CHARACTERIZATION AND ENERGY POTENTIAL ASSESSMENT OF THE FORESTRY RESIDUES FROM THE PAPER AND PULP INDUSTRY

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Abstract

The pulp and paper industry is the greatest consumer of biomass fuels and feedstock; as a result it generates biomass waste, which represents a great amount of heat energy available. Besides the waste generated in the industry, the paper and pulp production chain involves an important forestry activity, in which generally the wood is taken and the biomass residues are abandoned at the forest, that represents between 15 and 25% of the tree dry mass. This research focuses on the solid residues generated at the forest (leaves, barks, thin branches and thick branches) as well as the residues of the pulp and paper industry (fines, barks, chips and organic sludge), characterizing them as fuel. The objective is also estimate the electricity generation potential by the combustion of biomass residues through the steam Rankine cycle. The characterization is based on a range of analysis, studying the thermal degradation (thermal analysis - TG and DSC), and determining the heating value, the elemental, immediate and structural composition. Also, the ash elemental composition is established. The material used is taken from a hybrid of Eucalyptus urophylla x Eucalyptus grandis. The studied biomass is suitable to be used as fuel in industrial boilers. The forest residues, which have some disadvantages regarding to others biomass like wood, improved its characteristics as it remains at the forest for a period of time, decreasing its moisture and reducing the ash, chlorine and potassium contents. The sludge combustion could be energy deficient due to its high moisture content and its low heating value. The electricity generation potential is high, since the productivity of waste is large and its heating value is similar to the original wood. We conclude that without considering the logistics issues, the biomass waste has great energy potential, generally untapped.

1- INTRODUCTION

From an environmental perspective, the sustainability of development depends, among other measures, on the reduction of greenhouse gas emissions, conservation of soil and water, the rational use of fossil fuels and renewable natural resources. Between human activities, the production of energy is one of the most intensive uses of natural resources. On the other hand, it is also the biggest source of pollutants emission [1].

Currently, fossils fuels such as oil, coal and natural gas, represent the main source of energy in the world (approximately 80%). However, biomass is seen as the most promising source of energy to mitigate the effects of the emission of greenhouse gases. Today biomass contributes about 10 to 15% of the world energy demand and in developing countries the contribution of biomass is higher than in industrialized countries [2]. In addition to the neutrality of CO_2 emissions, biomass is relatively abundant and uniform around the world and can provide between 14 to 50% of the energy consumption of the world [3].

Biomass refers to any organic materials that are derived from plants or animals. A generally accepted definition is difficult to find. The definition given by Basu (2010) is *non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes* [4].

Compared to other renewable energy sources, biomass has few problems with energy storage, since biomass is stored energy. Moreover, biomass is a versatile fuel that can produce bio-gas, liquid fuels, charcoal, thermal energy and electricity. Biomass is considered a renewable energy source because their supply is not limited by the availability in the nature [5].

In Brazil, in 2008, renewable energy accounted for 43.8% of the energy matrix, from which 14.6% corresponded to hydropower and 29.2% to biomass, being 12.9% from forestry (firewood and charcoal). So, forestry biomass represented the third energy source of the energy matrix [1].

The pulp and paper industry is the largest consumer of biomass as fuel and feedstock in the world, generating waste such as bark, sawdust, shavings, lumber rejects ("overs") and sludge from waste water treatment, which represent a great amount of heat energy available in these products, making them useful energy sources. The production of pulp and paper requires large quantities of thermal and mechanical energy. These energy needs are met through the use of steam directly and by means of generating electricity. Therefore, this type of industry can be energetically self-sufficient. Most of the developments and improvements in boilers for biomass have been driven by the needs of this industry. Other options for generating energy from biomass such as pyrolysis and gasification, and the disposal of wastes from this industry as land disposal, composting and reuse as building material are being applied, although research is still needed for optimization of the processes [6, 7].

In addition of the waste generated at the plant, the pulp and paper production have a great forestry activity associated, which generates other biomass wastes that could be used as fuel. These wastes are the tree fractions that are not useful to make cellulose pulp, such as bark, leaves, thin branches and thick branches. These not useful fractions, which represent, between 15 to 25% of the dry mass of trees, are generally left in the forest without use and hinder the operations of new crops or new plantings. However, the total harvest of this material, could involve a negative environmental impact on soil quality [8].

Brazil is the fourth-largest pulp producer in the world, with a production of 13.9 millions of tons per year in 2012, overcomed by United Stated, China and Canada. The annual growth of the last decade was 5.7%. Regarding the paper production, Brazil is the ninth bigger producer in the world rankings [9,10].

In Brazil, the pulp and paper are mostly manufactured from eucalyptus wood (85.8%), but other species like pine (14.2%) have also been used. In 2012, 42% of the eucalyptus consumed by the Brazilian industry was destined to produce pulp and paper [9].

Considering that the eucalyptus is the forest species most planted in the world and that the pulp and paper industry is one of the largest consumers of wood, the use of forestry and industry biomass waste seems to be an attractive source of energy [11].

This research focuses on the solid residues generated at the forest as well as in the production of pulp and paper, characterizing them as fuel. The objective is also estimate the potential of electricity production by the combustion of biomass residues through the steam Rankine cycle.

2- MATERIALS AND METHODS

2.1- Sampling

The analyzed material were solid residues generated in the forest and in the pulp production. These material came from a forest of hybrid Eucalyptus (*urophylla x grandis*) forest, planted in the Sao Paulo State (latitude S 28°; altitude 760 m) and from a pulp and paper industry (Kraft process), which produce 670,000 $t.year^{-1}$ of pulp and 370,000 $t.year^{-1}$ of paper. This residues comprised of the tree fractions not useful to make pulp such as barks, branches (between 2 and 6 cm of diameter), tips (less than 6 cm of diameter) and leaves derived from the forest, in addition to fines (sawdust), barks, chips and sludge from the industry (Table 1). The studied forest residues were collected in three different conditions: the residues generated in the harvest day, residues that remained on the ground for 32 days and others which remained on the ground for 94 days. The forest was 6 years old and planted with a density of 1250 $tree.ha^{-1}$ (3.20 x 2.50 m). The productivity of this forest was 55 $m^3.ha^{-1}.year^{-1}$ including barks.

Forest	Industry
Barks	Barks + Slivers
Branches	Fines (sawdust)
Tips	Organic sludge
Leaves	Chips

Table 1. Biomass samples.

The samples preparation was made as the ASTM - E1757 standard. First, the samples were dried in an oven at 60°C until constant weight to determinate *in natura* the moisture content. The samples were ground in two cutting mill to homogenize them, being the first mill to cut up 9 mm and the second to make particles less than 0.5 mm. Quartering was not necessary to select the samples because the ground material was enough homogeneous.

2.2- analysis

A range of analysis was performed to study the characteristics of these samples of biomass and their ashes. These analyses, standards and/or methods employed and the laboratory where they were performed are shown in Table 2.

Analysis	Standard and/or method	Laboratory
Proximate composition		
Moisture	ASTM E871	Laboratory of Fuels – FEM – Unicamp
Ash	ASTM D1102 (575°C)	
Volatiles	ASTM E872	
Fixed carbon	By difference	
Ultimate composition		
C and H	ASTM E777	
N	ASTM E778	
S	ASTM E775	
Cl	ASTM E776	
O	By difference	
Heating value	NBR 8633	Laboratory of Pulp and Paper – Forestry Engineering Department - FUV
Structural composition		
Cellulose	HPLC-PAD	
Hemicellulose		
Lignin	TAPPI UM 250 TAPPI 222 om-98	
Extractives	TAPPI 264 cm-97	
Thermal analysis		
Thermogravimetry	STD Q600	CTBE – CNPEM
Differential spectral calorimetry		
Ash ultimate composition	EDS	Laboratory LME – LNNano - CNPEM

Table 2: Analysis performed to characterize the biomasses and their ashes.

The analyses described were performed in 15 samples of biomass and their ashes. These 15 samples were 4 from the industry (fines, barks+slivers, organic sludge and chips) and 11 from the forestry, 4 from the harvest day (barks, branches, tips and leaves), 4 which remained 32 days in the forest and 3 which remained 94 days in the forest.

The mass percentages of moisture, volatile matter, fixed carbon and ash content were determined in the proximate analysis. It was performed under standards ASTM E871, E872 and D1102 employing a muffle and an analytic balance (OHAUS, resolution de ±1 mg) to determinate the mass. Six replications were made with 2 g each one in ceramic crucibles.

The ultimate composition (C,H,O,N,S) was provided directly in the dry sample employed an Elemental CHNO analyzer, equipped with CHN TruSpec Micro; S - TruSpec S; O – TruSpec O.

The high heating value was obtained by the calorimetry pump methodology under the standard ASTM D240 with a PARR 6300 calorimeter.

Structural composition: The determination of cellulose, hemicellulose, lignin and extractives was provided under the standard TAPPI 264 cm-97 which, at first, the extractives contents were determined. On the extractive free wood lignin and carbohydrates were determined following TAPPI 222 om-98 and T249 cm-85 standards, respectively.

Thermal analysis: The thermal analysis were provided in the Brazilian Bioethanol Science and Technology Laboratory (CTBE) - (CNPEM) by an analyzer SDT Q600 doing thermogravimetry (TGA) and differential scanning calorimetry (DSC). The heating rate was 10 K/min and the samples masses 10±0.5 mg. Nitrogen was employed as atmosphere gas, with a flux of 100 ml/min, in the temperature range from ambient to 900°C.

Ash ultimate composition: By the energy dispersive X-ray spectroscopy (EDS) the ash ultimate composition was determined. This analysis was provided by the Electronic Microscopy Laboratory (LME) - National Nanotechnology Laboratory (LNNano) - CNPEM, by FEI Inspect F50 - High Resolution SEM equipment with a high sensitive and speed XEDS, which has an measurement uncertainty of ±1.5%.

2.2- Calculation of the electricity generation potential

Using simple equations (1) and (2), with some of the analysis results and bibliography data, were calculated the potential of electricity generation from the residues.

$$W_e = Q_{boiler} \times M \times \eta_{cycle} \times \eta_{ger} \tag{1}$$

$$\dot{W}_e = \frac{W_e}{3600 \times HPT} \tag{2}$$

Where:

- W_e (MJ.year^{-1}): electricity generated per year.
- $\dot{W}_e$ (MW): electric power.
- Q_{boiler} (MJ.kg^{-1}): thermal energy generated in the boiler per kilogram of fuel.
- η_{cycle}: thermal efficiency of the thermal cycle.
- η_{ger}: electricity generator efficiency, estimated in 98%.
- M (kg.year^{-1}): quantity of dry mass of each residue generated per year.
- 3600 (s.h^{-1}): conversion unities factor.
- HTP (h.ano^{-1}): plant working hours 7446 h.year^{-1}. Utilization factor of equipment: 85%.

The plant which provided the samples produces 670,000 t.year^{-1} of pulp and 370,000 t.year^{-1} of paper, generating waste as indicated in the Table 3.

Residues	Generation (t.year^{-1} – wet basis)	Moisture (%, wet basis)
Fines	34,000	30
Barks + Slivers	30,000	30
Organic sludge	48,000	40
Overs	6,000	30

Table 3: Pulp and paper waste generation.

Thermodynamic cycle

The adopted thermodynamic cycle was the Rankine cycle, using steam as the work fluid and with the following hypotheses to simulate the cycle:

- Isentropic and mechanical turbine efficiencies of 85 and 98% respectively.
- Isentropic and mechanical pump efficiencies of 70 and 90% respectively.
- Output turbine steam quality of 95%.
- Condensed pressure of 20 kPa.
- Pressure drop of 2% in each pipe stretch between equipment.
- Reheated cycle:
  - First step superheated steam parameters: 480°C and 11.5 MPa [7].
  - Second step superheated steam parameters: 480° C and 3.5 MPa (30% of the initial pressure).

Under these hypotheses, the thermal efficiency is 31%.

Boiler efficiency and thermal balance

The boiler efficiency is defined as the ratio of the useful energy (Q_{boiler}) and the available energy in the fuel (Equation (3)).

$$\eta_{boiler}^{HHV} = \frac{Q_{boiler}\left(MJ.kg_{dry\,fuel}^{-1}\right)}{HHV\left(MJ.kg_{dry\,fuel}^{-1}\right)} \tag{3}$$

A range of energy losses and hypotheses were considered in the thermal balance to simplify the calculation:

- Losses to environment by the heat transfer from the outer walls of the boiler (convection and radiation), considered in 2% of the HHV.
- Incomplete combustion losses, due to the presence of CO, H_2, CH_4 and others in the combustion gases, and fuel particles in the ashes. A value of combustion efficiency was adopted in order to include these losses.
- Heat losses by the enthalpy of boiler exhaust gases, which temperature was taken in 180°C.
- Dry air.
- Fuel and air inlet temperatures equal to reference temperature ($T_f = T_{air} = T_0$).
- Fuel moisture of 25% in dry basis.

The thermal balance remains as equation 4:

$$\begin{aligned} G_{s.s.} = (h_{s.s.} - h_{w.s.}) \\ &= HHV \times \eta_{comb} \times \eta_{H.T.} - G_{g9h}\left[h_{g9h}(T_{ch}) - h_{g9h}(T_0)\right] - 9H h_{fg0} \\ &- (H_2O)_f\left[h_{fg0} + c_{p_s}(T_{ch} - T_0)\right] = Q_{boiler} \end{aligned} \tag{4}$$

Where:

- $G_{s.s.}$; G_{g9h}: mass flow of superheated steam and semi-moist combustion gases, including only the water generated in the combustion, without the fuel moisture, per kilogram of dry fuel, $kg_x.kg_{fuel}^{-1}$.

- $(H_2O)_f$: fuel moisture, % (d.b.)
- $h_{s.s.}$; $h_{w.s.}$: enthalpy of superheated steam and water supply , kJ.kg^{-1}.
- HHV: higher heating value, kJ.kg^{-1}.
- h_{g9h}: gases enthalpy evaluated at exhaust gas temperature (T_{ch}) and reference temperature ($T_0 = 25°C$), kJ.kg^{-1}.
- c_{p_s}: steam water specific heat, kJ.kg^{-1}.K^{-1}.
- H: quantity of hydrogen in the fuel, $kg_{hydrogen}.kg_{fuel}{}^{-1}$.
- h_{fg0}: water vaporization enthalpy at reference temperature, kJ.kg^{-1}.
- η_{comb}: combustion efficiency.
- $\eta_{H.T.}$: efficiency related to the environmental heat transfer.

Based in literature data [12, 2, 6, 13, 5, 14, 15, 16], the combustion efficiency and air excess were fixed according to the furnace type (Table 4).

The combustion stoichiometry is solved using the biomass elemental composition and the air excess with the software *CEAgui (Chemical Equilibrium with Applications)* from *NASA*. Thus we determined the enthalpy, mass flow and composition of gases. With these results and the thermal balance, the boiler efficiency and Q_{boiler} were determined. After that, the electricity and power were calculated for each industry residue.

Furnace	Air excess (%)	η_{comb}
Fixed bed	40	92
Fluidized bed	25	98

Table 4: Combustion parameters chosen.

3- RESULTS AND DISCUSSION

3.1- Analysis

Moisture *in natura*

Table 5 shows the moisture (w.b.) of the samples collected in the forest. As expected, stands out the high moisture of the residues generated the harvest day. The barks are the tree fraction which shows higher moisture content with 61.7%. Leaves, branches and tips had 48.4%, 40.4% and 50.0% of moisture respectively. These results are similar to the noted in the literature, where the moisture at the harvester moment of the treetop (branches and leaves) is 52~53% and of the barks are between 64 e 66% (w.b.) [17, 18].

The high moisture content has a range of problems associated in conditioning biomass for energy proposes [19]. However, as is observed in Table 5, the moisture content decreases rapidly as the material stays in the forest. According to the collected samples and the results obtained at 32 days in the forest, the biomass moisture had reached a much smaller value, between 5 and 8%, which remained almost constant over time.

The natural drying depend on several factors, including environmental and climate conditions such as temperature and precipitations, conditions of the material, that is, if it was scattered or in heaps, the size and compaction of the material, barks and fines, elements size and distribution. The moisture hit by material collected is noticeably smaller than the data obtained in the literature, where it is estimated that hardly can be reached lower moisture content than 20% (w.b.) with natural drying [19]. According to other researches, sometimes more than a year is necessary of drying before could use the biomass for energy purposes [20]. The material was scattered in the forest, that it could be related with the low moisture content achieved, less than 8%. Also is noted that sampling was done in august, a dry period in Sao Paulo.

	Of Day	32 Days	94 Days
Leaves	48.4	5.8	7.9
Barks	61.7	4.5	7.2
Branches	40.0	8.5	8.0
Tips	50.0	8.2	-

Table 5: Forestry residues moisture in natura (%, w.b.).

The moisture of chips, fines and barks were 25.8%, 47.4% and 14.3% respectively, which may vary depending on the sampling. The organic sludge had a moisture content of 80%. This value is independent of the environment conditions since this sludge derived from the sewage treatment, leading the solids concentration to the range of 20 and 40%.

Proximate analysis

The proximate and structural compositions are shown in Table 6. All samples, except the organic sludge, exhibit values of volatiles and fixed carbon similar to literature data, in the range of 78 to 90% for the volatiles and 10 to 17% for the fixed carbon. The barks are the tree fraction which has a higher content of ash (4.5%), after that the leaves (3.2%), barks + slivers (1.8%) and branches (1%) in dry basis. The others samples, tips, chips and fines, have smaller contents of ash, being in the range from 0.2 to 0.7 % (d.b.). The fact that the barks are the fraction with higher content of ash, followed by leaves, branches and wood is also observed in the literature, although exist a big difference in the ash content depending on the eucalyptus species [21, 22, 23, 24, 25, 26, 8].

Sample	Volatiles	F.C.	Ash	Cellulose	Hemic.	Lignin	Extr.	Not Ident.
Leaves of day	80.1	16.6	3.2	15.7	11.0	37.5	32.7	-
Leaves 32 days	83.0	14.7	2.4	24.6	14.1	37.1	19.0	3.0
Leaves 94 days	82.1	15.3	2.6	22.9	13.1	38.1	18.3	5.0
Barks of day	80.4	15.1	4.5	44.1	11.9	21.9	14.2	3.3
Barks 32 days	86.2	8.9	4.9	40.0	11.7	25.1	10.8	7.6
Barks 94 days	78.9	17.1	4.0	44.4	13.0	23.7	10.2	4.7
Branches of day	84.3	14.8	0.9	38.2	14.7	31.4	6.7	8.1
Branches 32 days	88.3	10.6	1.2	38.3	14.6	31.4	4.8	9.9
Branches 94 days	83.7	15.6	0.8	39.6	14.8	30.9	4.7	9.3
Tips of day	89.5	10.2	0.3	37.9	14.8	32.0	6.8	8.2
Tips 32 days	87.4	11.9	0.7	42.8	13.8	31.0	3.1	8.7
Chips	87.0	12.8	0.3	46.5	13.3	29.9	2.7	7.3
Fines	92.8	7.0	0.2	46.6	12.1	30.7	3.3	7.2
Bark + Slivers	83.8	14.4	1.8	47.1	12.5	26.0	8.1	4.5
Organic sludge	64.7	2.1	33.1	20.1	3.9	21.9	19.9	1.0

Table 6: Proximate and structural composition (%, d.b.).

There are some changes in the volatiles and fixed carbon in the samples over the time. Firstly, the volatiles content of barks and branches decreased and fixed carbon increased for the harvest day to 94 days. In relation to ash contents, the forestry residues show the same behavior, where the ash content in the samples which were 94 days in the forest is lower than the samples of the harvest day. This behavior is related to ash leaching by rainwater [27].

The proximate composition of the organic sludge is really different, with 65% of volatiles, 2% fixed carbon and 33% of ash. The very high ash content is the most notable and harmful propriety for using this biomass as fuel, which is 100 times higher than chips ash content.

Compared with others biomasses that are frequently used as fuel, like pine wood, sugar cane bagasse and rice husk, the eucalyptus wood have similar characteristics as pine wood. However, the agriculture (or agro-industrial) wastes have some differences compared to the eucalyptus wood, especially in the ash, where the bagasse ash content is similar to the forestry residues (3.0%) and the rice husk achieves much higher values (19%) [28, 22]. From this point of view, and considering the widespread employment of bagasse as fuel in sugar and alcohol mills, could be attractive to employ forestry residues as fuel.

Structural composition

From the structural composition we determined the percentages (d.b.) of cellulose (glucans), hemicellulose (arabinans, galactans, xylans and mannans), lignin (soluble and insoluble) and extractives, which are shown in Table 6. The chips, that is the fraction employed to produce pulp and paper, had a content of cellulose, hemicellulose, lignin and extractives of 46.5%, 13.3%, 29.9% and 2.7% respectively. When the wood is employed energy generation, it is desirable to have more lignin and less cellulose and hemicelluloses [29].

As is observed in the Table 6, the extractives content had a fast decreasing over the time. Leaves had a reduction up to 60% of the original value in 32 days, barks and branches up to 70~75% in the same period of time. Between the 32 and 94 days is not observed a decrease. Extractives are the organic material with lower molar mass, thus they can be the firsts to degrade or leach [30].

Looking the forestry residues, leaves were the fraction with less cellulose (in the range of 16 to 25%) and the others as barks, branches and tips had a similar content among them (in the range of 38 to 44%). So that, wood is the tree fraction with more cellulose. The hemicellulose content had not much variation between chips and the forestry residues, being between 11 and 15%. Leaves where composed largely by lignin (37%) and extractives (32,7%).. The other fractions, like barks, branches and tips had respectively 22~25%, 30~31% e 31~32% of lignin. The extractives show a similar tendency, decreasing the content in the order: leaves > barks > branches > tips, where the leaves extractives content is more than 10 times higher than in chips.

Ultimate composition

The ultimate composition and higher heating value of each sample are shown in Table 7. Carbon is approximately the half of the mass in all tree fractions, 55% in leaves, 48% in barks and in the range of 52 to 53% for branches, tips, chips and fines. There is not great differences in hydrogen content among all tree fractions, compared to other biomass, where represents between 5 and 6% of the dry mass [22, 24, 25, 8].

Nitrogen had a higher percentage in leaves (1% aprox.) than in the other samples, in which both nitrogen and sulfur had a percentage lower than 0.2%. The nitrogen and sulfur content depend strongly on the forest fertilization. In addition, in fuels, low percentages of both are important in the environmental point of view [25, 8].

Sample	C (%)	H (%)	O (%)	N (%)	S (%)	Chloride (ppm)	HHV
Leaves of day	54.7	6.0	34.7	1.2	0.2	1339	21.1
Leaves 32 days	54.9	5.9	35.8	0.8	0.2	366	20.4
Leaves 94 days	55.1	6.0	35.1	1.0	0.2	112	20.5
Bark of day	48.1	5.5	41.7	0.1	0.1	4329	17.1
Bark 32 days	47.7	5.4	41.8	0.1	0.1	864	17.0
Bark 94 days	47.5	5.5	42.7	0.2	0.1	231	17.1
Branches of day	53.3	5.8	39.9	0	0.1	760	19.4
Branches 32 days	52.9	5.9	39.9	0.1	0.1	686	19.4
Branches 94 days	52.2	5.9	41.0	0	0.1	368	19.2
Tips do day	52.9	6.1	40.6	0	0.1	484	19.1
Tips 32 days	52.5	5.9	40.6	0.2	0.1	263	19.2
Chips	52.3	5.9	41.4	0	0.1	376	19.1
Fines	51.7	5.9	42.2	0	0.1	269	19.3
Bark + Slivers	50.0	5.7	42.3	0.1	0.1	423	18.3
Organic sludge	32.0	3.8	28.8	1.6	0.7	939	11.6

O(%) by difference.

Table 7: Biomass ultimate composition (d.b); High heating value (MJ.kg^{-1}).

The main components of a fuel (*C, H, and N*) do not show variation in the forestry residues related to the days of the material in the forest. However, chlorine, which is a very harmful element in boilers, detected as chloride, showed a really important reduction over the time in every sample. Bark is the tree fraction with highest content of chlorine, 4330 ppm in the harvest day sample, and this value decrease to 860 ppm in 32 days and to 230 ppm in 94 days. In other words, the barks chlorine content decrease 20 times in 94 days. Leaves had originally 1340 ppm of chloride and 32 days later had 366 ppm reaching up to 110 ppm in 94 days.

Compared to literature data, the ultimate composition of eucalyptus depends on the specie, but always with the same relation, for example: leaves are the fraction with more carbon and nitrogen content [24, 25, 8]. The pine wood elemental composition is really similar to the eucalyptus composition, but other biomass like bagasse and rice husk had lower carbon content [22].

The carbon and hydrogen content of the organic sludge are lower (32 and 3.8% respectively), but had more nitrogen (1.6%) and sulfur (0.7%).

Heating value

The higher heating value (HHV) showed results from 17.0 to 21.1 MJ.kg^{-1} to fractions of the tree and 11.6 MJ.kg^{-1} to the organic sludge (Table 7). Leaves are the fraction with higher HHV (20 MJ.kg^{-1}), which had a little decrease over the time, that may be related to the extractives reduction. HHV of branches, tips, chips and fines are not different from each other (19.1~19.4 MJ.kg^{-1}). Bark is the forestry residue with lower HHV (17.1 MJ.kg^{-1}) and is also the fraction with higher ash content.

Compared to other biomasses employed frequently as fuel, as pine, sugar cane bagasse and rice husk, the HHV of eucalyptus is similar to them and higher in some cases. The HHV of pine wood is higher than the eucalyptus, 20.0 and 19.1 MJ.kg^{-1} respectively. However, any forestry residue, including barks, has a higher or equal HHV than bagasse (17.3 MJ.kg^{-1}) and rice husk (16.1 MJ.kg^{-1}) [22].

Thermal analysis

Thermal degradation under inert atmosphere (pyrolysis) of chips had similar behavior that the data obtained in the literature for eucalyptus (and others biomasses too) [31, 32, 26, 33]. In the mass loss rate (DTG) in the Figure 1, two peaks are noted. The first one, at temperature below than 100°C, corresponds to the moisture evaporation and all samples have this peak. The second one, between 250°C and 400°C, has a peak in 360°C and a shoulder in 280°C [33]. This shoulder is considered as the hemicellulose degradation, and the peak as the cellulose degradation. The lignin has a lower devolatilization rate but in a larger range of temperature, so that the tail at the end of the main peak, between 400 and 500°C is due to the lignin degradation. The DSC plot (Figure 2) is not very exact because the equipment employed has a drift in the results, which begins at 420°C approximately for any sample. Considering this drift, two peaks of endothermic reactions are identified, the first one related to the moisture evaporation and the second one at the same temperature than the main peak.

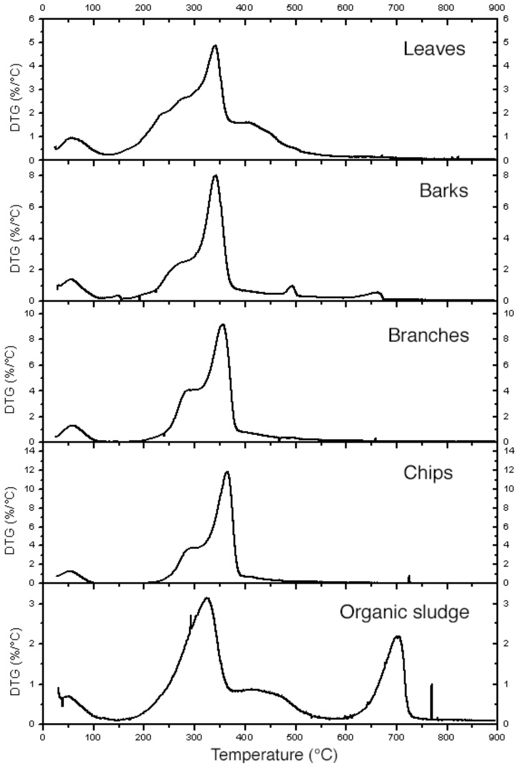

Figure 1: DTG of Biomasses

Branches had a similar ultimate, proximate and structural composition to the chips, so that, the behavior on the pyrolysis was similar too. There are observed the same two peaks in DTG and DSC curves. The peak shapes and the temperatures where they occur are very similar too. The thermal degradation of the barks, in addition to these peaks, shows three minor peaks in the mass loss rate at temperatures of 150, 590 and 660°C. Each one of these specific increases in the rate of thermal degradation is associated to endothermic reactions. The first one could be related to the extractives pyrolysis. Leaves pyrolysis behavior is even more different compared to chips behavior. Degradation begins at a lower temperature (150°C), and extend up to 550~600°C making a big peak, with a maximum at 350°C. In the way of increasing temperature, the first shoulder (220°C) could be generated by the extractives thermal degradation or devolatilization, the second one (270°C) by the hemicellulose, the peak (340 º) by the cellulose and the last shoulder (410°C) by the lignin.

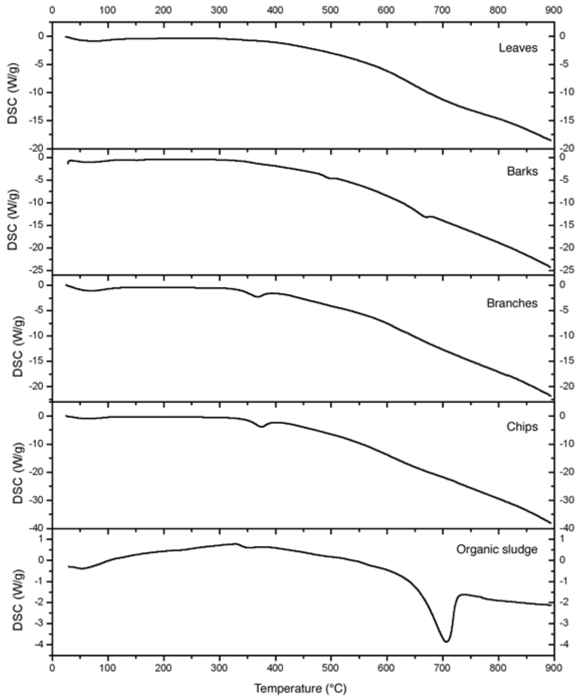

Figure 2: DSC of Biomasses

The thermal degradation of the organic sludge has a drying peak, another in the range of temperatures of the cellulose and hemicellulose degradation, one peak at 400°C by the lignin, and an another big peak (from 600 to 730°C), which has a strong endothermic reaction associated.

Ash ultimate analysis

Elements like alkaline metals (*Na* and *K*), alkaline earth metals (*Mg* and *Ca*), silicon (*Si*), sulfur (*S*) and chlorine (*Cl*), are the least desired in the elemental composition of the ash, since they are the main elements that take place in the fouling, slagging and corrosion.

The EDS analysis result is the elemental composition of the sample, but sometimes is better work as the oxide composition for ashes. So that, in Table 8 are shown the percentages in mass of the main oxides.

Observing the composition of each sample (Table 8), we noted that eucalyptus ashes are mainly composed by K_2O and CaO. In a background is found MgO, followed by P_2O_5 andNa_2O. Others elements have a less important representation.

The chlorine, which has a strong influence in the tubes corrosion, was found mainly in the leaves, barks and organic sludge ashes. In both leaves and barks, the ClO_2 had an important decreasing over the time that was noted in the biomass ultimate composition.

Among the alkaline metals, the oxide Na_2O had a percentage between 4 and 6% in the ashes of leaves, branches, chips and fines. The barks and organic sludge ashes had a lower quantity of this oxide, between 1 and 2%. The Na_2O percentage decreases a little with the environmental exposition. The other oxide of alkaline metal identified, K_2O, which had the biggest percentage decreasing over the time, is linked with the biomass degradation or leaching. This oxide decreases from 10% to 3% in the barks and from 36 to 12% in leaves in 94 days.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	ClO_2	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3
L.0d	3.87	10.13	1.55	2.59	8.49	2.65	5.97	36.03	23.31	0	3.67	1.75
L.32d	4.62	10.83	1.45	2.69	8.76	3.03	1.05	34.35	29.15	0	1.56	2.51
L.94d	1.56	10.15	1.82	3.08	7.79	3.55	0	12.08	57.09	0	0.80	2.08
Bark 0d	1.92	9.19	10.09	0.59	2.46	1.2	4.50	10.11	59.17	0	0.78	0
Bark 32d	1.08	10.97	0	0	2.45	0.71	0	4.84	79.41	0	0.55	0
Bark 94d	0.85	5.46	2.69	0.66	2.34	0.65	0	3.14	83.77	0	0.44	0
B.0d	3.13	10.03	13.32	0.8	4.59	1.72	0	22.35	41.35	0	2.70	0
B.32d	3.92	17.29	1.25	4.38	12.36	2.12	0	27.81	27.67	0.47	0.89	1.82
B.94d	2.88	12.84	0.83	0.94	6.55	2.23	0	12.36	60.50	0	0.88	0
T.0d	4.13	8.00	1.28	1.41	11.47	2.20	0	47.8	19.46	0	2.89	1.36
T.32d	5.70	20.27	0	0	10.03	2.27	0	29.78	30.81	0	1.13	0
Chips	5.63	6.63	1.43	1.86	7.12	3.84	0	28.67	41.79	0	0.86	2.18
Fines	4.12	10.28	6.83	6.86	5.95	2.75	0	13.64	41.78	0.42	1.34	6.03
B + ..	2.19	13.42	0.81	0.66	6.66	2.30	0.94	11.89	59.97	0	1.16	0
Sludge	1.40	2.15	9.63	10.3	2.75	3.10	1.37	0.30	63.72	0	0.56	4.73

Table 8: Ash composition - as oxides (% mass).

Results show an increase of CaO percentage in all samples as the material stay at the forest. CaO is one of the main oxides, so that, is seems that the CaO is difficult to return to the soil. This oxide had a higher percentage in the bark and organic sludge ashes. In all tree fraction samples, the oxide of magnesium, which is the other alkaline earth metal, had a percentage between 5 and 20%, and is not observed a variation over the time.

Considering sulfur, the percentage is equal or less than 4% in any sample, where bark ashes are which one with less percentage. Is not detected a tendency of increase or decrease of SO_3 over the time by the degradation or leaching. Thus, opposed to what happened with chlorine, sulfur is not easy to eliminate.

The silicon content was highest in the organic sludge ash (10%). In the other samples, the percentage of SiO_2 is less than 3%, where leaves were the tree fraction with more concentration.

Phosphorus had a less content in the barks and organic sludge (under 2%) than in the others sample, where the percentage in leaves were 5%, in chips and fines 4% and lastly 7% for branches and tips.

The rest of elements had a less representation in the ash ultimate composition, where Al_2O_3 was identified mainly in the organic sludge and barks, with a decrease over the time. MnO_2, with low percentages, had a decrease too. Finally, Fe_2O_3 and TiO_2 showed just traces.

Compared to other biomass, the most important difference is observed in the SiO_2, K_2O and CaO. On one hand, SiO_2 is the main oxide in biomass like bagasse, pine wood and rice husk, and the other oxides are not so important. On the other hand K_2O and CaO are the most relevants in the eucalyptus ashes and SiO_2 has juste a percentage under 3%. However, compared to others woods like poplar and willow, the ash ultimate composition is more similar to the eucalyptus composition, where ash from poplar wood has 10 and 50% of K_2O and CaO respectively, and ash from willow wood 15 e 41% of K_2O and CaO respectively [28, 34, 35].

3.1- Energetic potential

The energetic potential of the pulp and paper biomass wastes were calculated, discretizing by the residue type. The results are shown in Table 9.

		Fines	Barks+ Slivers	Overs	Organic Sludge	Total
	M x 10^6 (kg$_{wet}$.year^{-1})	34	30	6	48	118
	Moisture (% w.b.)	30	30	30	40	-
	M x 10^6 (kg$_{dry}$.year^{-1})	24	21	4,2	28	78
Fluidized bed	Q_{boiler} (MJ.kg$_{fuel}^{-1}$)	14.7	13.8	14.4	7.5	50.4
	η_{boiler}^{HHV}	75.9	75.4	75.6	64,3	-
	$W_t \times 10^7$ (MJ.year^{-1})	34.9	29.0	6.07	21.5	91.4
	$W_e \times 10^7$ (MJ.year^{-1})	11.3	9.40	1.97	6.97	29.6
	$\dot{W}_e$ (MW)	4.2	3.5	0.7	2.6	11.1
Fixed bed	Q_{boiler} (MJ.kg$_{fuel}^{-1}$)	13.4	12.6	13.1	6.7	45.8
	η_{boiler}^{HHV}	69.3	68.7	69.0	57.6	-
	$W_t \times 10^7$ (MJ.year^{-1})	31.8	26.4	5.53	19.2	83.0
	$W_e \times 10^7$ (MJ.year^{-1})	10.3	8.57	1.79	6.24	26.9
	$\dot{W}_e$ (MW)	3.9	3.2	0.7	2.3	10.0

Table 9: Energetic potential of the pulp and paper production wastes.

The residue with more energetic potential, both thermal and electric, was the fines due to the combination of be the most generated residue and with good fuel proprieties. Thus, could be generated 10.3~11.3x10 MJ.year^{-1} of electricity with a power of 3.9~4.2 MW depending on the employed technology. Overs are the residue whit good fuel proprieties but it is generated in too less quantities. The mixture of barks and slivers is the second residue whit high potential, because it is generated in less quantity and the boiler efficiency is a bit low.

The main waste is the organic sludge, generated in more quantity but his fuel proprieties are really bad.

So that, it could be generated between 6.2 and 7.0x10^7 MJ.year^{-1} of electricity (2.3~2.6 MW). To make the thermal balance calculation was employed a moisture of 40% (d.b.) as informed by the technical staff of the industry, although the value of moisture determined was 80%. If it is employ this moisture, the thermal balance is null. Thus, it is necessary a moisture reduction to use this biomass as a fuel.

The boiler efficiency is really similar in case of were burned fines, overs or barks+ slivers. This efficiency attains 75~76% to fluidized bed boilers and 69% to fixed bed boilers. In the organic sludge combustion, the efficiencies are lower, 64 and 58% for fluidized and fixed bed boilers respectively.

4- CONCLUSIONS

Based in the performed analysis to characterized these biomass and the calculation of the energetic potential, we concluded the following:

- The forestry residues moisture *in natura* is too high to be used as fuel (barks~60%; leaves and tips~50%; branches~40% - d.b.) being necessary a drying before using. According to the evidence, under specific environment conditions, the moisture content decrease to 5~8% in 32 days of remained in the ground.
- Some of the worst properties or characteristics in biomass such as high ash content, chlorine or others harmful elements, showed a reduction with the biomass degradation

or leach by the environmental exposition. The ash content decreased to 80~90% of the original value in all tree fractions, chloride decreased 20 times in barks, 10 times in leaves and up to the half in branches and tips.

- HHV had not an important value reduction with the environmental exposition. Leaves are the tree fraction with the more HHV (20~21 $MJ.kg^{-1}$) and barks with less (17 $MJ.kg^{-1}$).
- Compared to others residual biomass employed frequently as fuel, such as bagasse and rice husk, the forestry residues characteristics are similar or better.
- Fines and overs, generated in the plant, had the same fuel characteristics than chips, which is commonly employed as fuel. The mixture of barks and slivers showed some not good properties like their relatively high ash content.
- The organic sludge has not good fuel properties, mainly for their high moisture (80% w.b.), high ash content (33% d.b.), chlorine and sulfur, and low HHV (11.6 $MJ.kg^{-1}$).
- The thermal analysis determined that the pyrolysis of branches and chips are very similar. Barks and leaves showed some differences compared to chips, which could be associated to the higher content of extractives and lignin. Organic sludge was an exception, pyrolysis behavior was only endothermic.
- The ash ultimate composition of the tree fraction is similar to the poplar and willow wood composition, but really different compared to the bagasse, pine or rice husk ash composition. The difference are mainly in the CaO and SiO_2 content, where the first oxide is the main component in the first group and the second oxide is the main in the second group of biomass.
- Considering the energetic potential calculated, it was determined that the pulp and paper wastes have a high potential, excluding the organic sludge which could have a null energetic balance because of its high moisture. An industry which produces 670,000 $ton.year^{-1}$ of pulp and 370,000 $ton.year^{-1}$ of paper could generate $30x10^7$ $MJ.year^{-1}$ (11 MW) of electricity employing its waste.

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REFERENCES

[1] L. Couto y M. Dias Müller, «Florestas energéticas no Brasil,» de *Biomassa para energia*, 2008, pp. 93-111.

[2] A. A. Khan, W. De Jong, P. J. Jansens y H. Spliethoff, «Biomass combustion in fluidized bed boilers: Potential problems and remedies,» *Fuel Processing Technology,* vol. 90, pp. 21-50, 2009.

[3] S. Pérez, C. J. Renedo, A. Ortiz y M. Mañana, «Energy potential of waste from 10 forest species in the North of Spain (Cantabria),» *Bioresource Technology,* vol. 99, pp. 6339-6345, 2008.

[4] P. Basu, «Biomass Characteristics,» de *Biomass Gasification and Pyrolisis - Practical Design*, 2010.

[5] R. Saidur, E. A. Abdelaziz, A. Demirbas, H. M. S. y S. Mekhilef, «A review on biomass as a fuel for boilers,» *Renewable and Sustainable Energy Reviews,* vol. 15, pp. 2262-2289, 2011.

[6] J. B. Kitto y S. C. Stultz, «Wood and Biomass Installations,» de *Steam/Its generation and use*, 2005.

[7] M. C. Monte, E. Fuente, A. Blanco y C. Negro, «Waste management from pulp and paper production in the European Union,» *Waste Management,* vol. 29, pp. 293-308, 2009.

[8] S. Pérez, C. J. Renedo, A. Ortiz, M. Mañana y D. Silió, «Energy evaluation of the Eucalyptus globulus and the Eucalyptus nitens in the north of Spain (Cantabria),» *Thermochimical Acta,* vol. 451, pp. 57-64, 2006.

[9] ABRAF - Associação Brasileira de Produtores de Florestas Plantadas, «Anuário Estatístico ABRAF 2013 - Ano Base 2012,» 2013. [En línea]. Available: www.abraflor.org.br.

[10] Bracelpa - Associação Brasileira de Celulose e Papel, «Dados do Setor,» 2013. [En línea]. Available: www.bracelpa.org.br.

[11] M. G. R. Cannel, «Plantation Silviculture: Short Rotation Forestry for Biomass Production,» de *Encyclopedia of Forest Sciences*, 2004, pp. 872-877.

[12] A. Gungor, «Simulation of emission performance and combustion efficiency in biomass fired circulating fluidized bed combustors,» *Biomass and bio energy,* vol. 34, pp. 506-514, 2010.

[13] J. Koornneef, M. Junginger y A. Faaij, «Development of fluidized bed combustion—An overview of trends, performance and cost,» *Progress in Energy and Combustion Science,* vol. 33, p. 19–55, 2007.

[14] E. E. Silva Lora y M. Zampieri, «Classificação e balanço térmico das fornalhas para a combustão de biomassa,» de *Biomassa para energia*, 2008, pp. 155-178.

[15] M. L. Souza-Santos y J. Villanueva Chavez, «Preliminary studies on advanced power generation based on combined cycle using a single high-pressure fluidized bed boiler and consuming,» *Fuel,* vol. 95, pp. 221-225, 2012.

[16] C. Yim, L. A. Rosendahl y S. K. Kaer, «Grate-firing of biomass for heat and power production,» *Progress in Energy and Combustion Science,* vol. 34, pp. 725-754, 2008.

[17] J. O. Brito, L. E. G. Barrichelo, H. T. Z. Do Couto, E. C. M. Fazzio y L. Corradini, «Avaliação das características dos resíduos da exploração florestal do eucalipto para fins energéticos,» *Instituto de Pesquisas e Estudos Florestais - Circular Técnica N°62,* 1979.

[18] H. T. Z. Do Couto, J. O. Brito, M. Tomazello Filho, L. Corradini y E. C. M. Fazzio, «Quantificação dos resíduos florestais para produção de energia om povoamento de Eucalyptus saligna,» *Instituto de Pesquisas e Estudos Florestais - Circular Técnica N°26,* pp. 19-23, 1984.

[19] L. T. A. V. A. Ortíz, «Aprovechamiento de la biomasa forestal producida por la cadena monte-industria. Parte III: Producción de elementos densificados,» *CIS-Madera,* pp. 17-32, 2003.

[20] X. He, A. K. Lau, S. Sokhansanj, C. J. Lim, X. T. Bi y S. Melin, «Dry matter losses in combination with gaseous emissions during the storageof forest residues,» *Fuel,* vol. 95, pp. 662-664, 2012.

[21] G. Almeida, J. O. Brito y P. Perré, «Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: The potential of mass loss as a synthetic indicator,» *Bioresource Technology,* vol. 101, p. 9778–9784, 2010.

[22] L. A. B. Cortez, E. E. Silva Lora y E. Olivares Gómez, «Caracterização da biomassa,» de *Biomassa para energia*, 2008, pp. 31-62.

[23] R. García, C. Pizarro, A. G. Lavín y J. L. Bueno, «Spanish biofuels heating value estimation. Part II: Proximate analysis data,» *Fuel,* 2013.

[24] A. Heidari, R. Stahl, Y. H., A. Rashidi, N. Troeger y A. Asghar Ghoreyshi, «Effect of process conditions on product yield and composition of 3 fast pyrolysis of Eucalyptus grandis in fluidized bed reactor,» *Journal of Industrial and Engineering Chemistry,* 2013.

[25] R. Kumar, K. K. C. N. Padey y S. Mohan, «Study of age and height wise variability on calorific value and other fuel properties of Eucalyptus hybrid, Acacia auriculaeformis and,» *Biomass and Bioenergy,* vol. 35, pp. 1339-1344, 2011.

[26] W. B. Musinguzi, M. A. E. Okure, L. Wang, A. Sebbit y T. Løvas, «Thermal characterization of Uganda's Acacia hockii, Combretum molle, Eucalyptus grandis and Terminalia glaucescens for gasification,» *Biomass and Bioenergy,* vol. 46, pp. 402-408, 2012.

[27] S. Q. Turn y C. M. D. M. Kinoshita, «Removel of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching,» *Biornass and Bioenergy,* vol. 12, pp. 241-252, 1997.

[28] W. A. Bizzo, P. C. Lenço, D. J. Carvalho y J. P. Soto Veiga, «The generationofresidualbiomassduringtheproduction of bio-ethanolfromsugarcane,itscharacterizationand its useinenergyproduction,» *Renewable and Sustainable Energy Reviews,* vol. 29, p. 589–603, 2014.

[29] J. L. Gomide, J. Colodette, R. Chaves de Oliveira y C. M. Silva, «Caracterização tecnológica, para produção de celulose, da nova geração de clones de Eucalyptus do Brasil,» *R. Árvore,* vol. 29, nº 1, pp. 129-137, 2005.

[30] F. O. Silvéiro, L. C. A. Barbosa, C. R. A. Maltha, P. H. Fidêncio, M. P. Cruz, D. P. Veloso y A. F. Milanez, «Effect of storage time on the composition and content of wood extractives in Eucalyptus cultivated in Brazil,» *Bioresource Technology,* vol. 99, p. 4878–4886, 2008.

[31] A. G. Barneto, C. Vila y J. Ariza, «Eucalyptus kraft pulp production: Thermogravimetry monitoring,» *Thermochimica Acta,* vol. 520, p. 110–120, 2011.

[32] D. A. Mortari, I. Ávila y P. M. Crnkovic, «Study of thermal decomposition of sugarcane bagasse and ignition temperature of coal/bagasse blends using thermogravimetry,» *21 Brazilian Congress of Mechanical Engineering - COBEM,* 2011.

[33] H. Yang, R. Yan, H. Chen, D. Ho Lee y C. Zheng, «Characteristics of hemicellulose, cellulose and lignin pyrolysis,» *Fuel,* vol. 86, pp. 1781-1788, 2007.

[34] B. M. Jenkins, L. L. Baxter, M. J. T. R. y T. R. Miles, «Combustion properties of biomassa,» *Fuel Processing Technology,* vol. 54, pp. 17-46, 1998.

[35] A. A. Tortosa Masiá, B. J. P. Buhre, R. P. Gupta y T. F. Wall, «Characterising ash of biomass and waste,» *Fuel Processing Technology,* vol. 88, p. 1071–1081, 2007.

[36] S. Arvelakis, P. Arendt Jensen y K. Dam-Johansen, «Simultaneous Thermal Analysis (STA) on Ash from High-Alkali Biomass,» *Energy and Fuels,* vol. 18, pp. 1066-1076, 2004.