

OPTIMIZATION OF QUALITY OF CHARCOAL FOR STEELMAKING USING STATISTICAL ANALYSIS APPROACH

ERIC SERGES NOUMI^{1, 3, *}, JOEL BLIN^{1, 2,} and PATRICK ROUSSET^{2, 4}

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

² UPR 42 Biomass Energy, 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.

*Corresponding author: serges.noumi@2ie-edu.org

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

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 (y_{char}), the fixed carbon content (C_f), the bulk density (D), the compressive strength (R_m), friability (F) and the reactivity (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.

1- 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 [1]. Thus, about 7% of anthropogenic CO₂ emissions in the world are assigned to the steel industry [2]. 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 [3, 4]. 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 [5]. 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 [2-4, 6-17]. For example, **Gupta** [9] 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.**[6, 7] 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** [18] 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 [19]. 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 [20]. In Brazil, steelmakers use mainly charcoal to reduce iron ores [21], specifications of this combustible are those recommended by **Santos**, grouped in the table below [22].

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.** [23] and **M. Kumar et R.C. Gupta** [24] , 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).

2- MATERIALS AND METHODS

2-1 Raw material sampling and analysis

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. For macromolecular composition (lignin, extractives and holocelluloses content) and ash content, the samples were crushed and sieved, and the particle size fraction between 40 and 60 mesh were used.

The content of wood extractives was determined according to TAPPI 204 om-88, using the method of total extractives, substituting ethanol/benzene to ethanol/toluene. The lignin content was obtained by total sum of values of the soluble and insoluble lignin. The insoluble lignin was determined using **Klason** method and the soluble lignin was determined by spectrophotometry. The holocelluloses content was determined by difference, based on free wood extractives. The wood basic density was determined by water displacement method, according to ABNT NBR 11941 [25].

2-2 Charcoal preparation

The pyrolysis reactor used is cylindrical, of the batch type, with a useful volume of 400 cm³ corresponding to total wood volume of around 180 cm³. 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. The reaction temperature was monitored by two types of thermocouples, one inserted in annulus at the top of the reactor and the other in the heater system. The inert atmosphere and relative pressure were achieved by injecting nitrogen controlled by a backpressure regulator (Fig.1).

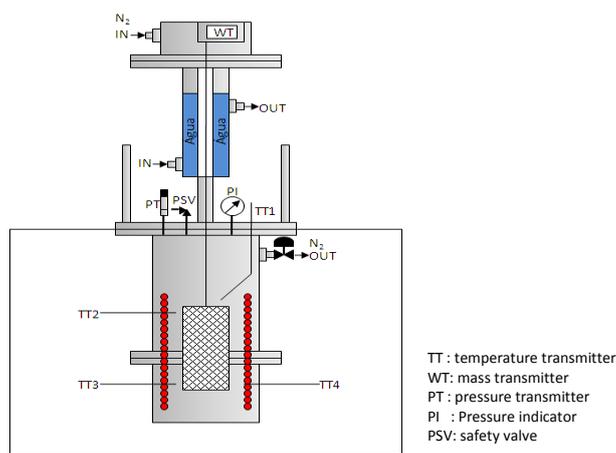


Figure 1 : General view of the pressurized pyrolysis reactor

We record the data on the mass of charcoal and the mass of sample and use to calculate the charcoal yield (y_{char}). The charcoal yield, expressed as a percentage, was the relation between the weight of the charcoal produced and the weight of wood put into the reactor.

2-3 Charcoal characterization

Physical (**bulk density**), chemical (**content of volatile, ash content, fixed carbon content, reactivity**) and mechanical (**friability, compressive strength**) properties of charcoal were characterized.

The **bulk density** ($\text{g}\cdot\text{cm}^{-3}$) was defined according to Brazilian standard NBR 9165/85. It was defined like mass of charcoal divided by the total volume it occupied as:

$$D = \frac{m_{char}}{W_r + (m_{sc} + m_{char})} \quad (1)$$

Where m_{char} the initial dry mass of charcoal, m_{sc} the mass of saturated charcoal and W_r the removed water. The volume was determined by coating a clod of known weight with a water-repellent substance and by weighing it while immersed in water [23].

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.**, [26].

The test of determination of **compressive strength** was done at **Laboratory of Forest Products (LFP)** at “**Serfio Florestal brasileiro**”. In view that don't exist a normalize test for characterization of the compressive strength (in $\text{kg}\cdot\text{cm}^{-2}$) 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 [27]. Before gasification we have post-pyrolysis stage to bring charcoal to gasification condition. The post-pyrolysis stage consisted of a temperature ramp ($40^\circ\text{C}/\text{min}$) 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 (CO₂, 70 ml/min) was introduced in the reactor. The main gasification reaction is the well-known Boudouard equilibrium 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 [28]. And in this conditions reactivity of char is represented by the intrinsic reactivity [29, 30]. The intrinsic reactivity R_{int} (mg/mg.min) is expressed by the following formula:

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

Where;

$m(t)$ the weight of char free of ash at time t ,

$\frac{dm(t)}{dt}$ is the reaction rate derived from the derivative (dTG) curve during gasification (mg/min).

2-4 Experimental protocol and method of analysis

In the present work, the effects of four independent variables, including three numerical variables (i.e., temperature between 350 and 600°C (X_1), heating rate between 1 and 5°C/min (X_2) and relative pressure between 2 and 6 bars (X_3)), and one categorical variables (i.e., the use of *E. Camaldulensis* or *E. Urophylla* as the starting material (X_4)) were investigated using General linear model (GLM). It handles models relating one or more continuous dependant variables to one or more independent variables. Six variables in response to the experiments were analyzed and discusses following a $2^{(4-1)}$ fractional factorial design: 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). Eight assays corresponding to 8 treatments were conducted. The values for the temperature (T), heating rate (h_r) and relative pressure (P) parameters were defined in accordance with earlier work [21, 23, 31-34] 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	Temperature (°C)	Heating rate (°C.min ⁻¹)	Relative Pressure (bars)
Level			
-1	350	1	2
1	600	5	6

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

A polynomial equation was developed to predict the dependant variables (chosen responses) as a function of independent variables (factors), as given by equation (1):

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \varepsilon \quad (1)$$

In this equation, Y is the predicted response, β_0 is the constant, x_i is the coded values of the independent variables, β_i is the linear term coefficient, ε is the random error, and n is the number of factors studied [35].

An analysis of variance (ANOVA) was applied to evaluate the fitness of the model. The goodness of fit of the polynomial model was expressed by the coefficients of determination, R^2 and R^2_{adj} , through equation (2) and (3), respectively:

$$R^2 = 1 - \frac{SS_{residual}}{SS_{model} + SS_{residual}} \quad (2)$$

$$R^2_{adj} = 1 - \frac{SS_{residual}/DF_{residual}}{(SS_{model} + SS_{residual})/(DF_{model} + DF_{residual})} \quad (3)$$

Here, SS is the sum of squares and DF is the degrees of freedom.

The statistical importance of the model was checked by determining the model's adequate precision ratio using equation (4) and (5) and by F-test:

$$Adequate\ Precision = \frac{\max(Y) - \min(Y)}{\sqrt{\bar{V}(Y)}} \quad (4)$$

$$\bar{V}(Y) = \frac{1}{n} \sum_{i=1}^n \bar{V}(Y) = \frac{p\sigma^2}{n} \quad (5)$$

Here, Y is the predicted response, p is the number of model parameters, σ^2 is the residual mean square and n is the number of experiments.

3- RESULTS AND DISCUSSION

3-1 Analysis of samples

The analyses of samples are shown in table 3.

Samples	Holocelluloses* (%)	Lignin*(%)	Extractives (%)	Ash (%)	Bulk density (kg/m ³)
E. Urophylla	68.68	28.4	2.8	0.11	659.2
E. Camaldulensis	67.1	31.06	1.72	0.12	609.9

*wood-free extractives

Table 3 : Chemical composition and bulk density of samples

The sum of the amount of celluloses and hemicelluloses is called holocelluloses, and it corresponds to the most significant mass fraction of wood. The holocelluloses contents for the two different samples are in agreement with other studies [34, 36, 37]. In view of the composition of the samples, we can say that the Eucalyptus Camaldulensis is the species that should give the highest charcoal yield. Eucalyptus Urophylla has the highest level of holocelluloses and these components do not contribute significantly to the yield of charcoal, but mostly to the production of non-condensable gases and condensable yield. With a relatively high density and lignin content, these woods have for the industrials the best quality parameters for the production of charcoal to use in industry. According to **Pereira** and al. [21], a minimum lignin content of 28% is required to wood for production of charcoal.

Although significant differences in ash content were observed between the 2 samples, the values < 0.2% can be considered low. Presence of inorganic is not desirable in charcoal, as these are not degraded during carbonization and they remain in charcoal and contributes to the reduction of Heat Heating Rate (**HHR**), and induce that some types of ferroalloys become brittle, less malleable and favourable to fissure.

3-2 Responses analysis and interpretation

Table 4 gives the obtained pyrolysis results for the 6 variables studied : charcoal yield (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)	hr (°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 4 : 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 (pyrolysis temperature, heating rate, relative pressure and nature of the biomass) and the responses (charcoal yield, fixed carbon content, bulk density, mechanical strength, friability and reactivity).

3-2-1 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 results are presented in table 5, in terms of coded factors

Table 5 : Analysis of variance (ANOVA) for the charcoal yield

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value (Prob> F)
X₁ : Temperature	483.761	1	483.761	657.42	0.0001***
X₂ : heating rate	5.56111	1	5.56111	7.56	0.0708*
X₃ : Pressure	10.8407	1	10.8407	14.73	0.0312**
X₄ : nature of sample	0.00070	1	0.00070	0.0	0.9773*
Total Error	2.20755	3	0.735849		
Total (corr.)	505.868	7			

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.995$; $R^2_{adj} = 0.989$

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 [38]. 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. Final polynomial equation of charcoal yield with only significant factor is:

$$Y_{char} = 40.46 - 7.77 * \text{Temperature} + 1.34 * \text{Pressure}$$

With the values of variables in the units of origin.

The fit of the model to the empirical data was tested by calculating the regression coefficients, R^2 and R^2_{adj} . The R^2_{adj} value of 0.989 was obtained for the charcoal yield. 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.

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 [23, 39, 40]. 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.

3-2-2 Fixed carbon content

As can be seen in table 6 who shows the ANOVA of fixed carbon content, 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.

Table 6 : Analysis of variance for the fixed carbon content

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value (Prob> F)
X_1 : Temperature	2350.58	1	2350.58	313.34	0.0004***
X_2 : heating rate	44.9826	1	44.9826	6.00	0.0918*
X_3 : Pressure	20.3688	1	20.3688	2.72	0.1980*
X_4 : nature of sample	5.91034	1	5.91034	0.79	0.4401*
Total Error	22.5049	3	7.50164		
Total (corr.)	2438.48	7			

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.9907$; $R^2_{adj} = 0.9784$

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. Final polynomial equation of charcoal yield with only significant factor is:

$$C_f = 70.77 + 17.14 * \text{Temperature} - 2.37 * \text{Heating rate} - 1.84 * \text{Pressure} - 0.99 * \text{Nature of Sample}$$

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.

3-2-3 Bulk density

Table 7 shows the ANOVA of 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.

Table 7 : Analysis of variance for the bulk density

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value (Prob> F)
X_1 : Temperature	6.48	1	6.48	0.01	0.9247*
X_2 : heating rate	8243.28	1	8243.28	13.42	0.0352**
X_3 : Pressure	346.56	1	346.56	0.56	0.5071*
X_4 : nature of sample	2053.5	1	2053.5	3.34	0.1649*
Total Error	1842.38	3	641.127		
Total (corr.)	12167.4	7			

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.8485$; $R^2_{adj} = 0.6466$

Final equation of bulk density is:

$$D = 340.55 - 0.9 * \text{Temperature} - 32.1 * \text{Heating rate} - 7.6 * \text{Pressure} - 18.5 * \text{Nature of sample.}$$

3-2-4 Mechanical strength

Table 8 shows the ANOVA of mechanical strength of charcoal. 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.

Table 8 : Analysis of variance for the mechanical strength.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value (Prob> F)
X_1 : Temperature	2.52001	1	2.52001	0.00	0.9584*
X_2 : heating rate	33409.8	1	22409.8	42.42	0.0074***
X_3 : Pressure	49.7376	1	49.7376	0.06	0.8178*
X_4 : nature of sample	1605.73	1	1605.73	2.04	0.2486*

Total Error	2362.97	3	787.657
Total (corr.)	38359.4	7	

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.9383$; $R^2_{adj} = 0.8562$

Final equation model of mechanical strength is:

$$R_m = 141.52 + 0.56 * \text{Temperature} - 64.62 * \text{Heating rate} - 2.87 * \text{Pressure} + 16.35 * \text{Nature of sample.}$$

3-2-5 Friability

Table 9 shows the ANOVA of 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 4 we see that in spite of the varying conditions of the pyrolysis the friability of charcoal obtained does not vary significantly.

Table 9 : Analysis of variance for the friability.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value (Prob> F)
X₁ : Temperature	0.201612	1	0.20162	0.05	0.849*
X₂ : heating rate	0.495013	1	0.495013	0.13	0.7454*
X₃ : Pressure	0.329004	1	0.32004	0.08	0.7905*
X₄ : nature of sample	5.7135	1	5.7135	1.46	0.3130*
Total Error	11.7143	3	3.90478		
Total (corr.)	18.6396	7			

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.3715$; $R^2_{adj} = 0.0$

3-2-6 Reactivity

The values reactivity obtained vary from 9.62 ($\mu\text{g} \cdot \mu\text{g} \cdot \text{min}^{-1}$) (corresponding to 49.7% of conversion of charcoal after one hour of gasification) to 16.84 ($\mu\text{g} \cdot \mu\text{g} \cdot \text{min}^{-1}$) (corresponding to 95.81% of conversion of charcoal after one hour of gasification). Table 10 shows the ANOVA of reactivity.

Table 10 : Analysis of variance for the reactivity.

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value (Prob> F)
X₁ : Temperature	28.804	1	28.80	38.33	0.0085**
X₂ : heating rate	0.85805	1	0.85805	1.14	0.3636*
X₃ : Pressure	0.01944	1	0.1944	0.26	0.6461*
X₄ : nature of sample	5.7624	1	5.7624	7.67	0.0696*
Total Error	575132	3	19171.1		
Total (corr.)	11123.3	7			

*** Most significant effect, ** less significant effect, * not significant effect; $R^2 = 0.9453$; $R^2_{adj} = 0.8725$

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 (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. Final polynomial equation of reactivity is:

$$R = 13.62 - 1.89 * \text{Temperature} - 0.32 * \text{Heating rate} - 0.18 * \text{Pressure} + 0.98 * \text{Nature of sample.}$$

This influence of pyrolysis temperature on the reactivity of char is similar to that reported by others workers [24, 41, 42]. Mackay and Roberts [42] 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 [43] and Sahu et al. [44], 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).

3-3 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

4- 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.

REFERENCES

- [1] Gielen D, Moriguchi Y. CO₂ in the iron and steel industry: an analysis of Japanese emission reduction potentials. *Energy Policy*. 2002;30:849-63.
- [2] Söderman J, Saxén H, Pettersson F. Future potential for biomass use in blast furnace ironmaking. In: Jacek J, Jan T, editors. *Computer Aided Chemical Engineering*: Elsevier; 2009. p. 567-71.
- [3] Griessacher T, Antrekowitsch J, Steinlechner S. Charcoal from agricultural residues as alternative reducing agent in metal recycling. *Biomass and Bioenergy*. 2012;39:139-46.
- [4] Xu C, Cang D-q. A Brief Overview of Low CO₂ Emission Technologies for Iron and Steel Making. *Journal of Iron and Steel Research, International*. 2010;17:1-7.
- [5] 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.
- [6] Fick G, Mirgaux O, Neau P, Patisson F. Using Biomass for Pig Iron Production: A Technical, Environmental and Economical Assessment. *Waste and Biomass Valorization*. 2014;5:43-55.
- [7] Fick G, Mirgaux O, Patisson F. Environmental assessment of biomass options for iron making. *Carbon Management Technology Conference, 7-9 February 2012, Orlando, Florida, USA2012*. p. 1-9.
- [8] Ghanbari H, Helle M, Saxén H. Process integration of steelmaking and methanol production for suppressing CO₂ emissions—A study of different auxiliary fuels. *Chemical Engineering and Processing: Process Intensification*. 2012;61:58-68.
- [9] Gupta RC. Woodchar as a sustainable reductant for ironmaking in the 21ST century. *Mineral Processing and Extractive Metallurgy Review*. 2003;24:203-31.
- [10] Mathieson JG, Rogers H, Somerville MA, Jahanshahi S. Reducing Net CO₂ emissions Using Charcoal as a Blast Furnace Tuyere Injectant. *ISIJ international*. 2012;52:1489-96.
- [11] Mathieson JG, Rogers H, Somerville MA, Jahanshahi S, Ridgeway P. Potential for the use of biomass in the iron and steel industry. *Chemeca 2011 (39th : 2011 : Sydney, NSW)*. Barton, A.C.T.: Engineers Australia; 2011. p. [1065]-[76].
- [12] Norgate T, Haque N, Somerville M, Jahanshahi S. Biomass as a source of renewable carbon for iron and steelmaking. *ISIJ international*. 2012;52:1472-81.
- [13] Norgate T, Jahanshahi S. Reducing the greenhouse gas footprint of primary metal production: Where should the focus be? *Minerals Engineering*. 2011;24:1563-70.
- [14] Norgate T, Langberg D. Environmental and Economic Aspects of Charcoal Use in Steelmaking. *ISIJ international*. 2009;49:587-95.
- [15] Orth A, Anastasijevic N, Eichberger H. Low CO₂ emission technologies for iron and steelmaking as well as titania slag production. *Minerals Engineering*. 2007;20:854-61.
- [16] Suopajärvi H, Fabritius T. Towards More Sustainable Ironmaking—An Analysis of Energy Wood Availability in Finland and the Economics of Charcoal Production. *Sustainability*. 2013;5:1188-207.
- [17] Suopajärvi H, Pongrácz E, Fabritius T. The potential of using biomass-based reducing agents in the blast furnace: A review of thermochemical conversion technologies and

- assessments related to sustainability. *Renewable and Sustainable Energy Reviews*. 2013;25:511-28.
- [18] Brito JO. Reflexões sobre a qualidade do carvão vegetal para uso siderúrgico. Piracicaba IPEF. 1993:6.
- [19] Sampaio R. Conversão da biomassa em carvão vegetal - Situação Atual com tendências 2025 - Estudo prospectivo do setor siderúrgico. *CGEE*. 2008:13.
- [20] J. Doat, G. Petroff. La carbonisation des bois tropicaux : essais de laboratoire et perspectives industrielles. *Revue Bois et Forêts des Tropiques*. 1975:55-72.
- [21] Pereira BL, Carneiro AdCO, Carvalho AMML, Colodette JL, Oliveira AC, Fontes MPF. Influence of chemical composition of Eucalyptus wood on gravimetric yield and charcoal properties. *BioResources*. 2013;8:4574-92.
- [22] Santos MAS. Parâmetros de qualidade do carvão vegetal para uso em alto-forno. In: UFMG, editor. *Forum Nacional Sobre Carvão Vegetal*, 1. Belo Horizonte, Brazil 2008.
- [23] Rousset P, Figueiredo C, De Souza M, Quirino W. Pressure effect on the quality of eucalyptus wood charcoal for the steel industry: A statistical analysis approach. *Fuel Processing Technology*. 2011;92:1890-7.
- [24] Kumar M, Gupta RC. Influence of carbonization conditions on the gasification of acacia and eucalyptus wood chars by carbon dioxide. *Fuel*. 1994;73:1922-5.
- [25] Brazilian Association of Technical Standards. NBR 11941 : Wood determination of basic density. Rio de Janeiro, Brazil 2003.
- [26] Silva MGD, Numazawa S, Araujo MM, Nagaishi TYR, Galvão GR. Carvão de resíduos de indústria madeireira de três espécies florestais exploradas no município de Paragominas, PA. *Acta amaz*. 2007;37:61-70.
- [27] Elyounssi K, Collard F-X, Mateke J-aN, Blin J. Improvement of charcoal yield by two-step pyrolysis on eucalyptus wood: A thermogravimetric study. *Fuel*. 2012;96:161-7.
- [28] Huo W, Zhou Z, Wang F, Yu G. Mechanism analysis and experimental verification of pore diffusion on coke and coal char gasification with CO₂. *Chemical Engineering Journal*. 2014;244:227-33.
- [29] Mermoud F, Salvador S, Van de Steene L, Golfier F. Influence of the pyrolysis heating rate on the steam gasification rate of large wood char particles. *Fuel*. 2006;85:1473-82.
- [30] Tagutchou JP. *Gazéification du charbon de plaquette forestières: particules et lit fixe continu*. Perpignan: Université Perpignan- Via Domitia; 2008.
- [31] Antal MJ, Croiset E, Dai X, DeAlmeida C, Mok WS-L, Norberg N, et al. High-Yield Biomass Charcoal†. *Energy & Fuels*. 1996;10:652-8.
- [32] Antal MJ, Mok WSL, Varhegyi G, Szekely T. Review of methods for improving the yield of charcoal from biomass. *Energy & Fuels*. 1990;4:221-5.
- [33] Numazawa S. *Contribution à l'étude de la pyrolyse lente sous pression du bois : Détermination des paramètres optima du procédé et caractéristiques des produits obtenus.*: Université de Technologie de Compiègne.; 2000.
- [34] Pereira BLC, Oliveira AC, Carvalho AMML, Carneiro AdCO, Santos LC, Vital BR. Quality of Wood and Charcoal from Eucalyptus Clones for Ironmaster Use. *International Journal of Forestry Research*. 2012;2012:8.
- [35] Shafeeyan MS, Wan Daud WMA, Houshmand A, Arami-Niya A. The application of response surface methodology to optimize the amination of activated carbon for the preparation of carbon dioxide adsorbents. *Fuel*. 2012;94:465-72.
- [36] Oliveira AC, De Carneiro ACO, Vital BR, Almeida W, Pereira BLC, Cardoso MT. Quality parameters of Eucalyptus pellita F. Muell. Wood and charcoal. *Scientia Forestalis/Forest Sciences*. 2010:431-9.

- [37] Santos RCD, Carneiro ADCO, Castro AFM, Castro RVO, Bianche JJ, Souza MMD, et al. Correlation of quality parameters of wood and charcoal of clones of eucalyptus. *Scientia Forestalis/Forest Sciences*. 2011;221-30.
- [38] Zabeti M, Daud WMAW, Aroua MK. Optimization of the activity of CaO/Al₂O₃ catalyst for biodiesel production using response surface methodology. *Applied Catalysis A: General*. 2009;366:154-9.
- [39] Antal MJ, Allen SG, Dai X, Shimizu B, Tam MS, Grønli M. Attainment of the Theoretical Yield of Carbon from Biomass. *Industrial & Engineering Chemistry Research*. 2000;39:4024-31.
- [40] Mok WSL, Antal MJ, Szabo P, Varhegyi G, Zelei B. Formation of charcoal from biomass in a sealed reactor. *Industrial & Engineering Chemistry Research*. 1992;31:1162-6.
- [41] Kumar M, Gupta RC, Sharma T. Influence of carbonisation temperature on the gasification of Acacia wood chars by carbon dioxide. *Fuel Processing Technology*. 1992;32:69-76.
- [42] Mackay DM, Roberts PV. The dependence of char and carbon yield on lignocellulosic precursor composition. *Carbon*. 1982;20:87-94.
- [43] Kashiwaya Y, Ishii K. Kinetic analysis of coke gasification based on non-crystal/crystal ratio of carbon. *ISIJ International*. 1991;31:440-8.
- [44] Sahu R, Levendis YA, Flagan RC, Gavalas GR. Physical properties and oxidation rates of chars from three bituminous coals. *Fuel*. 1988;67:275-83.