

# Brazilian Lignocellulosic Wastes for Bioenergy Production: Characterization and Comparison with Fossil Fuels

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The aim of this paper was to analyze energy-related properties of forestry and agricultural wastes for energy production purposes, and to compare them with fossil fuels. The forestry wastes used were red cedar, *Eucalyptus*, and *Pinus* wood shavings. The agricultural wastes analyzed were rice husk, coffee wastes, sugar cane bagasse, maize harvesting wastes, and bamboo cellulose pulp. The forestry wastes presented more suitable properties for bioenergy production than the agricultural wastes. Desirable energetic properties were found for coffee wastes. The opposite was verified for rice husks. Among the biomass studied, coffee wastes presented the highest equivalent in fossil fuel volume and hence may lead to the highest decrease in CO<sub>2</sub> emissions by fossil fuels used in Brazil for steam and heat production. The results suggests that CO<sub>2</sub> benefits can be obtained if bioenergy is generated in the same locale where biomass is produced, avoiding CO<sub>2</sub> cost of logistics and leading to greater end-use efficiency. The present work promotes the widespread use of different lignocellulosic wastes for bioenergy production and gives useful information for the planning and the control of power plants using biomass.

*Keywords:* Biomass; Carbon dioxide; Heating value

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## INTRODUCTION

Presently, the major energy concerns for most countries are the excessive use and dependency on non-renewable fossil fuels, the hazards of CO<sub>2</sub> emissions, and the increasing problem of global warming (Zhu *et al.* 2011). These concerns encompass many areas of inquiry, demanding scientific and technological development in order to diversify energy sources and to reduce consumption of fossil fuels so as to control the massive emission of greenhouse gases (GHG) into the atmosphere (Esteban *et al.* 2008; Moghtaderi *et al.* 2006). Biomass wastes from agriculture and forestry are renewable and CO<sub>2</sub> neutral energy resources. They also have a relatively low cost and widespread availability compared to fossil fuels, which can present an important role in reducing many countries' present dependence on fossil fuels and lowering GHG emissions (Moghtaderi *et al.* 2006; Jungmeier and Spitzer 2001). These initiatives are closely related to the possibility of using clean development mechanisms (CDMs), and they will be an important part of the future energy programs of many countries, especially agricultural countries (Yuan *et al.* 2011).

Despite worldwide concerns over environmental issues, there is growth and development of economic sectors, such as agricultural, industrial, and transportation, where fossil fuels are widely used. The U.S. Energy Information Administration (EIA) (2010) has estimated that world demand for energy will increase from approximately  $521903.3 \times 10^{15}$  J in 2007 to  $778321.2 \times 10^{15}$  J in 2035. Considering the currently used energy sources in the world and the EIA estimate, renewable fuels will represent only 13.5% of the total energy consumed in 2035. On the other hand, some countries that have agriculture as the main economy sector have taken advantage of such potential for using clean energy from agricultural and forestry crops (Wright 2006). Brazil, for instance, produces nearly 50% of its energy from renewable sources, of which 15.2% originates from hydropower and 32% from several types of biomass (MME 2010). According to McKendry (2002), biomass is the most common form of renewable energy widely used in developing countries.

Biomass may be considered as a range of biodegradable products including: 1) residue from agriculture and forestry activities; 2) vegetal waste from agriculture, forestry, and from the food production industry; 3) untreated wood waste and cork; 4) biodegradable by-products of the pulp and paper industry; 5) digestion of the biodegradable of separated municipal waste (IEA 2001).

Agricultural solid wastes deposits cause large-scale pollution of land, water, and air. Their inappropriate storage is a dramatic source of aesthetic pollution, eutrophication due to leaching or run-off, and hence perturbation of aquatic life. In addition, the uncontrolled releases of the gaseous products of waste decomposition into the atmosphere contribute to global warming (Mane *et al.* 2007; Viéitez and Ghosh 1999). Therefore, their energetic use is a feasible alternative to sustainability and avoids the above mentioned problems.

Biomass is often the only accessible and affordable source of energy in rural areas or remote locations (Demirbas 2004; Khambalkar *et al.* 2008). The conversion of biomass resources into useful energy products and services can be undertaken using a wide range of technological pathways. Electricity and heat can be obtained from biomass by the following procedures: 1) through direct combustion in a conventional steam boiler to cogenerate processing steam and electricity, 2) through co-firing coal and biomass in a pulverized, coal-fired boiler, 3) through direct combustion in a fluidized bed combustor, 4) through gasification in a gasifier to produce low calorific value gas for running a gas turbine, or 5) anaerobic digestion (Yuan *et al.* 2011; Moghtaderi *et al.* 2006).

Further scientific studies are needed in order to support the technological development of producing energy from biomass wastes. The major problem for local use of plant wastes is their variable dimensions and compositions due to the different production systems that generated them. Moreover, they present high moisture content and low density, which leads to high volume that decreases energy yield per biomass consumed and hinders transportation logistic. For this reason, they present different potentials for energy and must be studied for their choice and classification.

Many agricultural, forestry, and industrial wastes produced in Brazil present energy potential. A brief discussion of the availability of each waste used in this paper is presented. Coffee is one of the most consumed beverages in the world and it is the second largest traded commodity after petroleum (Mussatto *et al.* 2011). In 2011, Brazil's coffee production reached 43.5 million of 60 Kg coffee bags, placing the country as the largest producer in the world, for which Minas Gerais, Espírito Santo, Bahia, Paraná, and Rondônia are the main producing states (MAPA 2012). Coffee grain processing generates

a large amount of wastes. Close to 60% of the crude weight of the bean corresponds to the husk, while coffee parchment corresponds to 4.5% of the coffee cherry processing (Delfiol *et al.* 2012; Adams and Ghaly 2007).

Brazil is the third largest producer of maize in the world with 53.2 million of tons harvested in 2010. This crop is mainly cultivated in the South, Southeast, and Center-West regions of Brazil (MAPA 2012). The estimates of maize cob residual production may be considered approximately the same amount of maize produced (Melo-Silveira *et al.* 2012).

Sugar cane is Brazil's most widely planted crop. The country is responsible for more than half of the sugar commercialized in the world (MAPA 2012), and it is the world's second producer of ethanol (Elobeid and Tokgoz 2008). Sugar cane is produced in nearly the whole country. São Paulo is the main state with 60% of the total production. Other important regions are Paraná, Triângulo Mineiro, and Zona da Mata Nordestina (MAPA 2012; CONAB 2012). Crushing 1 ton of sugar cane yields 270 kg of bagasse at 50% of moisture content (Scaramucci *et al.* 2006).

Rice production in Brazil is distributed among the states of Rio Grande do Sul, Santa Catarina, and Mato Grosso. Considering that beneficiation of rice generates as byproduct rice husk that corresponds to about 23% of its initial weight, rice husk generation in Brazil could be estimated in 2.25 millions of tons in 2009/2010 (Della *et al.* 2002; MAPA 2012).

In the course of industrial saw wood transformation, only 40 to 60% of the log is used. The great amount of wood wastes is considered to have great potential for energy generation. In 2008 the production of saw wood from pine was about 10 millions of m<sup>3</sup>. Most industries are located in the south of Brazil. The eucalyptus saw wood industry is not well established in Brazil, but it is estimated that the demand for such products shall be 7 millions of m<sup>3</sup> in 2020, which will be produced mainly in Mato Grosso do Sul state (ABIMCI 2007).

CEPASA Company is located in Pernambuco and Maranhão states and invests in the production of high strength packaging papers such as cement bags. In order to achieve the needed levels of strength, the company extracts long fibers from bamboo (*Bambusa vulgaris* Schrad). CEPASA generates about 5 to 7% of fiber organic wastes from their production of 86000 ton each year.

The heating value, content of fixed carbon, volatile substances, ash, and cellulose/lignin contents are the most essential properties to be considered for potential energy analyses of lignocellulosic wastes (Erol *et al.* 2010; Akkaya 2009; Majumder *et al.* 2008; Moghtaderi *et al.* 2006). Several researchers have stated that elemental analyses may also be vital for biomass classification due to its high correlation with heating values (Yin 2010; Friedl *et al.* 2005; Sheng and Azevedo 2005). The density of lignocellulosic wastes is also very important for bioenergy production, since it establishes a relation between the mass and volume of the byproducts, considering the voids that certainly will influence the energetic yield of a material. High-density materials present a higher mass per volume and they have an advantage of resulting in a higher combustion yield.

The aim of this paper was to analyze energy-related properties of forestry and agricultural wastes for energy production purposes, and to compare them with fossil fuels regarding their equivalent amounts and CO<sub>2</sub> saved from fossil fuel burning. We first provide a complete chemical, physical, and energetic characterization of highly relevant Brazilian biomass wastes. Such data is important for further studies on bioenergy use for electric and heat power production. A second analysis consists of calculating the fossil

fuel equivalent of each biomass type, as much as the CO<sub>2</sub> amount that would be retained by fossil fuels by using CO<sub>2</sub> neutral biomass. We focus mainly on the potential of substitution of fossil fuels by biomass for heat production according to a Brazilian energetic scenario.

## EXPERIMENTAL

### Analytical Methods for Determining Energetic-Related Properties of Waste Biomass

The forestry biomass types studied were *Eucalyptus* wood (6-year-old *Eucalyptus urophylla*), Australian red-cedar wood (18-year-old *Toona ciliata*), and *Pinus* wood (35-year-old *Pinus* sp.). Waste slabs from lumber production of those species were selected, debarked, and transformed into shavings by a wood shaver machine. Rice husk, sugarcane bagasse, coffee wastes (husk and parchment), maize harvesting wastes (cob, straw, branches, and leaves), and residual kraft cellulose pulp from bamboo (*Bambusa vulgaris*) composed the agricultural wastes considered. Each biomass waste lot was divided into 5 samples corresponding to repetitions, which were used for all the analyses, from which an arithmetic average and standard deviation were calculated.

The materials were dried under room conditions and transformed into sawdust by a Wiley mill. A sieve set was used for classification. The fractions used for the analyses were as follows: 1) between 40 and 60 mesh for molecular proximate and ash analysis; 2) between 60 and 200 mesh for elemental and components analysis; and 3) 200 and 270 mesh for higher heating value analysis. The samples were conditioned at 20±3 °C and 60% UR until stabilization of moisture content.

Elemental constituents of the materials on a dry basis were investigated by using a Vario Micro Cube elemental analyzer. The ash contents of the wastes were determined according to standard M11/77 (ABTCP, 1974a) using a muffle furnace. The heating rate, initial temperature, and final temperature were 1.67 °C/min, 25, and 575 °C, respectively. The same final temperature was kept for the duration of 3 h. The oxygen content of the waste was determined by Eq. 1, as suggested by Bech *et al.* (2009).

$$O (\%) = 100\% - C (\%) - H (\%) - N (\%) - S (\%) - \text{Ash} (\%) \quad (1)$$

Total extractives and lignin contents were determined in accordance with standards M3/69 (ABTCP 1974a) and M70/71 (ABTCP 1974a). For total extractives analysis, a soxhlet apparatus was used, and the samples were extracted using a sequence of toluene-ethanol (5 h), ethanol (4 h), and water (2 h). Lignin content was determined by keeping 1 g of the samples in a cooled 72% H<sub>2</sub>SO<sub>4</sub> solution for 2 h. Afterwards, the samples were heated until boiling for 5 h, filtered and washed. Holocellulose content of the waste was determined by Eq. 2.

$$\text{Holocellulose} = 100 (\%) - \text{Lignin} (\%) - \text{Extractives} (\%) - \text{Ash} (\%) \quad (2)$$

The immediate analysis procedures were conducted in accordance with D-1762-64 (ASTM 1977). A bomb calorimeter (IKA C-200) was used to measure the higher heating values (HHV) of the wastes, following standard NBR 08633 (ABNT 1984). Eq. 3 was used to estimate lower heating values (LHV) of the wastes.

$$\text{LHV} = \text{HHV} - 5.72(9 \cdot \text{H} (\%) + \text{MC}) \quad (3)$$

In Eq. 3, LHV is the lower heating value (kcal/kg), HHV is the higher heating value (kcal/kg), H is the hydrogen content (% by dry mass), and MC is the moisture content (%).

Dry-basis moisture content of the wastes was obtained using infrared measurement equipment (Gehaka, model IV200). Basic density was determined using the beaker method (also named the water displacement method). 10 g samples with original particle geometry were saturated and then immersed in a 250 mL graduated cylinder containing 170 mL of water. The displacement of water volume was taken, which corresponded to sample volume, assuming a water density of 1 g/cm<sup>3</sup>. The samples were put in a forced air oven at 103±2 °C, and the dry mass was determined. Basic density was calculated dividing moisture-free mass by the saturated volume of the sample. The volume was determined using Archimedes' principle with water as the medium (Wakiyama *et al.* 2010; Azzini *et al.* 1981).

The energetic densities (GJ/m<sup>3</sup>) were calculated using Eqs. 4 and 5 (Rodrigues and Rousset 2009). They correspond to the amount of energy released by complete combustion of the material per unit of volume. The energetic densities were calculated using both HHV and LHV. LHV is important because it does not include the latent heat given up during condensation of the water produced during combustion. It represents the true energy amount produced by the complete combustion of the biomass. HHV is important to use for comparing different biomasses because it measures the maximum energy amount that a fuel may release since the latent heat of water is not lost.

$$\text{ED}_1 = \text{LHV} \cdot \text{BD} \quad (4)$$

$$\text{ED}_2 = \text{HHV} \cdot \text{BD} \quad (5)$$

In Eqs. 4 and 5, ED<sub>1</sub> is the energy density 1 (MJ/m<sup>3</sup>), ED<sub>2</sub> is the energy density 2 (MJ/m<sup>3</sup>), LHV is the lower heating value (MJ/kg), HHV is the higher heating value (MJ/kg), and BD is the basic density (kg/m<sup>3</sup>).

### Estimation for Comparison of Renewable Biomass Fuels with Fossil Fuels

This section focused on the comparison of fossil fuels with renewable fuels in relation to their energetic capacity and the amount of CO<sub>2</sub> released into the atmosphere. The analyses enable verification of the environmental advantages of using renewable fuels. The estimation of the amount of CO<sub>2</sub> that would be retained when renewable fuels are used instead of fossil fuels may be used by industries for future calculations of potential carbon credits. We used our own measured average values of ED<sub>1</sub> obtained in the previous stage of this work for biomass fuels to make comparisons with literature values of fossil fuels regarding equivalent energetic volume and CO<sub>2</sub> retention.

In similar studies of fuel cycle emission methodologies, first it is necessary to calculate the amount of biomass able to substitute fossil fuels. Then the calculation of the amount of CO<sub>2</sub> emitted by fossil fuel to operate energetic systems is provided (Gustavsson *et al.* 2011). It is assumed that the agricultural waste and the fossil fuel are being utilized for the same end use. Therefore energetic capacity of fossil fuels and biomass are mathematically equalized (Kumar *et al.* 2002). The next step is the quanti-

fication of the contribution from each biomass to the impact category (global warming). The reference substance for global warming is CO<sub>2</sub> (Hansen *et al.* 2006).

The analysis procedure developed by the Intergovernmental Panel on Climate Change (IPCC) and used by the SERHS-SP (2006) and CGEE (2008) for calculating CO<sub>2</sub> emission factors of non-renewable fuels was used. For fossil fuels, emissions were calculated (Herald 2003) using the information given in Table 1.

**Table 1.** Properties of Fossil Fuels

Fossil Fuel	LHV (kJ/kg)	Density (kg/m <sup>3</sup> )	EDff (MJ/m <sup>3</sup> )	EF (kg CO <sub>2</sub> /L)
Petroleum*	42705	867	37025.235	3.43
Diesel Fuel*	42622	851	36271.322	3.53
Fuel Oil*	39971	999	39931.029	2.94
Gasoline*	44196	738	32617.648	3.94
Natural Gas	50100**	0.654***	32.7654	0.01922****

LHV: lower heating value; SM: specific mass; EDff: energy density; EF: emission factor.

\* SERHS-SP (2006)

\*\*Demirbas (2004)

\*\*\*Granovskii *et al.* (2006)

\*\*\*\*Adapted from EPA (1998)

The following procedure was used to determine the volume of fossil fuel that is equivalent in energy to the complete combustion of 1 m<sup>3</sup> of biomass waste. First, the energy (MJ) provided by 1 m<sup>3</sup> of each biomass was calculated.

$$E_{\text{biomass}} = ED_{\text{1biomass}} * V_{\text{biomass}} \quad (6)$$

$E_{\text{biomass}}$  is the energy produced by 1 m<sup>3</sup> of each biomass waste analyzed in this work (MJ),  $ED_{\text{1biomass}}$  is the energy density (MJ/m<sup>3</sup>) obtained by Eq. 4, and  $V_{\text{biomass}}$  is the volume of biomass equals to 1 m<sup>3</sup>.

By using Eq. 7, it was possible to obtain the amount of fossil fuel that is required to produce the same amount of energy produced by biomass wastes studied in this work.

$$EqV_{\text{ff}} = E_{\text{biomass}}/ED_{\text{ff}} \quad (7)$$

$EqV_{\text{ff}}$  is the fossil fuel volume (m<sup>3</sup>) equivalent to 1 m<sup>3</sup> of biomass for energy production, and  $ED_{\text{ff}}$  is the energy density of the fossil fuel (MJ/m<sup>3</sup>) calculated using LHV (also considered for renewable fuels) and density (kg/m<sup>3</sup>).

In the present work the emission factor for biomass was considered to be zero. Certainly, a portion of CO<sub>2</sub> captured by the plant is returned to the environment through biomass processing (*e.g.*, combustion, gasification, *etc.*). In general, biofuels can be carbon neutral, carbon negative, or carbon sources, depending on how much CO<sub>2</sub> (and other greenhouse gases) is removed from or released into the atmosphere during crop growth and biofuel production (Tilman *et al.* 2006). For biomass to be considered as a CO<sub>2</sub> neutral energy resource it is assumed that CO<sub>2</sub> produced is absorbed by growing plants in a relatively short cycle (López-Rodríguez *et al.* 2009; Voivontas *et al.* 2001; Moghtaderi *et al.* 2006).

Moreover, aspects such as sustainability of agricultural and forestry systems and boundaries of biomass utilization must be taken into account for considering CO<sub>2</sub>

neutrality and hence the effectiveness of such calculations. The comparison proposed in this work simplifies those factors by comparing the CO<sub>2</sub> emissions of specifically residual biomass that is assumed to be used in the same place of its production. If the boundary conditions were extended to include the production, harvesting, and transportation of the biomass, then there is a net emission of CO<sub>2</sub>, but it is much smaller in magnitude than producing energy from fossil fuels.

Therefore, Eq. 8 allowed the calculation of the amount of CO<sub>2</sub> released from fossil fuels that would be retained by using biomass instead:

$$\text{CO}_{2\_ret} = \text{EF} * \text{EqV}_{ff} \quad (8)$$

CO<sub>2</sub>\_ret is the CO<sub>2</sub> mass (kg) prevented from releasing in the fossil fuels, and EF is the emission factor of fossil fuel (kg CO<sub>2</sub>/L).

## RESULTS AND DISCUSSION

### Physical and Chemical Characterization of Lignocellulosic Wastes

High C and H contents are advantageous properties for bioenergy production; however a high O content is not desirable, since it does not contribute to higher heating values. The heat content is related to the oxidation state of the natural fuels, in which carbon atoms generally dominate and overshadow small variations of hydrogen content (Huang *et al.* 2009; Demirbas 2004; Nordin 1994). Figure 1 depicts the elemental analysis of each waste.

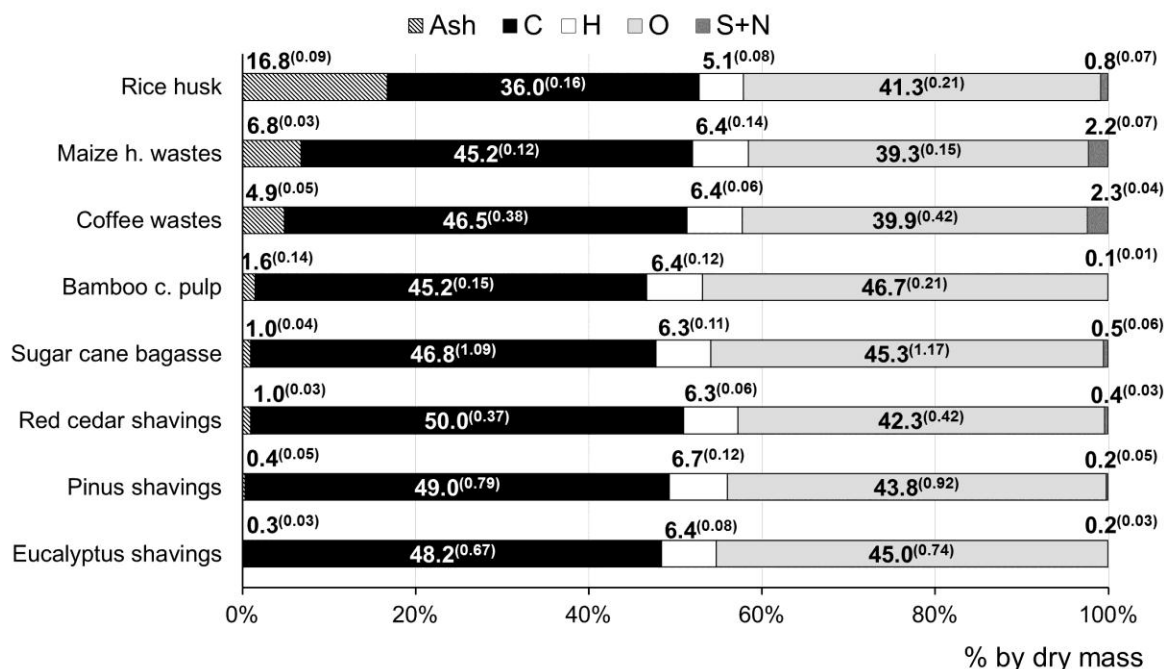


Fig. 1. Elemental and ash analysis of the wastes (standard deviation in parentheses)

*Pinus*, *Eucalyptus*, and red cedar shavings presented higher C contents. Among agricultural wastes, sugar cane bagasse and rice husk presented the highest and lowest values of C content, respectively. Maize harvesting wastes and coffee wastes had the lowest O contents. H values were nearly equal among most wastes, except for *Pinus* shavings and rice husk, which presented the highest and lowest contents, respectively.

The results found for wood shavings are in accordance with Kumar *et al.* (2010), who claimed that elemental analysis for woods is about 50% C, 6% H, and 44% O on a moisture-free basis. The differences between the woods are probably related to the different extractive types and contents (Ragland and Aerts 2003).

Among agricultural wastes, coffee wastes presented the highest C content and lowest O content, while the opposite was obtained for rice husk. The C and H contents of sugar cane bagasse were higher than those observed by Harun *et al.* (2009), at 44.5% C and 5.32% H. Seye *et al.* (2003) found similar C contents (46.7%) to the present work. The maize harvesting wastes and bamboo cellulose pulp did not show differences in C content, but the former presented a lower O content. Elemental analysis carried out by Wilaipon (2007) showed that maize cob is comprised of 40.5% C, 5.7% H, and 0.4% N.

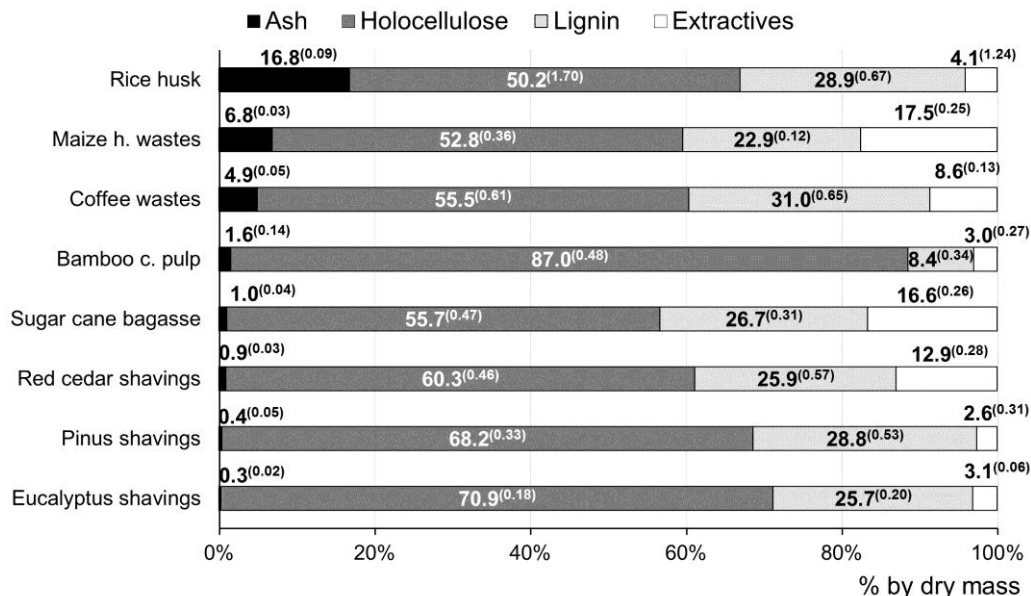
In addition to evaluating the energetic capacity of renewable fuels, it is also important to consider S and N contents if environmental aspects are taken into account (Kumar *et al.* 2010; Bilgen and Kaygusuz 2008). The differences among biomass wastes and the content of such components are related to soil nutrient balance, soil temperature, water stress, and type of soil. S is assimilated from the soil mainly as sulfates ( $\text{SO}_4^{2-}$ ), and the oxidation process involves microorganisms. N is mainly taken from the soil, and nitrate is the major form of absorption (Reif *et al.* 2012; Wang *et al.* 2012; Abbey *et al.* 2002). Therefore the content of those elements are influenced by growth conditions, while ash content also varies greatly among biomass (Demirbas 2004).

High N amounts released into the atmosphere may cause negative environmental impacts due to formation of nitrous oxides and nitric acid during pyrolysis and gasification (Yuan *et al.* 2011; Munalula and Meinckin 2009). Moreover, the substances in synthesis gas can form ammonium salt crystallizations by reacting with  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (water/steam), which affect the safety and long-term operation of gasification systems (Yuan *et al.* 2011). Among the wastes considered, bamboo cellulose pulp presented the lower value of N, while the highest value was found for coffee wastes.

The release of S to the atmosphere may cause acid rain and environmental degradation (Bilgen and Kaygusuz 2008). However, it has been reported that  $\text{SO}_2$  emissions are negligible in biomass fuels (García *et al.* 2012). *Eucalyptus* shavings, *Pinus* shavings, and bamboo cellulose pulp presented the lowest S contents, while the highest values were found for maize harvesting wastes and rice husk.

Average values of biopolymer analyses and ash contents are shown in Fig. 2. High lignin contents are advantageous properties for bioenergy production since this component presents higher carbon content in relation to cellulose and hemicelluloses and higher thermal stability due to its aromatic structure (Demirbas 2001a; Sharma *et al.* 2004). Protásio *et al.* (2012) and Demirbas (2001a) reported a high correlation between HHV and lignin content. Depending on their C content and chemical structure, some extractives may also increase HHV of biomass (Telmo and Lousada 2011). However, high ash content is not desirable, since it may decrease the heating value and makes biomass less desirable as a fuel (Kumar *et al.* 2010; Shafizadeh 1981; Brand 2010).





**Fig. 2.** Biopolymer and ash analysis of the wastes (standard deviation in parentheses)

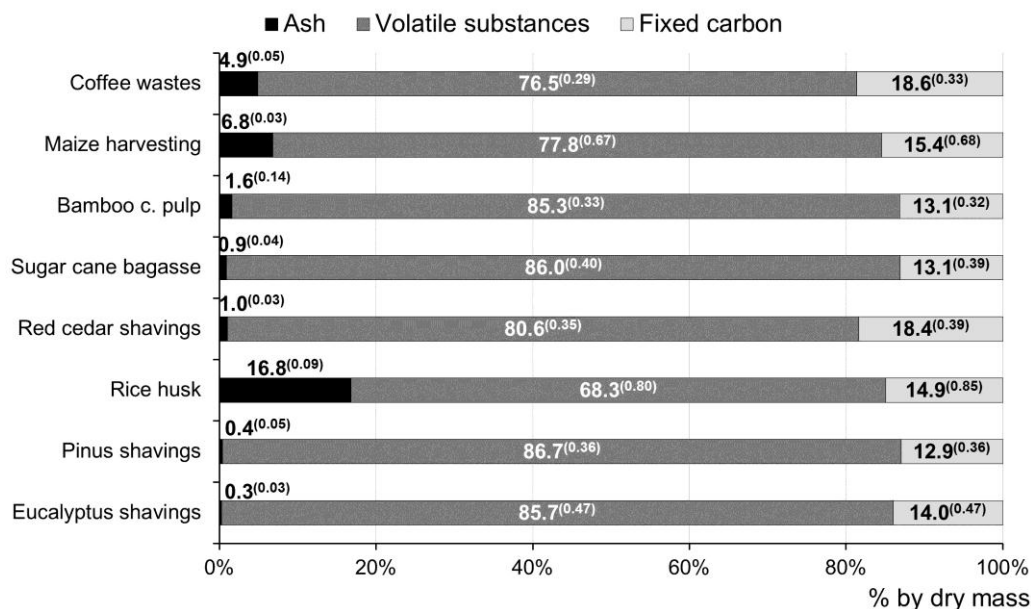
*Eucalyptus* and *Pinus* shavings presented the lowest ash contents, respectively. However, red cedar shavings and sugar cane bagasse presented equal ash contents. Among agricultural wastes, sugarcane bagasse presented the lowest ash content. Other agricultural wastes presented considerably higher ash content in the following order from the lowest to highest value: residual bamboo cellulose pulp, coffee husk, maize wastes, and rice husk. Biomass may be burned by direct combustion to produce steam, the steam turns up a turbine and the turbine drives a generator, producing electricity. Because of potential ash build up (which fouls boilers, reduces efficiency, and increases costs), only certain types of biomass materials are used for direct combustion (Demirbas 2001b). High ash content found for rice husk could limit its use.

Total extractive contents of *Eucalyptus* and *Pinus* shavings were similar, but both presented lower values than red cedar. Maize harvesting wastes and sugar cane bagasse presented the highest extractive contents. Besides presenting high heating values, some extractives facilitate the decomposition of the structural components of wood, decreasing their activation energy (Telmo and Lousada 2011; Guo *et al.* 2010).

Coffee wastes presented the highest lignin content among all wastes. Lignin content was similar for *Eucalyptus* and red cedar shavings, since they are both hardwoods. The lignin content of *Eucalyptus* was close to that found by Trugilho *et al.* (1996) for 2-year-old wood (24.48%). Among forestry wastes, *Pinus* shavings presented the highest lignin content. The lowest lignin content was found for bamboo cellulosic pulp. This is mainly attributed to the kraft pulping process, which causes extraction of a considerable fraction of these chemical components during the fiber individualization process. Rice husk and residual bamboo cellulose pulp presented the lowest and highest holocellulose contents, respectively. The average values found for proximate analyses are shown in Fig. 3.

Coffee wastes and red cedar shavings presented the highest fixed carbon contents among the wastes studied, followed by maize harvesting wastes, rice husks, and *Eucalyptus* wastes. The lowest values were found for *Pinus* shavings, sugar cane bagasse,

and bamboo cellulose pulp. The lowest content of volatile substances was found for rice husk.



**Fig. 3.** Proximate and ash analysis of the wastes (standard deviation in parentheses)

The fixed carbon content indicates the extent of non-volatile organic matter in the sample, which may also contain oxygen or hydrogen. Volatile matter of biomass fuels results from the thermal decomposition of the precursor and usually consists of H<sub>2</sub>O, CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, and tar, which is a complex mixture of condensable hydrocarbons, mainly levoglucosan, phenolic compounds, and carboxylic acids (Demirbas 2011b; Jurena and Hájek 2011; Lori *et al.* 2007; Parikh *et al.* 2007). Fuels with high fixed carbon contents and little volatile matter burn more slowly, which means that they may require a long time period in the furnace to burn completely (Brand 2010; Nogueira and Lora 2003). The knowledge of proximate analysis is important for the calculation of furnace projects for complete and direct combustion of biomass. The amounts of primary and secondary air that are injected in the furnace are determined according to oxygen necessary to completely burn volatiles and particles of biomass (Brand 2010). It has been reported that fixed carbon and volatile matter contents both have positive effects on the HHV (Majumder *et al.* 2008).

The average HHV and LHV values are depicted in Fig. 4. The heating value is an important parameter for the planning and the control of power plants using biomass. It may be defined as the enthalpy of complete combustion of a fuel with, for instance, all carbon converted to CO<sub>2</sub> and all hydrogen converted to H<sub>2</sub>O (Friedl *et al.* 2005).

Rice husk presented the lowest value for both HHV and LHV, which may have happened due to its low C, H, volatile materials, and fixed carbon contents, as well as high O and ash contents, besides its high ash content. In general, forestry wastes and coffee wastes presented higher values for HHV and LHV.

The highest HHV and LHV values were found for *Pinus* shavings, which corroborate the high values for H, lignin and extractive contents. Hardwoods represented by Red cedar and eucalyptus shavings had similar HHV and LHV. The mean difference in HHVs for softwoods, hardwoods, and non-wood biomass fuels is primarily caused by their differences in lignin type and content. The lignin types from grasses, softwoods, and

hardwoods differ somewhat in composition, mainly in methoxyl substitution and the degree of C-C linkage between phenyl groups.

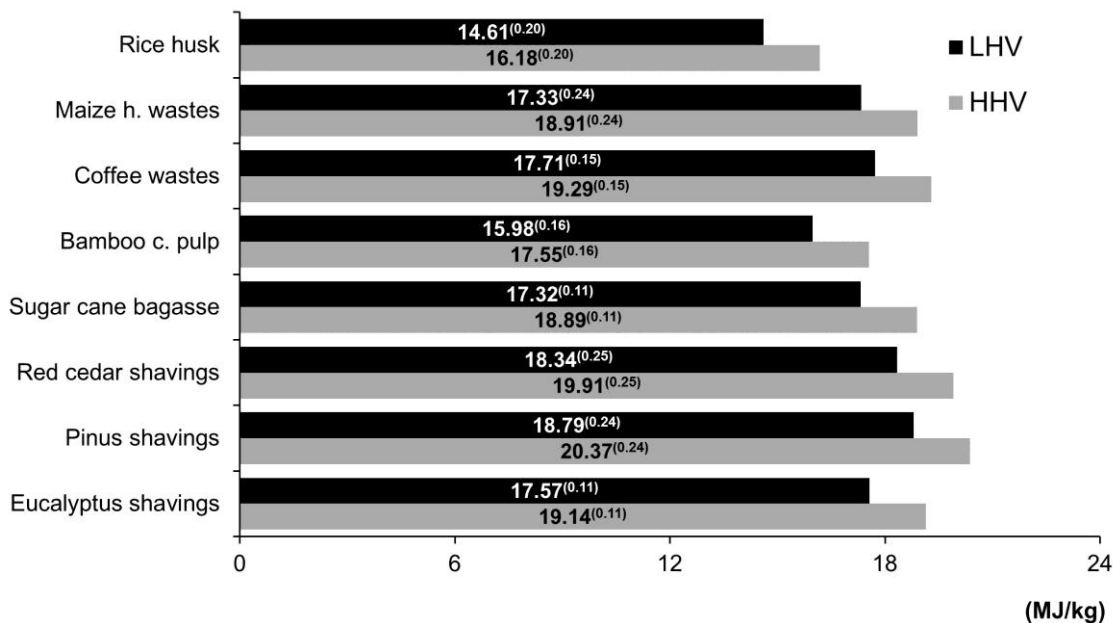


Fig. 4. HHV and LHV values (standard deviation in parentheses)

Guaiacyl lignin, which is found predominantly in softwoods, results from the polymerization of a higher fraction of coniferylphenyl propane units. Guaiacyl-syringyl lignin, which is typically found in many hardwoods, is a copolymer of both the sinapyl and coniferyl phenylpropane units; the fraction of sinapyl units is higher than in softwoods lignins. Lignin pyrolysis yields phenols via the cleavage of ether and C-C linkages. The aromatic and phenolic character is apparent in softwood lignin, as is the covalent C-C bonding that prevents reversion to monomers by mild processing. Hence a lower syringyl/guaiacyl rate usually increases heating power in softwoods (Mohan *et al.* 2006; Demirbas 2001a). Furthermore, Yin (2010) showed that elemental analysis has a good HHV predictive capability. HHV is also naturally related to high resin content in biomass (Naik *et al.* 2010).

Although the use of biomass for energy generation provides environmental advantages, the HHVs of all wastes studied are lower than those presented by gasoline, oil, and biodiesel, which were reported as 46.1 MJ/kg, 43.6 MJ/kg, and 39.09 MJ/kg, respectively (Lam *et al.* 2012; Ramírez-Verduzco *et al.* 2012).

Figure 5 presents the average basic and energetic densities of the wastes. High energy density values are advantageous properties for bioenergy production and represent the interaction between heating values and material densities.

The basic density for coffee wastes was the highest. Density depends on the plant species and tissue, and it is a very important parameter for evaluating the economic viability of using wastes. In general, biomass presents low density, which makes transportation and handling difficult and costly. The key to overcoming this problem is locating the energy conversion process close to a concentrated source of biomass, such as a sawmill (Demirbas 2001b). Coffee wastes presented the highest values  $ED_1$  and  $ED_2$ , followed by *Eucalyptus* shavings, while sugar cane bagasse and red cedar shavings had the lowest values (Fig. 5). Both HHV and basic density are important for bioenergy production.

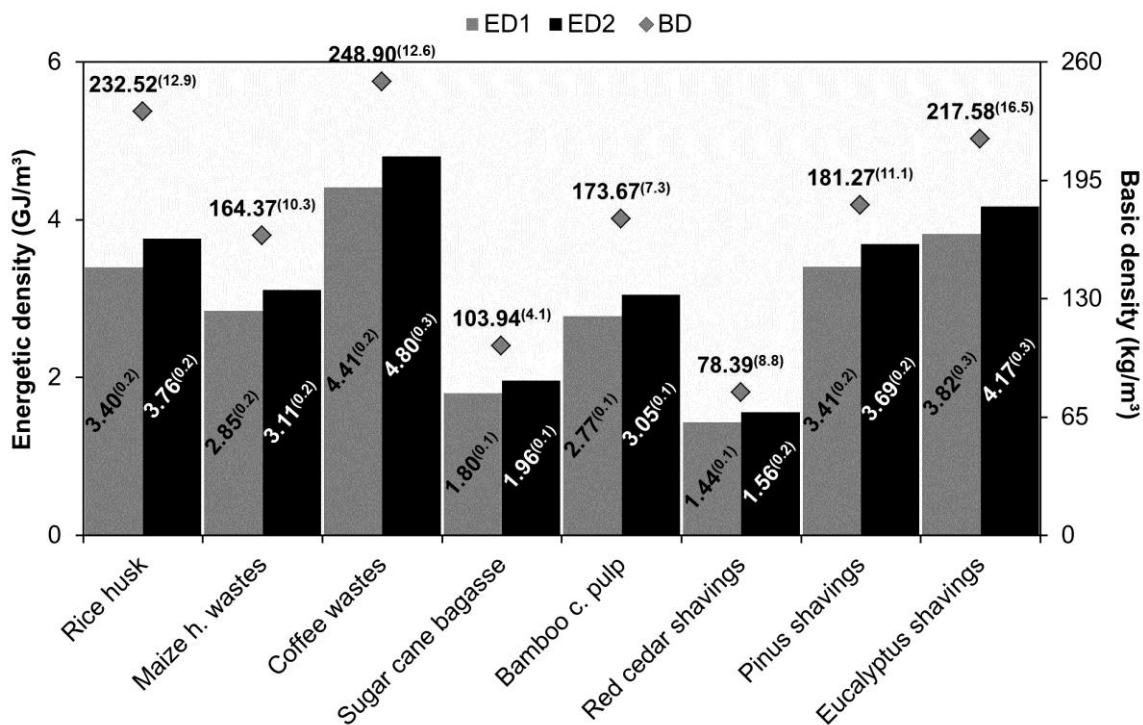


Fig. 5. Basic and energetic densities (standard deviation in parentheses)

In the case that one of these properties presents a low value, it may be compensated by high values of the other, as observed for bamboo cellulose pulp, which presented low HHV and LHV, but high ED<sub>1</sub> and ED<sub>2</sub>. Similarly, despite high HHV and LHV values, red cedar wood shavings presented low basic density values. Since ED<sub>1</sub> and ED<sub>2</sub> are calculated using LHV and HHV, respectively, their numerical difference represents the energy fraction that is lost for the environment during the complete combustion of the biomass due to water evaporation.

### Replacement of Fossil Fuels and CO<sub>2</sub> Retention

The results for fossil fuel volume (m<sup>3</sup>) equivalent to 1 m<sup>3</sup> of biomass for energy production are given in Fig. 6. Coffee wastes presented the highest equivalent volume in fossil fuels. Therefore, this result means that 1 m<sup>3</sup> of coffee wastes can replace either 100 L of fuel oil, or 119 L of petroleum, or 1221 L of diesel oil or 135 L of gasoline in order to produce the same amount of energy. The main advantage offered by coffee wastes is the high energy density found in the previous stage of this work, even though this waste presented lower heating value in relation to forestry wastes. On the other hand, low density of red cedar shavings shows that this residue is just able to substitute smaller amounts of fossil fuels for energy production.

Figure 7 depicts the amounts of CO<sub>2</sub> from fossil fuels that can be retained, considering biomass CO<sub>2</sub> neutral. Among the fossil fuels, the highest CO<sub>2</sub> emission reduction would be achieved by substituting gasoline and diesel oil for lignocellulosic wastes. Additionally, using these wastes could be useful for acquisition of carbon credits. Coffee wastes and eucalyptus shavings stood out as possible substitutes for fossil fuels, because of their high energy density.

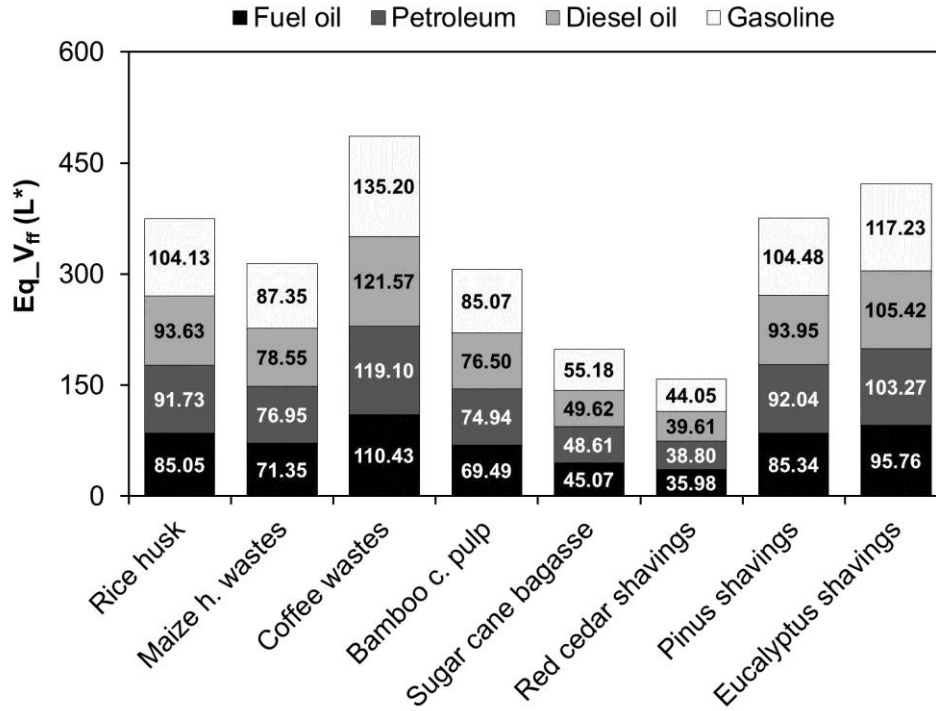


Fig. 6. Fossil fuels amounts (L) saved by biomass fuels (\*equal to 1 m<sup>3</sup> of lignocellulosic wastes)

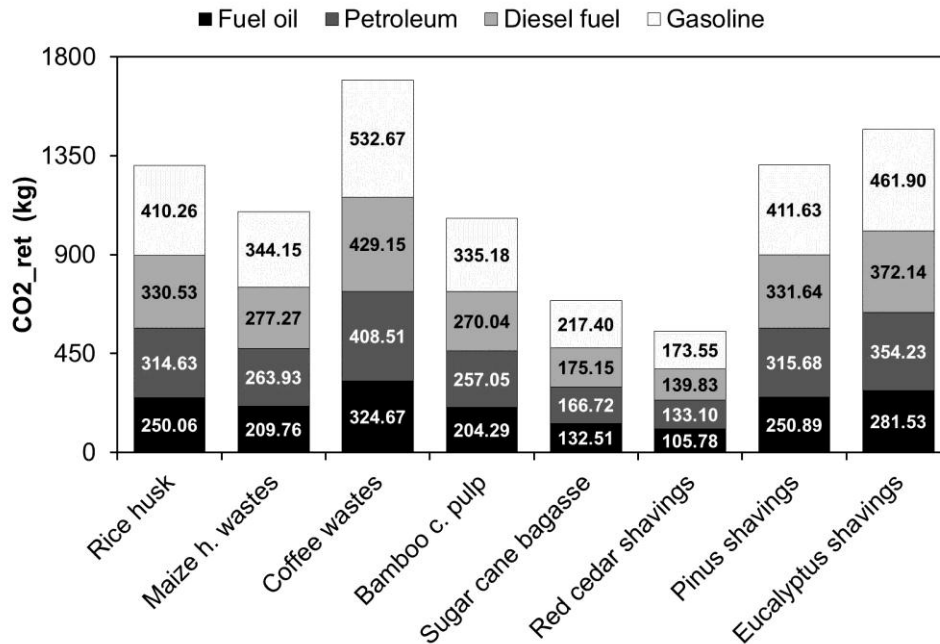
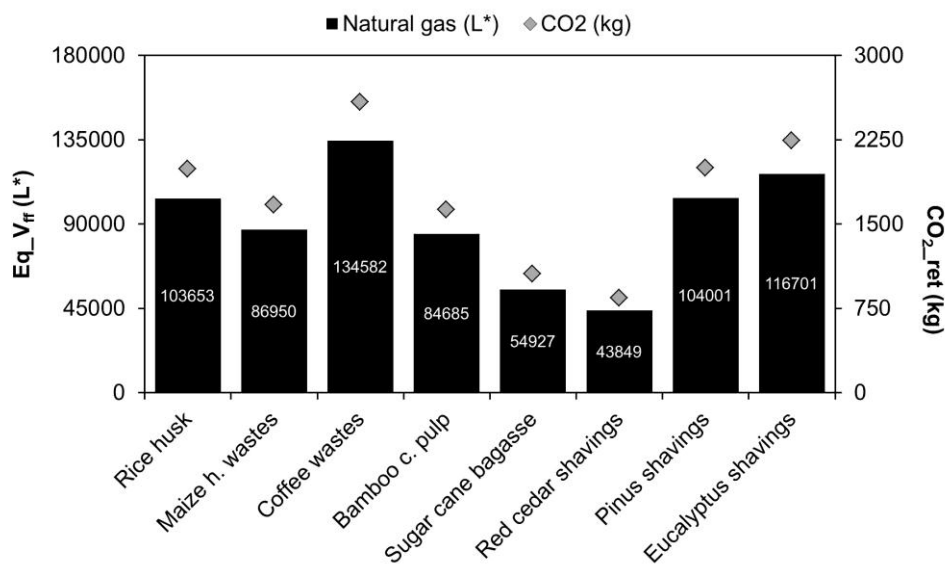


Fig. 7. CO<sub>2</sub> amounts (kg) from fossil fuels saved by biomass fuels

It should be noticed that the quantity of greenhouse gas emissions is regionally specific and varies significantly depending on the fuel used and the degree of cogeneration with heat (Fruegaard *et al.* 2009). Although the data presented above is important for comparing biomass with the main fossil fuels, including petroleum, some fuels are

more likely to be substituted by biomass for electricity and heat production. For example, the main energy sources of electric power in Brazil are hydro (83.7%), biomass, including firewood, charcoal and cane bagasse (5.9%), petroleum (3.1%), natural gas (2.9%), nuclear (2.8%), coal (1.5%), and wind (0.3%) (Brasil 2010). Brazilian coal is not so widely used for energy purposes because it presents low calorific power and high ash contents, thus requiring expensive processing treatment. This fuel is mainly used in iron and steel production rather than for energy. Compared to biomass, coal presents higher C content (84%), higher LHV, and lower volatile matter. On the other hand, biomass presents lower contents of ash and pollution elements, such as N and S (Beloševic 2010). Coal-fired power plants provide over 42% of the electricity supply for the world. At the same time, such plants account for over 28% of global CO<sub>2</sub> emissions (IEA 2010).

Although in Brazil fuel oil and diesel are the main fossil fuels used for electricity generation (Santos *et al.*, 2012), natural gas is widely used in other parts of the world. Therefore, the results of biomass equivalent in natural gas are depicted in Fig. 8.



**Fig. 8.** Natural gas amount (L) and CO<sub>2</sub> amounts (kg) economized by biomass fuels (\*equal to 1 m<sup>3</sup> of lignocellulosic wastes)

Once again, coffee wastes and red cedar shavings represent the higher and lower equivalent volume of natural gas and CO<sub>2</sub> retained. Natural gas is a fossil fuel that is limited in supply and very exposed to price volatility, which are factors of concern if moderate to large portions of electricity are required to be generated from this resource (Zhang *et al.* 2010).

It is important to notice that despite being renewable, biomass presents carbon dioxide emissions, and it may possibly not absorb in the next life cycle all the carbon emitted. Biomass currently requires fossil fuel combustion for its production, harvest, and supply; hence it would be a fallacy to simply identify bioenergy as emitting zero pollutants (Jing and Peidong 2011; Zhu *et al.* 2011; Gautam *et al.* 2010; Van Belle 2006). A wider approach including primary energy balances, CO<sub>2</sub> balances, transport modes, and distances would allow verifying if it is possible to transport biomass over long distances and still mitigate CO<sub>2</sub> emissions. Because of the modest energy requirement for recovery

and transport, it was observed in the literature that biomass can be transported long distances and still significantly offset CO<sub>2</sub> emissions from fossil fuels (Gustavsson *et al.* 2011). On the other hand, it has already been observed that the cost of transportation is very important because agricultural residues have low bulk density (Kumar *et al.* 2002)

Therefore, the results of this study with Brazilian wastes only show that CO<sub>2</sub> benefits can be obtained if bioenergy is generated in the same locality where biomass is produced, avoiding CO<sub>2</sub> cost of logistics and leading to greater end-use efficiency. In order to verify the possibilities of transporting Brazilian biomass, the data baseline must be expanded with further studies, including the above mentioned factors which would allow a life cycle assessment analysis.

## CONCLUSIONS

In general, forestry wastes presented more suitable properties for bioenergy production than agricultural wastes. Among the agricultural wastes, rice husks were the least satisfactory for bioenergy production, while coffee wastes presented favorable energetic properties. High basic density found for coffee wastes is related to species and location within the biomass. Differences in chemical composition are due to species characteristics and growth conditions. Except for coffee wastes, heating value properties are higher in forestry wastes, which are related to higher carbon content, lower ash content, and type of lignin. Among the biomass studied, coffee wastes present the highest equivalent in fossil fuel volume and hence may lead to the highest decrease in CO<sub>2</sub> emissions by liquid and gaseous fossil fuels used in Brazil for steam and heat production. This result is mainly attributed to the high HHV combined with high energy density presented by coffee husks. The present results with Brazilian lignocellulosic wastes suggests that CO<sub>2</sub> benefits can be obtained if bioenergy is generated in the same local where biomass is produced, avoiding CO<sub>2</sub> cost of logistics and leading to greater end-use efficiency. Furthermore, this work promotes the widespread use of different lignocellulosic wastes for energy production and gives useful information for the planning and the control of power plants using biomass, especially considering the Brazilian energy scenario.

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