Effect of wood properties and production process on stiffness of charcoal studied by ultrasonic technique

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Abstract

Charcoal can replace coke in blast furnaces avoiding the use of reducing agents derived from fossil fuels. However, the main limitation of charcoal is its lower strength, which is essential for supporting the iron ore load inside the blast furnaces. In order to improve and control the charcoal quality, the objectives were then to study (i) the influence of radial position of the raw material and carbonization temperature on charcoal density and rigidity, and (ii) the link between properties of wood and charcoal taking into account the previous factors. It was found that: (a) The charcoal MOE increased with the final temperature of pyrolysis, but the temperature effect was less significant for the density. (b) The charcoal properties were higher for samples cut near the bark, but an elevated carbonization temperature seemed to reduce this phenomenon. (c) The best predictors to estimate the charcoal quality were the wood density and the carbonization temperature.

Keywords: charcoal quality, carbonization temperature, juvenile wood, ultrasounds

Introduction

World steel production is dependent on coking coal. Steel is an alloy based primarily on iron, and the iron ore must be converted, or 'reduced', using carbon during the making process. The primary source of this carbon is coking coal. During the iron-making process, the heated air (1200°C) is blown into the blast furnace, and causes the coke to burn, producing carbon monoxide which reacts with the iron ore, as well as heat to melt the iron. Charcoal has often been compared to coke and can replace it in blast furnaces avoiding the use of reducing agents derived from fossil fuels. However, the main limitation of charcoal as replacement coke is its low compression strength, which is essential for supporting the iron ore load inside the blast furnaces. The effect of wood properties as well as parameters of carbonization process on the strength of charcoal has been studied. Wood density was found to be positively correlated to the apparent density of charcoal (Antal and Grønli 2003). Charcoals produced with dense woods were characterized by a higher mechanical resistance. Blankenhorn et al. (1978) showed, when carbonizing Black Cherry wood, that charcoal density decreased until 600 °C, then increased with the increase of temperature until 900 °C. Vieira (2009) observed that the acoustic modulus of elasticity of charcoal from *Eucalyptus* sp. increased with the increase of the carbonization temperature from 350 to 900 °C. Considering the radial position, the mechanical resistance increased from the pith to the bark. Trugilho et al. (1996) showed that juvenile wood produced a less resistant charcoal than mature wood. Moore et al. (1974) tested carbonized wood from Birch trees in a temperature range of 200-700°C. The compression strength of charcoal decreased up to approximately 500 °C then increased. These tendencies were also observed by Oliveira et al. (1982) for *Eucalyptus* sp. Ultrasonic velocity was measured for yucca, before and after carbonization (Krzesińska and Zachariasz 2007). It was found that the velocity of charcoal decreased

up to 300°C, then increased between 300-750°C and was quasi-constant for higher temperatures. From previous results obtained by the cited authors, it is known that charcoal density and compression strength are linked to wood density and rigidity. Furthermore, this link is function of the radial position and the pyrolysis temperature. In order to improve and control the charcoal strength, our questions were thus: How to predict the charcoal properties from the wood properties? And what will be the accuracy of such estimates? The mechanical strength of the charcoal beds in the Brazilian context of iron and steel furnaces is very important and contribute for reduce the specific consumption of the industrial units. The purpose of this work was to study (i) the influence of radial position and carbonization temperature on charcoal density and rigidity and (ii) the link between properties of wood and charcoal taking into account the previous factors. Density and longitudinal modulus of elasticity were measured on wood samples before and after pyrolysis according to three radial positions and two final temperatures.

Material and Methods

Sample preparation

A total of 35 trees of one hybrid of *Eucalyptus urophylla* ST Blake (6 years old) were harvested. The trees came from a plantation belonging to GERDAU S.A., and were located in the same plot at Santo Antônio do Amparo, Minas Gerais - Brazil (20°56'48" S e 44°55'09" O). The plot was characterized by a flat soil with moderate winds. Cubic samples (30 mm in L, R and T directions; N = 57) were cut at 1.30 m height and at three radial positions from pith to bark. For diameters less than 18 cm, only one cubic sample was cut (identified as 'middle', N = 13). In the other case, two cubic samples were prepared (identified as 'internal', N = 22, and 'external', N = 22). After cutting, the samples were conditioned in a climatic room at 20°C and 65% of relative air humidity.

Experimental protocol

The density of the wood samples was first determined (volume computed by measuring the dimensions with a digital caliper). The modulus of elasticity was then assessed by ultrasonic measurements in the longitudinal direction. In a second step, the cubic samples were pyrolized. The bulk density of the charcoal samples was measured according to the ASTM D2395-07 (volume by water immersion). The samples were waterproofed with a very thin layer of grease before obtaining charcoal volume (grease used as couplant for the ultrasonic tests). The modulus of elasticity of the charcoal samples was finally determined by ultrasounds.

Pyrolysis process

The cubic samples were pyrolized at two final temperatures: 500°C and 900°C. The samples population was previously divided into two batches: the samples were sorted according to the wood density, and the even ranks were associated to a pyrolysis temperature of 500°C (odd ranks with a temperature of 900°C). Pyrolysis was performed in a specific electric reactor developed by Cirad (Macro-ATG), using a heating rate of 1.5 °C/min. After carbonization, the samples were conditioned in a climatic room at 20°C and 65% of relative air humidity.

Ultrasonic testing

Two contact transducers were used in transmission mode. Each sample was placed between the piezoelectric transducers with silicon grease used as coupling medium. The emission frequency was set to 1 MHz, and the received signal was digitized with a 12-bit resolution and a sampling period of 0.1 µs (the average propagation time is 6.4 µs for wood). A computer algorithm calculated the propagation time by determining a threshold based on an analysis of the statistical properties of the signal noise. This determination method was appropriate in this case given that the signal-to-noise ratio was greater than 30 dB. The ultrasonic modulus of elasticity (MOE) was determined by the

conventional Equation (1), where ρ is the density, L is the sample length, and τ is the propagation time. The mean of three measurements was used to determine the MOE value of each sample.

$$MOE = \rho\left(\frac{L}{\tau}\right)^2 \quad (1)$$

Statistical analysis

The comparison between averages was carried out by a nonparametric Wilcoxon test because of the low number of samples. The kernel density estimation method (KDE) was chosen to build the probability density function graphs. Analysis of covariance evaluated the influence of variables related to wood, carbonization process and their interaction on the charcoal mechanical property. The descriptive statistics, comparisons between means and the analysis of covariance were performed using the R statistical software (version 3.1.1, 2014).

Results

Influence of radial position on wood properties

Table 1 - Descriptive statistics of wood density and MOE according to radial position. SD: standard deviation.

Radial position	Number of samples	Density ($kg.m^{-3}$)				MOE (MPa)			
		Min.	Max.	Average	SD	Min.	Max.	Average	SD
Internal	22	473	610	518	40	8939	12546	10397	964
Middle	13	491	616	556	40	10347	17912	14315	2272
External	22	484	697	588	54	9765	17202	14116	1924

The descriptive statistics of wood density and MOE according to radial position were summarized in Table 1. Figure 1 showed the associated probability density functions. The wood properties were found to be lower near the pith. The density values varied from 473 kg/m^3 near the pith to 697 kg/m^3 near the bark, and from 8939 MPa to 17912 MPa for MOE. The variation patterns of density were similar to those of MOE (Figure 1). The 'middle' and 'external' curves were superimposed (average density of 556 kg/m^3 and 588 kg/m^3, average MOE of 14315 MPa and 14116 MPa), and these curves were different from the 'internal' probability density function (average density of 518 kg/m^3, average MOE of 10397 MPa). From this last observation it was deduced that the samples population should be divided into two groups and not into three groups prior further analysis.

Table 2 - Wilcoxon unpaired tests for wood density and MOE according to radial position. Significance levels: 0.0001 '***'; 0.001 '**'; 0.01 '*'; 0.05 '.'; Non-significant 'ns'.

Wood Properties	Wilcoxon *p* (bilateral)		
	Internal vs. Middle	Middle vs. External	Internal vs. External
Density ($kg.m^{-3}$)	0.01*	0.12^{ns}	<0.001**
MOE (MPa)	<0.001**	0.84^{ns}	<0.001**

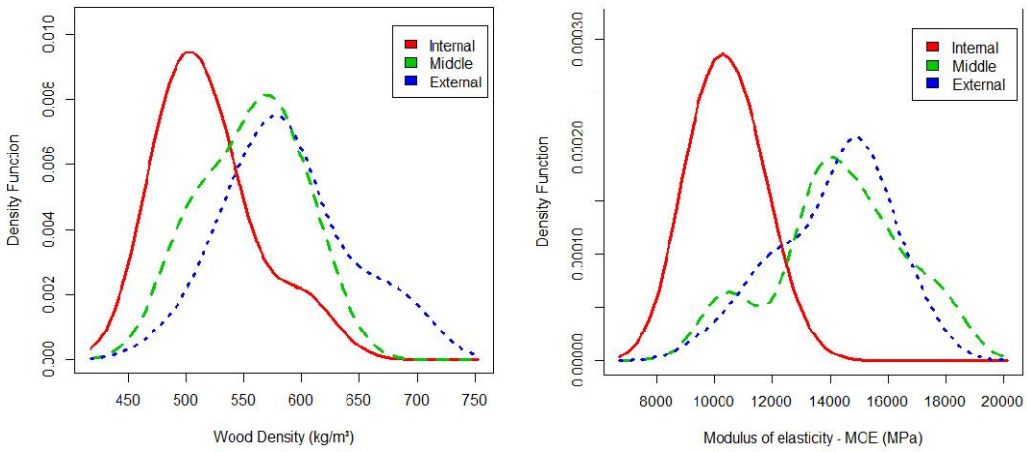


Figure 1 – Probability density function of wood density and MOE according to radial position.

The probability distributions were tested using the Kolmogorov–Smirnov test, and the Wilcoxon test was used to compare means. These tests led to the same conclusion, and confirmed the existence of two groups according to the radial positions. The Wilcoxon test results were presented in Table 2. In the following of the article, the samples population was thus divided into two groups identified as 'Internal' (N = 22) and 'Mid-Ext' (N = 35).

Influence of radial position and carbonization temperature on charcoal properties

Table 3 - Descriptive statistics of charcoal density and MOE according to radial position and carbonization temperature. SD: standard deviation.

Charcoal density (kg.m^{-3})										
Radial position	500°C					900°C				
	N	Min.	Max.	Average	SD	N	Min.	Max.	Average	SD
Internal	11	224	328	250	27.8	11	251	334	291	23.2
Mid-Ext	17	246	369	309	35.4	18	259	484	341	58.2
Charcoal MOE (MPa)										
Radial position	500°C					900°C				
	N	Min.	Max.	Average	SD	N	Min.	Max.	Average	SD
Internal	11	985	1346	1052	100.5	11	2962	4237	3379	387.1
Mid-Ext	17	1089	1592	1372	137.3	18	2880	6153	4047	850.5

The descriptive statistics of charcoal density and MOE according to radial position and carbonization temperature were presented in Table 3. Wilcoxon tests were used to study the influence of the two factors (Table 4). The radial position and the carbonization temperature had significant effects on the density and the elastic modulus. The MOE increased with the final temperature of pyrolysis, from 1052 MPa to 3379 MPa for the internal position, and from 1372 MPa to 4047 MPa for the Mid-Ext position (the charcoal was 3 times more rigid at 900°C than at 500°C). This effect was less pronounced for the density, from 250 kg/m^3 to 291 kg/m^3 for the internal position, and from 309 kg/m^3 to 341 kg/m^3 for the Mid-Ext position (the density was 1.13 times greater at 900°C than at 500°C). The difference between 309 kg/m^3 and 341 kg/m^3 was non-significant (p=0.106) with the Wilcoxon test. The charcoal MOE and density were found to be higher for the Mid-Ext position than for the internal position. The relative difference between the radial positions was reduced for 900°C. The density ratio (Mid-Ext/Internal) was 1.24 at 500°C and 1.17 at 900°C; the MOE ratio was 1.30 at 500°C and 1.20 at 900°C (this observation was shown at Figure 2, the curves were overlapped at 900°C). Thus, a high carbonization temperature seemed to soften the effect of radial position.

Table 4 - Wilcoxon unpaired tests for charcoal density and MOE according to radial position and carbonization temperature. Significance levels: 0.0001 '***'; 0.001 '**'; 0.01 '*'; 0.05 '.'; Non-significant 'ns'.

Charcoal properties	Combination of factors	Wilcoxon *p* (bilateral)
Density (kg.m^{-3})	Internal and 500°C / 900°C	0.002*
	Mid-Ext and 500°C / 900°C	0.106^{ns}
	500°C and Internal / Mid-Ext	<0.001**
	900°C and Internal / Mid-Ext	0.016*
MOE (MPa)	Internal and 500°C / 900°C	<0.001**
	Mid-Ext and 500°C / 900°C	<0.001**
	500°C and Internal / Mid-Ext	<0.001**
	900°C and Internal / Mid-Ext	0.016*

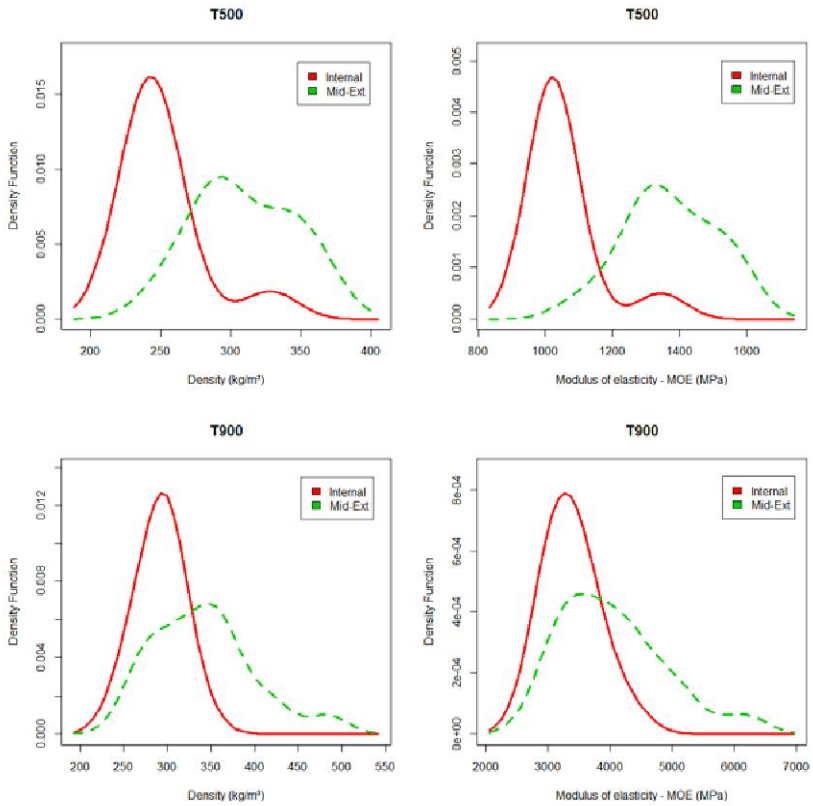


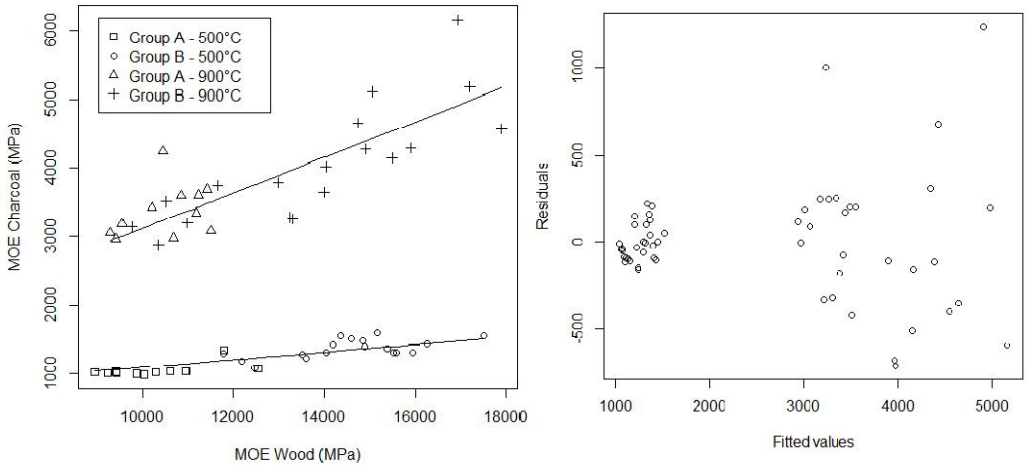
Figure 2 – Probability density function of charcoal density and MOE according to radial position (Internal, Mid-Ext) and carbonization temperature (T500, T900).

Link between properties of wood and charcoal according to radial position and carbonization temperature

The relationships between charcoal and wood properties according to the coupled effects of temperature and radial position were carried out with the analysis of covariance. The full influence of factors with interactions was initially taken into account for the modeling (wood density or MOE, final temperatures 500°C and 900°C, radial positions Internal and Mid-Ext). The models were then refined using the AIC criterion in a stepwise algorithm. At the end of the procedure, only the significant variables were kept in optimal models. The results were presented in Table 5. The effect of radial position was not present in the optimal models. The temperature effect was not included as an additive constant, but in the slope of the regression models (see the difference of slope in Figure 3).

Table 5 – Regression coefficients and model characteristics between charcoal and wood properties. T900: value of 1 for a temperature of 900°C and zero for 500°C. N = 57. RSE: Residual standard error.

Charcoal density (kg/m^3)				
Intercept	Wood density	Wood density * T900	RSE	Adjusted R^2
-151.1	0.792	0.060	17.3	0.89
Intercept	Wood MOE	Wood MOE * T900		
106.9	0.014	0.003	28.8	0.69
Charcoal MOE (MPa)				
Intercept	Wood density	Wood density * T900	RSE	Adjusted R^2
-1761	5.429	4.587	308	0.95
Intercept	Wood MOE	Wood MOE * T900		
543	0.055	0.203	335	0.94



(a) (b)

Figure 3 - Relationship between charcoal and wood MOE (a) according to carbonization temperature and radial position (Group A for internal position and Group B for Mid-Ext position). (b) Dispersion of residues. N = 57.

The best predictor to estimate the charcoal density was the wood density (Adjusted R^2 of 0.89 with wood density, and 0.69 with wood MOE). The standard error of the charcoal density estimation by the wood density was 17.3 kg/m^3 associated with an average charcoal density of 287 kg/m^3 at 500°C and of 322 kg/m^3 at 900°C. However, the models with wood density or wood MOE were quasi-equivalent to predict the charcoal MOE (Adjusted R^2 of 0.95 with wood density, and 0.94 with wood MOE). The standard error of the charcoal MOE estimation by the wood density was 308 MPa associated with an average charcoal MOE of 1251 MPa at 500°C and of 3794 MPa at 900°C. The difference of adjusted determination coefficient between charcoal density (0.89; 0.69) and charcoal MOE (0.95; 0.94) was due to the difference of dispersion (coefficient of variation of 17% for charcoal density, and of 56% for charcoal MOE, considering the 57 samples). The model between charcoal and wood MOE was presented as example at Figure 3a. The model equation was: Charcoal MOE = 543 + 0.055 Wood MOE + 0.203 Wood MOE*T900. This equation was equal to: Charcoal MOE = 543 + 0.055 Wood MOE for 500°C and Charcoal MOE = 543 + 0.258 Wood MOE for 900°C. The scatterplot of the residuals was presented at Figure 3b. It was observed that the standard error of the residuals was different between 500°C (RSE=110 MPa) and 900°C (RSE=474 MPa); the RSE model being equal to 335 MPa (Table 5). The residues at 900 °C were more scattered than those at 500 °C.

Discussion

The samples population was divided into two groups in order to study the effect of radial position. For small diameters, only one cubic sample was cut in the middle of the radius; otherwise, two samples were taken. The pertinence of the sampling location was a question during the study; this was solved by a statistical analysis allowing to group locations with similar properties. The radial variation observed for the wood properties (density and MOE) was explained by the transition juvenile to mature wood. The wood properties were lower near the pith. From references cited in introduction, the charcoal density and the mechanical properties of charcoal are linked to wood properties. This link is function of the radial position and the pyrolysis temperature. Our observations were in agreement with the references cited. In the same way, the charcoal properties were found to be higher for the external position than for the internal position: this observation was in agreement with the cited references (denser wood produced denser charcoal). It was observed that the charcoal MOE increased with the carbonization temperature, but this phenomenon was less pronounced for the charcoal density. The density is linked to porosity. The porosity of charcoal is closely associated to the wood porosity, the temperature of carbonization, and the speed of carbonization (Blankenhorn et al. 1978, Oliveira et al. 1982). Blankenhorn et al. (1978) indicated that for *Prunus serotina* Ehrh., the porosity increased with the increase of temperature up to 600 °C and then decreased with temperatures up to 900 °C. Thus, the density decreased until 600 °C, and increased with the increase of temperature until 900 °C due to the occurrence of lower weight loss in relation to shrinkage. The rigidity is linked to the density (amount of matter per unit of area) and to the rigidity of matter. At temperatures above 375°C, lignin is the key component of the charcoal formation. The majority of the carbohydrate polymers have degraded between 300-375°C and mainly products from lignin conversion remain. Lignin has the highest heat of combustion, the highest charcoal yield and also the lowest percent of volatiles. Lignin starts to decompose at about 200°C, but is much more stable to thermal decomposition as compared to carbohydrate polymers. The increase of resistance from 500 °C is due to the structural rearrangement of the charcoal components, especially carbon (Beall et al. 1974, Moore et al. 1974, Oliveira et al. 1982). According to Oliveira et al. (1982) this structural rearrangement is accompanied by the increase of apparent density of charcoal. The carbonized wood presents graphite-type crystalline forms despite being considered as non-graphitic material (Emmerich 1987). It was suggested that the bonding between carbon atoms is modified between 600 °C and 800 °C, which is the starting point to formation of macromolecules (from amorphous structure to crystalline structure) (Manabe et al. 2007). The increase of temperature, between 500°C to 900°C, induced an increase of charcoal density coupled with a structure more and more crystalline and rigid. The effect of radial position on the charcoal properties was found to be reduced by a high carbonization temperature. The juvenile wood is characterized by a high cellulose microfibril angle in the S2 cell wall layer and a low density (short fibers with thin walls and low percentage of latewood in the annual rings). In hardwoods the chemical composition shows little change from pith to bark, while softwoods have wood cores with lower cellulose and higher lignin. Above 500°C, the cellulose was largely converted and the chemical composition was quasi-constant from pith to bark; only the wood density variation should induced a variation in the charcoal properties. However, between 500°C and 900°C, the charcoal density increased due to shrinkage of cell walls. The hypothesis to explain the link between the radial position effect and the carbonization temperature was that the wood density variation was counterbalanced by the shrinkage variation along the radial axis. The effect of radial position was not present in the regression models linking the properties of wood and charcoal. The radial position should be seen as a hidden variable because the cutting position in the radius allowed maximizing the variation of the wood properties. It was also found that the temperature effect was included in the slope value of the regression models. It was expected that the constant was nil (or non-significant) because when the wood MOE tends to zero, the charcoal MOE should tend to zero. The fact that the best predictor to estimate the charcoal properties was the wood density was explain by the known correlation between wood density and wood MOE coupled with low measurement error on wood density compared to wood MOE. Figure 3b showed that the residues at 900 °C were more scattered than those at 500 °C. The measurement error of charcoal MOE was higher at 900°C. The sides of the samples were not flat but irregular due to the occurrence of shrinkage between 500-900°C.

Conclusions

The radial position and the carbonization temperature had significant effects on charcoal density and rigidity. The charcoal MOE increased with the final temperature of pyrolysis; this effect was however less pronounced for the charcoal density. Furthermore, the charcoal MOE and density were found to be higher near the bark, but a high carbonization temperature seemed to soften this effect of radial position. The relationships between charcoal properties and wood properties were modeled taking into account the full influence of factors with interactions. The effect of radial position was not present in the final models. The temperature effect was present in the slope of the regression models. The best predictor to estimate the charcoal density was the wood density. The models with wood density or wood MOE were quasi-equivalent to predict the charcoal MOE. The wood density was then the adequate variable to estimate both charcoal density and MOE. Careful controls of raw material and pyrolysis conditions are required to produce charcoal with sufficient properties to substitute coke in blast furnaces. Taking into account the final pyrolysis temperature, the wood density is an important property which allows controlling the charcoal density, rigidity and strength.

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