OPTIMIZATION OF PYROLYSIS CONDITIONS FOR PRODUCTION OF REDUCTANT CHARCOAL

Eric Serges Noumi[1, 3]; Joel Blin[1, 2]; Patrick Rousset[2, 4] and Angelica de Cassia Oliveira Carneiro[5].

Abstract Steel is one of the most important materials used in modern society. The majority of the steel produced today is based on the use of coke and contributes a lot to greenhouse gases emission. Many researchers have been laid on the possibility to replace part of the fossil-based energy source in iron making with renewable, biomass-derived reducing agent. The main problems of this replacement are some difference of in quality between coke and wood charcoal (more reactive, less strength and carbon content) It causes a little shutdown of production in blast furnace and additional cost to modify a furnace. The aim of this paper was to determine in a statistical manner how carbonizations parameters impact the charcoal quality, especially reactivity and mechanical parameter. We applied a random factorial design and used the General linear System procedure to perform the statistical analysis. The experimental study was carried out using ***Eucalyptus Urophylla*** and ***Eucalyptus Camadulensis*** wood and involved two carbonization temperature (350 and 600°C), two relative working pressure (2 and 6 bars) and two heating rates (1 and 5°C/min). Six response variables were analyzed and discussed following a random factorial design: the charcoal yield ($\boldsymbol{y_{char}}$), the fixed carbon content ($\boldsymbol{C_f}$), the bulk density ($\boldsymbol{D}$), the compressive strength ($\boldsymbol{R_m}$), friability ($\boldsymbol{F}$) and the reactivity ($\boldsymbol{R}$) of charcoal. Except for the friability of charcoal, all other property are well correlate with carbonization parameter. In the range of low carbonisation parameter, reactivity of charcoal is affected only by carbonization temperature.

Keywords: Pyrolysis, Biomass, Charcoal, Pressure, Reactivity, Multivariate analysis

INTRODUCTION

Conventional production of steel from iron ore reduction is great carbon consumer mainly from coke. However, the use of fossil coke as reducing agent is responsible for many pollution problems (Gielen & Moriguchi, 2002). Thus, about 7% of anthropogenic CO_2 emissions in the world are assigned to the steel industry (Söderman, Saxén, & Pettersson, 2009). In actual context of promotion of GHG reduction, integration of renewable fuels like charcoal to replace the coke in ore reducing process has become an issue great importance(Griessacher, Antrekowitsch, & Steinlechner, 2012; Xu & Cang, 2010). This issue is strongly encouraged by steelmakers who created a label "Green Steel" and it has been integrated to the main "**Bioenergy objectives**" in the European area ("Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.,"). Therefore, many research works have been conducted to evaluate appropriate technologies to integrate renewable carbon source in the process of reduction of the iron ore (Fick, Mirgaux, Neau, & Patisson, 2014; Fick, Mirgaux, & Patisson, 2012; Ghanbari, Helle, & Saxén, 2012; Griessacher et al., 2012; Gupta, 2003; John G. Mathieson, Rogers, Somerville, & Jahanshahi, 2012; John G Mathieson, Rogers, Somerville, Jahanshahi, & Ridgeway, 2011; Norgate, Haque, Somerville, & Jahanshahi, 2012; Norgate & Jahanshahi, 2011; Norgate & Langberg, 2009; Orth, Anastasijevic, & Eichberger, 2007;

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[1] International Institute of Water and Environment (2iE), Ouagadougou, Burkina Faso,

[2] French Agriculture Research Centre for International Development (CIRAD), Montpellier, France.

[3] University of Brasilia, Brasilia DF, CEP 70910-900, Brazil.

[4] Advanced Fuel Processing Laboratory (AFPL), the Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140 – Thailand ;Tel: +66 2 872 9014.

[5] Department of Forest Engineering, Federal University of Viçosa, 36570000 Viçosa, MG, Brazil.

Söderman et al., 2009; Suopajärvi & Fabritius, 2013; Suopajärvi, Pongrácz, & Fabritius, 2013; Xu & Cang, 2010). For example, **Gupta** (Gupta, 2003) studied ways to use charcoal in the various technologies of the steel industry such as blast furnaces, rotary kiln processes, etc. He concludes that, given the situation in the steel sector and even if the use of charcoal complicates the process, due to the evolution of global demand, it remains economically feasible. **Fick** et **al**.(Fick et al., 2014; Fick et al., 2012) have studied the use of multiple sources of biomass in the form of charcoal, bio-oil, syngas, terrified biomass and biogas as reducing agents. They concluded that the charcoal remains the most promising alternative technically and economically. Although many studies show that the reliability of the use of charcoal as reducers in the furnace, it remain some shadow areas on the appropriate characteristics that charcoal should have. **Brito** (Brito, 1993) pioneered this theme and he demonstrated that charcoal for reduction of iron ores must have an excellent mechanical strength and optimum density. In the same way, for **Sampaio** there are three essential criteria to the use of charcoal to reduce iron ores good gas permeability, acceptable mechanical strength and low reactivity (Sampaio, 2008). This affirmation was confirmed by **Doat J.** and **G. Petroff** who affirmed that the compressive strength, friability and chemical composition (fixed carbon content, reactivity) are the most important parameters to master (J. Doat & G. Petroff, 1975). In Brazil, steelmakers use mainly charcoal to reduce iron ores (B. L. Pereira et al., 2013), specifications of this combustible are those recommended by **Santos**, grouped in the table below (Santos, 2008).

Proprieties	Units	Charcoal	metallurgical coke	Steel quality charcoal
Fixed carbon	%	70-80	88	75-80
Volatile matter	%	25-35	1	Max 25
Humidity	%	1-6	1-2	Max 4
ash	%	0.5-4	10-12	Max 1
Suffers	%	0.03-0.1	0.45-0.7	Max 0.03
Resistance to compression	kg/cm^2	10-80	130-160	Min 30
granulometry	mm	9-100	25-75	40-50
Bulk density	kg/cm^3	180-350	550	Min 250

Table 1 : Charcoal and coke properties for steel use [21]

Although these criteria are well identified, and also it is recognized that properties of charcoal are function of carbonization conditions, few studies focuses on optimization of the pyrolysis parameters to produce charcoal having the best quality for reduction of iron ores. In this few studies, like that of **Patrick Rousset** and **al.** (Rousset, Figueiredo, De Souza, & Quirino, 2011) and **M. Kumar** et **R.C. Gupta** (Mithilesh Kumar & Gupta, 1994), all this desired quality parameters, mainly reactivity and density of charcoal are not taken in account in the objectives. The main parameter that these studies have aimed to optimize was the fixed carbon content of charcoal. Purpose of this article is to determine with statistical method how heating rate, pressure, temperature, and type of wood impact the pyrolysis condition and the quality of charcoal for use as reducing agent for the steel industry.

This study therefore aims to analyse the changes induced by pyrolysis temperature, heating rate and pressure on the charcoal yield (y_{char}), the fixed carbon content (C_f), the bulk density (D), the mechanical strength (R_m), friability (F) and the reactivity (R).

MATERIALS AND METHODS

For this study we use two short rotation forestry of Eucalyptus wood that are commonly used in Brazil for iron making: ***Eucalyptus camaldulensis*** and ***Eucalyptus urophylla***. The trees have 6 years old and were collected from Forestry Company, located in the state of Minas Gerais, Brazil. In order to limit variation due to the natural variability of wood and guarantee good reproducibility of the results we use a log without any bark, and free from defects to prepare a sample.

For carbonization and wood basic density test, the log of wood was cut in cubic sample with dimension 20 mm x 20 mm x 20 mm (longitudinal, radial and tangential). Samples were dried at 105°C for 8 h in an oven until use. The pyrolysis reactor used is cylindrical, of the batch type, with a useful volume of 400 cm^3 corresponding to total wood volume of around 180 cm^3. Heating rate was provided by an annular electric heating element with a power of 1.6 kW making it possible to work at up to 800°C, with heating rates of 10°C/min.

In the present work, the effects of four independent variables, including three numerical variables (i.e., temperature between 350 and 600°C ($\boldsymbol{X_1}$), heating rate between 1 and 5°C/min ($\boldsymbol{X_2}$) and relative pressure between 2 and 6 bars ($\boldsymbol{X_3}$)), and one categorical variables (i.e., the use of ***E. Camaldulensis*** or ***E. Urophylla*** as the starting material ($\boldsymbol{X_4}$)) were investigated using General linear model (GLM). Eight assays corresponding to 8 treatments were conducted. The values for the temperature (***T***), heating rate ($\boldsymbol{h_r}$) and relative pressure (***P***) parameters were defined in accordance with earlier work (Antal et al., 1996; Antal, Mok, Varhegyi, & Szekely, 1990; Numazawa, 2000; B. L. Pereira et al., 2013; B. L. C. Pereira et al., 2012; Rousset et al., 2011) and can be found in table 2. The duration of the final plateau was fixed at 1 h in accordance with earlier studies showed that in slow carbonization we don't need to prolong the plateaux beyond one hour.

Parameter Level	Temperature (°C)	Heating rate (°C.min^{-1})	Relative Pressure (bars)
-1	350	1	2
1	600	5	6

Table 2: Values of the parameters selected for the experimental design

Six variables in response to the experiments were analyzed and discusses following a $2^{(4-1)}$ fractional factorial design: the charcoal yield ($\boldsymbol{y_{char}}$), the fixed carbon content ($\boldsymbol{C_f}$), the bulk density (***D***), the mechanical strength ($\boldsymbol{R_m}$), friability (***F***) and the reactivity (***R***).

The bulk density (g.cm^{-3}) was defined according to Brazilian standard NBR 9165/85 (Rousset et al., 2011). **Content of volatile**, **ash**, and **fixed carbon** on a dry basis were determined according to the standards ABNT NBR 8112/86.

Friability of charcoal is the resistance of transform into fine particles. He is determined by the drum test, according to standard MB 1375/80 of ABNT. The procedure used is the same as described in the work of **Silva** and **al**., (Silva, Numazawa, Araujo, Nagaishi, & Galvão, 2007).

The test of determination of **compressive strength** was done at **Laboratory of Forest Products** (**LFP**) at "**Serfiço Florestal brasileiro**". In view that don't exist a normalize test for characterization of the compressive strength (in kg.cm^{-2}) of charcoal, we adapted test ASTM 143-94 and NFB 51-009 intended for natural wood. This test serves just to have the difference between charcoals coming from different carbonization conditions.

Reactivity test were performed through isotherm gasification of charcoal with CO_2 in TGA. In a typical run, the char (14-16 mg) was gasified in a TGA described in detail elsewhere (Elyounssi, Collard, Mateke, & Blin, 2012). Before gasification we have post-pyrolysis stage to bring charcoal to gasification condition. The post-pyrolysis stage consisted of a temperature ramp (40°C/min) from 40°C to 900°C, followed by 10 min stay at 900°C, and always under a nitrogen flow of 40 ml/min to prevent evolving gases from flowing back and condensing on the balance system. After stabilisation the gasification agent (CO_2, 70 ml/min) was introduced in the reactor. The main gasification reaction is the well-known Boudouard equilibrium reaction (1):

$$C+CO_2 \rightarrow 2CO \quad \textbf{(reaction 1)}$$

With the experimental conditions mentioned above, the gasification reaction takes place in a chemical regime, the phenomena of heat transfer and mass are negligible (Huo, Zhou, Wang, & Yu, 2014). And in this conditions reactivity of char is represented by the intrinsic reactivity (Mermoud, Salvador, Van de Steene, & Golfier, 2006; Tagutchou, 2008). The intrinsic reactivity ***R*** (µg/µg.min) is expressed by the following formula:

$$R = -\frac{1}{m(t)}\frac{dm(t)}{dt} \quad (2)$$

Where;

$m(t)$ the weight of char free of ash at time t, $\frac{\mathrm{dm(t)}}{\mathrm{dt}}$ is the reaction rate derived from the derivative (dTG) cuve during gasification (mg/min).

RESULTS AND DISCUSSION

Table 3 gives the obtained pyrolysis results for the 6 variables studied : charcoal yield ($\mathbf{y_{char}}$), fixed carbon content (C_f), bulk density (***D***), mechanical strength (R_m), friability (***F***) and reactivity (***R***) depending on the treatments numbered 1 to 8.

Experiment identification	**T (°C)**	**h_r (°C/min)**	**P(bars)**	**Sample**	**y_{char} (%)**	**C_f (%db)**	**R_m (kg/cm^2)**	**D (kg/m^3)**	**F (%)**	**R (µg/µg.min)**
3	**350**	**1**	**2**	**E. camaldulensis**	48.02	60.44	180.27	397.2	6.35	15.24
4	**350**	**5**	**6**	**E. camaldulensis**	47.97	48.77	88.09	324	8.74	14.29
1	**600**	**1**	**6**	**E. camaldulensis**	34.35	87.15	195.7	405.6	5.55	11.08
8	**600**	**5**	**6**	**E. camaldulensis**	34.18	87.02	30.86	294.2	5.82	9.62
6	**350**	**1**	**6**	**E. urophylla**	50.73	54.77	207.23	345	3.93	16.84
2	**350**	**5**	**2**	**E. urophylla**	46.26	50.55	88.28	299.6	3.37	15.73
5	**600**	**1**	**2**	**E. urophylla**	32.11	90.22	241.41	342.8	6.2	12.66
7	**600**	**5**	**2**	**E. urophylla**	30.13	87.27	100.39	316	6.09	13.56

Table 3 : Results for the 6 responses variables

As can be seen in the table, charcoal properties differed significantly according to species and pyrolysis conditions. We used static analysis based on **General Linear model** to identify any correlation between the variables factors and the responses. The fit of the model to the empirical data was tested by calculating the regression coefficients, R^2 and R^2_{adj}.

Charcoal yield

The yield of charcoal produced from ***E. Camaldulensis*** ranged from 34.18% to 48.02 % and for ***E. Urophylla*** from 30.13% to 50.73%. An analysis of variance was carried out for this response to assess the significance and fitness of the model. The R^2_{adj} value of 0.989 was obtained for the charcoal yield and this indicates that 98.9% of the total variation in charcoal yield could be explained by the quadratic model. The high R^2 value (i.e., close to unity) indicating that there was a good agreement between the experimental and predicted charcoal yield from the model. The results are presented in table 4, in terms of coded factors. Based on ANOVA results presented in this table, it can be concluded that the models were significant with p-values less than 0.0001 (model and term p-value < 0.05 indicates the model and the term are significant for 95% confidence intervals) to predict the response values (Zabeti, Daud, & Aroua, 2009). In this case, the temperature (**X_1**) and pressure (**X_3**) were significant model terms for charcoal yield with p-values less than 0.05. The heating rate and the nature of sample was insignificant to the charcoal yield which could be manually removed from the model to improve the regression model and optimization results.

	R^2	R^2_{adj}	**p-value (Prob> F)**				**Polynomial equation**
			X_1 : Temperature	**X_2 : heating rate**	**X_3 : Pressure**	**X_4 : nature of sample**	
Y_{char}	0.995	0.989	0.0001***	0.0708*	0.0312**	0.9773*	40.46 –7.77*X_1+ 1.34*X_3
C_f	0.9907	0.9784	0.0004***	0.0918*	0.1980*	0.4401*	70.77 +17.14*X_1
D	0.8485	0.6466	0.9247*	0.0352**	0.5071*	0.1649*	340.55 -32.1*X_2
R_m	0.9383	0.8562	0.9584*	0.0074***	0.8178*	0.2486*	141.52 -64.62*X_2
F	0.3715	0.0	0.849*	0.7454*	0.7905*	0.3130*	-
R	0.9453	0.8725	0.0085**	0.3636*	0.6461*	0.0696*	13.62 –1.89*X_1+0.98*X_4

*** Most significant effect, ** less significant effect, * not significant effect

Table 4 : Analysis of variance (ANOVA) for all responses

We can see that, the pyrolysis temperature have the higher effect on charcoal yield. And this impact is antagonist with charcoal yield while that of pressure is positive. These results corroborated those found in the literature (Antal et al., 2000; Mok, Antal, Szabo, Varhegyi, & Zelei, 1992; Rousset et al., 2011). Indeed, the increase in temperature causes the breaking of chemical bonds, which leads to the formation of volatile substances which emerge, with consequent gradual reduction of the mass of the sample. The fact that nature of sample did not impact on charcoal yield is probably due in that the two samples used have substantially the equal macromolecular composition, especially the lignin.

Fixed carbon content

As can be seen in table 4 that fixed carbon content also is highly dependent on pyrolysis conditions. The values obtained vary from 48.77% to 90.22% independently of nature of sample. The coefficients of regression calculated are, for R^2_{adj} we have 0.97 who mean that 97% of the total variation in fixed carbon content could be explained by the quadratic model. And for R^2 we have a high value 0.99, close to unity. This indicating that there was a good agreement between the experimental and predicted fixed carbon content from the model. Based on ANOVA results, the temperature (**X_1**) is the only variable having a significant effect on fixed carbon content. The increase of pyrolysis temperature also increases fixed carbon content. These results corroborated those found in the literature. To obtain charcoal with fixed carbon contents above 85% we must pyrolysis at high temperatures, around 600 °C.

Bulk density

The coefficient of determination obtained is within the acceptable range is 0.80. The polynomial model is sufficient to explain variations in the bulk density of charcoal. From all parameters studied, the heating rate is the only one with a significant effect on the bulk density of charcoal. Its increase causes a decrease of the apparent density of charcoal.

Mechanical strength

The coefficient of determination obtained is within very good. The heating rate also like for bulk density is the parameter with a significant effect. Their increase causes a decrease of the mechanical strength of charcoal.

Friability

The coefficients of determination obtained are very low, 0.37. The polynomial model cannot explain the change in friability according to variables of our study. In table 3 we see that in spite of the varying conditions of the pyrolysis the friability of charcoal obtained does not vary significantly.

Reactivity

The values reactivity obtained vary from 9.62 ($\mu g.\mu g.min^{-1}$) (corresponding to 49.7% of conversion of charcoal after one hour of gasification) to 16.84 ($\mu g.\mu g.min^{-1}$) (corresponding to 95.81% of conversion of charcoal after one hour of gasification). The coefficients of regression calculated are, for R^2_{adj} we have 0.8725 who mean that 87.25% of the total variation in fixed carbon content could be explained by the quadratic model. And for R^2 we have a high value 0.9453 and we can also concluded that there was a good agreement between the experimental and predicted fixed carbon content from the model.

Based on ANOVA results, the temperature ($\mathbf{X_1}$) is the only variable having a significant effect on reactivity of charcoal. This effect is antagonist, who mean that the increase of temperature induce the decrease of reactivity.

This influence of pyrolysis temperature on the reactivity of char is similar to that reported by others workers (Mithilesh Kumar & Gupta, 1994; M. Kumar, Gupta, & Sharma, 1992; Mackay & Roberts, 1982). Mackay and Roberts (Mackay & Roberts, 1982) report that low-temperature lignocellulosic chars gasify more rapidly than the high temperature chars. The reason for the decreases in reactivity of wood char with increase of pyrolysis temperature is believed to be due to increased structural ordering of carbon matrix. As suggested by Kashiwaya and Ishii (Kashiwaya & Ishii, 1991) and Sahu et al. (Sahu, Levendis, Flagan, & Gavalas, 1988), the improvement in structural ordering lowers the concentration of active sites (i.e., the number of sites available for reaction and hence results in a decrease of carbon reactivity).

Investigation of the optimum pyrolysis conditions to produce charcoal for blast furnace

To find the combination of experimental factors that gives a good result for several responses, we used the concept of optimization based multi-responses using a desirability function. In this concept, we determined the experimental region associated with combinations giving the highest desirability.

We know that for use in blast furnace, the charcoal should have a high mechanical strength and density, a low friability, a high fixed carbon content and a low reactivity. This properties which can be grouped in two group: physic-mechanical and chemical properties are gives in table 1. Table 1 gives some values of these parameters. From our results, we have seen that, mechanical strength and bulk density of charcoal are influenced by heating rate during pyrolysis while friability undergoes no significant change. And other hand, the values obtained for physical-mechanical properties for the samples analysed are above the threshold set. The chemical properties are the only ones that require an optimization. We will focus only on the most interesting of them for the process, i.e., fixed carbon content and reactivity of charcoal. From our results, we have seen that this two properties are influenced by pyrolysis temperature. The increase of pyrolysis temperature leads to increase of fixed carbon content and decrease of reactivity of charcoal. To obtain a charcoal with fixed carbon content above 85% and with low reactivity, we should proceed at higher temperatures above 550°C

CONCLUSIONS

The aim of our study was to analyse and optimize the parameters of pyrolysis to obtain charcoal for use as reducing agent for the steel industry. We use a statistical method named General linear model to analyse effect of parameters variables (temperature, heating rate and pressure) on the properties of charcoal. Pyrolysis temperature and heating rate are the most important factor during pyrolysis. The first affected more chemical property like the carbon content and the charcoal yield. The second have significant effect on mechanical properties. The pressure have just a little and positive effect on charcoal yield. Given the demand of the steelmaking sector, the best charcoal would appear to be obtained at high temperature above 550°C, high pressure and low heating rate.

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