THE INFLUENCE OF CARBONIZATION TEMPERATURE AND CARBONIZATION HEATING RATE IN THE CHARCOAL PRODUCTION

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Abstract. *The biomass heated over 200°C, in absence of air has a thermal decomposition (carbonization), generating gases, vapor and a solid residue (charcoal). Many factors influence the charcoal production: chemical-physical properties, size and form of the wood, water content, heating rate, external pressure, etc. Normally the carbonization is performed in the range 400-500°C, and the process temperature has high influence on the quality and quantity of charcoal produced. The present paper shows the analysis of the influence of carbonization heating rate on the properties of eucalyptus charcoal. The tests has been carried out in a macrotermobalance, under autogenerated atmosphere, with heating rates of 1, 2,5, 5, 10, 20 and 50°C/min and carbonization final temperature of 500°C.*

Keywords*: charcoal, biomass, eucalyptus , chemical kinetics, carbonization temperature*

1. Introduction

The reduction of the fossil fuel reserves and the concern with the environment have improved the use of renewed energy sources. Brazil is the world's greater charcoal producer and consumer (8.,66 Mton, 2003), and this charcoal is used mainly in the pig-iron and steel industries (82%, 7.1 Mton). Despite the charcoal being used since the beginning of the human civilization, the chemical kinetic and the heat and mass transfer mechanisms in the interior of the biomass during the carbonization are yet not very known. In order to improve the carbonization process efficiency, it is very important to know the carbonization process parameters and the way as they influence of the carbonization kilns performance and the produced charcoal quality.

2. Carbonization Gravimetric Efficiency

In Brazil, the firewood and charcoal are usually commercialized by volume, and the carbonization process "efficiency" in industrial kilns is evaluated through the Conversion Index **IC:**

$$IC = \frac{V_{wood}}{V_{charcoal}}$$

where $\mathbf{V_{wood}}$ is the volume of wood input (*estere*) and $\mathbf{V_{charcoal}}$ is the volume of charcoal output (mdc, m^3).

Table 1. Usual Factors for Conversion of *Estere* to Mass and to Volume of Eucalyptus and Pinus (st, kg, m^3)

Wood	Estere	Product	Mass		Volume			
	st		kg	%	st	%	m^3	%
Eucalyptus	1	Wood	577.6	95	0.87	87	0.61	87
		Bark	30,4	5	0.13	13	0.09	13
		Total	608	100	1	100	0.7	100
Pinus	1	Wood	545.2	94	0.82	82	0.57	82
		Bark	34,8	6	0.18	18	0.13	18
		Total	580	100	1	100	0.7	100

Source: BRACELPA

The *estere* is a brazilian measure unit of overall volume of a wood stack (height x depth x width), including the empty space between the wood logs (1 st = 1 m³ wood piled up). The measurement is made in the field with a measure

tape. When measuring the total volume, and not only the solid volume, the *estere* considers, beyond the wood, the empty spaces between wood logs. Thus, the wood mass in the *estere* is function of the piling up method, wood density, diameter, length and form etc. Over time all these factors can changes so much, and the precision of the wood mass contained in the *estere* is very approached, and depends on the number of the variable factors that can be controlled. For this reason, by the "Portaria Tecnica INMETRO nº97 (DOU 09/08/1999)", the use of the *estere* in wood logs commercialization operations will be not more allowed after January/01/2010.

The bulk mass of charcoal contained in 1 m^3 (mdc) can be estimated from the charcoal bulk density, but it also makes possible great errors due the approached volume measurement and the charcoal density variability. The errors in estimate the wood mass used and the charcoal produced, and the great chemical-physical properties changes during the carbonization process, make the carbonization efficiency evaluation by the Conversion Index IC and don't permit an accurate analysis about, the influence of different parameters involved in the carbonization process. The biomass carbonization process efficiency is better represented by the gravimetric efficiency $\eta_{charcoal}$, defined by:

$$\eta_{charcoal} = \frac{M_{charcoal}}{M_{biomass}} x\ 100$$

where $\mathbf{M_{charcoal}}$ is the output dry mass of charcoal (kg) and $\mathbf{M_{biomass}}$ the input dry mass of biomass (oven dried) (kg).

The use of input biomass dry mass, it is eliminated the influence of some variables factors such as density, size and form of the wood logs. Otherwise, by using the wood mass (oven dry), we cam define the real available biomass mass quantity for the charcoal production and eliminate the existing water mass in the green wood. The carbonization evaluation by the gravimetric efficiency, in spite of being the most recommendable way is not perfect yet, because it does not show the carbonization transformation progress. The charcoal hasn't a definded chemical composition. Some charcoals are near pure carbon, while others have only a partial carbonization process, and contain yet a large amount of oxygen and hydrogen.

3. Thermal Analysis

Thermal Analysis is a technique, where a physical parameter of a sample is analyzed while the sample is submitted to a controlled temperature heating. The temperature programme is most often a linear increase, but isothermal studies can also be carried out, when the changes in sample mass with time are followed. The Thermal Analysis is a simple tool, that allows to analyze and to understand problems that involve chemical-physical reactions and its mechanisms in function of the temperature.

The Thermogravimetry (TG) is based on the continuous measurement of the weight of a sample during the heating process. Normally a substance loses mass with the heating, due the humidity and volatile loss, due the pyrolysis and combustion reactions. By the thermogravimetry, it is possible to follow the heating process, determining the ignition point, water, volatile, fixed carbon and ashes contents, and informations about the thermal stability.

The thermogravimetry can be carried out in oxidant atmosphere (air or oxygen), up to the combustion. In this case, only remaining ashes are obtained at the end of the process. It also can be carried out in inert atmosphere (ex. N_2 or CO_2). In this case, have humidity and volatile release, and chemical and physical reactions. An example is the wood carbonization process studied in the present work.

By the Derived Thermogravimetry (DTG) the first derivative of the mass is measured in function of the time (**dm/dt**), or the temperature (**dm/dT**). By this method it is possible to determine the mass variation rate, and the beginning and the ending temperature (or time) in each stage of the process

The carbonization reaction speed is represented by the mass loss reaction rate (g/g.s):

$$\rho_m(t) = -\frac{1}{m_c(t)} \frac{dm_c(t)}{dt}$$

where **mc(t)** and **dmc(t)/dt** are, respectively, the mass and the derivative in the fixated time.

Preliminary studies (PINHEIRO, RESENDE and YOSHIDA, 1995) have determined the combustion and carbonization kinetic parameters of six eucalyptus species by thermogravimetry (TG) and derived thermogravimetry (DTG) analyses. The carbonization tests had been carried out in a Mettler TA4000 thermobalance in the range of 25 to 500°C, with a 10°C/min heating rate, in a 130 mL/min flow of ultrapure nitrogen atmosphere and sample mass ranging 15,989 mg to 15,425 mg. The results are shown in the figure 1.

The TG curves of figure 1, shows that in all the samples, that the volatile matter release begins at 175°C approximately. The DTG wood carbonization curves shows, only one maximum derivative peak at 354°C for all samples. The DTG curves of the all Eucalyptus carbonization tests, are similars, with no significant differences between the tested samples.

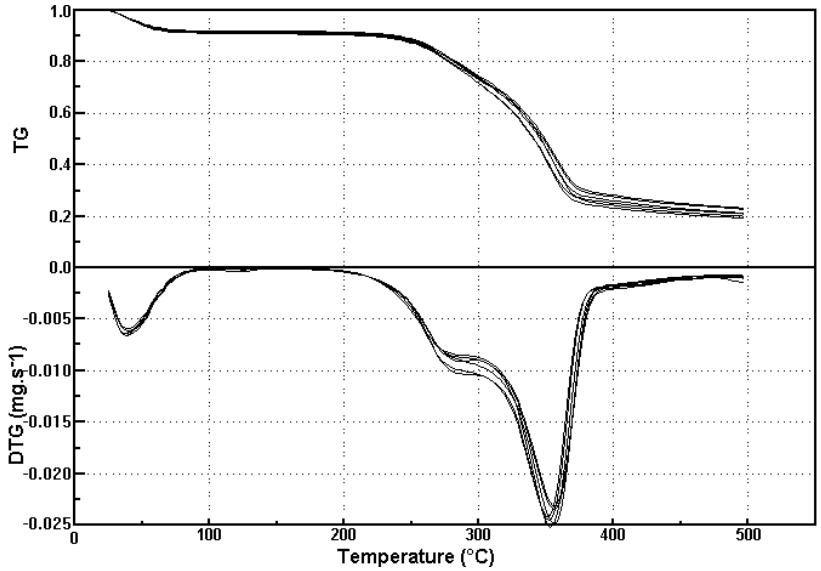

Figure 1. TG/DTG Eucalyptus Carbonization (10°C/min, N_2)

4. Temperature Influence

Initially, the temperature influence in the charcoal properties was analyzed in a carbonization test facility. A cylindrical carbonization pilot reactor (60 mm internal diameter and 160 mm depth) was manufactured with inox 310 steel. The pilot reactor have two openings in the superior cover for gases exit and thermocouples input. The reactor was placed inside a electrical furnace (Quimis, model Q.318D24), and it was heated up to the test temperature. A temperature controled system controls the electrical furnace temperature (and so the test temperature), and a thermocouple introduced inside the reactor determines the actual test temperature.

For the tests had been used Camaldulensis, Cloeziana and Citriodora Eucalyptus samples, with ages between 6,5 and 7,5 years and diameter of 30mm, obtained in the Mafla's Forests. The choice of the samples for test was preliminary made by visual analysis, auditing the one with cracks and nodes. The wood samples had been cut with a hand saw with 75 mm length cylinder. The heating of the wood was prevented, in order to don't produce any modification on its chemical-physical properties. The samples has been initially dried in electrical furnace at 105ºC for 48 hours.

The samples has been put in the reactor, the reactor was placed inside the electrical furnace and the furnace was heated up to the temperature test. After reaching the test temperature, the temperature was maintained for 10 hours, in order to make the complete sample carbonization. Several tests has been carried in the range of 200 to 650ºC, with 50ºC steps. The carbonization tests were accomplished in a self-generated atmosphere, using self carbonization liberated gases, simulating the conditions that occur in the industrial carbonization processes. After the carbonization time, the reactor is cooled until the room temperature.

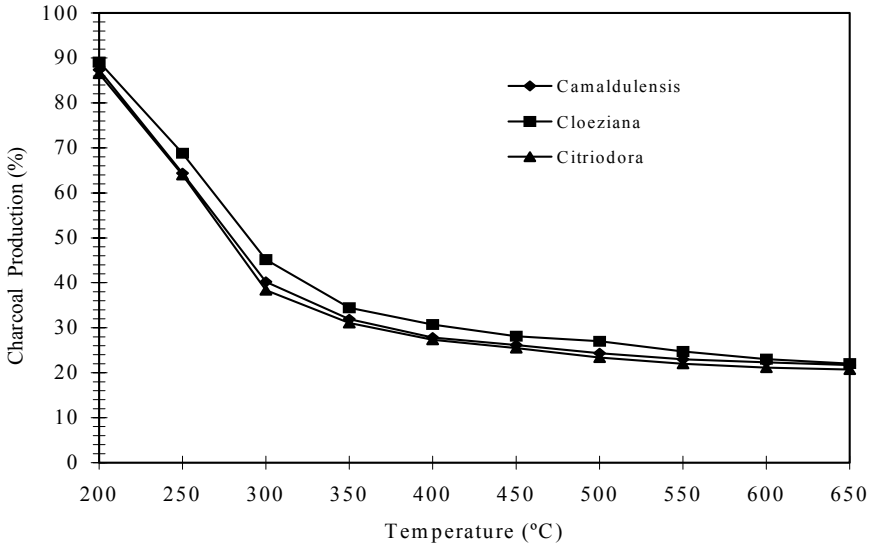

Figure 2. Charcoal Gravimetric Efficiency in Function of Final Carbonization Temperature.

The figure 2 shows the gravimetric efficiency in function of the final carbonization temperature. It can be show that the charcoal production decrease when the temperature increase. This production have a large variation in the range of 200 to 400ºC and is stabilized at 400ºC on around 30%. It also shows there's no great difference among the results obtained with all Eucalyptus species analysed.

The figures 3 and 4 shows the thermogravimetric analyses (TG and DTG) of the Eucalyptus Camaldulensis wood and its charcoals obtained in the carbonization reactor at several temperatures. The analyses had been carried through in a Mettler TA4000 thermobalance between 25 and 700°C, with a flow of 130 mL/min of artificial Air atmosphere with heating rate of 10°C/min. In the figure 3, the DTG curve show the existence of two peaks: the first one in the range of 200-380ºC corresponding to the decomposition reactions of cellulose and hemicellulose and other one at 380-550ºC corresponding to the lignin decomposition (Chauvette et al., 1985).

The thermal analysis curve of the original wood (Eucalyptus Camaldulensis) show a another peak at 290ºC, representing the hemicellulose decomposition. In the DTG of the charcoals produced at 200 and 250ºC this peak does not exist more, meaning that hemicelulose thermal degradation occurred during the carbonization process. The product obtained at this temperatures range can better be characterized as "brands" or torrified wood.

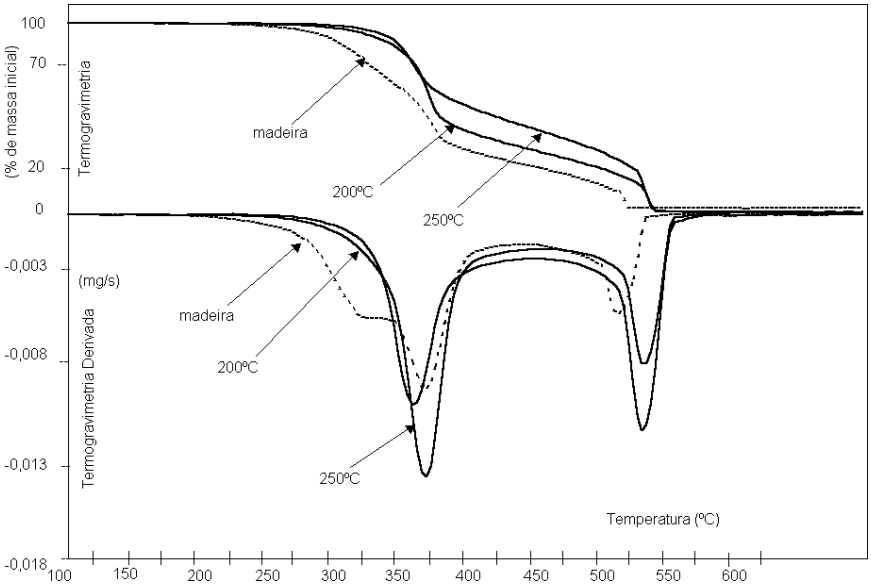

Figure 3. TG and DTG of Eucalyptus Camaldulensis Wood and Its Charcoal Produced at 200 e 250ºC

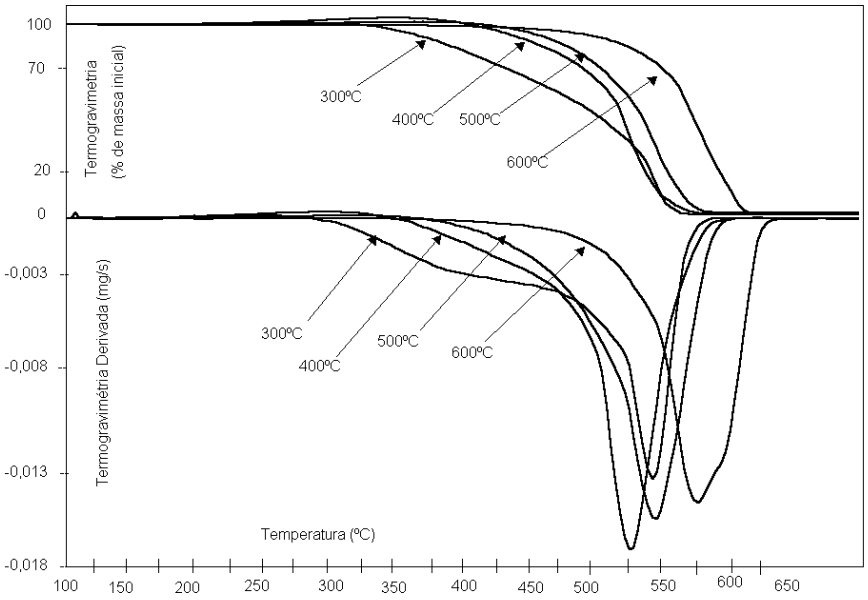

Figura 4. TG e DTG of Eucalyptus Camaldulensis Charcoal Produced at Range of 300 to 600ºC

In the charcoals obtained at final carbonization temperatures between 300 and 600ºC (figure 4) the DTG does not show the 290ºC peak. This means that in the carbonization processes, the hemicellulose and cellulose are firsts wood components that decomposes. The TG and DTG curves overlap means that does not exist other significant differences between the charcoals produced the different final temperatures of carbonization.

Goldstein [1977], showed that the thermal behavior of the wood, reflects the addition of the thermal behavoir of its three main components: Hemicellulose, Cellulose and Lignin. These, hemicellulose and cellulose (about 70% of wood composition), are the less stable components and they decompose between 225 and 375ºC. Therefore, it can be deduced that the loss of mass during the carbonization process is due the degradation of those two components. The lignin degrades slower because it is more stable, being the main component for the charcoal production. For temperature lower than 375ºC the production of condensed gases varies in function of the temperature due to thermal stability of the wood components that produce the condensed gases. Over 450ºC it can show that the production of condensed gases is very small because at this temperature the lignin reaches its maximum decomposition peak.

5. Construction of a MacroThermobalance

In order to analyze the phenomena that occur during the biomass carbonization and combustion, and that cannot be analyzed in a conventional thermobalance (heat conduction inside the sample, gases evaluation, identification of endothermic and exotermics reactions during the carbonization), a macrothermobalance was constructed.

Figure 5 shows a schematical scheme of the macrothermobalance constructed. A Ohaus, Model CT200 (202g x 0,01g), with precision ±0,01g electronic scale was used in the macrothermobalance construction. This scale have a sample sustentation device under the plate and a RS232serial port, in order to allow the data transmission of the weighting to a microcomputer PC. The microcomputer makes the data acquisition, the mathematical and graphical calculations. The data communication between the scale and the computer was carried by the software Telix (shareware) (http://www.delta.com/delta/deltacom/tfd/)

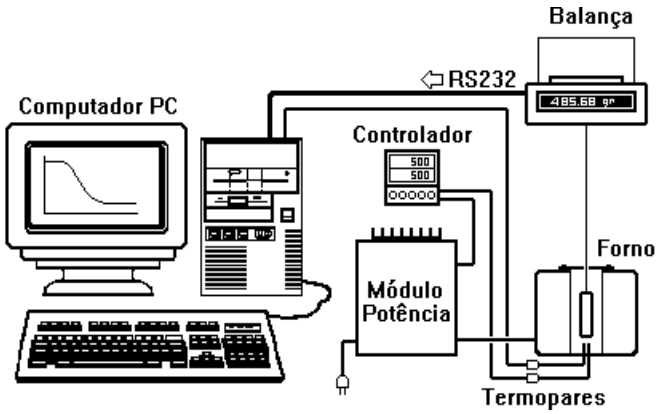

Figure 5. Macrothermobalance

The furnace used in the macrothermobalance was a 576W (120V) electric tubular oven. The oven has internal diameter of 50mm and length of 160mm. Inside of the oven was placed the carbonization reactor. The reactor was constructed with a inox AISI 304 steel pipe with 50mm diameter and 150mm length. The internal diameter of the reactor is 48mm. In the reactor was adapted a inox AISI 304 steel cover, with a inox pipe for output of combustion and carbonization products and with a small hole where it passes the inox wire (diameter 0,2 mm) that supports the sample to the device of the scale.

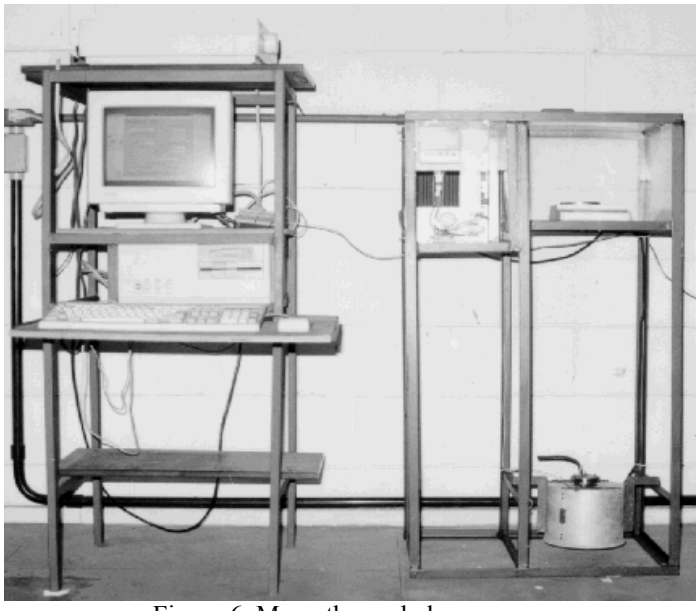

Figure 6. Macrothermobalance

To control the oven temperature it was used a PID temperature controller (Therma model Th2131-301). This PID controller allows to program the heating rate, in a linear slope, and settle a constant final temperature. The temperature had been measured with a type K thermocouple (chromel-alumel), diameter 1,5mm and length 50cm. The controller sends a control signal (4-20mA) to the power module ECI (3,2kW, 20A, 127V).

The data acquisition was carried out through a Daq-801 Quatech board (8 A/D inputs, 2 D/A outputs, 12bits, 40kHz and amplification 1000x). The choice of this acquisition board is due to its low cost (USS300,00 in Brazil). The data acquisition was carried by the software DaqEZ 1,0 (http://www.quatech.com/public/dez.htm).

The figure 7 shows the thermogravimetric tests at constant temperature (isothermal thermogravimetry) carried in the macrothermobalance. The sample was put inside the reactor at ambient temperature, and submitted to a high heating rate (75°C/min) until the test temperature was reached. It can be shown that higher is the final carbonization temperature, lower is the charcoal production.

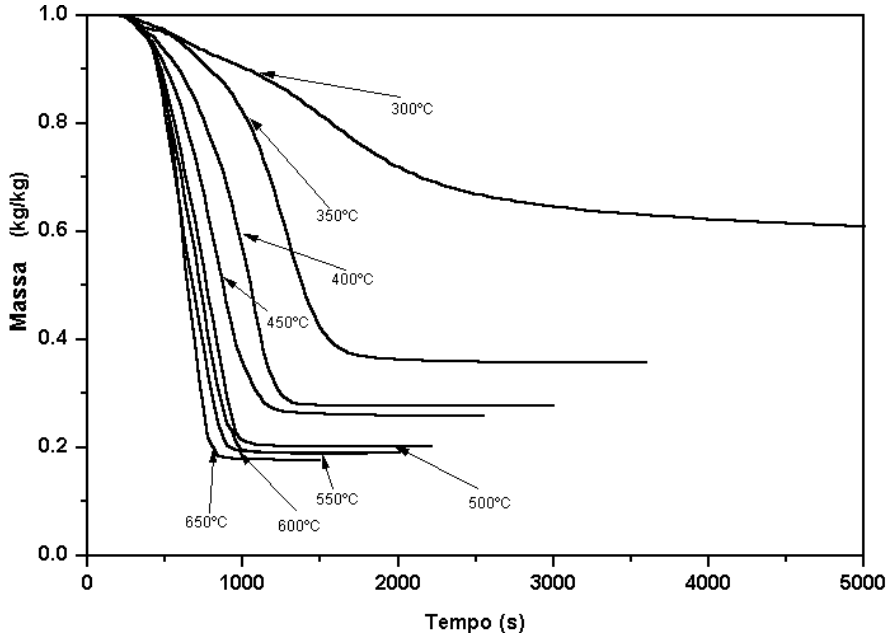

Figure 7. Influence of Carbonization Final Temperature

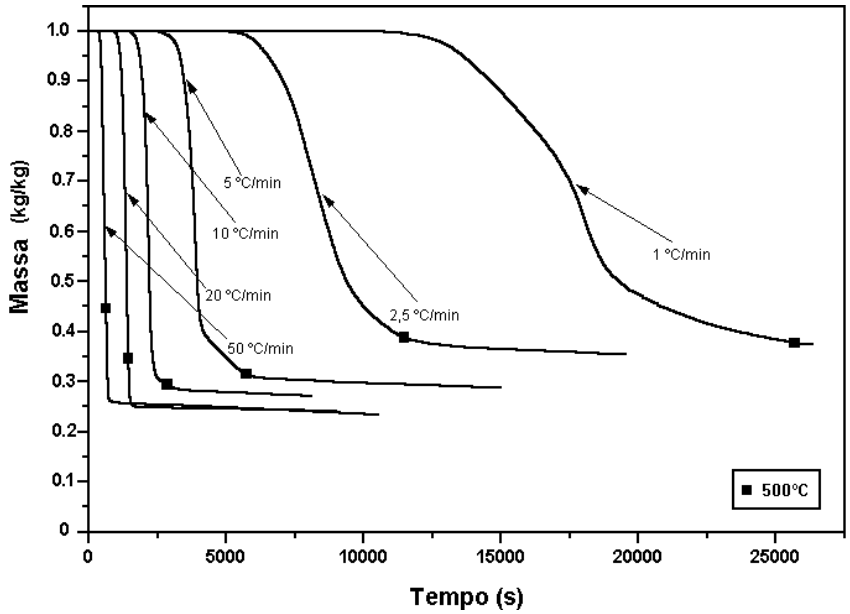

Figure 8. Influence of Carbonization Heating Rate

The figure 8 shows the influence of the heating rate in the carbonization process. In all the tests, the sample was heated up to 500°C, and maintained at this temperature until the end of all tests. Above 500°C the gain of fixed carbon

is very small compared to the huge amount of energy to reach this temperatures (Oliveira et alii, 1984). It can be showed that how higher is the heating rate, lower is the charcoal production. It can be showed also, at high heating rates, the sample continues to decompose, even after the reactor reached the programmed temperature (500°C). That is due the existence of a temperatures difference between the reactor and the sample interior. This temperature difference depends on the heating rate and of the heat and mass transfer mechanisms in the sample interior.

6. Conclusions

The tests carried out showed the influence of temperature and heating rate in the carbonization efficiency. It was verified that for all the analyzed species, lower is the temperature and lower is the heating rate, higher is the carbonization efficiency. These results are different of that obtained for Varhegyi et al [1988], carried in a traditional thermobalance, where the heating rate did not influenced the carbonization efficiency of the sugar cane bagasse. These results are today the reference and the most used for the all biomass carbonization.

For all the analyzed species, the optimum temperature in the carbonization process will be in the range 300-450°C, either in quantitative point of view (gravimetric efficiency), and in qualitative point of view (fixed carbon content). Lower is the carbonization heating rate, higher will be the charcoal production.

Despite of the results obtained in these experiments, it is very difficult to control the carbonization heating rate in a industrial kiln. This difficulty is due to the complex temperature profile and gas flow profile inside the kiln and also due to the heterogeneities of biomass characteristics (humidity, diameter, length, position). However, in an industrial carbonization kiln, the samples have a large diameter ant its internal heating rate is function of the internal kiln temperature. Thus, according to the obtained results it is necessary to control the carbonization kiln in order to operate at lower temperature and lower heating rate.

Field tests carried out at JG brick kiln carbonization Plant at CarboJota, it was verified that with a correct kiln operation, it is possible to increase the charcoal gravimetric efficiency from 22-23% to 35%, at most part of the time, and in some tests it was possible to obtain 40%.

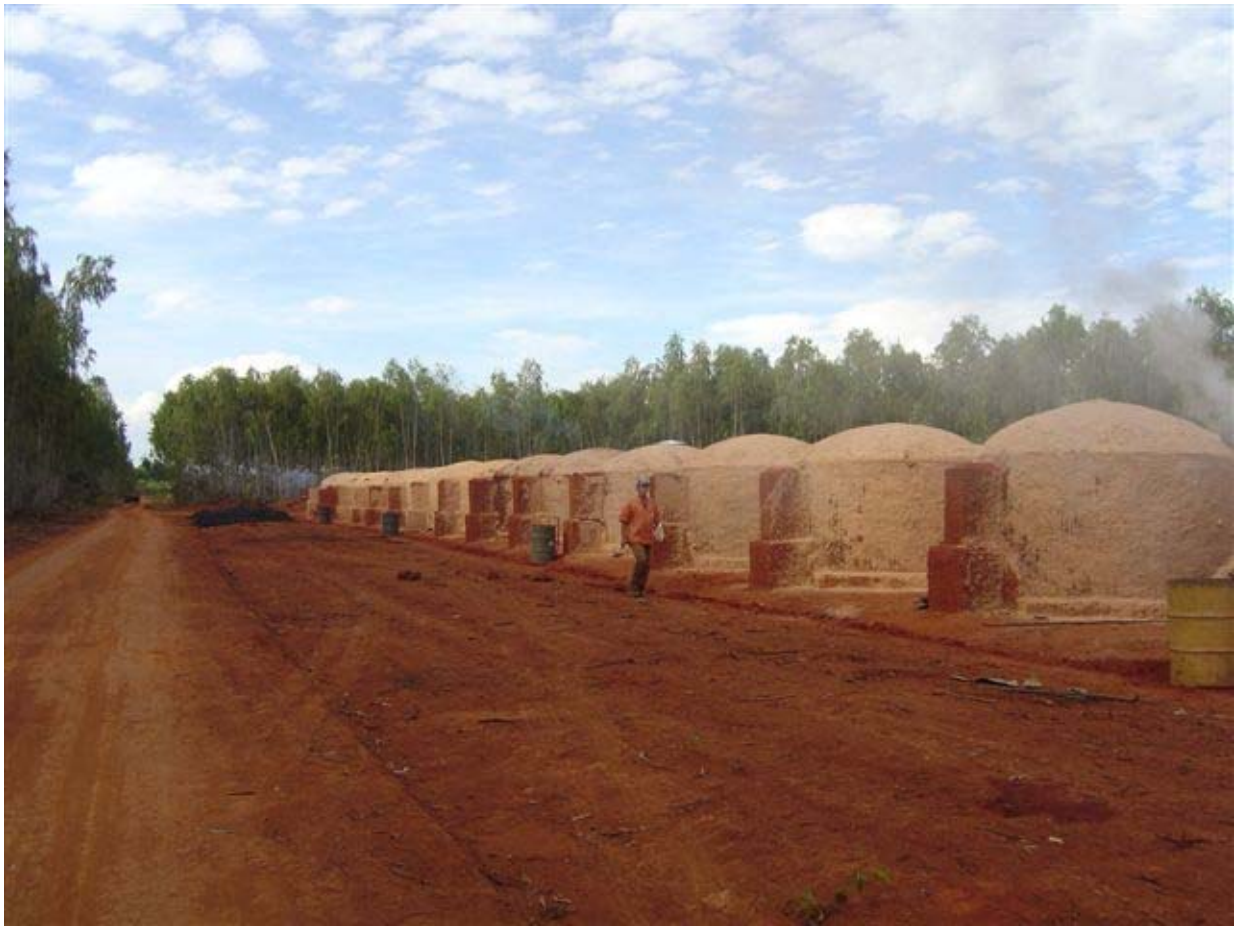

Figure 9. JG brick kiln carbonization Plant at CarboJota

7. References

BRASIL, 2004. Ministério de Minas e Energia. Balanço Energético Nacional 2004. Brasília, 169p, ISS 010-1-6636

ANTAL, Michael Jerry JR; MOK, William S.L.; VARHEGYI, Gabor; SZEKELY, Tamas. Review of Methods for Improving the Yield of Charcoal from Biomass. Energy & Fuels, v.4, n.3, p.221-225, May/June 1990.

CETEC - Fundação Centro Tecnológico de Minas Gerais. Experiências em Escala de Laboratório para Determinar a Influência da Idade, Umidade e Temperatura de Carbonização sobre Propriedades do Carvão. Relatório de Projeto. Belo Horizonte: 1980.

CHAUVETTE, G.; HEITZ, M.; RUBIO, M.; KHORAMI, J.; CHORNET, E.; MENARDI, H. TD/DTG: Method for the Caracterization do Solid Residues Derived from Liquifation of Lignocellulosics. Thermochimica Acta, v.84, p.1-5, 1985.

FIGUEIREDO, Francisco José. Desenvolvimento de uma MacroTermobalança para Análise da Carbonização da Biomassa. Belo Horizonte: UFMG, Dissertação (Mestrado em Engenharia Mecânica), Escola de Engenharia, Universidade Federal de Minas Gerais.

GOLDSTEIN, I. S., Ed. Wood Technology: Chemical Aspects. Washington, Am. Chemical Society, 372p., 1977.

OLIVEIRA, J. B.; MENDES, M. G. e GOMES, P. A. Carbonização da Madeira – Modelo Físico e Influência das Variáveis de Processo. Metalurgia (ABM), v.40, n.319, p.315-19, Jun.1984.

PINHEIRO, Paulo César da Costa; RESENDE, Dimas José de; YOSHIDA Maria Irene. Análise da Combustão e Carbonização do Eucalipto por Termogravimetria. In: XIII Congresso Brasileiro de Engenharia Mecânica (COBEM 95), II Congresso Ibero-Americano de Engenharia Mecânica (CIDIM-95), 12-15 Dezembro 1995, Belo Horizonte, MG, Actas-Anais- Proccedings... Rio de Janeiro: ABCM, Associação Brasileira de Ciências Mecânicas, 1995, CD-ROM.

SEYE Omar. Influência da Temperatura de Carbonização nas Propriedades do Carvão Vegetal de Eucaliptus. Belo Horizonte: UFMG, 08 de Maio de 1998 79p, Dissertação (Mestrado em Engenharia Mecânica) Escola de Engenharia, Universidade Federal de Minas Gerais.

VARHEGYI, Gabor; ANTAL, Michael J.; SZEKELY, Tamas; TILL, Ferenc; JAKAB, Emma; SZABO, Piroska. Simultaneous Thermogravimetric-Mass Spectrometric Studies of the Thermal Decomposition of Biopolymers. 2. Sugarcane Bagasse in the Presence and Absence of Catalysts. Energy & Fuels, v.2, n.3, p.273-277, May 1988.

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