisture which are important parameters to evaluate the stability of the briquette when subjected to conditions of transport and storage were also studied. Mixing residues from coffee production chain and Pine wood improve the characteristics of the briquettes in relation to the resistance to compression, linear expansion, hygroscopic equilibrium moisture, apparent density and energy density. The best mixing ratio between all treatments was 75% Pine for all parameters evaluated.

Keywords: Solid biofuels; Agricultural and forest biomass; Briquetting

1. INTRODUCTION

The coffee industry is responsible for the generation of large amounts of residues, which without treatment can represent serious environmental problems (Schwan *et al.*, 2014). These solid residues are often not used as feedstock for energy production, since they have undesirable characteristics when used *in natural* condition, such as high heterogeneity, high moisture, low density, irregular shape and particle size, which leads to difficulties in handling, transport and storage. Thus, it is necessary to develop and evaluate technologies and pretreatments, that can mitigate these undesirable biomass characteristics, making it a more attractive and competitive fuel in the energy market, such as production of solid fuels (briquettes, pellets and charcoal), liquids, biogas, bio-oil, as well as several chemical products.

Briquetting is and alternative and efficient process that uses lignocellulosic residues to increase its energy density of the biomass (De Paula Protásio *et al.*, 2011). According to Granada *et al.* (2002), biomass briquetting is a densification process that improves the characteristics of the residual biomass by increasing energy density, reducing transport costs, and producing a uniform fuel. The briquetting process consists of an application of pressure to a mass of particles, with or without addition of a binder, and with or without heat treatment. However, for the production of briquettes using lignocellulose residues, knowledge about the process and final product quality is necessary, which can be evaluated by means of physical, chemical and mechanical characterization.

There is still little information about the energy potential of residues from coffee production chain through the briquetting process. Therefore, the use of traditional biomasses implemented in the production of briquettes such as pine wood may be attractive as mixtures with coffee residues for determining the energetic behavior of the biomasses. The pine wood is rich in natural resins (Brito *et al.*, 2008), which gives it high calorific power. It also has a high content of lignin and silica in its composition. Thus it does not require the addition of natural binders or the addition of lignin itself to act as a binder in the compaction of biomass in briquettes production.

With this background, the present work aims to use the briquetting process to compact the biomasses from coffee production chain and mix with pine wood by gradual addition to produce a solid fuel of regular shape and high energetic density and resistance, providing greater operational efficiencies in appropriate firing systems.

2. MATERIALS AND METHODS

The experiment was conducted in two steps: i) Classification, physical and chemical characterization of biomasses; and ii) Production of briquettes and their physical, mechanical and chemical characterization.

Three residual biomasses were evaluated: coffee wood, pine wood (forest biomasses), and parchment of coffee cherry (agricultural biomass). The residues from coffee (*Coffea Arabica* L.) were provided by a rural farm in the municipality of Paula Cândido, MG, Brazil (20°49'50.0" S 42°55'03.3" W). The pine wood were collected in commercial plantation, from experimental units of the zootechny department of the Federal University of Viçosa, MG, Brazil.

Classification and physical – chemical characterization of biomasses

The biomasses were ground in an electric hammer mill, Weg®, with a fixed speed of 3520 rpm, which was linked with a sieve with a 2 mm opening. The coffee wood samples were previously separated into (I) stem, (II) primary branch and (III) secondary branch according to their diameter. The granulometry classification of the all biomasses used in this study was carried out using a sequence of sieves with two different openings (40 *mesh* and 60 *mesh*).

The measurement of moisture was determined according to DIN EN 14774-1 (DIN, 2010a) standard procedure, in an oven at 105 ± 2ºC.

According to previous tests developed in the laboratory, Table 1 shows the obtained results for structural composition and basic density of the biomasses.

Table 1. Structural composition and basic density of the biomasses

Components	**Biomasses**				
	Pine	Stem	Primary branch	Secondary branch	Parchment
Basic density(kg.m^{-3})	406.00	598.70	*nd*	*nd*	*nd*
			Structural composition (%)		
Total Extractive	3.92	10.58	13.09	13.95	21.95
Total Lignin^{b}	30.35	29.57	29.85	32.25	26.59
Holocelluloses^{b}	68.90	68.28	67.88	63.61	67.50

$^{\mathbf{b}}$ dry ash free basis. *nd* not determined

For approximate analysis (volatile matter, fixed carbon and ash content), the granulometry of the biomasses was reduced even more, using a Wiley type laboratory mill according to the TAPPI 257 cm-85 standard procedure (TAPPI, 1985). It was posteriorly classified in sieves of 40 *mesh* and 60 *mesh*. For the analysis, the sawdust fraction that passed through the sieve of 40 *mesh* and was retained in the sieve of 60 *mesh* was used. The ash content was determinate according to DIN EN 14775 standard procedure (DIN, 2009); the volatile matter analysis were performed according to DIN EN 15148 standard procedure (DIN, 2010d); and the fixed carbon was calculated of the difference between 100 and the sum of volatiles and ash biomass content.

The bulk density was determinate according to DIN EN 15103 (DIN, 2010c) standard procedure. The higher heating value (HHV) was obtained according to DIN EN 14918 (DIN, 2010b) standard procedure, using an adiabatic calorimetric pump IKA300.

Briquettes production and characterization

The recommended moisture range for manufacture briquettes varies from 8% to 15% dry basis (DIN, 1996). Hence, the particles of the biomasses were conditioned until the moisture reached 8 ± 0.5% dry basis.

The briquettes were produced in a piston-press-type, laboratory-scale briquetting machine from Lippel®, model LB 32. The temperature of compressing was 120°C and pressure equal to 8.27 Mpa, during 4 min, with a cooling time of 8 minutes. The briquetting conditions were defined experimentally from preliminary tests. Pine was mixed in ratios of 0%, 25%, 50%, 75% and 100% with stem, primary branch, secondary branch, mixture of wood parts of coffee shrub (stem, primary branch and secondary branch), and parchment of coffee cherry, totaling a mass of 20 g of residue of each composition of raw material used for briquette production.

The briquettes were evaluated by visual analysis for length variations and mass loss during the briquetting process. After cooling, the briquettes were kept in an air-conditioned chamber at temperature of 23±1 °C and relative moisture of 60±10% until reaching equilibrium hygroscopic moisture. The visual analysis were measurement before and after conditioning in the climatic chamber.

The quality of the briquettes was assesses through the following analyses: Hygroscopic equilibrium moisture content (HEMC), was determined according to DIN EN 14774-1 (DIN, 2010a) standard procedure; Apparent density, was measured in triplicates by mercury immersion method according to (Vital, 1984); Compact rate, was determined by dividing the apparent density of briquette between the bulk density of ground biomass; Energy density, was obtained with the value of the apparent density times the Net heating value (NHV); The NHV, was determined using the following equation (1), according to Annex E of DIN EN 14918 (DIN, 2010b) standard procedure:

$$\text{NHV (Kcal/Kg)} = ((\text{HHV (Kcal/kg)} - 600 * (9 * \text{Hydrogen content (\%)} / 100)) * (1 - \text{Hygroscopic moisture (\%)})) - (600 * \text{Hygroscopic moisture (\%)}) \qquad (1)$$

The tensile strength by diametrical compression for briquettes was measurement according to the guidelines of norm NBR 7222 (ABNT, 2011) with adaptations (De Paula Protásio *et al.*, 2011), in triplicate. The test was carried out in an universal test machine, Contenco brand, UMC-300 model. The result of maximum load was obtained by the Pavitest software 2.7.0.7, coupled to the equipment.

Experimental design

The experiment was carried out in a completely randomized factorial design (5x5), considering five mixing ratios of residues (0%, 25%, 50%, 75% and 100%), five mixing biomasses (stem, primary branch, secondary branch, mixture of wood parts and parchment), and ten replicates, giving a total of 250 sampling units.

The effects of the mixing proportions of Pine with coffee residues were analyzed, and 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)

For hygroscopic moisture (%), maximum load (Kgf), apparent density (Kg.m^{-3}) and energy density (MJ.m^{-3}) properties, models were defined with the aid of program R for explaining the distribution of the data. The comparison between the treatments was done by the identity model test (Regazzi e Silva, 2004).

3. RESULTS AND DISCUSSION

3.1 Characterization of the lignocellulosic residues

The Table 2 shows the granulometry composition in percentage, of the biomass used in the production of the briquettes produced in this study.

Table 2. Granulometry composition of the lignocellulosic residues used in the produccion of briquettes

Biomass	Particle size (mm)		
	Ø < 0.31	0.31 ≥ Ø < 0.47	0.47 ≥ Ø ≤ 2
Pine	60.3%	19.0%	20.7%
Stem	51.2%	22.2%	26.6%
Primary Branch	47.5%	21.4%	31.1%
Secondary Branch	45.1%	16.6%	38.3%
Parchment	21.9%	35.3%	42.8%

The biomass granulometry after milling is one of the most important initial characteristic of the raw material destined for compaction process. The particle size distribution of the coffee wood residues presents a similar behavior; it contains a high percentage (45.1%-51.2%) of particles with diameters lower to 0.31mm, 16.6% to 22.2% with diameters between 0.31 mm and 0.47 mm, which corresponds to the particles that passed through the 40 *mesh* sieve and were retained in the 60 *mesh* sieve, and the rest of the parts with diameter between 0.47 mm and 2 mm, which correspond to the particles retained in the 40 *mesh* sieve. The parchment has a granulometry distribution with the lowest presence of fines and 42.8% of particles densities between 0.47mm and 2mm, apparently due to the rounded form of its structure. Probably, those biomasses that presented more resistance to trituration produced fractions with higher granulometry, which can decrease the homogeneity, strength (Mani *et al.*, 2006), durability and resistance of briquettes (Kaliyan e Morey, 2009). On the other hand, pine sawdust presents high presence of fines particles (60.3%). According to Guo *et al.* (2016) e Sudhagar *et al.* (2004), when a large proportion of the raw material is of smaller particles size (≤ 2mm), resulting a uniform, high quality and high volumetric density briquettes. The reason for this trend is that the increased compacting pressure will lead to the biomass material particles being closely packed due to reduction of void ratio and plastic deformation of the sawdust particles, therefore resulting in the increased density of the briquettes (Mitchual *et al.*, 2013). Additionally, if the raw material is finer, it gives a larger surface area for bonding which results in the production of briquette with higher density (Mani *et al.*, 2006).

Table 3 shows a chemical characterization of the lignocellulosic residues used in the production of briquettes.

Table 3. Chemical characterization of the lignocellulosic residues

Parameter	Biomasses					
	Pine	Stem	Primary branch	Secondary branch	Wood mix*	Parchment
HEMC *(wt %)*	12.23 a	10.96 a	8.70 c	9.28 b	9.65 b	11.09 a
V^a *(wt %)*	82.46 a	79.76 ab	80.67 a	76.50 bc	79.57 ab	73.80 c
FC^a *(wt %)*	16.79 b	18.09 ab	17.05 ab	19.36 ab	14.62 d	20.09 ab
Ash^a *(wt %)*	0.75 d	2.15 c	2.27 c	4.14 b	2.63 c	5.91 a
HHV *($MJ.kg^{-1}$)*	20.71 a	20.12 b	19.75 bc	19.72 c	19.86 bc	18.92 d

HEMC: Hygroscopic Equilibrium Moisture Content; V: Volatiles; FC: Fixed Carbon; HHV: Higher Heating Value. ^{a} dry basis. *Mixture of Stem, Primary Branch and Secondary Branch

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

The hygroscopic moisture of the biomasses used in the production of the briquettes ranged from 8.70% to 12.23%. Preliminary tests were carried out to determine the moisture on dry basis of the raw material mixtures that favored the mechanical properties of briquettes. Considering that, the mechanical resistance and durability of the briquettes rise with increasing humidity (Kaliyan e Morey, 2009). Studies recommend that the biomass for the production of briquettes must have a moisture content between 8%-15% (Quirino, 2002; Oliveira, 2015), values below this range made the particle agglomeration difficult because of the high friction forces in the compression channels, and above the range, the dimensions (diameter and length) of briquettes are not stable (Kalinauskaitė *et al.*, 2013). Of the evaluated biomass, all residues of the coffee shrub had humidity within the range when they are in hygroscopic balance, being an advantage in the energy balance already that reduces energy in the drying stage of the material mixtures. However, several studies have shown that the ideal moisture for the production of briquettes is variable, possibly due to the chemical composition of the raw material and the shape of the particles (Mani *et al.*, 2006; Serrano *et al.*, 2011).

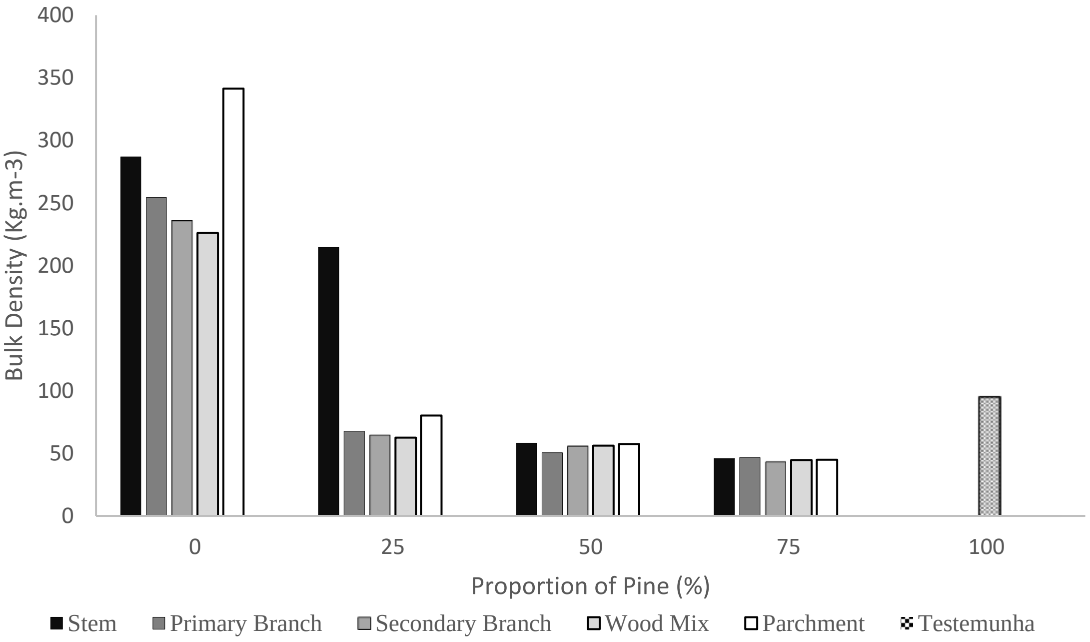
For the volatile matter, the wood residues presented a higher percentage than the parchment. Pine sawdust followed by the primary branches present the highest values with no significant difference, i.e. 82.46% and 80.67%, respectively. The volatile matter is the part of fuel that is released as gases when the material is degraded and is mainly responsible for the supply of energy during combustion. Solid fuels with high contents of volatile matter are more susceptible to thermal degradation during combustion (Fernandes *et al.*, 2013). The values obtained are similar to those found for wood (82%) (Mckendry, 2002) and higher than other materials used in briquettes production, such as rice husk (65.47%), sugarcane bagasse (73.78%) (Jenkins, 1990), shea mel (66.3%) (Munir *et al.*, 2009), paper sludge (48.7%) and coal (33.1%) (Yanfen e Xiaoqian, 2010).

The fixed carbon content (FC) was proportionally inversely to the volatile matter; thus, the FC for parchment (20.09%) was higher than the wood residues (14.62%- 19.36%). According to Lora e Nogueira, (2003) high FC indicates that the materials tend to burn more slowly, requiring longer residence time compared to fuels with a low FC. This suggests that the burn rate of briquettes with parchment in its composition, may be slower than the other samples.

Ash content imply the presence of metals but also inorganic materials, mostly in the form of oxides (Raj *et al.*, 2015). In this way, the parchment present a strong inorganic composition, evidenced by the highest value of ash (5.91%) followed by wood residues (0.75% - 4.14%). According to Obernberger e Thek, (2010), the ash content in the feedstock does not influence the densification process, however if the ash content is greater than 10%, it will cause wear on the equipment matrix. As the objective of this study was the production of solid biofuels (briquettes), it is desirable that the samples present low ash values, producing a higher heating value, as well as increasing the volatile content and reducing the fixed carbon.

The higher heating value (HHV) was relatively high for all biomasses, considering the parchment showed a lower heating value, most likely due to a high content of inorganic material and a low content of lignin in its structural composition. Compare to other fuels used for manufacture briquettes, such as rice husk (16.36 MJ.kg^{-1}) (Diniz et al., 2004), whet straw (16,40 MJ.kg^{-1}), timothy grass (16,30 MJ.kg^{-1}) (Nanda *et al.*, 2013), sugarcane bagasse (17.33 MJ/kg) (Jenkins, 1990) and eucalyptus wood 19.03 MJ/kg (Soares *et al.*, 2015), the samples presents attractive values, thus increasing the efficiency and reducing the process costs, due to the higher values of HHV, less material will be needed to attend an specific energy demand.

The average values obtained for the bulk density of the biomasses used in the production of briquettes in function to the proportion of pine, are presented in Fig. 1.



*Wood Mix – Mixture of Stem, Primary Branch and Secondary Branch

Fig. 1. Bulk density of pine wood with gradual addition of residual biomasses of coffee production chain.

The bulk density of the mixtures with 0% of pine had higher average values, being higher in approximately 87.25% in relation to the mixtures with 75% of pine, which presented the lowest values of this property. The parchment present the highest value (341.48 $Kg.m^{-3}$), because of the basic density of the material and its particles flat format. This result may significantly influence the quality of the briquette produced due to the accommodation of the particles at the time of compaction. Bulk density is an essential feature in the economic viability of renewable energies, since it influences factors such as transport costs and energy density. In this sense, lignocellulosic residues with high bulk density values are desirable for the production of briquettes. In this case, the increase of residual biomasses of coffee production chain and mixed with pine wood increased the bulk density property. This result is indicative of the superiority of coffee residue in bulk for energy use.

3.2 General and visual aspects of briquettes

The briquettes produced mixed pine in ratios of 0%, 25%, 50%, 75% and 100% with residues of coffee production chain shows satisfactory visual appearance, having good uniformity and absence of cracks, also presenting a smooth and shiny surface indicating that there was sufficient plasticization of the lignin, as can be observed in Fig.2.

Fig. 2. Briquettes produced with different mixtures of residues. PW = Pine Wood. CS = Coffee Stem. B1 = Primary Branch. B2 = Secondary Branch. Mix = Stem + Primary Branch + Secondary Branch. CP = Cherry Parchment.

One way of evaluating the briquetting process is through the compaction rate of the particles, which represents the percentage between the apparent density of the briquette and the bulk density of the particles. Higher values of the compaction rate indicate a reduction of the volume of the briquette, which probably achieves a density gain. Table 4 shows the average values obtained for the compaction rate in relation to the proportion of pine.

Table. 4. Compaction rate of the Briquettes produced with different mixtures of residues

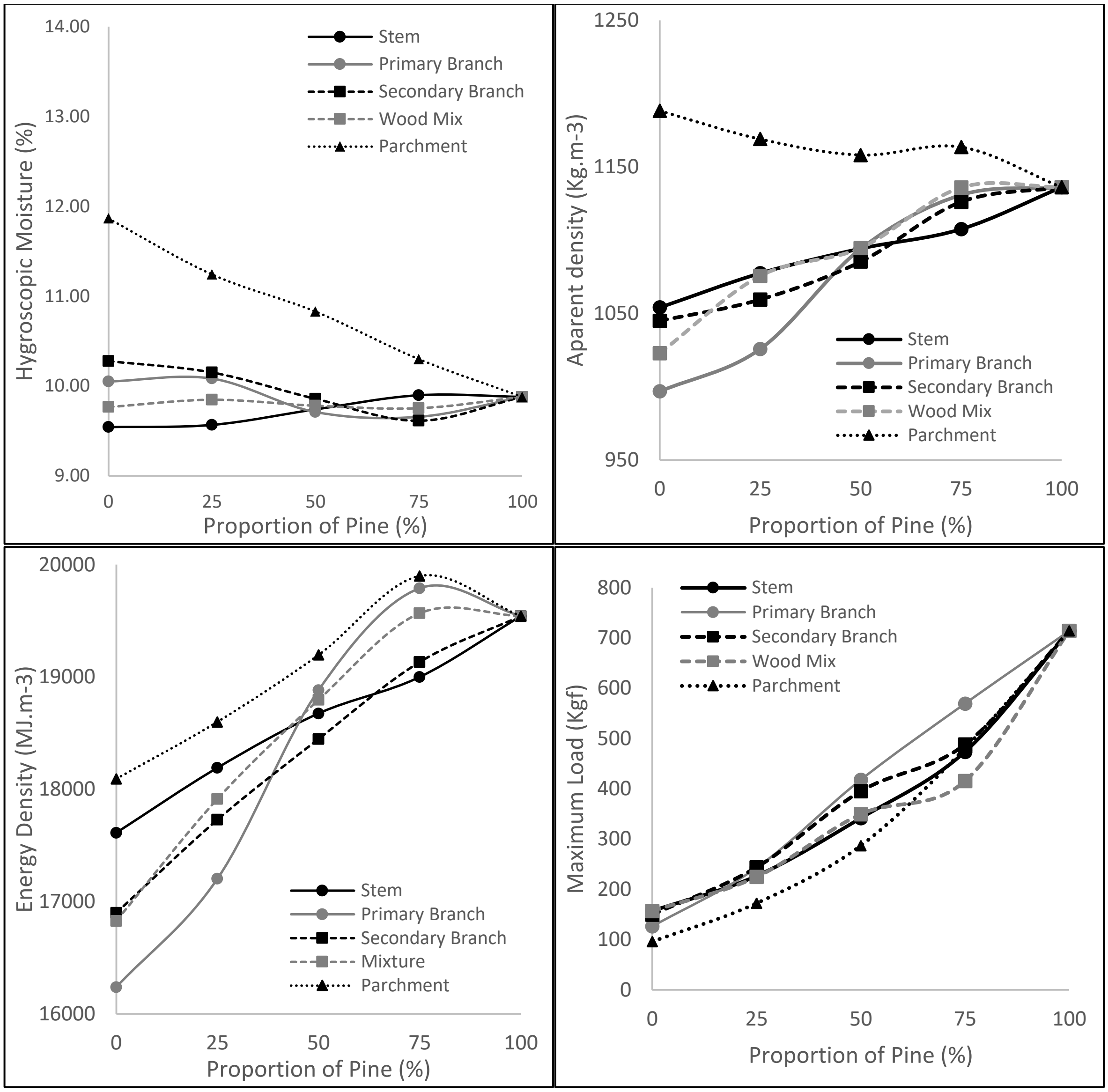
Pine content (%)	Biomasses				
	Stem	Primary branch	Secondary branch	Wood Mix*	Parchment
0	3.67	3.92	4.43	4.53	3.48
25	5.02	15.16	16.25	17.23	14.58
50	18.81	21.64	19.30	19.52	20.13
75	24.12	24.29	25.86	25.41	25.88
100	11.78	11.78	11.78	11.78	11.78

***Mixture of Stem, Primary Branch and Secondary Branch**

In the Table 4, it was observed that mixtures with 75% of pine and 25% of biomass from coffee residues shows higher compactions rates. In addition, the increase in the percentage of residual coffee biomass in the briquettes decreased the compaction rate. This result showed that the fines of the biomasses, after the compaction, obtained a greater reduction of volume. However, the treatment with 100% of pine did not reveal the highest values in this property, as expected, probably due to the difference in basic density between the pine wood and residual coffee biomass. It was also observed that lower compaction rate evidence a higher bulk density of the material, considering that the pressure and temperature used in the briquetting process was the same for all treatments. The biomass with higher bulk density would require higher pressures, because these materials present greater resistance to densification. In this sense, the addition of residual coffee biomass in briquettes, mostly at 50% and 75% can contribute to increase the density without need of spending more energy to increase the pressure in the compaction stage.

3.3 Physical – chemical characterization of briquettes

The average values of hygroscopic equilibrium moisture content, compressive strength, apparent density and energy density of briquettes are presented in Fig. 3. Hygroscopicity and compressive strength are important for evaluating the physical structure of the biomasses in relation to impacts of storage and transportation. Apparent density and energy density study the storage and the energy efficiency of the briquettes, respectively (Rodrigues *et al.*, 2010). According to the identity model test, a single model can be adjusted to the treatments produced with mixtures of pine and stem, primary branch, secondary branch and mix wood (stem, primary branch and secondary branch), as show the Table 5.



Observed and estimated values of the Hygroscopic Equilibrium Moisture (%) (3A), Apparent Density (Kg.m-3) (3B), Energy Density (MJ.m-3) (3C) and Maximum Load (Kgf) (3D) in function of the proportion of Pine.

Fig. 3. Physical properties of Briquettes produced with mixtures of pine wood and residual biomass of coffee production chain

The Fig. 3A. Shows the hygroscopic equilibrium moisture content (HEMC) of the briquettes. This property is of great importance because, briquettes with low HEMC (5 – 12%) (Tumuluru *et al.*, 2011) can favors transportation, in that the amount of energy per transported volume is much higher, also the low HEMC confers to briquettes its compact shape, increasing its physical and mechanical resistance (Avelar *et al.*, 2016). Another factor to be consider is that high values of HEMC, being more difficult to ignite the briquette, and obtaining low energetic density values, because of the inverse relation between the HEMC and net heating value (Tumuluru *et al.*, 2011). In this sense, the mixtures of pine and (I) stem, (II) Primary branch, (III) Secondary branch and (IV) wood mix could be adjusted to a only one model equation (Table 5), because generally was not affected by the mixing proportion of Pine. The briquettes will be handle more efficiently during storage and transportation due to the lowest values of HEMC. For the mixtures of pine and parchment, the increase of pine proportion decrease the briquette HEMC.

The evaluation of the variation of the apparent density after the densification of the biomasses is essential in the production of bioenergy, since a decrease of the briquettes density can raise the costs of transport and decrease the energy density. The apparent density of the briquettes (Fig. 3B) increases with the proportion of pine into the mixture for the treatments with (I) stem, (II) primary branch, (III) secondary branch and (IV) wood mix. This is due to the higher compaction rate of the briquettes with greater percentage of fines. For the briquettes with parchment in its composition, the mixing proportion of pine did not significantly affect the apparent density between the samples, probably for the high basic density of the parchment. The values observed in this work are similar to briquettes produced with eucalypt sawdust (1060 kg.m^{-3}), corn residues (1159 kg.m^{-3}), and coffee husk (1248 kg.m^{-3}) (De Paula Protásio *et al.*, 2011).

The energy density (Fig. 3C) indicates the energy potential of the briquette per volume unit. The energy density of the treatments with (I) stem, (II) primary branch, (III) secondary branch and (IV) wood mix into the briquettes composition increased due to the high HHV of the biomasses. The energy density of briquettes with parchment in its composition presents the highest average values, due to high bulk density. The increase of energy density is attractive for bioenergy because the transport and storage cost are reduced. In this way, for the same volume, briquettes of Parchment with 25% of Pine generate 18% more energy than briquettes of stem with 0% of pine.

The tensile strength by diametral compression and maximum force indicates the ability of briquettes to withstand mechanical impacts during storage and transport.

Therefore, briquettes with low resistance tend to disintegrate more quickly, which can cause problems in the combustion chamber. Kaliyan e Morey (2009) concluded that the size of the particles, the chemical composition, mainly the lignin content, compaction rate and hygroscopic equilibrium moisture content influence the tensile strength of the briquettes. In this study, it was observed that the resistance to diametral compression and maximum force increase with the increase of the pine briquettes content, the highest values observed were of the briquettes with 100% of pine. This result is probably due to the low volumetric expansion after the densification of the mixtures because of the presence of fines; the compression rate; the low HEMC and the lignin content of the pine.

Table 5. Adjusted equation for the physical – chemical properties of Briquettes

Property	Treatment	Adjusted Equation	R^2
Hygroscopic moisture	General model*	$y = 0.00004x^2 - 0.0054x + 9.94$	0.59
	Model for parchment	$y = 0.00003x^2 - 0.0229x + 11.84$	0.99
Compressive strength	General model*	$y = 0.0286x^2 – 2.6885x + 150.04$	0.99
	Model for parchment	$y = 0.045x^2 – 1.6835x + 96.95$	0.99
Apparent density	General model*	$y = - 0.0043x^2 – 1.5405x + 1027.40$	0.99
	Model for parchment	$y = 0.00001x^2 - 0.44x + 1184.90$	0.85
Energy density	General model*	$y = - 0.1897x^2 – 46.601x + 16835$	0.99
	Model for parchment	$y = - 0.1855x^2 – 35.338x + 17995$	0.93

*****Adjusted equation for briquettes except for treatments with parchment in its composition

4. CONCLUSION

In this study, it was demonstrated that the residues from coffee production chain such as stem, primary branch and secondary branch of coffee shrub and parchment of coffee cherry can be used as combustible material in the combustion processes when mixed with pine, adding economic value to this biomasses.

Mixing residues of coffee production chain with different proportions of pine wood improved the characteristics of the briquettes in relation to the resistance to compression, linear expansion, hygroscopic equilibrium moisture, apparent density and energy density. The best mixing ratio between all treatments was 75% pine for all parameters evaluated.

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ARTIGO III

FAST OXIDATIVE PYROLYSIS AS A SUSTAINABLE WAY FOR RESIDUES FROM PULP INDUSTRY AND COFFEE PLANTATION TO A RENEWABLE FUEL

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 woods were investigated under inert and oxidative conditions at the heating rates of 10, 25 and 50 ^{o}C/min. For EW, the process produced 37.7% gases, 22.64 % heavy bio-oil, 17.07% light bio-oil and 15.35% bio-char, and for CS, the process produced: 47.35% gases, 14.67% heavy bio-oil, 23.2% light bio-oil, and 14.75% bio-char. As the bio mass 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 (6.31 times bigger for EW and 4.26 bigger for CS). The bio-char presented the Higher heating value (21.19 MJ kg^{-1} for CS and 22.08 MJ kg^{-1} 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.

Keywords: Fast oxidative pyrolysis, Fluidized bed reactor, Waste, Coffee shrub, Eucalyptus

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). Renewable, abundant and clean energy alternate resources are required to address CO_2 emission. 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 chemicals (Baskar et al., 2012; Basu, 2013). 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., 2013; Rocha et al., 2015; Sellin et al., 2016).

According to Brazilian Tree Industry (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 2.25 million ha (Ministry of agriculture, 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 Foreign Agricultural Service, 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 A, 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 et al., 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 A, 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., 2016). Additionally, fast pyrolysis of agro-industrial residues does not compete with food security (Anex et al., 2010; Trippe 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, 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, 1998). Pyrolysis in inert athmosphere 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., 2015).

The types of reactors, such as the bubbling and circulating fluidized bed reactor, among others, and the main parameters for fast pyrolysis have been widely reported. However values of residence time and temperature influence this type of conversion (Bridgwater, 2012). According to Joubert et al. (2015) a rapid removal and rapid cooling of the vapors generated in the pyrolysis is of paramount importance in raising the efficiency of the operation. 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^{-1} (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 was 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 results obtained by Kim (2015) were similar to those of other researchers.

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 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. It is important to note that the bio oils generated by fast pyrolysis and can be fast quite different. Also bio-oils from different raw materials exhibit variances. For example, according to the literature, bio-oils from coffee grounds have a greater amount of carbon, nitrogen, water, heating value and a lower amount of oxygen when compared to bio-oils from woody biomass. Therefore, it is important to obtain data on the bio-oil generated by the oxidative pyrolysis of residues from the woody biomass of coffee and eucalyptus plantations so that their suitability to bio-oil generation can be ascertained.

2. MATERIALS AND METHODS

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 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 biomass 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 analyses were carried out in triplicate and a mean value corrected for moisture content is reported.

The thermal behavior of the biomass materials was studied under inert (N_2) and oxidative (Air) atmospheres using a DTG60H-SHIMADZU. TGA, DTG and DTA experiments were performed at heating rates of 5, 25 and 50^{o}C min^{-1} (gas flow of 30 ml min^{-1}) from room temperature to 500 ^{o}C.

Pyrolysis Plant and Experimental Procedure

Fast oxidative pyrolysis experiments have been performed in a fully controlled, continuously operated pilot-scale plant (SDB-20) as shown in Fig. 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 (Amutio et al., 2012; Mesa-Pérez et al., 2013; Sellin et al., 2016).

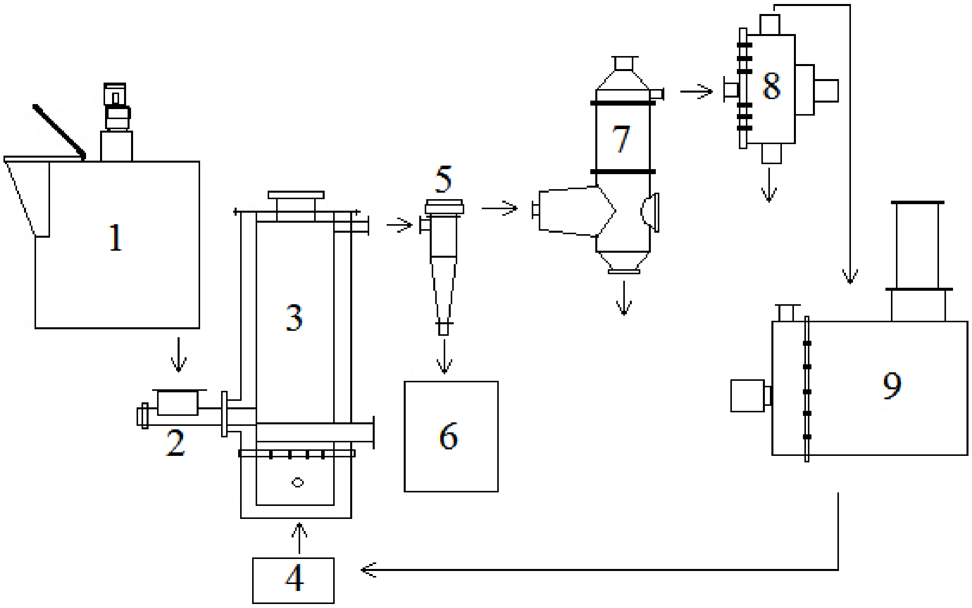

Fig. 1. Scheme of the SDB-20 pilot plant, flow diagram. 1) Hopper/silo; 2) screw feeder; 3) fluidized bed reactor; 4) compressor; 5) cyclone; ; 6) char storage system; 7) and 8) bio-oil extraction system; 9) combustion chamber.

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^{-1} for the CS and 15.06 kg h^{-1} 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 ± °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 $13Nm^3$ h^{-1} for air and 7 Nm^3 h^{-1} 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 1300 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.

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 (HHV), measured by a bomb calorimeter (Parr 6300 Calorimeter) and density, measured using a scale and graduated cylinder.

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 (HHV) data 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.

3. RESULTS AND DISCUSSION

After analyzing the properties of used biomass resources, the pyrolysis of eucalyptus wood (EW) and coffee shrub (CS) 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. All the tests occured with no major operational problems.

3.1 Biomass analyses

The results of the proximate analysis, ultimate analysis, and ash composition of residual biomasses studied are presented in Table 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 1, wood of 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% (Demirbas, 2004; Rocha et al., 2015).

Moisture in the EW was 16.56%. This value is outside the recommended range for the pyrolysis process, between 7% and 15% (Fernandes et al., 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 (Demirbas A, 2009).

The higher heating values (HHV) of samples are similar to other lignocellulosic biomasses which, nowadays, are being evaluated as raw materials in pyrolysis (Greenhalf et al., 2013; Mesa-Pérez et al., 2014, 2013; Sellin et al., 2016). 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 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 (1.45 for EW and 1.52 for CS) and O/C (0.49 for EW and 0.71 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.

Table 1. Heating Value, Proximate and Ultimate Analysis.

	Eucalyptus wood waste	Coffee shrub	Sugar cane straw (A)	Elephant grass (B)	Wheat straw (C)	Banana Leaves (D)	Sugar cane bagasse (E)
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^{-1})							
HHV	18.1	19	18	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	50.3	49.6	43.2	41.2	44.9	43.5	50.57
H	6.1	5.98	6.7	5.5	5.71	6.2	6.05
O	33.1	44.1	33.2	46.6	43.8	42.3	42.55
N	3.3	0.071	0.3	1.8	0.63	0.86	0.73
S	0.4	0.032	0.2	*nd*	*nd*	0.95	0.1
O/C	0.49	0.71	0.58	0.85	0.73	0.73	0.63
H/C	1.45	1.52	1.85	1.59	1.52	1.7	1.43

[a] dry basis; [b] dry ash free basis; *nd*-not determined; M − moisture; V − volatiles; FC − fixed carbon; HHV − higher heating value; LHV− lower heating value

From Mesa-Pérez et al. (2013) (A), Mesa-Pérez et al. (2014) (B), Greenhalf et al. (2013) (C), Sellin et al. (2016) (D), Rocha et al. (2015) (E)

The TG and DTG curves in inert and oxidative atmosphere of eucalyptus wood and coffee shrub are shown in Fig. 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 °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 hemicellulose 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 °C that is associated to the char combustion.

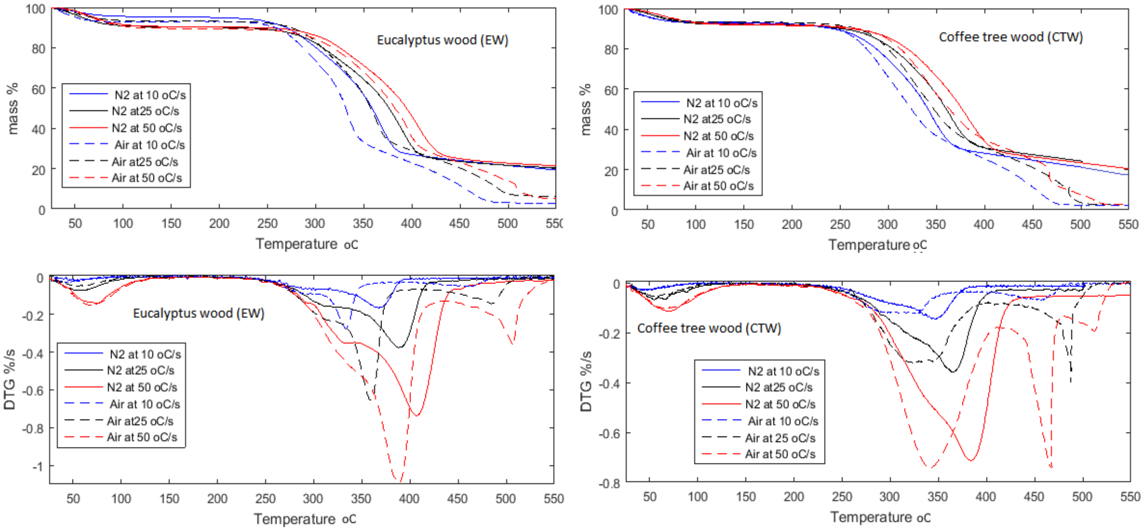

Fig. 2. Thermal behavior of eucalyptus wood (EW) and coffee shrub (CS) by TGA and DTA.

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

The temperatures for the onset of active pyrolysis occurs in a range between 223 and 240 ^{o}C. 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 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.

Table 2. Thermogravimetric Properties of the Samples

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

nd not determined

3.2 Yield of products

The Table 3 shows the product yields obtained in the experiments carried out are expressed on on basis of the driy 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 (Mesa-Pérez et al., 2013; Sellin et al., 2016). 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 °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 °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 (EW) and coffee shrub (CS) 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.

Table 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]			
	Reactor capacity	Process temperature	Fluidization agent	Liquid		Char	Gas
				Heavy bio-oil or organics	Light bio-oil or reaction water		
	kg h^{-1}	°C		wt %	wt %	wt %	wt %
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 (A)	12	500	Air	17	10	23.3	49.6
Wheat straw (B)	1	525	Nitrogen	21.39	12.54	28.05	26.99
Pine wood (C)	1	480	Nitrogen	47	11	15	23
Willow SRC (D)	1	500	Nitrogen	40.51	10.81	19.28	19.89

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

From Sellin et al. (2016) (A), Greenhalf et al. (2013) (B), (Westerhof et al., 2010) (C), (Greenhalf et al., 2012) (D)

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.

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^{-1} 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 Fig. 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).

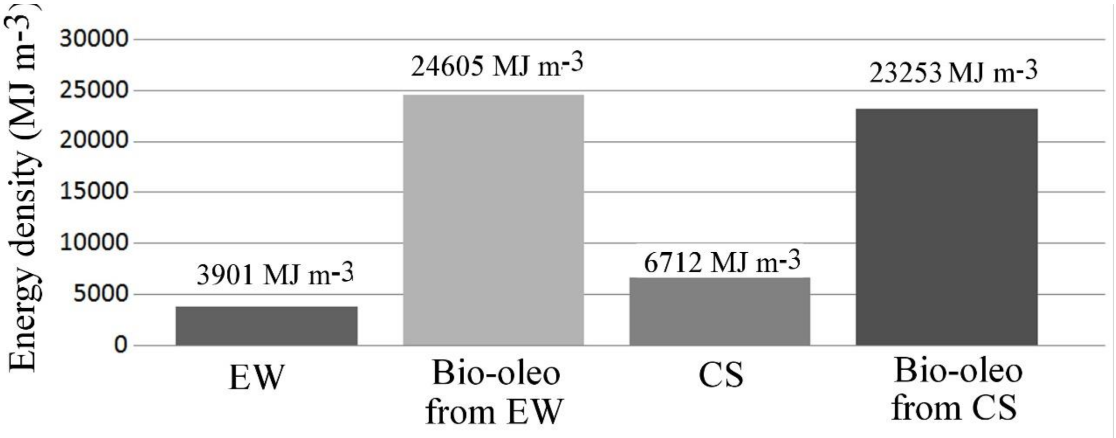

Fig. 3. Comparison between the energy density (MJ m^{-3}) of bio-oils and biomasses.

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 4. The physical and chemical characteristics of bio-char depend on the biomass specie and the experimental conditions of the fast pyrolysis process (Bridgwater, 2012) . The bio-char generated in oxidative fast pyrolysis of residues from pulp industry (EW) and coffee shrub (CS) presented the Higher heating value (26.06 MJ kg^{-1} for CS and 27.16 MJ kg^{-1} for EW) inside the range found for vegetal biomasses as showed in table 4.

Table 4. Analyses of the bio-char from oxidative pyrolysis.

	Bio-char from				
	Coffee shrub	Eucalyptus wood waste	Banana leaves (A)	Sugar cane straw (B)	*Pinus insignis* (C)
Proximate analysis (wt %)					
M	2.58	3.45	1.68	1.9	*nd*
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

From Sellin et al. (2016) (A), Mesa-Pérez et al. (2013) (B), Amutio et al. (2012) (C)
nd not determined

3.5 Energy efficiency

Table 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^{-1} for EW and 14412 kcal h^{-1} 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.

Table 5. Energy efficiency for products from pyrolysis of studied.

	Energy of products (kcal h^{-1})	Energy efficiency		Energy density (MJ m^{-3})
		Based on TPEa (%)	Based on TUE b (%)	
Products 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	*nd*
Gases	36808.61	68.80	72.39	*nd*
Products from coffee shurb				
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	*nd*
Gases	10977.72	64.31	76.17	*nd*

[a] Total primary energy (TPE, 53502 kcal h^{-1} for EW and 17069 for WCT). [b] Total useful energy (TUE, 50845 kcal h^{-1} for EW and 14412 for WCT). *nd*-not determined

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 (3901 MJ m^{-3} EW and 6712 MJ m^{-3} for CS).

4. CONCLUSION

The oxidative fast pyrolysis of eucalyptus wood (EW), from pulp industry and coffee shrub (CS), from coffee plantations in a fluidized bed reactor was investigated.

The physicochemical 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^{-1}) 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^{-1} for CS and 26.2 MJ kg^{-1} 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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CONCLUSOES GERAIS

Pela facilidade de operação e pela quantidade de energia que é gerada a partir da biomassa in natura é adequado, desde que observada suas características (Propriedades físicas, químicas e mecânicas), estabelecer a melhor rota de conversão das biomassas do cultivo de café. Pode-se observar que as propriedades da madeira do cafeeiro demostraram grande viabilidade de utilização dos processos de conversão para a produção de energia, apresentando valores baixos de umidade e de teor de cinzas e um alto teor de voláteis e de poder calorífico superior, porém o teor de carbono fixo é baixo. O pergaminho apresenta alto teor de cinzas o que prejudica o potencial calorifico e a eficiência dos processos de conversão termoquímica. Entretanto, a princípio e no geral, as características físicas e químicas são favoráveis aos processos de conversão termoquímicos.

A partir da caracterização das biomassas in natura, dos ensaios de pirólise rápida e da caracterização dos produtos, conclui-se que as biomassas provenientes dos resíduos das plantações do cafeeiro são potenciais candidatas à produção de bioenergia por pirólise rápida. Elas podem ser utilizadas como fontes convencionais de biomassa, assim como resíduos da cadeia produtiva de cana de açúcar, madeira de pinus e eucaliptos, entre outros, para produção de energia por meio de tecnologias de conversão termoquímica.