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Potential assessment of eucalyptus grown for biorefinery processes

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ABSTRACT

With the predictability of oil shortage, there is a strong demand for renewable and sustainable raw materials. In this scenario, lignocellulosic material stands out as a potential solution. With the use of bio-refinery, they can be processed into high value added products through chemical, biochemical and thermochemical processes. A great source of lignocellulosic biomass today is the wood of Eucalyptus, which has high levels of production and productivity in Brazil, reaching numbers between 60-80 m3ha1year-1. In order to achieve a more efficient utilization of biomass in a biorefinery concept, it is necessary first to perform chemical analyses to define the operating conditions of the conversion processes, since heterogeneity and high chemical complexity is an inherent property of the biomass. In this context, this study aimed to chemically characterize and investigate the potential of three species of Eucalyptus (*E. urophylla*, *E. saligna* and *E. dunnii*) grown in Rio Grande do Sul state for biorefinery purposes. Results of higher heating value for *E. urophylla*, *E. saligna* and *E.dunnii* were similar (19.10, 19.10 and 19.15 MJ/kg respectively). However, cellulose content results for *E. s*aligna (47.5%±2.40) were highlighted, being slightly higher than those for *E. urophylla* (42.75%±1.34) and *E.* dunnii (43.10%±1.13). Hemicelluloses content for *E. u*rophylla (23.25%±0.78) was slightly superior to the others (20.35%±2.05 for E. saligna and 18.80%±2.40 for E. dunnii). Finally, it was concluded that the analysed species of Eucalyptus have high potential for biorefinery in thermochemical processes. The species *E. urophylla* has the greatest potential for biorefinery processes using hemicelluloses, and the species *E. saligna* has greater potential for biorefinery processes utilizing cellulose.

Key words: Chemical characterization, lignocellulosic biomass, Heating Value, cellulose.

INTRODUCTION

In view of an expected shortage of oil, there is a great demand for renewable and sustainable raw materials in the near future (Shafiee 2009). Therefore, the replacement of petroleum-based processes or other non-renewable sources for biorefinery process is of great interest (Santos et al., 2013). Today, 41.2% of Brazil`s energy grid is already derived from renewable sources, with an increased growth forecasted for the coming years. Also, biomass represents more than half of the total renewable sources in Brazil, which makes the country a world reference in power generation through biomass (Empresa de Pesquisa Energética 2016).

An important feature of Brazil is its high productivity achieved with certain woody crops, which is highly advantageous for energy forestry. Currently, most of planted forest area is allocated to the energy sector, with another large portion intended for pulp and sheet (Associação Brasileira de Produtores de Florestas Plantadas 2013). With new possibilities for energy gain, more investment would go to the forestry sector, adding value to the planted wood. Most of Brazil`s energy forestry consists mainly of Eucalyptus varieties, comprising 6.95 million hectares of planted forest in 2014 (Instituto Brasileiro de Geografia e Estatística 2016). This area used for forestry of Eucalyptus is justified by the high productivity of this crop achieved in Brazil, reaching values between 60-80 m3ha^{-1}year^{-1} (Stape et al., 2010).

In this context, biorefinery turns out as an important renewable solution for industry processes, using woody biomass for energy production and development of new high added-value products. With increasing energy forestry area and the increase of waste in the timber industry, the development of techniques to make the most of the available natural resources is necessary.

Currently, there are many researches and developments in biorefinery processes: chemical (transesterification, hydro processing and Fischer-Tropsch reactions for the production of biofuels), biochemical (fermentation and the use of enzymes for biofuels), and thermochemical processes (combustion, gasification and pyrolysis for the production of biofuels and energy) (Santos et al., 2013).

To properly select biorefinery processes and final product obtained, a biomass characterization is highly recommended. (Eichler 2015). Chemical, elemental and immediate composition of biomass directly affects the choice of the best bioproducts to be obtained and the type of process used. For example, (I) with elemental analysis, it is possible to know the weight fractions of the chemical elements (carbon, hydrogen, nitrogen, sulphur and oxygen) constituents of the biomass, essential for the combustion process; (II) the immediate analysis refers to fixed carbon, volatiles and moisture present in the biomass, necessary data to choose the best thermal process used; (III) with the Calorific Value , the amount of energy released as heat during the complete combustion of biomass can be determined; (IV) establishing the chemical composition of cellulose, hemicelluloses, lignin and extractives present in biomass show its potential for specific biorefinery processes such as second generation alcohol (Santos et al., 2012). Understanding the constituents present in biomass is paramount in transformation or conversion processes, generating information from both qualitative as quantitative characters.

In this context, this study aimed to chemically characterize and investigate the potential of three species of Eucalyptus (*E. urophylla*, *E. saligna* and *E. dunnii*) grown in Rio Grande do Sul state for biorefinery processes.

MATERIALS AND METHODS

Feedstock

Raw material used in the experiments was wood chips of three different Eucalyptus species with 9 years of age (*E. urophylla*, *E. saligna* and *E. dunnii*) grown in Guaiba city in Rio Grande do Sul state, Brazil. The material was harvested with proper equipment in April 2015, left for 90 days in the field for drying, and transported to the pulp mill in Guaiba city for log processing and chipping. The wood chips were separated for each variety in 2kg bags, and mixed so that chips from bottom and top of the tree log were in the same sample.

The experimental methodology for physicochemical characterization and other analyses of biomass were performed all in duplicate, at the Institute of Petroleum and Natural Resources at the Pontifical Catholic University of Rio Grande do Sul and the Federal University of Viçosa in Minas Gerais.

Pre-processing

For elementary, chemical and immediate analysis, wood chips were previously ground as required for those analytical procedures, in order to reduce the wood sample particles diameter. To this end, chips were placed in a knife mill and reduced particle size to pass through a 40 mesh sieve, being retained on a 60 mesh sieve (0.42 mm>particle diameter> 0.25 mm).

Proximate analysis

In the proximate analysis, moisture, ash, volatile and fixed carbon contents were measured. Analyses were performed according to NBR 8112 standard.

Ultimate analysis

Analysis of Carbon, Hydrogen, Nitrogen and Oxygen contents is performed to determine their proportions in the samples. The process is based on an automated colorimetric method named Pregl-Dumas. Samples were burned at 950 °C in non-dispersive Elemental Analyser TRUSPEC, LECO brand, equipped with an infrared detector. The sulphur content analysis was performed on Leco SC-632 type Elemental Analyser equipped with an infrared detector.

Heating value

Materials were assessed for High Heating Value (HHV), with a calorimeter bomb, model Parr 6300. This analysis was performed in duplicate, according to NBR 8633/84 standard.

Another way to obtain HHV is through calorific value of some formulas that uses elemental or immediate composition values to estimate Heating Values of some solid fuels. Such formulas allow an estimate for Heating Value, although since those use different compositions, their final result can vary for each type of solid fuel. To evaluate the estimate values for lignocellulosic biomass as the Eucalyptus biomass, three formulas were used to identify whether the numbers obtained in the formulas (Dulong, Yokoyama and Channiwala) were similar to the results obtained with the calorimeter bomb.

Dulong formula consists of applying percentage values of fuel elementary composition to evaluate the superior calorific power. According to Dulong, the total calorific fuel value is the sum of the calorific value of each fuel element regardless of the amount of oxidation states occurs (Basu 2006):

$$HHV\,(kJ/kg) = (C * 33\,823) + 144\,249 * (H - \mathrm{O}/8) + \mathrm{S} * 9\,418$$

C, H, O, S are the percentages of Carbon, Hydrogen, Oxygen and Sulphur, respectively.

According to Vital et al. (2013) the calorific value can also be estimated by Yokoyama of formula (Santos et al., 2013). This formula uses carbon solid fuel composition for estimation.

$$HHV\,(MJ/kg) = 0.4571 * C - 2.7$$

Another formula that estimates the gross calorific value is the Channiwala formula that uses data from immediate analysis (Parikh et al., 2005):

$$HHV\,(MJ/kg) = 0.3536 * FC + 0.1559 * VC - 0.0078 * AC$$

FC, VC and AC are the percentage of Fixed Carbon, Volatile Content and Ash Content, respectively.

Chemical characterization

The chemical characterization of eucalyptus samples was performed in Pulp and Paper Laboratory of the Federal University of Viçosa. The following chemical analysis was carried out: cellulose content, hemicelluloses, lignin (soluble, insoluble and total) and total extractives.

Determination of carbohydrate content was performed using hydrolysis of polysaccharides according to Saeman method, followed by quantification of the resulting sugars by ion-exchange chromatography (Dionex IC-3000) with a pulsed amperometric detection (HPAE-PAD).

RESULTS AND DISCUSSION

Density

Chart 1 shows the average values of chips basic density of the three species of eucalyptus (*Eucalyptus urophylla*, *E. saligna* and *E. dunnii*), along with comparisons with results for the same species obtained by other authors.

Chart 1. Mean basic density of Eucalyptus species.

Species	Density (g/cm^3)	Reference
E. urophylla	0.56	This Work
E. urophylla	0.54	Vital, 2013
E. urophylla	0.55	Queiroz, 2004
E. saligna	0.49	This Work
E. saligna	0.50	Vital, 2013
E. saligna	0.46	Foelkel, 1971
E. dunnii	0.52	This Work
E. dunnii	0.51	Vital, 2013
E. dunnii	0.55	Lopes, 2007

As it can be seen, among the species studied, there was a slight difference in absolute values, where *E. urophylla* had higher average basic density values (0.56 g/cm^3) and *E. saligna* obtained the lowest absolute average basic density values (0.49 g/cm^3).

However, compared with literature values obtained by Vital et al. (2013) for the same species (0.54 g/cm^3 for *E. urophylla* and 0.50 g/cm^3 for *E. saligna*) of the same age and the same part of the plant assessed (wood without shell), it can be seen that there are no major differences between values.

Specific gravity is used as a quality parameter for various industrial processes. For example, for direct wood burning to obtain thermal energy, low densities can result in a rapid burning of the material, and thus little energy generated per unit volume. On the other hand, high density wood obtains larger amounts of thermal energy per unit volume. However, higher densities also lead to higher initiation time for wood burning (Vale et al., 2002). The same author suggests a specific gravity in the middle range between 0.65 and 0.80 g/cm^3 for burning and obtaining thermal energy.

In Kraft technique studies, low density Eucalyptus wood, in some cases, is the most recommended material for pulp production. It provides higher screened yield, higher pulp viscosity, requiring lower alkali charge in cooking, obtaining lower solids content in the residual liquor, and lower consumption of chemicals in bleaching (Queiroz et al., 2004).

Proximate analysis composition

For the evaluation of the main thermochemical processes, an immediate analysis is needed, aimed at discovering the values of ash, volatile and fixed carbon from biomass. In Chart 2, results of immediate composition of wood chip samples performed for three species of eucalyptus are shown, as well as data from other authors, for comparison purposes.

Chart 2. Immediate composition of Eucalyptus species.

Species	Volatiles (%)	Ashes (%)	Fixed Carbon (%)	Reference
E. urophylla	87.80	0.10	6.14	This Work
E. urophylla	87.34	0.40	11.66	Nakai, 2014
E. urophylla	85.35	0.90	13.75	Eufrade Junior , 2015
E. saligna	87.09	0.15	8.09	This Work
E. saligna	84.80	0.50	14.70	Santos, 2010
E. saligna	84.50	0.55	15.05	Souza, 2013
E. dunnii	85.77	0.30	9.31	This Work
E. dunnii	86.27	0.36	3.16	Scremin, 2012
Eucalyptus sp.	81.70	0.27	18.03	Macedo,2012

It is observed that the ash content of *E. urophylla* analysed (0.15%) was below the values found by Nakai (2014) (0.40%), and Eufrade Junior (2015) (0.90%) for the same species. The same happened with the ash content for E. *saligna* (0.15%), which was also lower than values found for the same species by Santos (2010) and Souza (2013), with 0.50 and 0.55 % respectively.

In the case of *E. urophylla*, the volatile content (87.80%) was similar to the values found by Nakai (2014) (87.34%), and Eufrade Junior (2015) (85.35%). Nevertheless, the fixed carbon content of *E. urophylla* (6.14%) was much lower than the values found in literature (11, 66% and 13.75%). The same was true for *E. saligna* analysis, where the fixed carbon value (8.09%) was below the values found in literature by Santos (2010) (14.70%), and Souza (2013) (15.05%). The *E. saligna* species volatile content (87.09%) was slightly higher than that in literature, only about 2-3% higher compared to values of Santos (2010) (84.80%) and Souza (2013) (84.50%).

Volatile content refers to volatile fraction of the residual biomass, composed of gases such as hydrogen, hydrocarbons, carbon monoxide and carbon dioxide (Santos et al., 2013). In the formation of gas during the heat treatment, tar formation can be related to the amount of volatile materials, so that during wood burning, biomass with higher volatile concentrations can obtain higher yields of condensable gases (Vale et al., 2002). Therefore, for the production of bio-oil through pyrolysis of biomass, biomass with higher volatile content would be recommended. In this case, samples of *E. saligna* and *E. urophylla* are recommended for this type of biorefinery, due to high volatile content values with 87.09% and 87.80%, respectively.

Ash content refers to biomass inorganic components, mineral oxides residue obtained by complete combustion of the material (Santos et al., 2013). Reis et al. (2012) show that the amount of ash content causes a decrease in the Higher Heating Value. Therefore, it can be assumed that samples of *E. urophylla* and *E. saligna* are recommended for thermochemical energy conversion processes, since they possess lesser amounts of mineral matter 0.10% and 0.15%, respectively.

The fixed carbon content is an important indicator of the quality of coal in the steel industry (Santos et al., 2013), being also important for energy production, directly affecting the amount of energy obtained by burning. Vale et al. (2002) noted that high levels of fixed carbon in the fuel have a slower burning, with longer residence times in the combustion reactors. Higher fixed carbon content also positively influences the increase of biomass gross calorific value (Reis et al., 2012).

Elemental composition

Elemental composition is the elementary mass percent of biomass components and it is an important biomass quality parameter. Chart 3 shows the percentages of carbon, hydrogen, nitrogen, sulphur and oxygen obtained by comparing literature data along with elemental analysis of the samples.

Chart 3. Elemental composition of Eucalyptus species.

Species	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)	Oxygen (%)	References
E. urophylla	53.76	5.65	0.01	0.00	40.59	This Work
E. saligna	54.47	5.47	0.25	0.02	39.80	This Work
E. dunnii	54.24	5.68	0.00	0.00	40.08	This Work
E. urophylla	43.90	7.40	0.40	0.09	47.50	Eufrade Junior, 2015
E. urophylla	46.76	6.14	0.11	0.00	47.00	Reis, 2012
E. dunnii	43.84	6.74	0.06	0.00	49.36	Alho, 2012
Eucalyptus sp.	47.20	6.50	0.50	0.10	44.00	Vital, 2013
Eucalyptus sp.	49.50	5.75	0.14	0.03	44.00	Vital, 2013
E. grandis	48.30	5.89	0.01	0.01	44.20	Vital, 2013

In the results for the three species of Eucalyptus analysed, there was no significant difference between them for all elemental compositions. The content of carbon (53.76%, 54.47% and 54.24%), hydrogen (5.65%, 5.47% and 5.68%), nitrogen (0%, 0.02% and 0%), sulphur (0%, 0.02% and 0%) and oxygen (40.59%, 39.80% and 40.08%) for the *E. urophylla*, *E. saligna* and *E. dunnii*, respectively, varied up to a maximum of 1% between the results obtained for the various species. It is also important to note that the results of carbon percentage (53.76%) were about 10% higher than the results found by Eufrade Junior (2015) (43.90%) for the same species (*E. urophylla*). The same happened to the result of carbon content obtained for E. dunnii (54.24%), which also reached about 10% higher than that found by Alho (2012) (43.84%) for the same species. The carbon content is directly related to the calorific power where Vital et al. (2013) reports that an increase of 1% of carbon may amount 0.39 MJ/kg of HHV.

It is noticeable that the results of hydrogen percentage (average 5.6%) were slightly lower than those found in literature by Eufrade Junior (2015) (7.40%) and Alho (2012) (6.74%) for *E. urophylla* and *E. dunnii*, respectively. Reis et al. (2012) points out that the decrease in hydrogen content is undesirable for energy production, as the increase of 1% of this level can lead to gains of 515 kcal/kg in HHV.

The content of nitrogen and sulphur of *E. dunnii* samples and *E. urophylla* were in error limit of the method (0.01%), showing that the value of these elements in the biomass were extremely low. Only the specie analysed E. saligna remained with relatively high nitrogen rates (0.25%), compared to the others (0% for both *E. urophylla* as for *E. dunnii*) and compared to values found by Reis et al. (2012) for *E. urophylla* (0.11%) and data found by Alho (2012) for *E. dunnii* (0.06%). After combustion, elements like nitrogen and sulphur reacts with oxygen to form nitrogen oxides and sulphur oxides, which can be highly toxic and polluting gases (Reis et al., 2012).

Oxygen content results were on average of 40.16%, a figure slightly below all the values found in literature. For the author Vital et al. (2013), the average values of oxygen content for wood species of Eucalyptus sp. were 44%, while for Eufrade Junior (2015) and Reis et al. (2012), these values in *E. urophylla* were on average 47.5 and 47%, respectively. The increase in the biomass oxygen content tends to lower the calorific value of the fuel (Reis et al., 2012).

As shown by Basu et al. (2006), percentage values of the elemental composition allow us to perform stoichiometric calculations for various uses in thermochemical processes. For combustion and gasification, these values allow us to calculate: the amount of CO_2 and H_2O produced in the complete combustion; the amount of air needed for gasification of the fuel; the amount of adsorbent required for cleaning sulphur from the fuel gas; Higher Heating Value and Lower Heating Values (Basu et al., 2006).

Calorific value

The results obtained and calculated for the Higher Heating Value are shown in Chart 4, together with published results achieved experimentally for the same species. Besides the HHV obtained by calorimeter bomb, results of the elemental and immediate compositions for such theoretical estimates were also used as shown in Chart 4 (Santos et al., 2013).

Chart 4. Higher Heating Value of Eucalyptus species.

Species	HHV (MJ/kg)	Reference
E. urophylla	19.10±0.01	This Work
E. urophylla	18.97	Dulong*
E. urophylla	21.87	Yokoyama*
E. urophylla	15.58	Chaniwalla*
E. urophylla	18.70	Eufrade Junior, 2015
E. urophylla	18.05	Counto, 2013
E. saligna	19.10±0.14	This Work
E. saligna	19.10	Dulong*
E. saligna	22.19	Yokoyama*
E. saligna	16.43	Chaniwalla*
E. saligna	19.39	Couto, 2013
E. saligna	17.95	Couto, 1984
E. dunnii	19.15±0.07	This Work
E. dunnii	19.26	Dulong*
E. dunnii	22.09	Yokoyama*
E. dunnii	16.66	Chaniwalla*
E. dunnii	19.08	Pereira, 1997
E. dunnii	19.01	Brand, 2014

*Values calculated by formulas.

It is noticeable that, for the results obtained by the experiment using bomb calorimeter, there was no significant variation between the results of different species where *E. urophylla* and *E. saligna* had the same value (19.1 MJ/kg), and only *E. dunnii* value was slightly higher (19.15 MJ/kg).

The values found by Pereira et al. (1997) (19.08 MJ/kg) and Brand (2014) (19.01 MJ/kg) and those obtained in this study (19.15 MJ/kg) for *E. dunnii* species showed no significant differences, where the value found corroborates with those in literature. The values calculated by Yokoyama´s formulas (22.09 MJ/kg) and Chaniwalla (16.66 MJ/kg) differ from the average of the values obtained (19.15 MJ/kg), while the theoretical value using Dulong equation (19.26 MJ/kg) was closer to the average of the values obtained and the results found in literature.

The same thing can be observed in *E. urophylla* HHV values and *E.* saligna, where those obtained in the experiment (both 19.10 MJ/kg) and calculation using Dulong´s formula (18.97 MJ/kg and 19.10 MJ/kg, respectively) are similar to the results in literature for the same species (18.70 MJ/kg Eufrade Junior (2015) for *E. urophylla* and 19.39 MJ/kg Couto and Muller (2013) for *E. saligna*). However, values calculated from Yokoyama`s formula (21.87 MJ/kg for *E. urophylla* and 22.19 MJ/kg for *E. saligna*) and Chaniwalla´s formula (15.85 MJ/kg for *E. urophylla* and 16.43 MJ/kg for *E. saligna*) are relatively different.

According to Brand (2010), the main factors influencing gross calorific values are: chemical composition, type of biomass, moisture and ash contents.

Chemical characterization

Average values of cellulose, hemicelluloses, lignin and extractives are shown in Chart 5, along with values found in literature for some species of Eucalyptus, making an average of values for comparison purposes as well.

Chart 5. Chemical composition of Eucalyptus species.

Species	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractives (%)	Reference
E. urophylla	42.75±1.34	23.25±0.78	27.25±0.21	3.45±0.07	This Work
E. saligna	47.50±2.40	20.35±2.05	29.55±0.07	1.45±0.07	This Work
E. dunnii	43.10±1.13	18.80±2.40	28.90±0.01	3.75±0.07	This Work
E. urophylla	47.40	18.60	30.60	2.88	Gomide, 2005
E. urophylla	49.70	19.60	28.20	1.99	Gomide, 2005
E. grandis	44.00	12.40	25.60	0.38	Rocha, 2015
E. grandis	40.20	15.70	26.90	0.38	Rocha, 2015
E. grandis x urophylla	45.80	22.40	27.80	3.52	Gomide, 2005
E. grandis x urophylla	44.10	22.00	29.90	3.45	Gomide, 2005
Average	44.95	19.23	28.30	2.36	

Results of extractives obtained for *E. urophylla* (3.45%) and *E. dunnii* (3.75%) were slightly higher than the mean calculated value (2.36%) and higher than values found by Gomide et al. (2005) for *E. urophylla* (2.88 and 1.99%), but very similar to those found by the same author for hybrid *E. urophylla* x *E. grandis* (3.52 and 3.45%). The value of *E. saligna* extractives obtained was lower than the overall average, being higher only comparing to values found by Rocha (2015) for *E. grandis* (0.38%).

Extractives content affect some physical properties of wood as colour, smell and resistance to microorganisms (Santos et al., 2013). As part of the extractives is volatile, they are important for timber firing, helping to keep the flame of combustion. Thus, high levels of extractives are beneficial for power generation, but detrimental for the production of charcoal, since it reduces gravimetric yield (Santos et al., 2013).

The results of extractives obtained from *E. urophylla* (3.45%) and *E. dunnii* (3.75%) show that both would be favourable for energy production, since they have higher content of extractives compared with the result for *E. saligna* (1.45%).

Lora and Venturi (2012) point out that the correlation content values of cellulose, hemicelluloses and lignin affect several biorefinery processes. Biomass pre-processing for second generation ethanol production is dependent on the chemical composition of biomass, where the type of pre-treatment is chosen depending on the content of cellulose, hemicelluloses and lignin.

Yang et al. (2007), showed that wood composition also directly affects gas composition obtained from pyrolysis and the pyrolysis temperature used in the process. The same author observed individual differences between cellulose, lignin and hemicelluloses in the pyrolysis of each of the contents, where cellulose pyrolysis in a fixed bed is between 315-400 °C with increased formation of CO; the pyrolysis with hemicelluloses produce higher CO_2 content, and lignin pyrolysis produces higher H_2 content with pyrolysis in the range of 150-900 °C.

Cellulose

It is important to notice that the value obtained from cellulose content for *E. saligna* (47.5%) was slightly higher than the others and the average value (44.95%), but similar to those found by Gomide et al. (2005) for *E. urophylla* (47.4 and 49.7%). Values obtained from *E. urophylla* (42.74%) and *E. dunnii* (43.1%) were significantly lower than the average value calculated, being only above the cellulose content found by Rocha (2015) for *E. grandis* (40.2%).

Ferreira et al. (2006) state that higher cellulose content increases pulp yield during cooking process. This is particularly important for species type selection for specific production of paper, where high levels of cellulose favours pulp production directed to "tissue" like paper. High levels of hemicelluloses are favourable for pulp production intended for "printing and writing" like paper (Ferreira et al., 2006).

Yang et al. (2007) shows that differences in cellulose content in the biomass lead to different final compositions of synthesis gas, where higher cellulose concentrations can produce larger amounts of CO in the final pyrolysis gas composition.

Higher concentrations of cellulose in biomass favours second generation ethanol production, according to Santos et al. (2013), depending on the recovery yield of cellulose due to the pre-treatment used.

Hemicelluloses

The results for hemicelluloses content were above average (19.23%) for *E. urophylla* (23.25%) and *E. saligna* (20.35%), but slightly below average for *E. dunnii* (18.8%). The result obtained for *E. urophylla* was above other results from the same species, compared with those found by Gomide et al. (2005) (18.6 and 19.6%), far above the results by Rocha (2015) for *E. grandis* (12.4 and 15.7%) and similar to the first author results for *E. grandis* x *E. urophylla* hybrids (22.4 and 22%).

The results obtained from *E. saligna* (20.35%) and *E. dunnii* (18.80%) were in a difference of +/- 1% of the average (19.23%), being above the results found by Rocha (2015) (12.40% and 15.70%).

Macedo (2012) point out that materials with higher content of hemicelluloses tend to create more volatile products, compared to the high content of lignin materials. The same author concluded that high levels of holoceluloses are positively correlated with income condensable gases in burning processes.

Machado et al. (2016) stress the importance of recovery and use of hemicelluloses to produce furfural, a substance used in plastics industry, as the world market for this chemical has been increasing.

Lora and Venturi (2012) also points out that some microorganisms such as Z. mobillis are able to utilize pentose sugars for fermentation and ethanol production. With that, specific pre-treatments could be made to release sugars from both hemicelluloses and celluloses for subsequent fermentation.

Lignin

In Chart 6, contents of soluble lignin, insoluble lignin and total lignin of clones were analysed; reviewed literature and an average of all values for comparison were shown.

Chart 6. Soluble lignin, Insoluble lignin and total lignin of Eucalyptus species.

Species	Soluble Lignin (%)	Insoluble Lignin (%)	Total Lignin (%)	Reference
E. urophylla	5.00±0.99	22.25±0.78	27.25±0.21	This Work
E. urophylla	3.50	27.10	30.60	Gomide, 2005
E. urophylla	3.30	24.90	28.20	Gomide, 2005
E. saligna	4.50±0.28	25.05±0.35	29.55±0.07	This Work
E. saligna	1.00	30.62	31.63	Trugilho, 2003
E. saligna	1.00	30.10	31.10	Trugilho, 2003
E. dunnii	5.30±0.14	23.60±0.14	28.90±0.01	This Work
E. urograndis	3.40	26.60	30.00	Ferreira, 2006
E. urograndis	3.40	25.70	29.10	Ferreira, 2006
E. grandis	2.70	20.60	23.30	Barbosa, 2008
E. urograndis	2.40	27.80	30.20	Barbosa, 2008
Average	3.23	25.85	29.08	

Soluble lignin values found in this study are above average (3.23%) and above all the researched results in literature, where the values of this content for *E. urophylla*, *E. saligna* and *E. dunnii* were, respectively, 5%, 4.5% and 5.3%.

Insoluble lignin values were below average (25.85%), where only the result of *E. saligna* was near average with 25.05%. However, the result of *E. saligna* remained below the values found by Trugilho et al. (2003) (30.62 and 30.1%) for the same species. For *E. dunnii*, (23.6%), the insoluble lignin was fairly below average value (25.85%).

For *E. urophylla*, the insoluble lignin was (22.25%), slightly lower than that found for Gomide et al. (2005) for the same species, where literature values were 27.1% and 24.9%.

For total lignin values, the results obtained were similar to the average (29.08%), where the values of *E. urophylla*, *E. saligna* and *E. dunnii* were respectively 27.25%, 29.55% and 28.9%. The result for *E. urophylla* was more than 1% different from the average and below results found by Gomide et al. (2005) for the total lignin in the same species (30.6% and 28 2 %).

The same is observed for the total lignin value obtained for *E. saligna* (29.55%) where Trugilho et al. (2003) found higher values for the same species (31.63% and 31.1%).

According to Yang et al. (2007), in the presence of high methoxyl and aromatic rings, cracking and deformation of lignin in fixed bed pyrolysis releases more H_2 and CH_4 gases, which have high calorific value. These gases are highly favourable for the production of synthetic gas for energy transformation (Basu 2006).

Santos et al. (2013) point out that, due to lignin having a carbon content approximately 50% higher than that found in polysaccharides, their potential for energy production is greater. The heating value of lignin (5995 kcal/kg), estimated by Brand (2010), is greater than the average value of the heating value of Eucalyptus shelled (4 600 kcal/kg). This shows that high amounts of lignin in the biomass composition may increase the calorific value.

Rocha (2015) stated that lower levels of lignin in the wood equals to less amount of lignin to be removed in pulp delignification, reducing the kappa number. This is associated with the residual lignin content in pulp, where the higher the kappa, the greater the amount of residual lignin from pulp and more difficult and expensive the whitening process is.

Yuan et al. (2012) states that lignin is a major contributor to biomass recalcitrance. It generates high costs for biorefinery processes, stressing the importance of choosing specific purification methods, depending on the final use of the lignin.

CONCLUSIONS

The results for the three species of Eucalyptus (*E. urophylla, E. saligna and E. dunnii*) corroborate its use for biorefinery in thermochemical processes such as combustion, pyrolysis and gasification. According to analyses, it emphasizes the use of species studied *E. urophylla* for hemicelluloses biorefinery due to its relatively high content. The results indicate the use of the species *E.* saligna analysed in cellulose biorefinery processes for its high biomass content. As this was a preliminary study with focus on characterization and evaluation of potential, further research is needed in forestry biorefinery for a better understanding of the subject.

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