

Use of Charcoal and Partially Pirolysed Biomaterial in Fly Ash to Produce Briquettes: Sugarcane Bagasse

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1. Introduction

Currently, many scientists worldwide are studying the recycling or reuse of waste materials to make useful products. For example, silicate-based wastes have been studied for use as raw material in the ceramic industry. Although numerous types of waste have been studied, sugarcane bagasse ash (SCBA) has been overlooked, probably because this type of residue is more common in developing countries that produce sugar and alcohol from sugarcane. Bagasse is a by-product of the cane sugar industry. Brazil is the world's largest producer of alcohol and sugar from sugarcane and has an extensive alternative program for automobile fuel. The new technology of flex-fuel (alcohol/gasoline) vehicles, developed in the 1990s and applied to new cars in 2003 revived the Brazilian PROALCOOL program. Today, several million flex-fuel cars are in use, and more than 85% of the new cars produced in the country run on this system (PróAlcool 2011; History of ethanol fuel in Brazil 2011; Goldemberg 2008).

In the production of sugar and alcohol, sugarcane is ground and the resulting juice is extracted to obtain sugar or used in a fermentation process to produce alcohol. The fibrous matter that remains after sugarcane has been crushed to extract the juice is called bagasse (or "bagaço," in Portuguese). There are many applications and much research effort is directed at exploring the potential of bagasse as a renewable power generation source, for the production of bio-based materials (for example, bioethanol and briquettes or pellets), cattle feed, building materials, etc. Basically, bagasse is a fibrous material containing cellulose (~50%), hemicellulose and lignin as the major (~95%) compounds. There are also waxes, inorganic materials and/or salts inside the plant tissues that will result in the final ash (oxides and carbonates) after firing (Pandey et al. 2000).

Although there is a great deal of research in Brazil on sugarcane bagasse briquetting, showing the many advantages of using briquettes instead of bagasse, factories still burn bagasse. Currently, sugarcane bagasse is used as a primary fuel source in sugar mills. It is burned in a boiler to produce steam which is utilized in the factory's processes and also to power turbines for the production of electrical energy. Today, the cogeneration of electricity by sugar and alcohol mills accounts for ca. 5% of the total electricity produced in Brazil

(BEN 2010; SYS 2001). However, most factories do not participate in this production, which can achieve in the future a rate of about 15% of the market. The combustion yields ashes (bottom and fly ashes) containing high amounts of organic material (~35% by weight of charcoal and bagasse debris) and silica as the major inorganic component. Fly ash contains more charcoal than does the bottom ash. The inorganic fraction can be used by the ceramic industry and the organic one can be used to produce fuel briquettes (Teixeira et al. 2010b). Fly ash is the solid material that is removed from the gases leaving the boiler to the industry chimneys. In general it consists of a mixture of inorganic materials, charcoal, and partially pyrolyzed material (bagasse debris). Depending on the source and makeup of the material being burned, the components of the fly ash produced vary considerably. Its composition includes substantial amounts of inorganic substances (generally oxides and carbonates) and carbon matter (organic material), which can be detected by loss on ignition or by thermogravimetric analyses. In fly ash from coal, the carbon concentration is low (< 6%), but with biomass for burning, such as sugarcane bagasse, there can be a very high carbon content, as much as 35%. This value can be reduced by improving the efficiency of the firing process or using briquettes instead of burning crude bagasse. Therefore, for this residue to be used as raw material, it is interesting to separate out the charcoal to produce briquettes and to improve the quality of the inorganic part for use in the ceramic industry. Due to the difference in grain size distribution and in density of organic and inorganic fly ash compounds it is possible to separate the two fractions using sieves, hydrocyclones or other processes (Teixeira et al. 2010b, Ahmaruzzaman 2010; Rodríguez-Pedrosa et al. 2010; Zandersons et al. 1999).

The estimated 2009/2010 Brazilian sugarcane harvest was 629 Mton to produce sugar (44.7%) and alcohol (55.3%) (BEN 2010). The volume of ash (fly and bottom) that would be produced from this harvest is approximately 3.2 Mton (1000 kg cane → 250 kg bagasse → 6 kg ash) (Teixeira et al. 2010a). In this chapter, we will show some of the possible utilizations of sugarcane bagasse and will discuss the separation, characterization and utilization of the charcoal in the fly ash of the fired bagasse, to produce briquettes.

2. Energy in Brazil and proalcohol

Brazil has the most renewable energy sources in the industrialized world with 46.8% of its primary energy production from renewable resources such as hydropower plants (13.9%), firewood (10.2%), sugarcane products (18.8%) and others (2.8%). Figure 1 shows the evolution of primary energy production in Brazil over the past 40 years. The non-renewable energy sources (oil, natural gas, coal and uranium) still represent about 53% of the energy produced and consumed in the country. Hydropower plants are responsible for generating over 76% of the electricity in the country. It is worth noting that the global energy matrix is composed of 13% renewable in the case of industrialized countries, falling to 6% among developing nations. The Brazilian energy model has great potential for expansion, which results in a number of opportunities for long-term investment. The estimate of the Ministry of Mines and Energy for the period 2008-2017 indicate public and private contributions of R\$ 352 billion (~US\$ 207 billion) for the expansion of national energy programs (BG, 2009; BEN, 2010).

The Brazilian domestic energy supply (BEN 2010) shows the participation of each kind of energy source in the country's energy matrix (Fig. 2) in the last seven decades. It is interesting to note the increase in the consumption of oil and electricity, with a

corresponding decrease in consumption of wood, after the World War II until the 1970s. With the oil crisis in the 1970s and 1980s there was a stabilization in the consumption of oil

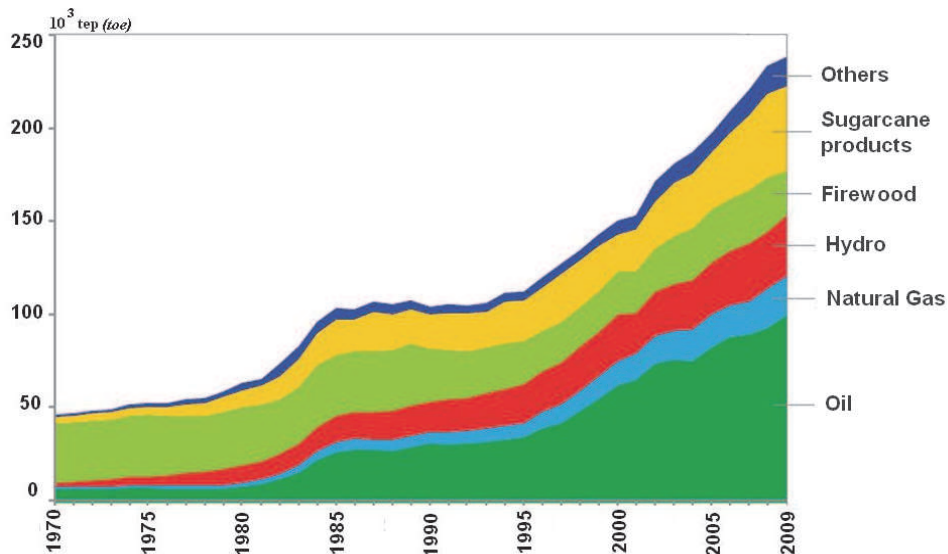


Fig. 1. Brazilian Primary Energy Production (BEN 2010)

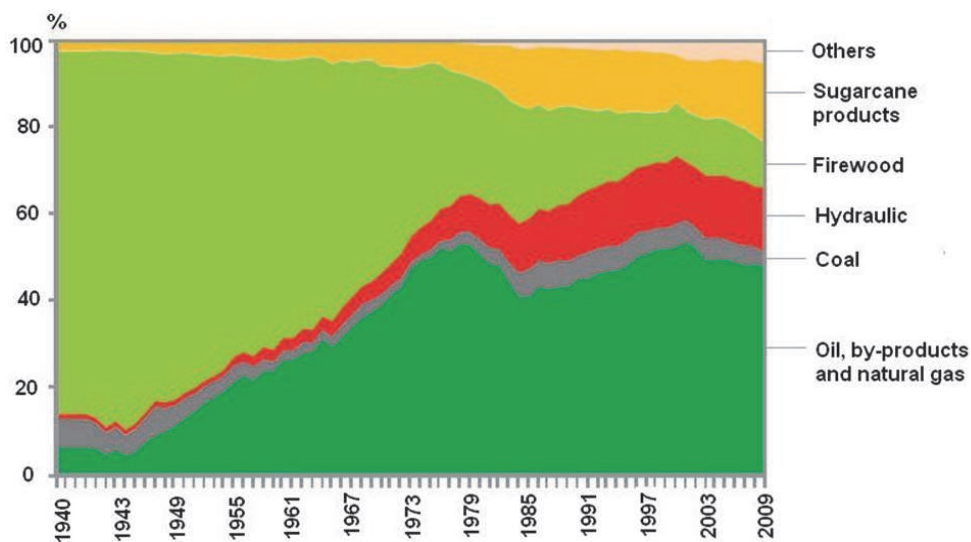


Fig. 2. Brazilian Domestic Energy Supply (BEN 2010)

and increased production of hydraulic power and ethanol, with the Brazilian alcohol program. At the height of this program, between 1975 and 1985, there was a decrease in consumption of oil products including gasoline, which was replaced by alcohol. Table 1 shows the trend in energy production for each sector, every 20 years, for the last 40 years.

The progress in energy production from renewable resources happened mainly in the sugarcane industry. Brazil's sugarcane-based ethanol fuel program allowed the country to become the world's second largest producer of ethanol, and the world's largest exporter. In response to the 1973 oil crisis, the Brazilian government began promoting bioethanol as a fuel. The National Alcohol Program - *Pró-Álcool* (In Portuguese, **Programa Nacional do Álcool**), was a nation-wide program financed by the government to phase out automobile fuels derived from fossil fuels, such as gasoline, in favor of ethanol produced from sugarcane. Several important political and technological developments led Brazil to become the world leader in the sustained use of bioethanol. Government policies and technological advances also allowed the country to achieve a landmark in ethanol consumption, when ethanol retail sales surpassed 50% of the market share of the gasoline-powered vehicle fleet in early 2008.

Year	1970	1990	2009
Oil by-products and natural gas	38,0	43,7	46,6
Coal and by-products	3,6	6,8	4,7
Hydraulic and electricity	5,1	14,1	15,2
Firewood and charcoal	47,6	20,1	10,1
Sugar cane products	5,4	13,4	18,2
Others¹	0,3	1,9	5,2
Total	100	100	100

Table 1. Domestic Energy Supply (BEN 2010)

The Brazilian National Alcohol Program (known as **Proalcohol**) (History of ethanol fuel in Brazil, 2011; PróAlcool, 2011) was established on November 14, 1975 as a result of two serious international crises in the 1970s: in the sugar market and oil market that pushed the average price of a barrel of oil at U.S. \$ 2.91 in September 1973 to \$ 12.45 in March 1975. At the time, Brazil imported about 80 percent of the crude oil consumed in the country. The program was a success for nearly 15 years. By the end of 1980, there were more than 4 million cars and light trucks running on pure alcohol, which accounted for a third of the country's fleet of motor vehicles. However, at this time, ethanol production and sales of cars running on pure ethanol dropped due to several factors (gasoline prices fell sharply, Brazilian inflation, sugar prices increased sharply, a shortage of ethanol fuel supply, and the

¹ Including others renewable energy and uranium

reduction of ethanol subsidies by the government). In 1990, production of neat ethanol vehicles fell to 10.9% of the total car production as consumers lost confidence in the reliability of ethanol fuel supply, and began selling or converting their cars back to gasoline fuel. Confidence in ethanol-powered vehicles was restored with the introduction in the Brazilian market of flexible-fuel vehicles starting in March 2003 when Volkswagen launched in the Brazilian market the **Gol 1.6 Total Flex**, the first commercial flexible fuel vehicle capable of running on any blend of gasoline and ethanol. Some months after others car companies launched their flex-fuel cars in the Brazilian Market. By 2010, there were 12 carmakers in Brazil (Chevrolet, Citroën, Fiat, Ford, Honda, Kia Motors, Mitsubishi, Nissan, Peugeot, Renault, Toyota and Volkswagen) that produced 70 flex fuel models. Flexible-fuel vehicles accounted for 22% of the car sales in 2004, 73% in 2005 and 87.6% in July 2008, with a record 94% set in August 2009. In the year 2010, there were more than 2.6 million cars and light commercial of the flex type produced in Brazil, representing more than 86% of the total manufactured that year (ANFAVEA, 2010). The fleet of **flexible-fuel vehicles in Brazil** is the largest in the world, and since their inception in 2003, a total of almost 12 million cars and light trucks have been produced as of December 2010. The first flex-fuel motorcycle was launched in March 2009, and by December 2010, a total of 515,726 units of the two flexible-fuel motorcycles available in the market had been sold, representing an 18.1% market share of the new motorcycle sales in Brazil in 2010. In addition to the establishment of flexible-fuel cars that use ethanol, the Brazilian government also made it mandatory for gasoline to be blend with ethanol, fluctuating from 1976 until 2010 between 10% and 20-25%, depending on the results of the sugarcane harvest and the levels of ethanol production from sugarcane, resulting in blend variations even within the same year. Brazilian flexible-fuel vehicles are optimized to run on any mix of E20-E25 gasoline and up to 100% hydrous ethanol fuel (E100) (History of ethanol fuel in Brazil, 2011; PróAlcool, 2011; Goldemberg, 2008).

A review article was published in 2008 (Goldemberg, 2008) by a leading authority on energy in Brazil. In this article he describes the rationale for the ethanol program in Brazil, its present 'status' and its perspectives. The environmental benefits of the program, particularly the contribution of ethanol to reducing the emission of greenhouse gases, are discussed, as well as the limitations to its expansion. According to the data presented in 2008, ethanol was used as biofuel to replace about 3% of the gasoline produced from fossil fuels consumed in the world at that time.

Besides the production of ethanol fuel the sugarcane industry co-generates electricity from the burning of bagasse, a byproduct of the production of sugar and alcohol. Today, many alcohol/sugar mills produce electrical energy only for their own use. Most modern plants produce excess energy that is sold to the electricity distributors. Currently, the total contribution from energy co-generation in sugar and alcohol factories to the electricity production is about 5%, and it is estimated that in some years the sector will provide about 15% of the total electricity produced in the country. The conversion of bagasse in energy is given approximately by the relation: 1ton (moist bagasse, 48-52% humidity) → 2.2 ton steam (65 kg/cm²) → ~363 kW. At the moment, for the technology available in Brazil, the ideal condition for the sugarcane sector is to use boiler working pressure of 65 kg/cm² and temperature of steam of 500°C.

2.1 Biomass and residues: Bagasse

The utilization of organic and agricultural residues for energy is considered to be an important element in any strategy to achieve renewable energy goals and to reduce waste

disposal and environmental pollution. This is a global concern that is reflected in the great number of published papers and international conferences, whose main theme is energy production from biomass. There is a wide range of biomass materials that are byproducts, residues (or wastes) from some other process, operation or industry. Many of these have a valuable energy content that can be usefully exploited. Biomass is a natural renewable carbon resource that is large enough to be used as a substitute for fossil fuels.

In many countries, particularly those with the poorest population, it is still common practice to burn organic waste (biomass), such as municipal solid waste, used tires, wood scraps, cardboard, plastics, etc., in garbage dumps or in inappropriate places. This practice produces bad odors and pollutes the air, soil and, in some cases, surface waters. Furthermore, it is meaningless practice considering the waste of energy, environmental pollution and health problems that can result. With increasing world population, demand for more energy and the increase in waste production makes burning even more inappropriate. Nowadays, in many countries, especially developed countries, measures are being adopted that are more interesting from the standpoint of environmental and economic development. In these countries, some solid wastes are collected separately (selective collection) and then go through a sorting process (metals, glass, papers, wood, plastics; composting of organic matter). Ultimately, the remainder is buried or incinerated. Direct incineration of unsorted waste is currently the main route practiced by the waste industry to produce energy (Ryu et al. 2007). The flow diagram (Fig. 3) shows the main processes to convert sugar cane bagasse into energy.

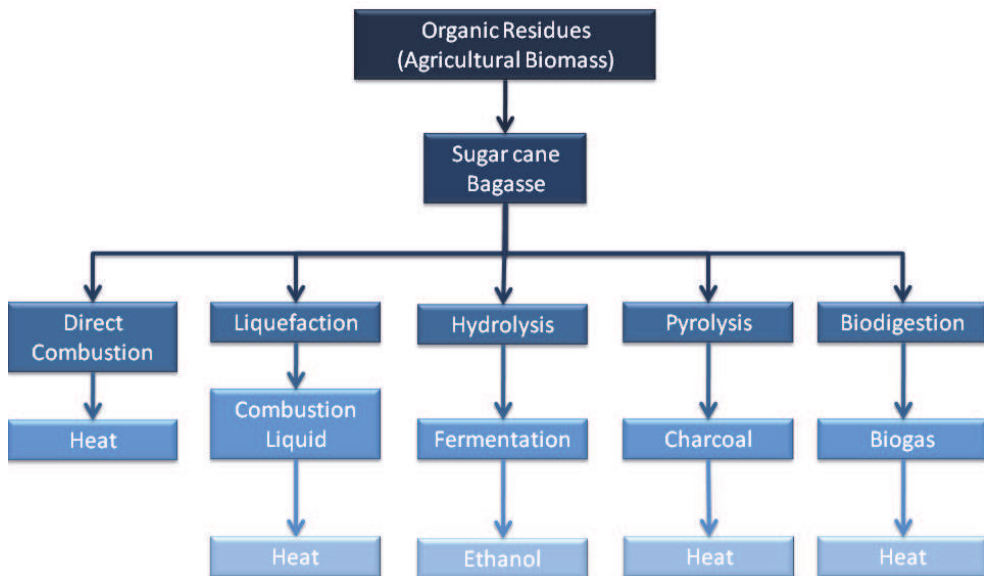


Fig. 3. Schematic diagram of the processes of energy conversion of biomass

Due to its extensive cultivable area, Brazil is one of the largest producers of agricultural products and therefore produces a large volume of biomass residues (around 330 million

metric tons/year). Currently, sugarcane bagasse is the most abundant biomass residue generated in Brazil (Felfli et al. 2011).

In the sugar/alcohol industry, sugarcane is crushed to extract the juice used to produce sugar or fermented to produce alcohol. The fibrous matter that remains after the juice extraction is bagasse. The chemical composition of this lignocellulosic waste found in the literature varies widely due to differences in the types of plants, soil where it is grown and analysis conditions (on a washed and dried basis). Considering the ranges found in the literature (Goldemberg et al., 2008; Aguiar, 2010; History of ethanol fuel in Brazil, 2011) its basic composition (in weight %) is: cellulose (41 - 55%), hemicellulose (20 - 27.5%), lignin (18 - 26.3%) and others (~7%).

Sugarcane bagasse can be used either for energy production or for non-energy applications, and currently, there is much research on the uses of sugarcane bagasse (Pandey et al. 2000; Silva et al., 2010). Advances in industrial biotechnology offer potential opportunities for economic utilization of agro-industrial residues (or lignocellulosic residues) such as sugarcane bagasse. For example, it can be used as paper-making material and for cellulose derivatives (methylcellulose, cellulose acetate and microcrystalline cellulose) (Andrade 2001, Covey 2006, Yousef 2005, Pasquini et al., 2005; Vieira et al., 2007; Ilindra and Dhake 2008, Aguiar, 2010; Sun et al., 2004); it can also be utilized as a source of raw material in the chemical industry to produce xylose, xylitol and furfural and their derivatives (Cunha 2005; Lavarack 2002; Aguiar, 2010, Zhang et al., 2007). As it is rich in fermentable sugars (but not directly available), it has aroused the interest of researchers for the production of ethanol with chemical pre-treatments such as enzymatic or hydrolysis (Aguiar, 2010, Dawson and Boopathy, 2008; Botha and Von Blottnitz, 2006). In addition, bagasse can be used in various other ways: as a constituent of animal feed (Hossain et al., 2009; Fontana et al., 1995; Teixeira et al., 2007; Leme et al., 2003), to produce useful materials for the construction industry and furniture manufacturing, such as plywood, particleboard and other engineered wood products (Widyorini et al., 2005; Lu et al., 2006; Maldas and Kokta, 1991; Stael et al., 2001; Tabarsa et al., 2010); and as an adsorbent for environmental remediation to remove oil by-products from contaminated water (Silva 2007).

Nowadays, there are many companies around the world producing paper products (e.g., tableware) made of sugarcane bagasse. These products have many advantages over plastic goods: they are 100% biodegradable, nontoxic, harmless, recyclable, microwaveable and resistant to different temperatures (hot or cold). It can substitute for virgin paper and cellulose in many applications, saving the countless trees used to produce these products.

2.2 Ashes from sugarcane bagasse

For energy production, sugarcane bagasse can be burned as the raw product or in the form of briquettes. Despite the advantages of biomass briquetting (Granada et al. 2002; Yamaji et al. 2010; Felfli et al. 2011) and the huge production of biomass waste in Brazil (Felfli et al. 2011), the briquetting of biomass is insignificant when considering the volume of waste produced annually. Although briquetting results in more energy per unit volume and improves the transport and storage conditions for the sugarcane mills, it is nowadays cheaper to burn the sugarcane bagasse in the raw form at the place where it is produced. Currently, most of the sugarcane bagasse is burned in boilers to produce steam which is utilized in the factory's processes and also to power turbines for the production of electrical energy. The combustion of bagasse yields ashes (bottom and fly ashes) containing high amounts of charcoal (unburned carbon) and silica as the major inorganic component.

Aluminum, calcium, iron and magnesium oxides are the main minor components. The chemical properties of fly ash are associated with the type of material used in the thermal conversion, characteristics of the furnace, temperature of the process and ash extraction system (Rodríguez-Pedrosa et al. 2010; Ahmaruzzaman M. 2010). The loss on ignition (LOI) test and thermal gravimetric measurements show that the organic matter (carbon and biomass unburned) content in the ash from different types of biomass can range from 0 to 80 wt% (Frías et al. 2011; Batra et al. 2011; Rodríguez-Pedrosa et al. 2010; Ahmaruzzaman 2010). In general, the combustion of biomass and organic residues produces more unburned carbon compared to burning coal. The quantity and quality of the ash produced during the combustion process depends on the material burnt and on the technology used. The sugarcane bagasse ash (SCBA) has a high content (about 35 wt%) of carbon and fine particles of bagasse (partial combustion of the biomass) depending on the characteristics of the furnace and the speed of the bagasse combustion process (Teixeira et al. 2010b; Batra et al. 2011; Zandersons et al. 1999). Because of its high concentration of unburned carbon, fly ash can be used in many important environmental applications, such as adsorbent for the removal of various pollutants (Ahmaruzzaman 2009, 2010; Batra et al. 2011; Purnono et al. 2010; Ahmedna et al. 2000; Tai et al. 2009; Wang et al. 2010).

Approximately 65% weight of SCBA is inorganic material. Fly ash contains more charcoal than the bottom ash, and nowadays, in the most modern factories the bottom ash is mixed with the fly ash inside the water channel that comes from the gas washer. The inorganic fraction can be used by the ceramic industry (Teixeira et al., 2008) as non-plastic material to produce bricks and roof tiles, to produce glass-ceramic materials (Teixeira et al., 2010b) or as pozzolan in cementitious materials (Frías et al. 2011; Dutta and Das 2010; Cordeiro et al. 2009).

For each ton of cane processed, between 250 and 300 kg of bagasse are generated, which has a moisture content of 40 to 50%. Considering that about 300 kg of bagasse is produced per ton of sugarcane milled, and considering the amount of sugarcane (630 Mton) harvested in the 2009/2010 season, it can be estimated that 3.2 Mton of ash and about 1 Mton of carbon and unburned biomass were produced in this harvest.

In previous studies (Teixeira et al. 2010a, 2010b), we have demonstrated the feasibility of recovering unburned carbon (soot from bagasse) and bagasse debris from fly ash to produce charcoal briquettes. Although we used in these works a by-product of burning sugarcane bagasse, this can be extended to by-products of combustion processes for any fossil fuel or biomass.

2.2.1 Ashes preparation

Fly ash is the solid material suspended and carried by the exhaust gases, which is collected by electrostatic precipitators, filters or gas washers. Fly ashes are generally highly heterogeneous, consisting of a mixture of inorganic materials, charcoal and, in general, not totally burned material (partially pyrolyzed material). The boiler gas cleaning systems follow two main routes: dry (cyclones and electrostatic separators) and wet (gas washer or scrubbers). The gas-cleaning systems adopted by the sugarcane industry is the wet route (gas washer) because they are simpler to design, less expensive, and provide great efficiency. The scrubber's water treatment consists of waste flocculation and a subsequent rapid sedimentation of flocculated solids. The sludge containing the solid material, extracted in the decanter, is transported to a concentration step in a rotating screen and filter type blanket (suction strainer) where the water with solid waste (ash flay) is then filtered (Fig. 4 and Fig.5). Another option to decrease the moisture content of ash is passing it through an

endless thread (Teixeira et al. 2010b). The water returns to the tanks and can be reused, and sludge is transported to deposits to be then spread over the ground. According to the process used and the working conditions (climate), the final ash moisture can vary from 40 to 60% by weight. The amounts of organic and inorganic materials also vary (about 35 and 65 wt%, respectively), as will be shown later in the thermogravimetric analysis.



Fig. 4. System for treatment of water from gas washer to remove the ash using decanters and porous blankets.



Fig. 5. Blanket type filter system (with suction strainer) to remove water and reduce moisture from the ashes

Since SCFA has a high content of charcoal and organic debris, it would be interesting to separate the two fractions (organic and inorganic) for use as raw material suitable for the production of goods useful to society. In briquette production, it is important to separate the combustion by-product with a minimum concentration of the inorganic fraction (useful for the cement and ceramic industries).

There are several methods (for example, cyclonic separation, flocculation and flotation processes) (Rubio et al. 2007, Martignoni et al. 2007) to separate the two fractions but none of them allows complete separation, i.e., there is always a certain amount of ash in the charcoal. Due to the difference in the grain size distribution and in density of organic and inorganic fly ash compounds many different processes can be used to separate them. In this work, we will discuss the separation process using sieves and a hydrocyclone.

2.2.2 Ashe characterization and charcoal separation

Fly ash samples were collected at the solid/water exit of the gas washer at the Alto Alegre mill, nearby Presidente Prudente city in São Paulo State, Brazil. As the charcoal is concentrated in the coarser fraction of the ash, it can be concentrated using sieves. Therefore, we used two different procedures to separate charcoal from ash: (1) ashes were passed through a 1 mm (18 mesh) sieve and (2) ashes were passed through a 0.125 mm (120 mesh) sieve; afterwards, the coarse fraction was passed through a hydrocyclone (Fig. 6). A hydrocyclone (Arterburn, R.A., 2010) is a device that classifies, separates or sorts particles, in a liquid suspension based on the ratio of their centripetal force to fluid resistance. It may be used to separate solid particles of different density (different materials for same grain size) or of different particle size (materials with same density). A hydrocyclone has two exits on its axis: the smaller one on the bottom (for underflow or reject purpose) and the larger one at the top (for overflow or accept purpose). The underflow is generally the denser or thicker fraction, while the overflow is the lighter or more fluid fraction. Internally, centrifugal force is countered by the resistance of the liquid, with the effect that larger or denser particles are transported to the wall for eventual exit at the reject side with a limited amount of liquid, whilst the finer, or less dense particles, remain in the liquid and exit at the overflow side through a tube extending slightly into the body of the cyclone at the center.

In the first procedure, the coarser charcoal fraction (grains > 1mm) that was separated using a 1 mm sieve, was analyzed to determine the calorific value (or heat of combustion) and the final concentration of ash, using a bomb calorimeter, according to Brazilian standards (ABNT-NBR 8633). The results show that this fraction has lower ash content (13.2 wt%) and high calorific value (6,140 kcal/kg). Compared with the literature (Quirino & Brito, 1991), it can be observed that the briquette of sugarcane bagasse generates more energy and lower amount of ash than charcoal briquettes from different sources. As the fraction smaller than 1 mm has a large amount of charcoal, a sieve less than 1 mm (0.125 mm) was used to separate the charcoal in the second procedure.

In the second procedure, the ash was first passed through a 115 mesh (125 mm) sieve. Before going through the hydrocyclone, the three samples, crude and sieved (115 mesh, 125 mm) fractions, were submitted to thermal gravimetric (or thermogravimetric) analysis (TGA) to determine changes in sample weight in relation to change in temperature. This technique determines the amount of ash and charcoal in the samples. The TGA results (Fig. 7) show that the inorganic residue of the ash fired at 800°C is 64.06 wt% for the crude ash, 48.53 wt% for the coarser ash (> 125 mm) and 83.21 wt% for the finer ash (< 125 mm). As observed in previous work (Teixeira et al. 2010b), sieving improves the concentration of

charcoal in the samples. The sample moisture measured by TG ranges from 5.7 to 7.2 wt-%. TG data for the finer fraction (< 125 μm) confirms that it holds only 14.86 wt% of charcoal (Teixeira et al. 2010a).

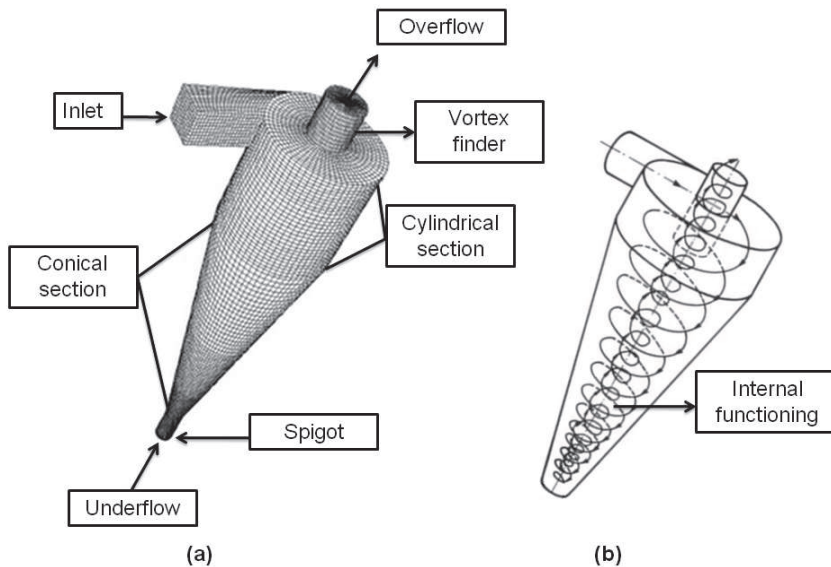


Fig. 6. (a) Illustration of a Hydrocyclone; (b) Internal functioning of the Hydrocyclone

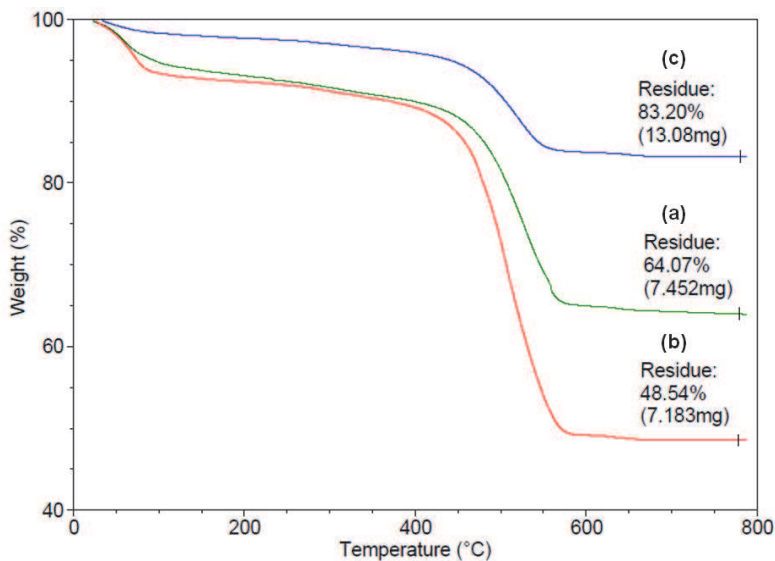


Fig. 7. TGA data of the SCBA: (a) in natura (64.15%), (b) >125 μm (48.60%) and (c) <125 μm (83.21%)

The quality of the sieved coarser charcoal (> 0.125 mm, 120 mesh) was improved, diminishing its fraction of inorganic material using a hydrocyclone (Fig. 8) to separate the fine parts (principally inorganics) and to concentrate the organic particles in the coarser fraction. Although the particles have the same size distribution, there are differences in density between the organic and inorganic particles, and the denser particles will exit preferentially at the bottom (underflow). As the minerals have densities greater than $2\text{g}/\text{cm}^3$ while the charcoal density is less than $1\text{g}/\text{cm}^3$, this device is suitable for the selective concentration of charcoal.

The hydrocyclone used has a 250 mm diameter, exit dimension of 40 mm, one $\frac{3}{4}$ HP (1 HP = 746 W) centrifugal pump (maximum $14\text{ m}^3/\text{h}$) and two 150-liter barrels connected by 40 mm plastic tubes and valves for controlling the feed pressure and liquid inflow; the valves control the amount of time that the overflow (the lighter or finer fraction) passes through the hydrocyclone in a loop circuit. Samples were collected at different times (1, 2, 4, 5 and 20 min) for analysis. This hydrocyclone was used to separate charcoal from SCBA to produce charcoal briquettes.



Fig. 8. Hydrocyclone system (with hydraulic pump) used to separate the charcoal from the SCBA. The charcoal with water goes out of the hydrocyclone through the vortex finder (overflow) and the inorganic components go to the tank (reservoir) through the spigot (underflow)

The X-ray fluorescence (XRF) data show that the ash contains SiO_2 as the major inorganic component (usually over 70% by weight). Among the minor components, Al_2O_3 , Fe_2O_3 , K_2O , CaO and TiO_2 were the most prominent. The chemical composition of SCBA may be different depending on the type of sugar cane and composition of the soil where it is cultivated. The X-ray diffraction (XRD) data for SCBA shows patterns that suggest that the major crystalline phase is quartz (Teixeira et al. 2008), corresponding to the SiO_2 fraction demonstrated in the chemical analysis (Fig. 9).

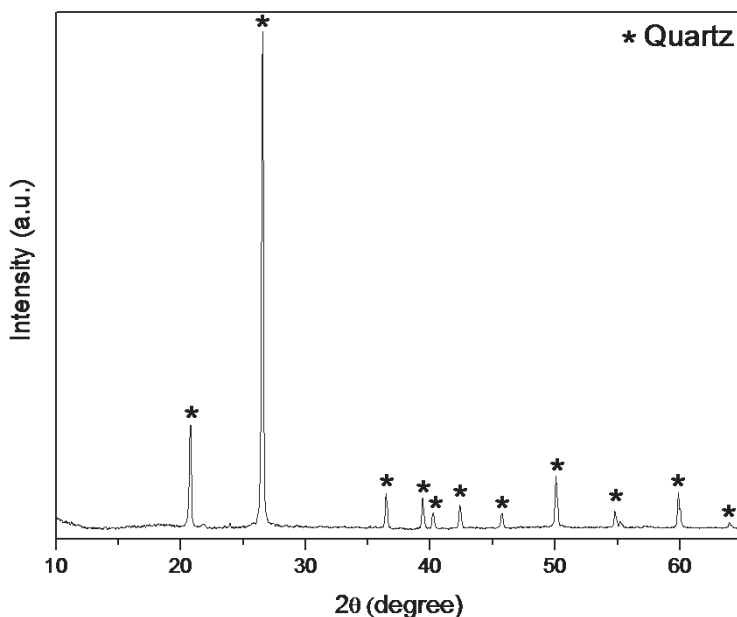


Fig. 9. X-ray diffraction (XRD) pattern of the inorganic fraction of the SCBA showing that it is composed mainly of quartz

2.2.3 Briquetting

Charcoal is a friable material, and therefore, to press it in the form of briquettes, it is necessary to use a binding material to strengthen the briquettes. In this work, cassava (or manioc) starch was used, taking into account that it is widely produced in tropical countries (Charcoal Briquette, 2002; Smith, 2004; Fontes et al., 1991). The binder was prepared in the usual manner, i.e., the starch was added to boiling water until polymer molecules (gum or porridge) were formed (FAO, 1987; Smith, 2004). The briquettes were prepared in two different ways. In the first method, the coal powder was mixed with a gum (8 wt%) to form a homogeneous paste, which was pressed. In the second method, the briquettes were prepared by mixing the moist charcoal powder with starch (8% by weight), and heating at 100°C to form the binder and then pressing it. The cylindrical briquettes (30 mm diameter) (Fig. 10) were pressed using a manual uniaxial hydraulic press and a steel cylindrical mold. An applied compression force of 5 tons was maintained for 1 min for each sample. After some thermal tests, we concluded that it was better to use the second method for preparing the briquettes (Teixeira et al. 2010).

After drying, the briquettes were submitted to various analytical methods and characterization tests to determine their mechanical strength, density, calorific value, moisture and residual ash.

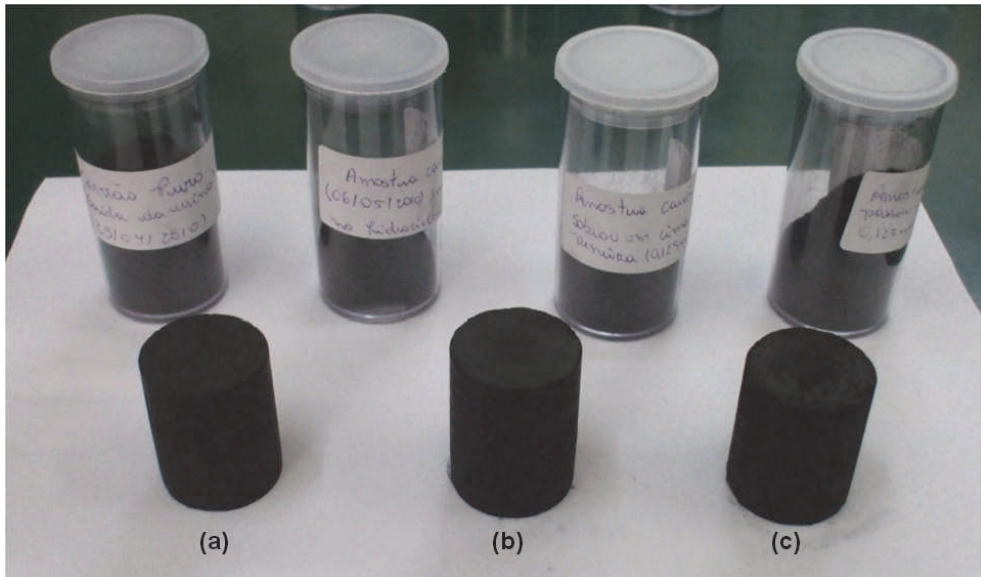


Fig. 10. Charcoal briquettes ($\phi = 30$ mm) with different preparation: (a) only moist charcoal, (b) charcoal powder mixed with gum (8 wt%) and (c) moist charcoal mixed with starch (8 wt%) and heated at 100°C to form the binder

Briquettes prepared with coarse (> 1 mm) charcoal were analyzed and the most important results have been previously published (Teixeira et al. 2010). The mechanical strength value obtained was 7 Mpa, for axial compression of the cylindrical briquette. This value is close to those obtained for briquettes produced using different kinds of wood. The briquette density (measured using caliper and balance) varies between 0.91 to 1.33 g/cm^3 . These values are close to those found for wood briquettes manufactured using another type of binder (1.08 g/cm^3) (Fontes et al. 1991). However, this density range is lower than that obtained for briquettes made with eucalyptus charcoal and tar as the binder (1.41 g/cm^3) (Brito & Nucci, 1984). As mentioned before, these briquettes showed a calorific value of $25,700$ kJ/kg and a residual quantity of ash of approximately 13 wt%.

The moist charcoal obtained in the second procedure, where the coarse fraction (> 0.125 mm) was passed through the hydrocyclone (for 1, 2, 4, 5 and 20 min), was filtered to remove the excess water and used to prepare the briquettes. The charcoal powder was mixed with starch (8% by weight) and then heated at 100°C (to form the binder). Similarly, the briquettes were pressed uniaxially in a cylindrical shape (30 mm diameter). After air-drying (two days in an open place), density of the briquettes was determined using a caliper and analytical balance. Samples of the briquettes were collected and analyzed using a thermal gravimetric instrument. Table 2 shows the briquette density and percent residue (ash) after TG measurements (up to 800°C) (Teixeira et al. 2010).

Time (min)	01	02	04	05	20
Residue (%)	18.56	18.77	19.99	19.89	16.92
Density (g/cm ³)	0.95	0.90	0.75	0.90	0.87

Table 2. Residue and density of the briquettes after (TG) thermal analysis (up to 800°C)

These results indicate that there were no significant changes in briquette density (~0.90 g/cm³) or in the resultant ash (19%) after firing it at 800°C. Therefore, one minute is sufficient time to separate the charcoal from the ash using the hydrocyclone. This period corresponds to the use of three hydrocyclones, similar to the one used, in series.

The briquette calorific value (heat of combustion) measured using a calorimeter bomb was 28,326 ± 920 kJ/kg (6,767 ± 220 kcal/kg), which is approximately the same as for charcoal from wood. The axial compression test shows that briquette resistance was higher than 3,300 N (ϕ = 3cm, 48 kgf/cm²), which is a sufficient value for handling, piling and transporting bags of charcoal.

Figures 11 and 12 show the results of the thermal gravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis of the charcoal (1 min) and of briquettes prepared by mixing moist charcoal and starch (8 wt-%) and heating at 100°C.

Natural fibers are a complex mix of organic materials (Alvarez et al. 2004). Sugarcane bagasse (SCB) is a natural fiber (lignocellulose) that is not totally pyrolyzed in the boiler of the sugar/alcohol industry. As a result, there is residual natural fiber inside the coarse charcoal particles. Therefore, the thermal decomposition of the charcoal will show the reaction steps of both materials (fiber and charcoal) degrading. Furthermore, cassava starch is added as a binder to the charcoal to raise the mechanical resistance of the briquettes. Lignocellulosic materials are composed of cellulose, hemicellulose and lignin. Therefore, the thermal decomposition of the charcoal shows an overlapping of decomposition peaks of charcoal, fiber and starch. The TGA/DSC curves in nitrogen atmosphere show two decomposition steps at temperatures higher than 200°C. At a temperature of 350 to 400°C the molecular structure of lignocellulosic biomass is degraded (Zandersons et al. 1999). In air (or oxidant atmosphere), besides the material's thermal decomposition, its thermoxidative degradation will also occur. The peaks' positions depend on the heating rate, so the peak near 300°C is attributed to the first peaks representing the thermal decomposition of starch, hemicellulose and cellulose (Alvarez et al. 2004; Suárez et al. 2010; Guiotoku et al. 2010). The lignin peak is wider and appears between 200°C and 500°C superposing on the other peaks (Alvarez et al. 2004). Its maximum degradation rate occurs above 448°C (Guiotoku et al. 2010) and depends on the kind of lignin. During the thermal degradation of wood components, stable substances are formed around 450 to 530°C and after the completion of the reaction. With regard to charcoal, its combustion in an air atmosphere occurs in this same temperature range. The type of material (or wood) used to produce the charcoal and the pyrolysis conditions influence its temperature of combustion (Suárez et al. 2010). Suárez A.C. et al. (2010) observed that DSC curves show two exothermic peaks, at ~337°C and 477°C, which overlap with those peaks observed for lignocellulosic materials. These overlapping peaks result in a broad peak (between 400 and 600°C), observed in both samples (Fig. 11 and 12), which is characteristic of the charcoal from SCBA (Fig. 11). Accordingly, the thermal analysis results show that all materials in the briquette composition (charcoal, lignocellulosic material and starch) are degraded in the

same temperature ranges. It was observed (Teixeira et al. 2010a) that starch degradation shows three major peaks between 300 and 500°C, and that the transformation of the starch into binder changes only the second degradation peak to a higher temperature (from 470°C to 500°C, approximately). The starch thermal decomposition peak remains at the same temperature at 318°C.

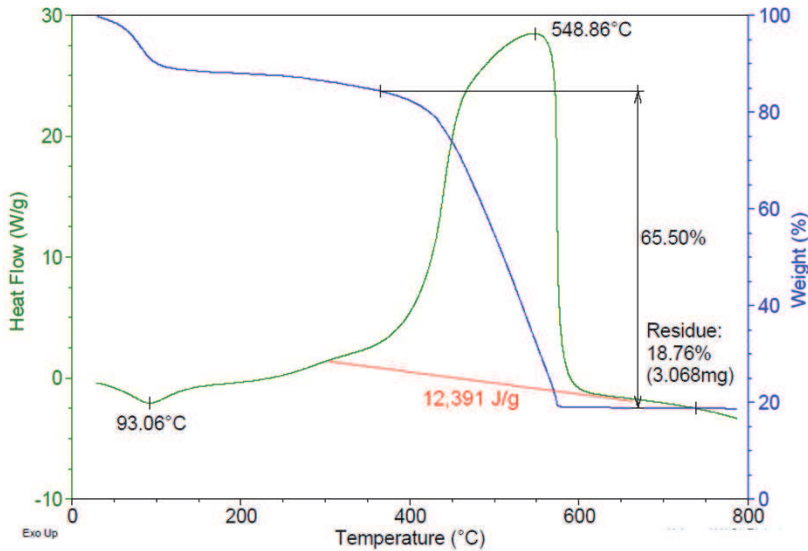


Fig. 11. TGA and DSC data of the charcoal (1 min)

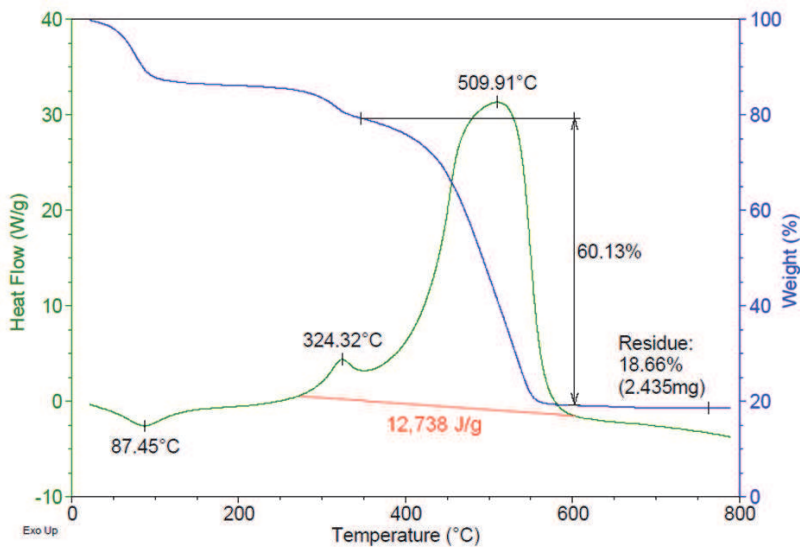


Fig. 12. TGA and DSC data of the charcoal mixed with starch and heated (at 100°C)

3. Conclusion

Brazil is an outstanding position in the production and consumption of charcoal on the international scene, and about 55% of the raw material for the production of charcoal originates from native forests, mainly in areas of the Cerrado. The other 45% comes from homogeneous planted forests of rapidly growing tree species (pine or eucalyptus). The area of planted forests grew on average 20% per annum between 2003 and 2008, with a big drop in 2009 due to an international crisis. Due to its large territory and intense sunlight, the use of plants (carbonized wood) as a source for reducing iron ore (and a source of energy to produce heat) is a valid alternative in countries such as Brazil. The technology used in charcoal production is primitive, mostly we use the same process as a century ago. It is a predominantly artisanal process with low efficiency in which only part of the wood (30-40%) is transformed into charcoal by pyrolysis or a carbonization process. The remainder is released into the atmosphere as gases. The main consumer sectors of charcoal are pig iron, steel and iron-alloy and to a lesser extent, trade and households. Charcoal has many advantages compared to coal. It is renewable, less polluting and virtually free of sulfur/phosphorus, and the technology for its manufacture has been largely consolidated in Brazil. For the forestry economy, the more relevant range of companies with regard to charcoal use includes independent producers of pig iron, which are suppliers of raw material for the steel industry. In 2010, Brazil produced 11.6 million cubic meters of charcoal from planted forests, of which 66.2% were consumed by independent pig iron makers. The trend is for the consumption of native wood to steadily decrease over the years, being replaced with wood from planted forests, and due to the greater control exercised by the inspection agencies and to the increased social pressures on natural resource preservation. (ABRAF 2011)

The use of charcoal in Brazil as a thermal reduction agent in steel production started in Minas Gerais (MG). The lack of coal reserves and abundant availability of native vegetation favored conditions for the use of charcoal. Currently, the consumption of charcoal in Brazil in steelmaking is concentrated in the state of Minas Gerais (MG), the largest consumer. The second steel center is in Carajás, located in the states of Maranhão (MA) and Pará (PA), where the use of charcoal obtained from native vegetation dominates, and in third place at present is the state of Mato Grosso do Sul (MS; Corumbá, Aquidauana and Ribas do Rio Pardo), the youngest pig iron center in the country, surpassing the state of Espírito Santo (ES) (EPAMIG 2010).

In 2009 (BEN 2010), 25,178 x 10³ tons of wood were used for charcoal production. In this year, firewood and charcoal accounted for approximately 10% of domestic energy supply while sugarcane products made a contribution of 18% (Table 1).

According to the AMS Statistical Yearbook (2008), in 2007 the state of São Paulo (SP) accounted for approximately 3% of domestic consumption of charcoal (1140 x 10³mdc²). Considering that 1mdc is equivalent to an average of 200 kg of charcoal, SP statewide consumption was on the order of 228 x 10³ tons of charcoal in 2007. Part of this charcoal is imported from other states, mainly Mato Grosso do Sul (MS).

According to CONAB (2009), the state of São Paulo accounts for approximately 58% of the sugarcane (364 Mton) production in Brazil. Considering that 6 kg of ash are produced per

²mdc: cubic meter of charcoal

tonne of milled sugarcane and that ash is approximately 33% by mass charcoal and sugarcane debris, then approximately 720,000 tons of charcoal mixed with SCBA were produced in SP State. As shown in the TGA results (Figs. 11 and 12), charcoal has about 19% by mass of ash (residue after firing at 800°C). Therefore the amount of material (charcoal and bagasse debris) that is present in the ash and that may be briquetted is approximately 580,000 tonnes. This value is approximately twice the amount charcoal produced in SP State.

One difficulty in using this charcoal is the fact that it is produced in industries of different sizes throughout the state. However, if one considers the current value of cubic meters of charcoal, the freight value which is becoming increasingly expensive due to the distance between the sites of production and use, and mainly the environmental benefits, the commercial use of this material should be further assessed in the short term.

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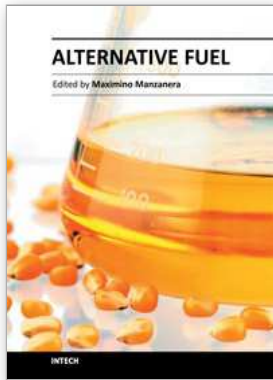
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