Pressure effect on the quality of eucalyptus wood charcoal for the steel industry: A statistical analysis approach

P. Rousset a,⁎, C. Figueiredo b, M. De Souza c, W. Quirino c

a UPR 42 Biomass Energy, French Agriculture Research Centre for International Development (CIRAD), Brasilia DF, 70818-900, Brazil
b University of Brasilia, Brasilia DF, CEP 70910-900, Brazil
c Laboratory of Forest Product, Brazilian Forest Service (LPF-SFB) Brasilia DF, 70818-900, Brazil

A R T I C L E   I N F O

Article history:
Received 22 February 2010
Received in revised form 18 April 2011
Accepted 9 May 2011
Available online 31 May 2011

Keywords:
Pyrolysis
Biomass
Charcoal
Pressure
Multivariate analysis

A B S T R A C T

Brazil is the leading producer and consumer of charcoal, 75% of which goes to the steel industry alone. The carbonization processes are generally small-scale technologies that are difficult to control, with relatively low gravimetric yields. New technologies are currently being developed to improve those figures. One such technique is pressurized pyrolysis. Recent studies have shown that using pressure can increase gravimetric yields by 50% and considerably reduce carbonization time. The purpose of this paper was to study statistically how pressure impacts on the quality of the resulting charcoal. We applied a random factorial design and used the General Linear System procedure to perform the statistical analysis. The experimental study was carried out on the wood of Eucalyptus grandis and involved three relative working pressures (0, 5 and 10 bars), two carbonization temperatures (450 and 600 °C) and three wood moisture contents (0, 15 and 110%). Five response variables were analyzed and discussed following a random factorial design: charcoal yield (ychar), fixed carbon yield (yc), bulk density (D), fixed carbon content (fc) and gross calorific value (GCV). The best "steel" quality charcoal seemed to be obtained with an anhydrous wood, a pressure of 10 bars and a temperature of 600 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

For a long time in world steelmaking, charcoal was used exclusively as a fuel and reducing agent. Brazil is one of the few countries in the world that offers major potential for biomass production and use. It is the world’s leading producer of charcoal with annual production estimated at 9 million tons [1]. Around 75% of that production goes to the steelmaking sector [2]. Unfortunately, most of the kilns used to carbonize wood are not mechanized and the technologies used still remain outdated [3]. In order to guarantee sustainable development of the steelmaking sector, companies need to be modernized developing and adopting new, more efficient carbonization technologies [4].

Of the promising technologies like continuous hot rinsing gas retort (Lambiotte, Reichert) or discontinuous batch retort (DPC, CML), we have chosen pressurized carbonization. This process has been studied for several years by the University of Hawaii and CIRAD [5]. The aim of this paper was to determine in a statistically valid manner how pressure impacts on charcoal quality. The goal for this study was to investigate causality and, in particular, to draw conclusions on how changes in the value of independent variables (pressure, temperature and moisture content) affected dependent variables charcoal yield (ychar), fixed carbon yield (yc), bulk density (D), fixed carbon content (fc) and gross calorific value (GCV). There are some publications on pressurized pyrolysis from the classic work by Antal and Mok [6,7] to the present day [8] but there are no published data yet for a complete multivariable statistical analysis.

2. Background

Global warming presents an enormous challenge to the steel industry, which is both carbon-intensive and energy efficient. Lean production can provide some short-term emission mitigation, at the level of the Kyoto requirements. In the middle term, more use of scrap will also help alleviate emissions. But to reach much larger reductions in GHG emissions, on a par with the likely targets that will be set after the Kyoto period, the steel industry will have to imagine new production paradigms, which constitutes its most formidable challenge for the years to come [9].

About 8 million t of pig iron are already produced in Brazil today, with eucalyptus trees, charcoal ovens and small blast furnaces fed with this charcoal. Charcoal production has always relied on extremely diverse technologies that are more or less adapted to the environmental conditions in which they are used. In recent years, the increasing scarcity of wood or its high production costs, along with rising labor costs, or the possibility of mechanizing handling...
operations and, generally, international determination to optimize the productivity of materials, have given rise to new carbonization technologies and to sometimes major modifications to existing technologies.

The most common Brazilian (and simplest) model to produce charcoal is the “Rabo Quente” basic kiln, which accounts for at least 95% of the kilns in operation [10]. Charcoal yields are very low, usually under 20% (drying base). The charcoal is generally very heterogeneous due to limited control of the carbonization process. According to Sampaio [11], a charcoal of steelmaking quality has to satisfy 4 criteria: its reducing power, its gas permeability, its physical strength and its reactivity.

Table 1 gives the quality criteria for a charcoal and a coke intended for the steelmaking industry [12].

Pyrolysis is one of the main three biomass energy conversion pathways. Antal and Gronl [13] gave a complete review summarizing knowledge on the production and properties of charcoal accumulated over the past 38 millennia. By controlling the main reaction parameters, namely temperature, heating rate, carbonization time and pressure, it is possible to maximize mass and energy yields and steer the reaction towards the desired products [14].

Recent work has revealed an increase in charcoal yields when pyrolysis is carried out under pressure, leading to char coal conversion approaching theoretical yields of 42 to 62% dry basis, accompanied by a significantly shorter carbonization time [15,16]. The average distribution of products and by-products generated by carbonization showed that liquid and gaseous by-products accounted for almost 70% of the initial mass of the wood. They also accounted for 40 to 50% of its initial energy. In atmospheric conditions, changes in the fixed-carbon yield over time reveal the existence of two distinct phases: A first phase which primarily involves the pyrolysis of hemicelluloses and cellulose, during this phase, the fixed-carbon yields continuously increase with the pyrolysis time to reach a maximum. The second phase, which begins with slow lignin decomposition, is characterized by a decrease in the fixed-carbon yield as the residence time increases. The value of the maximum can be as great as that obtained under high-pressure pyrolysis and approached the theoretical value [14].

The role played by secondary reactions of condensable vapors seems to be of prime importance both with and without pressure. Indeed, with the thermolysis of biopolymers at atmospheric pressure, released monomeric structures (e.g. levoglucosan), oligomeric structures (e.g. cellobiosan) and other by-products of degradation in the vapor phase. These extremely reactive products form condensable substances and carbon-rich tars [7].

With pressurized pyrolysis, the reactional phenomena are different. The pressure increases the residence time of the vapor phase in the solid matrix (cell wall). The highly reactive substances repolymerize into a more stable structure, in crystal form, called secondary charcoal. Solid yields are then higher and accompanied by water vapor and light gasses [17]. A hot pressure treatment of cellulose samples was studied by thermogravimetric analysis (TGA) [18]. The results showed that part of the cellulose remained unconverted and another part only partially converted under the mildest pre-treatment conditions, 300 °C at 100 bars. Elevation of the temperature to 350 °C or the pressure to 150 bars resulted in a high level of cellulose conversion [8]. Antal gives an example of the high-pressure cellulose degradation mechanism [13]. In general, it would seem that the state of equilibrium for pressurized pyrolysis follows Le Chatelier’s principle [19]. That principle shows that if pressure is applied in a closed gaseous system, the latter will tend towards a new state of equilibrium minimizing the formation of gaseous molecules in order to reduce the volume [20,21]. The reader will find more details in the recent review [22] which reports on the state of the art in modeling the chemical and physical processes of wood and biomass pyrolysis.

A clearer understanding of the phenomena taking place during pressurized pyrolysis can be obtained from studies conducted on mineral charcoal. A number of studies related to the coking pressure developed during the carbonization process have been carried out. Some of them have focussed on the mechanism of the generation of coking pressure. There is strong evidence to suggest that the relative amount of heavy compounds in the primary tars is related to the coking pressure generated by the coals studied [23]. Griffin et al. [24] discovered the existence of competition between secondary reactions involving the volatile matter produced and its ejection from the solid. Those observations confirmed strong dependency between mass transfers and pressure, so that an increase in pressure was reflected in an overall reduction in volatile emissions, hence in tar and gas yields [21]. Phuoc and Dubetaki [25] had already found that transport rates for low pressures were rapid, whereas at high pressure, as for biomass, there were reactions leading to the recombination of volatiles in the solid matrix. Internal transport would therefore seem to have been relatively slow, compared to chemical kinetics, if the size of the particles, the heating rate and pressure were increased. There would seem to exist two reaction levels depending on temperature. Below 560 °C, pressure would seem not to affect yields, whilst beyond that it would appear to be the temperature that has a negligible effect. However, they found that the heating temperature and particle size during pressurized pyrolysis had little effect on material yields [26].

3. Experimental

3.1. Material

The Eucalyptus grandis W. Hill ex Maden used was 6 years old and was collected in the Federal District of Brazil. Six logs without any peeling, and free from defects, were sawn into 50-mm thick, quartersawn boards. For comparative studies on the effects of temperature levels and treatment duration, the wood samples were taken from a single longitudinal section in order to limit variation due to the natural variability of wood and thus guarantee good reproducibility of the results. Sample dimensions were 10 mm × 10 mm × 150 mm (Longitudinal, Radial and Tangential) before treatment, in order to match the volume of the reactor chamber and allow good treatment uniformity. No pre-treatments were used to improve charcoal yields from these samples. The samples were divided into 3 batches with different relative humidities (RH) They were then dried or saturated respectively to obtain an average moisture content of 0, 15.5 or 110% (drying base) using a dryer (T = 103 °C) or a climate chamber (T = 22 °C and RH = 85%).

Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Charcoal</th>
<th>Steel quality charcoal</th>
<th>Steel quality coke</th>
<th>Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon (%)</td>
<td>65–75</td>
<td>74–77</td>
<td>88</td>
<td>88–92</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>25–35</td>
<td>25–22</td>
<td>1</td>
<td>7.8–11</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>2–3</td>
<td>1–1.5</td>
<td>10–12</td>
<td>0.1–0.5</td>
</tr>
<tr>
<td>Alkalis</td>
<td>High</td>
<td>&lt;20%</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Resistance to compression kg/cm²</td>
<td>10–80</td>
<td>50–100</td>
<td>130–160</td>
<td>–</td>
</tr>
<tr>
<td>Ash Basicity (C + M)/(S + A)</td>
<td>Basic</td>
<td>C + M÷5 + A</td>
<td>Acid</td>
<td>Acid</td>
</tr>
</tbody>
</table>
3.2. Reactor

The pyrolysis reactor was cylindrical, of the batch type, with a useful volume of 400 cm$^3$ corresponding to a total wood volume of around 180 cm$^3$, i.e. 12 samples per treatment. Heating was provided by an annular electric heating element with a power of 1.6 kW making it possible to work at up to 900 °C, with heating rates of 15 °C/min. The reaction temperature reaction was monitored by two type K thermocouples, one inserted in an annulus at the top of the reactor and the other in the heater system. The inert atmosphere and relative pressure (14 bars) were achieved by injecting nitrogen controlled by a back-pressure regulator (Fig. 1). Finally, we wanted the temperature history of the wood sample to be very close to that of the set temperature acting on the gas flow. This was ensured by a high heat transfer coefficient at the interface and by choosing a small sample thickness to reduce the time constant related to thermal diffusion in wood. This time constant $\tau$ read as:

$$
\tau = \frac{t^2 \rho C_p}{\lambda}
$$

where $t$ is the half-thickness of the sample (m), $\rho$ the wood density (kg·m$^{-3}$), $C_p$ the specific heat capacity of wood (J·kg$^{-1}$·K$^{-1}$) and $\lambda$ the thermal conductivity of wood (J·s$^{-1}$·m$^{-1}$·K$^{-1}$). Using usual values for wood ($\rho = 800$ kg·m$^{-3}$, $C_p = 1250$ J·kg$^{-1}$·K$^{-1}$ and $\lambda = 0.15$ J·s$^{-1}$·m$^{-1}$·K$^{-1}$) and with a total thickness of 10 mm, the time constant $\tau$ was less than 166 s. This value was very small relative to the treatment duration, thereby ensuring uniform treatment throughout the section.

3.3. Experimental protocol

Thirty-six assays were conducted, corresponding to 18 treatments and two replicates. We used a General Linear System (GLM) procedure from a Statistical Analysis System (SAS) program. It handles models relating one or more continuous dependent variables to one or more independent variables. Five variables in response to the experiments were analyzed and discussed following a $3^2 \times 2$ random factorial design: the charcoal yield ($y_{char}$), the fixed carbon yield ($y_{fc}$), the bulk density ($D$), the fixed carbon content ($fC$) and the gross calorific value ($GCV$). The values for the moisture content ($MC$), pressure ($P$) and temperature ($T$) parameters were defined in accordance with earlier work [6,16] and can be found in Table 2. The heating rate and duration of the final plateau were fixed at 4 °C/min and 3 h respectively, even though earlier studies showed that high-pressure carbonization significantly increased charcoal yields without needing to prolong the plateaux beyond one hour.

The carbonization order was chosen at random. The experimental error had a degree of freedom of 18, which was highly acceptable according to Montgomery [27]. The general model for variance analysis was that described by the following equation:

$$
Y_{ijk} = \mu + [MC_i + P_j + T_k + (MC \times P)_{ij} + (MC \times T)_{ik} + (P \times T)_{jk} + (MC \times P \times T)_{ijk}] + e_{ijk}
$$

where $MC$ is the Moisture Content, $P$ the Relative Pressure and $T$ the Temperature.

Proximate/ultimate analyses were performed and the heating value (dry basis) was measured. Proximate analysis was conducted to determine the fraction of ash (Ash) and volatile matter (VM). The fixed carbon (FC) content was obtained by difference. The values of proximate analysis were obtained in accordance with the procedure of the Brazilian Association of Technical Standards ABNT NBR 8112/86. The gross calorific value (GCV) was provided by a Parr 1261 analyser according to Brazilian standard NBR 8633/84. The bulk density (g cm$^{-3}$), mass of the charcoal divided by the total volume it occupied, was defined according to Brazilian standard NBR 9165/85 as

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

where $m_{char}$ was the initial dry mass of charcoal, $m_{sc}$ was the mass of the saturated charcoal and $W_r$ was the removed water. The volume was determined by coating a clod of wood with a thin layer of plasticine, heating it up to the heating temperature, cooling it down to room temperature and submerging it in a water bath. The change in volume was recorded.

![Fig. 1. General view of the pressurized pyrolysis reactor.](image-url)
known weight with a water-repellent substance (paraffin) and by weighing it while immersed in water, using Archimedes’ principle [28]. Precision in calculating bulk density required correction for the difference in weight of the wire in air and in water. However, the error was negligible with thread or a 28-gage wire.

### 4. Results and discussion

#### 4.1. Overall results

Table 3 gives the averages obtained for the 5 variables studied, charcoal yield ($y_{char}$), fixed carbon yield ($y_{fc}$), bulk density (D), fixed carbon content ($fC$) and gross calorific value (GCV) depending on the treatments numbered 1 to 18. As pressure was the differentiated factor in this study, we classed the data by increasing order of pressure for each temperature. Then, each response variable was isolated and classed by decreasing order, thereby enabling identification of the best treatment for the variable in question. Statistical analysis was used to identify the effects and trends for parameters MC, P and T along with their second and third order interactions.

In statistics, an analysis of variance (ANOVA) is a collection of statistical models, and their associated procedures, in which the observed variance is partitioned into components due to different explanatory variables. All the variables, apart from bulk density, generally displayed a coefficient of variation under 7%, indicating a good control over the operating conditions (Table 4).

We performed analyses of type III sum of squares to analyze which parameters significantly interfered ($\alpha = 0.05$) with the five response variables, along with the effect of second and third order interactions on the quality of the charcoals produced. Among the parameters studied, pressure was the factor with the greatest impact on 4 of the 5 response variables. The carbonization temperature and the second order interaction between pressure and temperature ($P \times T$) significantly influenced 3 of the 5 variables (Table 5).

Wood moisture content had a significant impact on the fixed carbon yield and bulk density, whereas the second order interaction between moisture and pressure ($MC \times P$) only affected bulk density. The interaction between moisture and temperature ($MC \times T$) did not provide any significant response for any of the 5 variables studied. Bulk density was the variable that suffered most from interference by the different parameters taken separately, such as temperature and pressure, and by the ($MCxP$) second order interaction and the ($MC \times P \times T$) third order interaction. Gravimetric yield and fixed carbon content were significantly influenced by the pressure, the end temperature and the ($P \times T$) interaction. Lastly, the fixed carbon yield was significantly affected by the impact of moisture and pressure taken separately, with the calorific value only being affected by the carbonization temperature and the ($P \times T$) interaction. The P-value is discussed in the following sections where results for each response variables are reviewed.

One of the main applications of ANOVA is multiple comparisons testing whose aim is to check if the parameters for the various categories of a factor differ significantly or not. Numerous tests have been proposed for comparing the means of categories. Tukey’s test is the most used (HSD: Honestly Significant Difference). It is a single-step multiple comparison procedure and statistical test generally used in conjunction with an ANOVA to find which means are significantly different from one another. The test compares the means of every treatment to the means of every other treatment; that is, it applies simultaneously to the set of all pairwise comparisons and identifies where the difference between two means is greater than the standard error would be expected to allow. For example, in our case where 18 treatments are applied to biomass, we want to know not only if the treatments have a significant effect, but also if the treatments have different effects. We applied this test to each of the response variables. We identified 6 statistically equal groups for the charcoal yield, 5 for the fixed carbon yield, 2 for both the bulk density, the fixed carbon content and the gross calorific value. The results are shown in Table 6.
Table 4
Summary statistics for the experimental factorial design performed considering a mean of two replicates.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std dev</th>
<th>R²</th>
<th>Coef. of variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal yield (wt. %)</td>
<td>29.300</td>
<td>43.500</td>
<td>35.506</td>
<td>4.942</td>
<td>0.900</td>
<td>6.15</td>
</tr>
<tr>
<td>Fixed carbon yield (wt. %)</td>
<td>26.100</td>
<td>30.000</td>
<td>28.050</td>
<td>1.244</td>
<td>0.86</td>
<td>2.47</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>0.320</td>
<td>0.660</td>
<td>0.393</td>
<td>0.077</td>
<td>0.81</td>
<td>12.64</td>
</tr>
<tr>
<td>Fixed carbon content (wt. %)</td>
<td>68.300</td>
<td>89.700</td>
<td>80.206</td>
<td>9.178</td>
<td>0.96</td>
<td>3.21</td>
</tr>
<tr>
<td>Gross cal. value (kcal kg⁻¹)</td>
<td>7015.000</td>
<td>8226.000</td>
<td>7669.889</td>
<td>475.195</td>
<td>0.96</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Table 5
Analysis of variance of the Moisture Content (MC), Pressure (P) and Temperature (T) parameters, along with their first, second and third order interactions for the five response variables analyzed; "*" = significant at 5%; ns = not significant at 5%. The p-values are in italic.

<table>
<thead>
<tr>
<th>Variable</th>
<th>MC</th>
<th>P</th>
<th>T</th>
<th>(MC×P)</th>
<th>(MC×T)</th>
<th>(P×T)</th>
<th>(MC×P×T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal yield (wt. %)</td>
<td>ns</td>
<td>*</td>
<td>*</td>
<td>ns</td>
<td>ns</td>
<td>*</td>
<td>ns</td>
</tr>
<tr>
<td>Fixed carbon yield (wt. %)</td>
<td>0.1127</td>
<td>&lt;0.0001</td>
<td>&lt;0.0001</td>
<td>0.9383</td>
<td>0.6652</td>
<td>0.0331</td>
<td>0.9265</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>0.0061</td>
<td>&lt;0.0001</td>
<td>0.4102</td>
<td>0.8313</td>
<td>0.0923</td>
<td>0.3743</td>
<td>0.8538</td>
</tr>
<tr>
<td>Fixed carbon content (wt. %)</td>
<td>0.0015</td>
<td>0.0031</td>
<td>0.9471</td>
<td>0.0027</td>
<td>0.1826</td>
<td>0.2022</td>
<td>0.0431</td>
</tr>
<tr>
<td>Gross caloric value (kcal kg⁻¹)</td>
<td>0.2179</td>
<td>0.0029</td>
<td>&lt;0.0001</td>
<td>0.6892</td>
<td>0.6444</td>
<td>0.0239</td>
<td>0.7581</td>
</tr>
</tbody>
</table>

For greater clarity, we chose for each response variables the 5 most favorable treatments out of the 18 applied.

4.2. Charcoal yield

Table 5 shows that P, T and PxT second order interaction were the only variables having a significant impact on charcoal production. It can be seen that the highest values of charcoal yield, 40% and over, were obtained for the highest pressures at a temperature of 450 °C (Table 3). These results corroborated those found in the literature with Eucalyptus, with yields exceeding 42% at 10 bars and 450 °C. We noted moisture content did not affect charcoal yields as we used a retort reactor with an outside energy source. Fig. 2 shows the effect of the Temperature, Pressure and Pressure x Temperature second order reaction on charcoal yield. Means are statistically different when we increase temperature from 450 to 600 °C. The same results are observed for the pressure. Whilst, overall, charcoal yields increased, only the switch from 0 to 5 bars or 0 to 10 bars for both the two temperatures positively and significantly affected charcoal production. Between 5 and 10 bars, there are no significant differences. We found values very close to those obtained in the literature with Eucalyptus, with yields exceeding 42% at 10 bars and 450 °C. We noted that the greatest increases were obtained for low pressures. These results corroborated those obtained by Numazawa [16] for pressures under 10 bars, beyond which the pressure had little effect [13]. Sjoestroem and Chan also concluded that increasing pressure did not seem to increase char yield. The fixed-carbon yield they obtained

Table 6
Classification by Tukey’s test in increasing order for the 5 response variables: charcoal yield, fixed carbon yield, bulk density, fixed carbon content and gross caloric value. For each group, the means with the same letter were not significantly different at 5% (α = 0.05).

<table>
<thead>
<tr>
<th>Significant minimum difference</th>
<th>Ranking</th>
<th>Means (wt. %)</th>
<th>Exp. N°</th>
<th>MC (wt. %)</th>
<th>P (bars)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal yield (6 groups)</td>
<td>8.77</td>
<td>43.5ᵃ</td>
<td>5</td>
<td>0</td>
<td>10</td>
<td>450</td>
</tr>
<tr>
<td>Fixed carbon yield (5 groups)</td>
<td>2.78</td>
<td>30.0ᵇ</td>
<td>6</td>
<td>0</td>
<td>10</td>
<td>600</td>
</tr>
<tr>
<td>Bulk density (2 groups)</td>
<td>0.19</td>
<td>0.66ᵃ</td>
<td>17</td>
<td>110</td>
<td>10</td>
<td>450</td>
</tr>
<tr>
<td>Fixed carbon content (2 groups)</td>
<td>10.35</td>
<td>89.7ᵃ</td>
<td>8</td>
<td>15.5</td>
<td>5</td>
<td>600</td>
</tr>
<tr>
<td>Gross caloric value (2 groups)</td>
<td>501.69</td>
<td>8226ᵃ</td>
<td>18</td>
<td>110</td>
<td>10</td>
<td>600</td>
</tr>
</tbody>
</table>
approached the theoretical value more when the isotherm temperature decreased, even at atmospheric pressure [30]. Other works showed the thermochemical equilibrium calculations indicate that a moderate temperature (\(b \approx 400 ^\circ C\)) greatly favors the production of carbon and predict an insignificant effect of pressure on charcoal yield [14]. These results reveal that pressure is not the only factor that increases fixed-carbon yield and that slow pyrolysis is highly recommended for the first phase, i.e. up to 50% mass loss from the wood samples [31]. The combined effect of pressure and moisture content did not have any significant effect on charcoal production. For each pressure, the gravimetric yields obtained at the different moisture contents were considered statistically equivalent. We found the highest positive variations (+12.3% on average) between 0 and 5 bars.

### 4.3. Fixed carbon yield

Pressure and moisture content were the two factors that significantly affected the fixed carbon yield (Table 6). For pressure, we found that the fixed carbon yield had a tendency to rise with a significant gain between a pressure of 0 and 5 bars (+7.14%) as opposed to 1.75% between 5 and 10 bars. For moisture content, we found that there was an overall decrease, but with smaller variations: −2.1% and −1.8% (Fig. 3). As for charcoal yield, Tukey's test showed for the first 5 results that the means of the fixed carbon yields were not significantly different. When looking at the results for the 18 treatments carried out, we had to reach the tenth rank (T16) before we had statistically different means. Treatment T6 gave the best result \((Y_{\text{char}} = 34.2\%, Y_{\text{fixed-c}} = 30\%, \text{fixed-C} = 87.6\%)\). It differed from T5, with the best charcoal production, through its higher temperature (600 °C). Under the same pressure conditions, but with a lower temperature and a 1-hour carbonization time, Antal [15] obtained 46.1%, 32.8% and 70.6% for charcoal yield, fixed carbon yield and fixed carbon content respectively. According to the same author, the fixed carbon yield values generally exceeded the expected theoretical yields by 80%. For low temperature isotherms, favor secondary solid–vapor reactions, actually increase the fixed-carbon yield. Elyounsi and his co-author [14] obtained with eucalyptus the maximum value of the fixed-carbon yield reached in the vicinity of 50% mass loss were very high and approached those obtained under high pressure for alder, birch, oak, pine, spruce and eucalyptus wood. They amounted to 32% for the Eucalyptus samples at 360 °C.

The composition of the biomass, and especially the lignin content, has a positive impact on the fixed carbon yield [15]. Water vapor production at high pressure would seem to have led to the formation of polyhydric non-volatile phenols by saponification of ether bonds between the lignin fragments. A free radical mechanism has been suggested as a major route during the early lignin degradation stages followed by a combined free radical and concerted pathway at elevated temperatures [32]. Recent studies have shown that for temperatures over 280 °C, severe recondensation reactions lead to considerable enrichment of resistant interunit bonds in thermally-treated lignins [33]. Regarding the effect of water content, some studies have shown the impact of steam flow on the yield and the properties of the products obtained in pyrolysis of selected samples of agricultural and forestry wastes. The steam would contribute to the formation of solid residues [34].

### 4.4. Fixed carbon content

The fixed carbon content was affected by pressure, the final temperature and the P×T interaction. We traced variations in the fixed carbon yield and the fixed carbon content depending on the P×T pair (Fig. 4). The fixed carbon content tended to decrease as pressure increased. The statistical analysis showed the decrease to be more significant between 0 and 5 bars at 450 °C, recording a drop of 8.3% compare to a drop of 1.2% between 5 and 10 bars. The best fixed carbon concentrations were obtained with the higher temperature treatments.

![Fig. 2. Effect of T(a), P(b) and the PxT(c) second order interaction on charcoal production (average value). ns = not significant; * = significant.](image-url)

![Fig. 3. Effect of pressure and water content on the mean of fixed carbon yields. (ns) = not significant; (*) = significant.](image-url)
4.5. Bulk density

The analysis of variance showed that bulk density was the variable most affected by the interference of the different parameters: T, P, MC×P and MC×P×T. The best four treatments were obtained for the saturated samples carbonized at a pressure of 0 and 5 bars (Table 6). The values obtained (0.42 to 0.66 g/cm³) were in average over those obtained on different 6 and 7-year-old eucalyptus clones under the same conditions (increase of +23.5 to +94.1%) [35]. Independently from the treatment pressure and temperature, the bulk density of the charcoal remained the same for an anhydrous sample or one with 15% relative humidity. Between a 15% and a 110% moisture content, the density of the charcoal increased significantly (+18%) reaching a value of 0.45 g/cm³. When only considering the pressure variable, the density increased 19% on average between atmospheric pressure and 10 bars. The Tukey test showed a significant difference only between these 2 values. From 0 to 5 bars and 5 to 10 bars, the means variations are not statistically different. Fig. 5 shows the changes in bulk density depending on the (P×MC) interaction. For a saturated sample, pressure strongly affected density, with a gain of 20% and 33% when it rose from 0 to 5 bars and 5 to 10 bars respectively. Only the increase between 5 and 10 bars was statistically significant. It was interesting to note that between carbonization at atmospheric pressure and carbonization at a pressure of 10 bars, the density underwent a significant increase of 60%, reaching an average rather than a 0.57 g/cm³. Some studies established a linear relationship between the bulk density of wood and carbonized wood [36]. To explain the pressure effect, more mechanical and chemical investigations are necessary.

4.6. Gross caloric value

The analysis of variance showed that this variable was only influenced by the temperature and the Pressure x Temperature interaction (Table 5). This parameter was closely linked to the fixed carbon content. We obtained the best results for high temperatures, with 7222 kcal/kg and 8117 kcal/kg for 450 and 600 °C respectively, i.e. an increase of 12% all parameters combined. The mean GCV values depending on the first order P×T interaction. GCV was found to decrease when pressure was increased at 450 °C, whereas the tendency was reversed at 600 °C. Tukey’s test showed that these variations for a given temperature were not significant. Only the variations obtained between 450 °C and 600 °C were statistically significant (Table 7). The main explanation comes from the correlation with their lignin content. There is a highly significant linear correlation between the high heating value (HHV) of the biomass fuel and the lignin content [37].

5. Conclusions

i. This study was based on a strict experimental design and a statistical analysis based on the GLM procedure from a Statistical Analysis System (SAS). Five variables in response to the experiments were analyzed and discussed: the charcoal yield (ychar), the fixed carbon yield (yF), the bulk density (D), the fixed carbon content (F) and the gross caloric value (GCV). The results showed excellent reproducibility of the assays with a coefficient of variation approaching 7%.

ii. Although the carbonization temperature is generally the most important factor during pyrolysis, pressure alone significantly affected 4 of the 5 variables studied. If it was in interaction with the temperature, then all the response variables were significantly influenced.

iii. Bulk density was the response variable that was most influenced by the experimental variations. It was alone in being significantly affected by the third order (MC×P×T) interaction. It increased by 19% between 0 and 10 bars with a maximum value of 0.66 g/cm³. The values obtained with saturated samples were higher than those obtained with anhydrous samples or samples with a 15% moisture content.

iv. Pressure had a positive effect on charcoal yields, with more pronounced effects at 450 °C. The highest value was obtained on anhydrous wood at 450 °C and a pressure of 10 bars. Increasing pressure from 0 to 5 bars independently of the temperature gave the best results with values varying from 32.4 to 36.4%, i.e. an increase of more than 12%. For pressures approaching 10 bars, the charcoal yield stabilized. Our assays showed that the moisture content had no effect on charcoal yields.

v. The results obtained for fixed carbon yields tallied with those found in the literature. This variable was significantly affected by the moisture content of the sample and the operating pressure. The best results were obtained for high pressures,
whatever the temperatures. The highest value (30%) was obtained with anhydrous samples at a pressure of 10 bars at 600 °C.

vi. The fixed carbon content was significantly influenced by the pressure, temperature and second order (P × T) interaction. The fixed carbon content tended to decrease as pressure increased. The statistical analysis showed that the decrease was significant between 0 and 5 bars at 450 °C, recording a drop of 8.3%. The best fixed carbon concentrations were obtained for the high pressure treatments, with values between 87.6 and 89.7%. The maximum value (89.7%) was obtained for a sample stabilized at 15.5% humidity at atmospheric pressure and at 600 °C.

vii. The calorific value increased in line with the fixed carbon content. This response variable was significantly affected by the temperature and the second order (P × T) interaction. At 450 °C, pressure had a negative effect on GCV. Only the variations obtained between 450 °C and 600 °C were statistically significant with mean values of 7222 kcal/kg and 8117 kcal/kg respectively. The maximum value (8226 kcal/kg) was obtained for a saturated sample at a pressure of 10 bars at 600 °C.

viii. Given the demands of the steelmaking sector, the best charcoal would appear to be obtained with an anhydrous wood, a pressure of 10 bars and a temperature of 600 °C. The fixed carbon yield was found to be 30%, the apparent density 0.4 g/cm3, the fixed carbon content 87.6% and the calorific value 8090 kcal/kg.

Acknowledgments

Laboratory work was supported by the Forestry and Geoprocessing Technology Foundation (Funtec). Part of that work was supported by a grant from CIRAD. We thank Professor Lúcio José Vivaldi from the University of Brasilia (UnB) and Professor Vincenzo Esposito Vinzi from the ESSEC Business School for their technical support in the statistical analysis.

References