RAUL DE ABREU NETO

INFLUENCE OF WOOD DENSITY AND FINAL TEMPERATURE OF PYROLYSIS ON THE MECHANICAL PROPERTIES OF CHARCOAL

LAVRAS–MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-graduação em Ciência e Tecnologia da Madeira, área de concentração em Ciência e Tecnologia da Madeira, para obtenção do título de Doutor.

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INFLUENCE OF WOOD DENSITY AND FINAL TEMPERATURE OF PYROLYSIS ON THE MECHANICAL PROPERTIES OF CHARCOAL

INFLUÊNCIA DA DENSIDADE DE MADEIRA E TEMPERATURA FINAL DA PIROLISE NAS PROPRIEDADES MECÂNICAS DO CARVÃO

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-graduação em Ciência e Tecnologia da Madeira, área de concentração em Ciência e Tecnologia da Madeira, para obtenção do título de Doutor.

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"... standing upon the shoulders of giants"

Sir Isaac Newton

ABSTRACT

Hardness, stiffness, porosity and crystallinity have been considered important indicators of mechanical quality of many materials. However, there is a lack of specific methodologies to evaluate mechanical properties of charcoal, making it difficult to standardize the tests. New techniques for properly classifying charcoal are necessary and non-destructive methods can be an efficient alternative to classifying charcoal in terms of quality. The hypothesis of this study is that hardness and stiffness obtained by non-destructive methods can be used as a new criterion for classifying quality of charcoal in terms of mechanical performance in blast furnaces. Therefore, the aim of this study was to determine to what extent wood density and final pyrolysis temperature affect hardness, stiffness, surface area and crystallinity of charcoal for steel use. For this, nine plant materials were pyrolyzed at final temperatures of 300, 450, 600 and 750°C, were analysed: stiffness, by ultrasound; surface area, by BET method; crystallinity, by X-Ray diffraction; dynamic hardness, by Portable Hardness Tester and classification of density and hardness by Near Infrared Spectroscopy. Mean dynamic hardness of untreated wood was 29.8 MPa, the stiffness was 3,920 MPa and the density was 0.791 $g.cm^{-3}$. In general, pyrolysis temperature decreases mechanical properties of material. Increase temperature from 300 to 750°C decreases hardness, 10.89 to 3.05 MPa, the stiffness from 2,794 to 1,278 MPa and density from 0.634 to 0.444 $g.cm^{-3}$. Charcoals produced at temperature at 450, 600 and 750°C exhibit similar behaviour, with low absorbance compared to wood and thermally treated material at 300°C, indicating homogenization of charcoal caused by pyrolysis temperature. NIR spectroscopy models were successfully developed for estimating pyrolysis final temperature, charcoal density and its dynamic hardness. The statistics of the models indicate that NIR spectroscopy is an efficient solution to quickly estimate density and hardness of charcoal. Considering the genetic materials, the highest values of wood stiffness were presented by *C. citriodora* and *E. deglupta*, same materials presented highest density and dynamic hardness, confirming high positive correlation between wood properties. Correlation between density and stiffness was R^2=0.87, for charcoal R^2=0.99. Correlation between density and hardness was R^2=0.93, for charcoal R^2 = 0.69. Correlation between stiffness and hardness of wood was R^2=0.79, final pyrolysis temperature negatively affects correlation between these properties. The surface area of pyrolyzed samples at 300 and 450°C were close to zero, while the pyrolyzed samples at 600 and 750°C were 358 and 327 m^2/g, respectively. In general, charcoals presented a typical behaviour of micro pores. Spectra obtained by X-ray diffraction show a change in spectral pattern of materials submitted to different pyrolysis temperatures, increased pyrolysis temperature increases formation of graphite crystals. At temperature of 750°C, similarity of spectra obtained by X-ray diffraction of different species, as well as similarity in adsorption curves of N_2 indicate the efficiency of pyrolysis process in charcoal homogenization.

Keywords: Dynamic hardness. Stiffness. Superficial area. Crystallinity. Mechanical properties.

RESUMO

Dureza, rigidez, porosidade e cristalinidade têm sido considerados importantes indicadores de qualidade mecânica dos materiais. No entanto, faltam metodologias específicas para avaliar propriedades mecânicas do carvão, dificultando a padronização dos testes. Novas técnicas para classificar o carvão vegetal em termos de qualidade são necessárias e métodos não destrutivos podem ser uma alternativa eficiente. A hipótese deste estudo é que a dureza e rigidez obtidas por métodos não destrutivos podem ser utilizadas como novo critério para classificar a qualidade do carvão em termos de desempenho mecânico em altos-fornos. Portanto, o objetivo deste estudo foi determinar em que medida a densidade da madeira e a temperatura final da pirólise afetam a dureza, rigidez, área superficial e cristalinidade do carvão vegetal para uso em aço. Nove materiais vegetais foram pirolisados nas temperaturas finais de 300, 450, 600 e 750°C, foram analisados: rigidez, por ultra-som; área de superfície, pelo método BET; cristalinidade, por difração de raios X; dureza dinâmica, por Durometro Portátil e classificação de densidade e dureza por Espectroscopia de Infravermelho Próximo. A dureza dinâmica média da madeira foi de 29,8 MPa, a rigidez foi de 3.920 MPa e a densidade foi de 0,791 $g.cm^{-3}$. Em geral, temperatura de pirólise diminui as propriedades mecânicas do material. Aumento da temperatura de 300 para 750°C diminui a dureza, 10,89 para 3,05 MPa, a rigidez de 2,794 para 1,278 MPa e densidade de 0,634 para 0,444 $g.cm^{-3}$. Carvões produzidos a 450, 600 e 750°C exibem comportamento similar, com baixa absorbância em relação à madeira e material termicamente tratado a 300°C, indicando homogeneização do carvão vegetal causada pela temperatura de pirólise. Modelos de espectroscopia NIR foram desenvolvidos com sucesso para estimar a temperatura final de pirólise, densidade de carvão e dureza dinâmica. Modelos estatísticos indicam que a espectroscopia NIR é eficiente para estimar rapidamente a densidade e a dureza do carvão vegetal. Considerando os materiais genéticos, os maiores valores de rigidez da madeira foram apresentados por *C. citriodora* e *E. deglupta*, os mesmos materiais apresentaram maior densidade e dureza dinâmica, confirmando alta correlação positiva entre as propriedades da madeira. Correlação entre densidade e rigidez foi R^2=0,87, para o carvão vegetal R^2=0,99. Entre densidade e dureza foi R^2=0,93, para o carvão R^2=0,69. Entre a rigidez e dureza da madeira foi R^2=0,79, a temperatura final da pirólise afeta negativamente a correlação entre essas propriedades. A área superficial das amostras pirolisadas a 300 e 450°C foi próxima de zero, enquanto as amostras pirolisadas a 600 e 750°C foram 358 e 327 m^2/g, respectivamente. Em geral, os carvões apresentaram comportamento típico de micro poros. Espectros obtidos por difração de raios-X mostram mudança no padrão espectral de materiais submetidos a diferentes temperaturas de pirólise, o aumento da temperatura de pirólise aumenta a formação de cristais de grafite. À temperatura de 750°C, a similaridade dos espectros obtidos por difração de raios X das diferentes espécies, bem como a similaridade nas curvas de adsorção de N_2, indicam a eficiência do processo de pirólise na homogeneização do carvão vegetal.

Palavras-chave: Dureza dinâmica. Rigidez. Área superficial. Cristalinidade. Propriedades mecânicas.

SUMÁRIO

CHAPTER 1:

General introduction

Steel industries are main charcoal consumers in Brazil (Indústria Brasileira de Árvores – IBA, 2017) and require high quality charcoal for metal production. These industries use iron ore and charcoal in the blast furnace to produce pig iron, steel, and iron. Inside the blast furnaces, charcoal generates heat, reduces iron ore naturally (Gupta, 2003; Suopajarvi et al., 2013) and supports ore loading (Oliveira and Almeida, 1980).

As wood used to produce charcoal directly influences its quality (Oliveira et al., 2010; Dufourny et al. 2018), such industries seek raw materials with adequate traits as high density (Brito and Barrichello 1977, Santos et al., 2011, Nones et al., 2015), stiffness (Babich et al., 2010, Castro et al., 2016) and hardness (Hirata et al., 2001). In this thesis, these mechanical properties are supposed to indicate charcoal quality, in terms of supporting ore loading with blast furnaces. Besides wood properties, pyrolysis process causes physical, anatomical and mechanical changes, which can influence charcoal characteristics. Pyrolysis temperature affects cellular composition and causes components degradation (Oliveira et al., 2010) changing fibrous wood into carbonized material composed mainly of graphitic carbon (Xu et al., 2017), altering the charcoal quality and stiffness (Veiga et al., 2018).

Process and vegetal material are known to influence the density (Trugilho and Silva, 2001), stiffness (Veiga et al., 2018) and hardness (Zickler et al., 2006) of charcoal. However, there are no standard methods for evaluating mechanical properties of charcoal pieces. Moreover, pyrolysis temperature is prone to alter surface area and crystallinity of charcoal changing the product quality. Although surface area of charcoal is important for mechanical performance, this characteristic does not receive much attention and few data on adsorption/desorption of charcoal is available in literature. Surface area has been commonly studied in activated charcoal (Bansal et al., 1988). The crystallinity is known to affect wood thermal expansion at low temperature (Zhao et al., 2016), but the influence of pyrolysis temperature on crystallinity of charcoal is poorly understood.

There are methods for evaluating wood hardness, such as Brinell and Janka, but these tests when applied to charcoal may be imprecise as charcoal is a brittle material. Veiga et al. (2018) evaluated stiffness of charcoal and reported lack of specific methodology difficult its study. Thus,

new solutions are necessary to evaluate and classify charcoal mechanical properties, and non-destructive equipment can be effective in this demand.

The starting hypothesis of this study was: charcoal's mechanical properties depends more on pyrolysis conditions, especially carbonization temperature, than on wood density that will give rise to charcoal.

For this purpose, the following devices and techniques were tested on charcoal:

1) The Portable Hardness Tester (DPM-3) - an equipment developed at UNESP to measure wood dynamic hardness (Assis et al., 2017) can be an alternative to evaluate dynamic hardness of charcoal;

2) Ultrasound - an effective tool in inferring physical and mechanical properties of wood and indirectly allows estimating material elastic constant (Ballarin and Nogueira, 2005) can be used to measure stiffness of charcoal.

3) Near Infrared Spectroscopy (NIRS) - a technique used to identify chemical composition of material (Baillères et al., 2002) can be used to evaluate physical, anatomical and mechanical properties. Costa et al. (2018) and Ramalho et al. (2017) used NIRS to identify different species of wood and classify charcoal by production temperature, the equipment has potential to classify charcoal by mechanical hardness;

4) Surface area by BET method (Brunauer et al., 1938), and 5) Crystallinity by X-Ray diffraction (Lopes et al., 2013) of charcoal.

In this study, the starting hypothesis is that hardness and stiffness can be used as a new criterion for classifying quality of charcoal in terms of mechanical performance in blast furnaces. Therefore, the main aim of this study was to determine to what extent wood density and final pyrolysis temperature affect hardness, stiffness, surface area and crystallinity of charcoal for steel use.

CHAPTER 2:

Dynamic hardness of charcoal varies according to the final temperature of carbonization

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ABSTRACT

Hardness has been considered to be one of the most important mechanical indicators of material quality. Here, an automated portable hardness tester was used to evaluate dynamic hardness (DH) of vegetable charcoal for industrial application, correlating these results to vegetal material and final temperature of carbonization. Wood specimens from nine vegetal materials were pyrolysed at final temperatures of 300, 450, 600, and 750 °C. A total of 45 wood specimens were used as the sample control. DH of wood and charcoal was determined by an automated portable hardness tester. Wood specimen DH varied from 12.9 to 44 MPa. Wood density (ρ) presented a high positive correlation (r = 0.94) with wood DH. The heavier wood species (ρ = 988.6 kg m−3) is on average 1.93 times denser than the lighter wood (ρ = 512 kg m−3), while the harder wood (DH = 44 MPa) is 3.41 times harder than the softer material (DH = 12.9 MPa). Charcoal specimen DH significantly varies with the final temperature of carbonization: DH was 10.89 MPa for charcoal specimens produced at 300 °C, 3.05 MPa for charcoal produced at 450 °C, 3.44 MPa for charcoal produced at 600 °C, and 4.59 MPa for charcoal produced at 750 °C. Hardness variation between vegetal materials also decreases with the final temperature of carbonization. These findings are important, especially for industries that use the Eucalyptus charcoal as a reducing agent and supporting material in blast furnaces for producing “green steel”. In this industrial segment, a homogeneous product is necessary and the control of the characteristics of the raw material becomes essential.

Keywords: reducing agent; mechanics; hardwood; supporting material; load resistance

1 INTRODUCTION

Steel industry uses iron ore and coking coal in the blast furnace for producing iron. The process consists of converting iron ore into pig iron and steel, which is done using reducing agents based on carbon and hydrogen (Gupta et al. 2003). Coal can be replaced by vegetable charcoal produced from pyrolysis (Suopajarvi et al. 2013, IBA 2017). Charcoal presents many advantages over mineral coal because it is renewable, it is less polluting, it has a low ash content, it is practically free of sulfur and phosphorus, it is more reactive, the production and transport process is not centralized and provides foreign exchange savings with the elimination of imports of fossil fuels (Arantes et al. 2013).

Brazil has been pointed out as the only country that industrially uses charcoal as a source of carbon monoxide and heat in blast furnaces for steel production (Protásio et al. 2014). The main consumers of the charcoal are pig iron, steel and iron-alloys industries, and to a lesser extent, trade and residential consumers (IBA 2017). According to Vieira et al. (2013) one of the problems faced by the Brazilian steel industry is the heterogeneity of the charcoal used in the steel fabrication with reference to physical, mechanical and chemical properties and the low yield in the carbonization processes currently used.

Variations in wood and in the carbonization processes led to variations in gravimetric yield and charcoal quality (FAO 1985, Moutinho et al. 2016). High wood density, lignin content and low ash content are characteristics which may be considered as wood quality-indices for charcoal production (Santos et al. 2011, Oliveira 1990), Regarding to the quality of charcoal, higher fixed carbon (FC) and lower ash and volatiles contents are associated with high lignin content and low holocellulose and extractives contents in wood (Santos et al. 2011).

Many studies have been done to understand the influence of temperature on gravimetric yield, fixed carbon and volatile material content of charcoal. For instance, Trugilho and Silva (2001)have measure the influence of temperatures between 300 and 900°C on the charcoal quality produced with Jatobá (*Himenea courbaril*). The authors reported differences in the fixed carbon, volatile material and ash content as a function of final temperature of pyrolysis. Pinheiro et al. (2005)have evaluated the effect of temperature between 200 and 650°C and heating rate on the charcoal properties of *Eucalyptus microcorys* concluding that the temperature between 300 and 450°C result in charcoal with satisfactory gravimetric yield, around 30%.

However, the mechanical properties of charcoal are important for industrial use and there are few studies on this key issue.

Charcoal has two main functions in the blast furnace, provides energy for the process in the form of heat and is the reducing agent of iron ore1 but also the charcoal layers must mechanically withstand the weight of the iron ore inside the blast furnaces (Costa et al. 2015).According to Assis et al. (2016) the mechanical characteristics of charcoal are also controlled by the characteristics of precursor material raw, for instance specific gravity, moisture, chemical composition, anatomical features and also by the two key carbonization settings: final temperature and heating rate.

To our knowledge, there is no standardized method for evaluating strength characteristics of vegetable charcoal. Traditional methods to evaluate mechanical behavior of charcoal are neither precise nor repeatable. Among the mechanical properties of the charcoal, the friability has been determined by means of the drum test (Coutinho et al.1988). To carried out the mechanical characterization in the charcoal sample, 500 grams of material are placed in a fixed rotating drum that rotates at 30 rpm around a horizontal axis 30 cm in diameter and 25 cm in length.

After 500 rotations, the material is sieved, separated and weighed according to their granulometry. The amount that passed through the 13 mm mesh is considered as fine. Regarding friability, it is known that in highly friable charcoal (due to factors such as manufacturing process, storage, screening, transportation and others), there may be losses of up to 25% of the material in the form of fines. The compression test can be used to measure the charcoal strength in order to predict its mechanical behavior when subjected to a load (Costa et al. 2017). According to Mendes et al. (1982) charcoal with higher compressive strength should exhibit less degradation during use. However, there is no standardized test to mechanically characterize vegetable charcoal.

The hardness has been considered to be one of the most important indicators of wood quality (Hirata et al. 2001, Hansson, 2006), as it has a high correlation with other key mechanical properties of the material, like the crushing strength parallel and perpendicular to the fibers 20 and ultra-structural features (Tze et al. 2007).In nanoscale, few studies have been done by using nanoindentation tests for investigating charcoal hardness at the scale of single wood cell walls. Using this approach, Zickler et al. (2006) have evaluated the mechanical properties of wood charcoal as a function of the pyrolysis temperature while Das et al. (2015) have investigated the structure–mechanics properties of waste derived biochar.

A Brazilian research group has developed a new device for evaluating dynamic hardness in wood and wood product (Assis et al. 2017). The portable equipment is based on a displacement transducer and an embedded electronic processor and can be applied to charcoal specimens for evaluating their mechanical resistance. Here, we believe that charcoal hardness can be a new criterion for classifying charcoal quality in terms of mechanical performance into blast furnace.

Therefore, the aim of this study was to evaluate the influence of final temperature of carbonization of charcoal on the dynamic hardness. Moreover, the effect of density of the precursor wood on dynamic hardness of the charcoal was evaluated.

2 MATERIAL AND METHODS

2.1 Vegetal Material

Wood specimens of *Corymbia citriodora* and several *Eucalyptus* species and hybrids from progeny test and commercial plantations presenting a high variation in terms of wood density were investigated in this study (Table 1).

Table 1. Description of the genetic materials studied.

Code	Vegetal material	Age(years)	Origin
1	*Eucalyptus saligna*	37	Progeny test
2	*Corymbia citriodora*	37	Progeny test
3	*Eucalyptus pilulares*	37	Progeny test
4	*Eucalyptus deglupta*	37	Progeny test
5	*Eucalyptus cloesiana*	37	Progeny test
6	*E. urophylla* x *E. grandis*	6.0	Commercial plantation
7	*Eucalyptus microcorys*	37	Progeny test
8	*Eucalyptus dunnii*	37	Progeny test
9	*E. urophylla* x *E. grandis*	6.5	Commercial plantation

Corymbia citriodora and six (6) *Eucalyptus* species from progeny test planted at Federal University of Lavras, Lavras, Brazil (spacing density: 400 plants / ha) and harvested at 37 years old were investigated. This progeny test was deployed on the Federal University of Lavras campus which is located in a transition zone between the Cerrado and Atlantic Forest biomes (21°14'S and 45°00'W); altitude of approximately 900 meters the climate is Cwb type, according to Köppen classification.

Relating to planted forests, two hybrids of Eucalyptus clones from forestry industries were also studied: i) *Eucalyptus urophylla* x *E. grandis* hybrids (6.5 years old) commercially cultivated by *Vallourec* do Brasil and used as charcoal to produce steel and ii) *Eucalyptus grandis* x *E. urophylla* hybrids (6 years old) commercially cultivated by *Cenibra Nipo-Brasileira* S.A., an important Pulp & Paper industry player. These vegetal materials represent the large genetic variation among Eucalyptus trees for industrial applications in Brazil. Charcoal specimens coming from these same Eucalyptus wood samples were also investigated in Ramalho et al. (2017).

2.2 Specimen preparation

Planks cut from the logs each genetic material were processed for producing 225 specimens (25 from each vegetal material) with size of 25 mm (Radial) × 25 mm (Tangential) × 40 mm (Longitudinal) with well-defined surfaces and free of defects. The wood pieces were placed in a temperature-controlled room at 21°C and 65% relative humidity until moisture stabilization. Under such environmental conditions, the wood moisture is expected to stabilize at 12%.

Prior to carbonization treatment, wood density was calculated for each specimen using the ratio between oven dried mass and its volume determined by immersion method as described in NBR 11941.26 Hence wood specimens were previously oven-dried at 103°C ± 2°C until constant mass and their dry mass recorded for calculating the gravimetric yield.

2.3 Pyrolysis process

The wood specimens were pyrolysed in a muffle furnace (electrical type; Q318M model; Quimis, São Paulo, Brazil). Five (5) specimens (repetition) of each of the nine (Moutinho et al. 2016) woods species were submitted to pyrolysis process using an electrical muffle furnace in according to procedure described in Neves et al. (2011) and Protásio et al. (2017). Wood pieces were charred within a metal capsule placed inside the furnace for avoiding influx of oxygen. Four (4) carbonization processes were performed varying the final temperature: 300°C, 450°C, 600°C, and 750°C. Thus, 180 specimens of charcoal were produced (9 materials x 4 temperatures x 5 repetitions). For the charcoal production, the initial temperature of pyrolysis was set as 100°C and the heating rate was set for 1.67°C min^{-1}. The residence time at final temperature was 30 minutes and the cooling period by natural convection was 16 hours.

To avoid "carbonization parameter effect" the wood specimens (previously oven dried) from different material were taken at random and carbonized together in the same pyrolysis process.

2.4 Characterization of charcoal

Gravimetric yield was calculated after each carbonization as the ratio between the mass of charcoal and the mass of oven-dried wood, in percentage. Charcoal density was carried out by the hydrostatic method which is based on water immersion as described in NBR 1194126 with adaptations for charcoal.

2.5 Dynamic hardness testes

Dynamic hardness (DH) of wood and charcoal were determined by an Automated Portable Hardness Tester - DPM3 (Figure 1 A) according to procedure fully described in Assis et al. (2017).

Five wood specimens per genetic material were tested totalling 45 (5 x 9) values of DH of wood. Concerning the charcoal, five specimens per genetic material were produced under four different temperatures totalling 180 (5 x 9 x 4) charcoal specimens. The equipment DPM3 was originally developed for testing wood specimens. According to Assis et al. (2017) the energy of indentation of a mass of 1 kg dropping 20 cm is 1.96 Joules. However, since charcoal is a brittle material, the use of the DPM3 device was adapted: the dropping component was released from 10 cm height for the analyses in the charcoal (instead of 20 cm, commonly used to wood tests). In preliminary tests, we noticed that the charcoal specimens suffered crushing and total defragmentation when the dropping component was released from the maximum height. The indentation was performed on the radial-longitudinal surface of the charcoal samples as shown in the Figure 1.

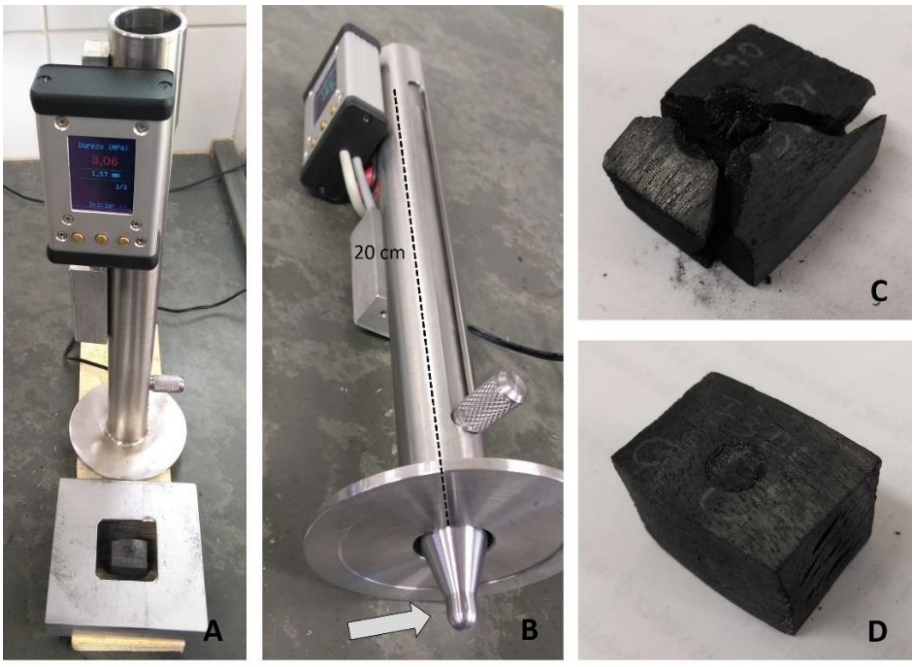

Figure 1. Automated Portable Hardness Tester – DPM3 (A), dropping component and indenter – arrow (B) and indentation after the dynamic hardness test on charcoal specimen produced under 300°C (C and D).

3. RESULTS AND DISCUSSION

3.1 Wood density and dynamic hardness of the wood specimens

The mean dynamic hardness of wood specimens was 29.83 MPa while the mean wood density was 791.5 kg m^{-3}. Variation in wood density and dynamic hardness (DH) of the wood specimens by vegetal material (VM) is presented in Figure 2.

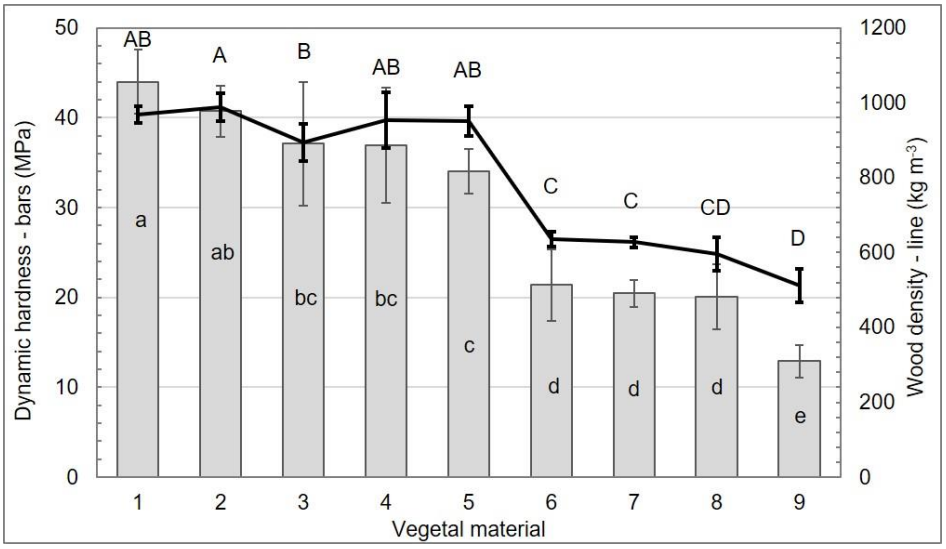

Figure 2. Average and standard deviation of dynamic hardness (MPa) and wood density (kg/m³) of the investigated wood specimens per vegetal material. Means of wood density (line) followed by the same capital letters and means of dynamic hardness (bars) followed by the same lower case do not differ to 5% of significance by the Tukey test.

The heavier wood species (VM 1, ρ = 989 kg m^{-3}) is, in average, 1,93 times denser than the lighter wood (VM 8, ρ = 512 kg m^{-3}) while the harder wood (VM 2, DH = 44 MPa) is 3.41 times harder than the softer material (VM 8, DH = 12.9 MPa). Thus, the wood of these vegetal material presents more variation in dynamic hardness than in wood density.

A strong relationship between dynamic hardness and density of 45 wood specimens is shown in Figure 3.

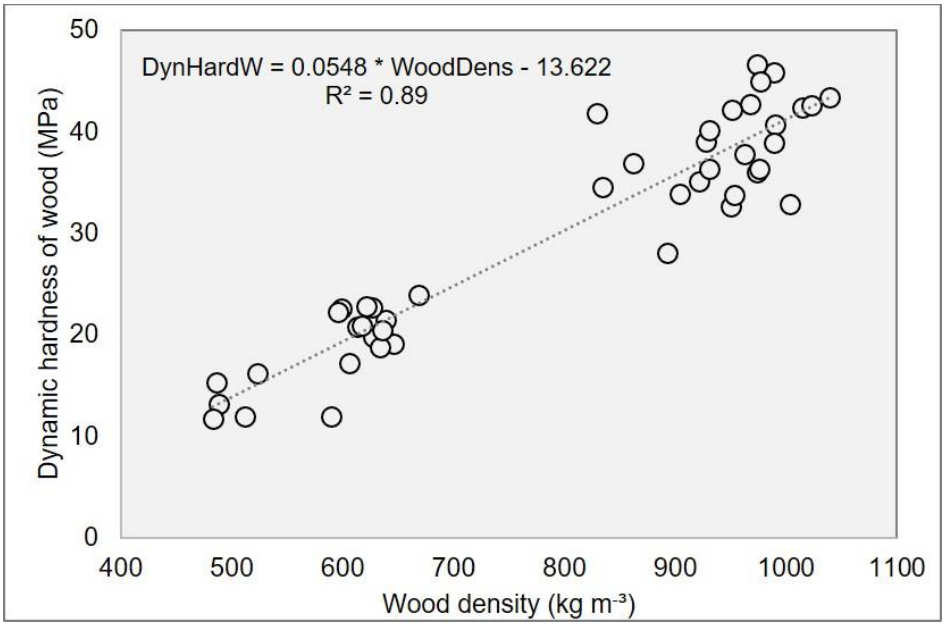

Figure 3. Relationship between dynamic hardness and density of wood.

There is high correlation between hardness and density. In short, wood with higher densities also exhibit greater dynamic hardness (Figure 3). The high correlation between hardness and density is in agreement with the findings reported by Antal and Mok (1990) and Chrzazvez et al. (2014), who evaluated the relationship between density and mechanical strength. According to data found in the literature, there is a positive correlation between the basic density of wood and the elasticity modulus, the compressive strength parallel to the carbon fibers, the gravimetric yield and density of charcoal (Veiga et al. 2018, Moutinho et al. 2017). Moreover, charcoal produced with denser woods present higher density and lower friability (Doat et al. 1975).

3.2 Final temperature influences the charcoal hardness

The variation of dynamic hardness of wood (29.83 MPa, in average) and of charcoal specimens produced under 300°C (10.98 MPa), 450°C (3.05 MPa), 600°C (3.44 MPa) and 750°C (4.59 MPa) is shown in Figure 4. Interestingly, the hardness of charcoal specimens decreases with thermic treatment (pyrolysis conditions) from 300°C to 450°C and then remains statistically equivalent at 600 and 750°C. The variation among vegetal material also decreases with the final temperature of carbonization. According to Xu et al. (2017): “when the carbonization temperature

surpassed 325°C, the compositions difference between different layers of wood cell walls became invisible and graphitic carbon began to appear in carbonized wood". Therefore, above 350°C the material raw loses its fibrous character and becomes a new material.

In regard to wood carbonization, the higher the final temperature the higher the polymers degradation (Trugilho et al. 2001) and consequently the higher the fixed carbon and ash content and also higher calorific value. Furthermore, the volatiles and gravimetric yield decrease with final temperature increase. To sum up, the charcoal quality is controlled by the final temperature. Higher temperature lead to homogeneous charcoal from a chemical point of view, independently of the precursor material quality (Ramalho et al. 2017, Andrade et al. 2012). The results presented in Figure 4 are in accordance to these statements. The large difference in dynamic hardness of wood specimens between vegetal material (from 12.9 to 44 MPa, in average, between contrasting vegetal material) drastically decreases when the material is subjected to pyrolysis, especially at 450°C (from 1.6 to 5.5 MPa, in average, between contrasting vegetal material). Xu et al. (2017) observed that cellulose, hemicellulose and lignin were no longer identifiable above 325°C from analyses with Raman confocal microscope. They stated that the chemical compositions of the layers become homogeneous above 325°C, and it is no longer possible to observe differences between the wood cell walls.

Here, the findings of Figure 4 reveal that the increase of final temperature until 450°C decreases the DH of vegetal materials from 29.8 MPa (wood), in average, to 3.05 MPa (charcoal of 450°C). The findings clearly demonstrate that dynamic hardness decreases while temperature increases until 450°C, regardless the genetic material.

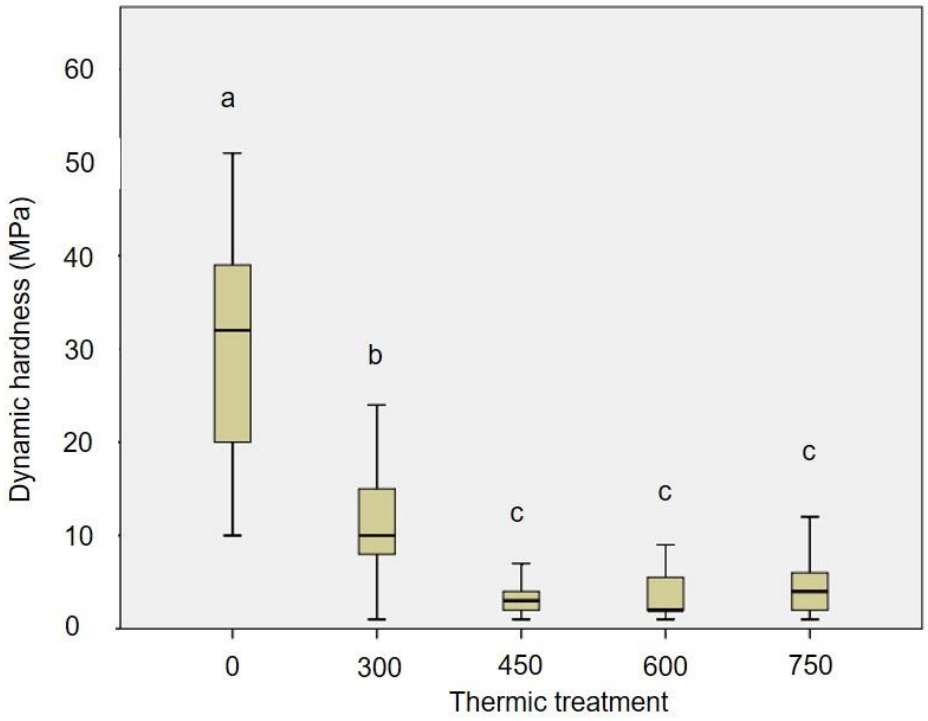

Figure 4. Variation of dynamic hardness of wood and charcoal produced under 300, 450, 600 and 750°C. Means followed by the same letters do not differ to 5% of significance by the Tukey test.

It can also be observed that the DH variation between the wood sample is higher than those for 300°C charcoal, which is greater than the DH variation found for charcoal specimens of 450, 600 and 750°C. In the pyrolysis process, many chemical reactions occur and these reaction phenomena are bounded to final temperature (Antal and Grønli 2003). Therefore, knowledge of the target final temperature and other carbonization parameters, such as heating rate and pressure, are important for improving the mechanical performance of charcoal (Assis et al. 2016).

Contrary to our findings, Zickler et al. (2006) have observed increased hardness as a function of temperature increase on samples of spruce wood (*Picea abies* Karst.) with 15 × 15 × 15 mm^3 size. Specimens pyrolysed at temperature of 220°C presented hardness of 0.4 GPa whereas specimens pyrolysed at 700°C resulted in hardness of 4.5 GPa.

However, the authors performed a hardness study by the indentation method at the scale of single wood cell walls, monitoring the depth of nanoindentation with continuous loads in surface areas of 50 × 50 μm^2. Besides this, Das et al. (2015) have found that hardness increased in samples

pyrolysed at 900°C comparing to samples pyrolysed at 350°C. The authors investigated hardness of pine saw dust biochar's made at four pyrolysis temperatures via nanoindentation and calculated from the load–displacement data. Both methods differ from the dynamic hardness evaluated in the present study. The methods differ in scale and the mechanical properties obtained by static methods are different from those obtained by dynamic tests.

To our knowledge, there are no reports concerning dynamic hardness in charcoal specimens. Thus, comparison between our results with literature information for other mechanical properties should be done with caution.

It seems intuitive that the dimensions, anatomy structure and chemical composition of the wood pieces and carbonization parameters like peak temperature, heating rate and pressure affect the mechanical properties of charcoal. However, information concerning the relationships between physical and structural characteristics of charcoal is contrasting.

Blankenhorn et al. (1972), Beall et al. (1974), Oliveira and Almeida (1980) and Oliveira et al. (1982) have shown that the higher the final carbonization temperature, the more resistant is the structure of charcoal whereas Andrade and Della Lucia (1995) have reported opposite results.

Oliveira et al. (1982) reported that compressive strength increased with increasing temperature from 300 to 900°C and suggested that the amount of fiber per area may influence this behavior. Assis et al. (2016) have stated that a significant increase in charcoal mechanics is achieved by carbonization at a final temperature above 500°C.

Here, the results shown in Figure 4 indicate that the dynamic hardness of the charcoal decreased with increasing carbonization temperature. Andrade and Della Lucia (1995) also observed that the compressive strength decreases to 500°C. They explain that the increased porosity of the charcoal, due to the output of volatile materials, may have contributed to this result. Baileys and Blankenhorn (1982) also observed the increase of pores in charcoal produced at a temperature of 500°C. According to Manabe et al. (2007) carbonization under high temperature induces a reorganization of the crystalline structure, since the increase of carbonization temperature resulted in the formation of micropores of charcoal. From Raman spectroscopy results, the authors observed that charcoal changed its physical-chemical structure mainly in the temperature range between 600°C and 800°C.

3.3 Effect of vegetal material on dynamic hardness of charcoal

Wood presenting high density tend to produce less brittle and denser charcoal (Veiga et al. 2018). Therefore, charcoal produced from dense woods are expected to exhibit higher mechanical strength. Chrzazvez et al. (2014) states compressive strength depends on charcoal formation temperature and has no impact on amount of fragments produced after material rupture.

The findings of Figure 4 allow to conclude that the influence of the original vegetal material on the charcoal mechanics decreases with the increase of the final pyrolysis temperature. The carbonization at 450°C produces charcoal with the lower DH variation between vegetal material (Figure 4).

Pinheiro et al. (2005) have analysed the effect of the temperature and carbonization heating rate on the charcoal characteristics of *Eucalyptus camaldulensis*, *E. cloeziana* and *Corymbia citriodora* at 6.5 to 7.5 years old and found that for all species analysed, the lower the final temperature and the heating rate, the higher the carbonization yield. They concluded that the temperature between 300°C and 450°C optimized the pyrolysis process for all species analysed for both gravimetric and fixed carbon content.

Figure 5 shows a large variation in the values of dynamic hardness as a function of the plant material. This result was expected because, as found in the literature, charcoal quality is interrelated to the characteristics of the wood that produced it8 and mechanical strength is positively correlated with wood density (Brito and Barrichelo 1980, Antal and Grønli 2003).

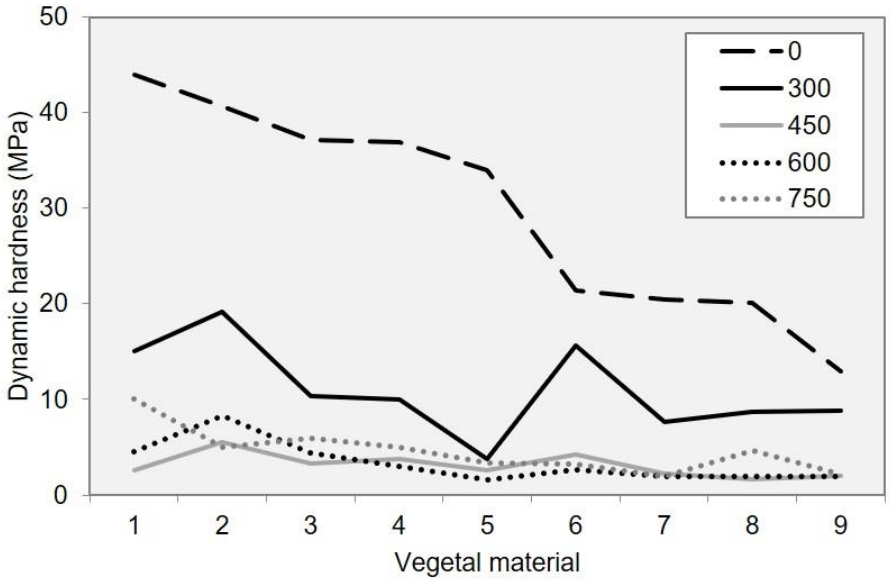

Figure 5. Thermic treatment and vegetal material interaction for dynamic hardness of wood and charcoal.

However, in regard to dynamic hardness, this study showed that increasing final carbonization temperature tend reduce the hardness of charcoal specimens.

The steel industry prefers homogenous materials, because woods with the same characteristics have similar behavior inside the blast furnace, this increase the yields in charcoal. In addition, this choice reduces the consumption of the product and increases the efficiency of the process (Assis et al. 2016).

However, our results showed that raw material has minimal influence on mechanical strength of charcoal produced above 450°C.

3.4 Effect of dynamic hardness on carbonization yield

Figure 6 shows the relationship between the dynamic hardness and the yield of charcoal produced under different temperatures.

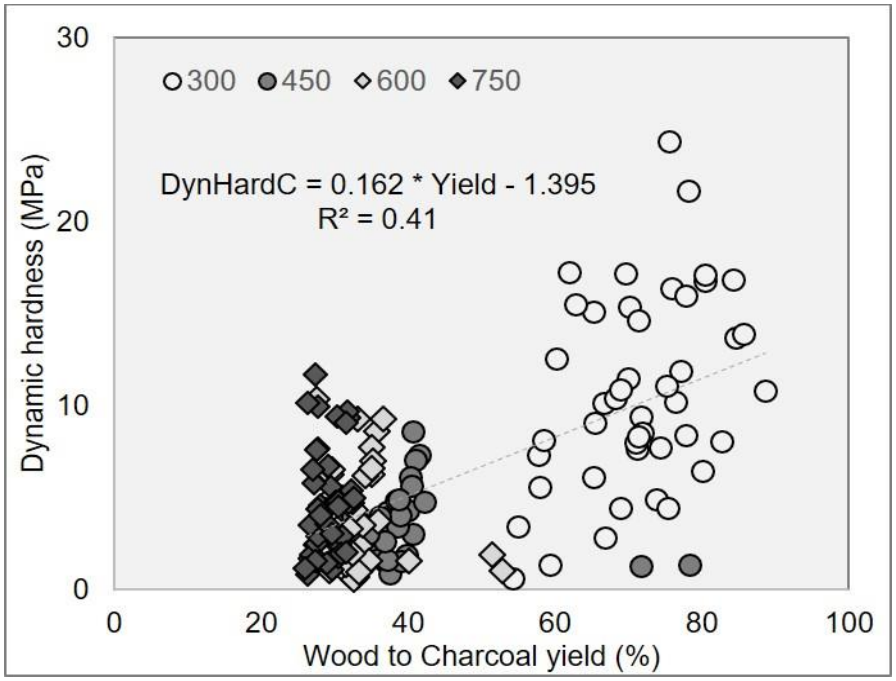

Figure 6. Relationship between dynamic hardness and wood to charcoal yield, produced under 300, 450, 600 and 750°C.

Figure 6 shows the low correlation between the dynamic hardness and the charcoal yield, with $R^2 = 0.41$. In spite of this, it is possible to observe the influence of temperature by the clusters as function of thermic treatment.

The yield of the charcoal decreased with increasing temperature. After the carbonization process at 300°C, the product that precedes the charcoal, considered thermally treated wood, presents great variation in terms of dynamic hardness (Figure 6). Due to the low carbonization temperature the product preserves many characteristics of the precursor wood. Carbonization at 300°C produces a material with a high gravimetric yield, very variable dynamic hardness (depending on the variation of the precursor wood) and its resistance (~ 10 MPa) is 1/3 of the wood (~ 30 MPa).

Charcoals produced at 450, 600 and 750°C showed a tendency to decrease yield when compared to a temperature of 300°C and different cluster could be observed in Figure 6.

The charcoals produced at a temperature of 450, 600 and 750°C showed lower dynamic hardness variation (Figure 3), suggesting a lower influence of the raw material on the carbon resistance, which becomes more homogeneous under high temperatures. Moutinho et al. (2007)

reported differences in yield of *Eucalyptus* wood (30% to 35%) and *Corymbia* sp (40%) while Oliveira et al. (1982) and Pereira et al. (2013) found a yield of 32% in *Eucalyptus* at 450°C and equal pyrolysis parameters. Vella et al. (1989) obtained a yield of 33% in *Eucalyptus tereticornis* also at 450°C, With different heating rate (0,42; 0,63; 0,64; 1,05 e 1,25°C/min).

These findings are important, especially for industries that use the Eucalyptus charcoal as reducing agent and supporting material in blast furnaces for producing "green steel" and need to monitor the properties of the carbonaceous material so that its products have uniform performance. According to Ramalho et al. (2007) most industries are searching for genetic selection of their vegetal material, so that these trees present greater uniformity in their properties and higher quality for the production of charcoal. However, this study shows that controlling carbonization processes is more important than selecting vegetal material (by using wood density as selection criterion, for instance), at least for mechanical performance of charcoal into blast furnaces.

4 CONCLUSIONS

Dynamic hardness (DH) of *Eucalyptus* charcoal decreased with the increase final temperature of carbonization. The DH was 10.89 MPa for charcoal specimens produced at 300°C, 3.05 MPa for 450°C, 3.44 MPa for 600°C and 4.59 MPa for charcoal of 750°C. The DH variation of charcoal between vegetal material also decreases with the temperature of carbonization, suggesting a lower influence of the precursor wood. Controlling carbonization processes is more important than selecting vegetal material, at least for mechanical performance of charcoal into blast furnaces. This study can serve as a reference for the mechanical classification of charcoal quality in industries.

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CHAPTER 3:

Estimating hardness and density of wood and charcoal by near infrared spectroscopy

Paper submitted to: *Biomass and Bioenergy*

ABSTRACT

Hardness has been considered an important indicator of wood quality and presents high correlation with density. However, there are few studies on how much this correlation is influenced by final pyrolysis temperature and, as far as we know, there is no specific methodology to evaluate hardness charcoal. In this context, it is necessary to develop a fast, reliable and efficient methodology to classify charcoal mechanical properties. Therefore, the aim of this study was to establish multivariate models for estimating dynamic hardness and apparent density of wood and charcoal based on near infrared spectra. For this, nine wood specimens were examined. *Corimbia citriodora*, six *Eucalyptus* species from progeny test and two hybrids of *Eucalyptus* clones from forestry industries. Specimens were pyrolyzed in 300°C, 450°C, 600°C, and 750°C. The apparent density of wood and charcoal was determined according to standard NBR 14984 andhydrostatic method, respectively. Dynamic hardness of wood and charcoal were determined by an Automated Portable Hardness Tester. Materials submitted to thermal treatment have different spectral signatures than those obtained by the wood. Charcoals produced at temperature at 450, 600 and 750°C exhibit similar behaviour, with low absorbance compared to wood and thermally treated material at 300°C, indicating homogenization of charcoal caused by pyrolysis temperature. NIR spectroscopy was able to detect: Pyrolysis final temperature, density and dynamic hardness. Charcoal pyrolyzed at 450°C presented model with highest coefficient of determination and smaller mean square error. PC1 accounts for 99.9% of the variability of analysed data while PC2 accounted for 0.08% of the remaining data variability, totalling 100% of the explanation of variance, for all pyrolyzed samples data. With these results it can be affirmed NIR spectroscopy is an efficient equipment to estimate density and hardness of charcoal.

Keywords: NIR; mechanical properties; automated portable hardness tester, hardness

1 INTRODUCTION

Brazil produces and consume seven million tons of charcoal per year, being the largest producer in world (Faostat, 2014). Steel industries are charcoal main consumers (IBA, 2017) and require charcoal quality compatible for metal production, such as charcoal high density (Brito and Barrichello 1977, Santos et al., 2011, Nones et al., 2015) and hardness (Zickler et al., 2006). It's knows wood used to produce charcoal directly influences its quality (Oliveira et al., 2010; Dufourny et al. 2018) and pyrolysis temperature can change charcoal mechanical characteristics (Costa et al., 2018). In blast furnaces, charcoal has to provides energy for process in form of heat and is the reducing agent of iron ore (Gupta, 2003; Suopajarvi et al., 2013), moreover, charcoal layers must mechanically withstand the weight of iron ore (Oliveira and Almeida, 1980; Costa et al., 2015), emphasizing the importance of charcoal mechanical properties, especially hardness.

Steel industries should know wood characteristics to select suitable raw material and control production process. According to Santos et al. (2011) and Moutinho et al. (2016), choice vegetable material can to improve charcoal gravimetric yield and to obtain high concentration fixed carbon and lower ash content. For instance, Pinheiro et al. (2005) analysed effect of temperature and pyrolysis heating rate on charcoal characteristics of *Eucalyptus camaldulensis*, *E. cloeziana* e *Corymbia citriodora* between 6.5 and 7.5 years and verified temperature between 300°C and 450°C optimized pyrolysis process and carbonization yield.

There are conventional laboratory methodologies used to measure wood hardness, such as Janka and Brinell. However**,** Janka hardness test is only applicable under laboratory conditions, due to forces difficult to control under field conditions (Colenci, 2006; Rohanová, 2007), and can cause some materials to rupture during the evaluation (Doyle, 1980; Doyle and Walker, 1985). Brinell method may present inaccuracy in indentation measurement, the sunken around edge may render it subjective and imprecise (Hansson e Antti, 2006; Heräjärvi, 2004; Colenci, 2006). As exposed, there are methods to evaluate wood hardness, however, these tests may be imprecise, costly and time consuming. Moreover, wood and charcoal characteristics are different (Nisgoski et al., 2014; Silva et al., 2018), due to the physical, anatomical and mechanical changes caused by the pyrolysis process (Ronewicz et al., 2016). Methods allowing quick and reliable predictions of physical and mechanical charcoal properties can be useful for monitoring charcoal quality in iron and steel industries.

Hardness has been considered an important indicator of wood quality (Hirata et al. 2001, Hanssone Antti, 2006), and presents high correlation with density (Zickler et al., 2006, Swaczyna et al., 2011). However, there are few studies on how much this correlation is influenced by final pyrolysis temperature. As far as we know, there is no specific methodology to evaluate hardness charcoal. In this context, it is necessary to develop a fast, reliable and efficient methodology to classify charcoal mechanical properties and non-destructive methods can be effective in this demand.

Portable durometer originally used for evaluating dynamic hardness in woods (Assis et al., 2017) has presented suitable results for evaluation of charcoal produced under different temperatures (Abreu et al., 2018). These results suggest the equipment can be used as a reference for the mechanical classification charcoal quality in steel industry.

Near infrared (NIR) spectroscopy has been used to identify materials chemical composition. Technique offers advantages such as speed, simplicity in sample preparation and effectiveness to evaluate chemical, physical, anatomical and mechanical properties of material (Tsuchikawa and Schwanninger, 2013). In addition, it can be used in field, in industrial production line and in *online* processes for any biological material (Pasquini, 2003).

NIR technology has been applied for qualitative studies related to charcoal for discriminating the precursory raw material and productive processes of charcoal. For example, Labbé et al. (2006) have discriminated charcoal produced from four wood species used for manufacture of distilled beverages using mid infrared. Monteiro et al. (2010) have applied this approach for distinguishing pyrolysis process and charcoal origin (*Eucalyptus* and native species). Devrieux et al. (2010) have discriminated Ipê (*Tabebuia serratifolia* (Vahl) Nichols) and *Eucalyptus grandis* Hill ex Maiden wood and charcoal powders. Nisgoski et al. (2015) have distinguished four species belonging to two families. Muñiz et al. (2016) have differentiated species of wood and charcoal marketed as angelim. Ramalho et al. (2017) used this solution for segregating charcoal specimens produced from wood coming from planted and native forest in temperatures of 300, 500 and 700 degrees. Costa et al. (2019) have applied NIR spectroscopy coupled with multivariate statistics in order to classify into categories and estimate the quality of commercial vegetable charcoal for domestic use. They reported models able to correctly classify

up to 95% of charcoal specimens by charcoal supplier or by charcoal quality in terms of fixed carbon content based on NIR signature.

Few studies have been carried out for quantitative analysis of charcoal properties by NIR. Labbé et al. (2006) estimated carbonization temperature and Andrade et al. (2012) estimated fixed carbon content, volatile material content and gravimetric yield of *Eucalyptus* charcoal based on NIR spectra. Costa et al. (2018) have established multivariate models to estimate gravimetric carbonization yield, apparent relative density and final carbonization temperature of *Eucalyptus* charcoal by NIR spectroscopy. Their models were able to predict final carbonization temperature and gravimetric carbonization yield presenting cross-validation coefficients (R^2cv) between reference and estimated data of 0.96 and 0.85, respectively, but it was not possible to predict apparent relative density based on charcoal spectral signature.

Therefore, the aim of this study was to establish multivariate models for estimating dynamic hardness and apparent density of wood and charcoal based on near infrared spectra.

2 MATERIAL AND METHODS

2.1 Vegetal Material

Nine wood specimens were examined (Table 1). *Corimbia citriodora* and six *Eucalyptus* species from progeny test planted at Federal University of Lavras, Lavras, Brazil and harvested at 37 years old were investigated. Two hybrids of *Eucalyptus* clones from forestry industries were also studied: *Eucalyptus urophylla* ×*Eucalyptus grandis* hybrids, harvested at 6.5 years old and *Eucalyptus grandis* × *Eucalyptus urophylla* hybrids harvested at 6 years old.

Table 1. Description of the genetic materials studied.

Code	Vegetal material	Age (years)	Origin
1	*Eucalyptus saligna*	37	Progeny test
2	*Corymbia citriodora*	37	Progeny test
3	*Eucalyptus pilulares*	37	Progeny test
4	*Eucalyptus deglupta*	37	Progeny test
5	*Eucalyptus cloesiana*	37	Progeny test
6	*E. urophylla* x *E. grandis*	6.0	Commercial plantation
7	*Eucalyptus microcorys*	37	Progeny test
8	*Eucalyptus dunnii*	37	Progeny test
9	*E. urophylla* x *E. grandis*	6.5	Commercial plantation

2.2 Specimen preparation

Wood pieces were cut and processed, with 25 (repetition) samples each genetic material, were dimensioned with 25 mm (Radial) × 25 mm (Tangential) × 40 mm (Longitudinal), totalling 225 specimens.

Prior to carbonization treatment, wood density was calculated for each specimen using the ratio between oven dried mass and its volume determined by immersion method as described in NBR 11941 (ABNT, 2003). Hence wood specimens were previously oven-dried at 103°C ± 2°C until constant mass and their dry mass recorded for calculating gravimetric yield.

2.3 Pyrolysis process

Wood specimens were pyrolysed in muffle furnace (electrical type; Q318M model; Quimis, São Paulo, Brazil). Five (5) specimens (repetition) of each of nine woods species were submitted to pyrolysis process using an electrical muffle furnace. Wood pieces were charred within a metal capsule placed inside the furnace for avoiding influx of oxygen. Four (4) carbonization processes were performed varying final temperature: 300°C, 450°C, 600°C, and 750°C. Thus, 180 specimens of charcoal were produced (9 materials × 4 temperatures × 5 repetitions). For charcoal production, pyrolysis initial temperature was set as 100°C and heating rate was set for 1.67°C min^{-1}. Residence time at final temperature was 30 minutes and cooling period by natural convection was 16 hours. Wood specimens from different material (previously oven dried) were taken at random and carbonized together in same pyrolysis process, to avoid “carbonization parameter effect”.

Charcoal specimens were produced at 300, 450, 600 and 750°C to simulate temperature range adopted in real situations in most Brazilian industries.

2.4 Charcoal characterization

2.4.1 Dynamic hardness testes

Dynamic hardness of wood and charcoal were determined by an Automated Portable Hardness Tester - DPM3 according to procedure fully described in Assis et al. (2017) and Abreu Neto et al. (2018).

Five wood specimens per genetic material were tested totaling 45 (5 × 9) values of wood dynamic hardness. Five charcoals specimens per genetic material were produced under four different temperatures totaling 180 (5 × 9 × 4) charcoal specimens.

2.4.2 Recording NIR spectra

Acquisition of NIR spectra was performed by Bruker FT-NIR (model MPA, Bruker Optik GmbH, Ettlingen, Germany), connected to computer to collect stored spectra data the OPUS program, Version 7.5. Based on a Fourier transform equipped with an integrating sphere, spectra of each sample were obtained by means of 16 scans performed, within the 12,500 to 3,600 cm^{-1} range at 8 cm^{-1} resolution equipment. Each spectrum consisted of 2,307 absorption values, according to the procedure described in Ramalho et al. (2016). Specimens of wood and charcoal were kept in acclimatized room at a temperature around 20°C and relative humidity around 65%. Under these conditions charcoal specimens reached equilibrium moisture of approximately 6%.

2.5 Multivariate data analysis

Data multivariate analysis was performed with Unscrambler software ® (CAMO AS, Oslo, Norway, v. 9.7), Principal Component Analysis (PCA), Partial Least Squares regression (PLS-R) were adjusted based on NIR spectra and hardness, apparent density and final carbonization temperature values.

From data of hardness, apparent density and final pyrolysis temperature, calibration was performed to predict characteristics of further samples based on their NIR spectrum. The calibrations and Cross-validation were performed based Ramalho et al. (2016) with number of

latent variables determined based on the minimization of the standard error of validation and maximization of coefficient of determination of validation.

Models were adjusted from original spectra and mathematically treated with first derivative, second derivative, normalization and normal variation (SNV), for development of models of apparent density and hardness of wood and charcoal. Selection of models were based on coefficient of determination for calibration (R^2c), mean quadratic error for calibration ($RMSE_C$), coefficient of determination for cross validation (R^2cv), mean square error for cross validation ($RMSE_{CV}$) and Latent variables (LV).

3 RESULTS AND DISCUSSION

3.1 Near IR Spectra of wood and charcoals

NIR spectra obtained by integrating sphere of wood and thermally treated materials at final pyrolysis temperatures of 300, 450, 600 and 750°C are shown in Figure 1.

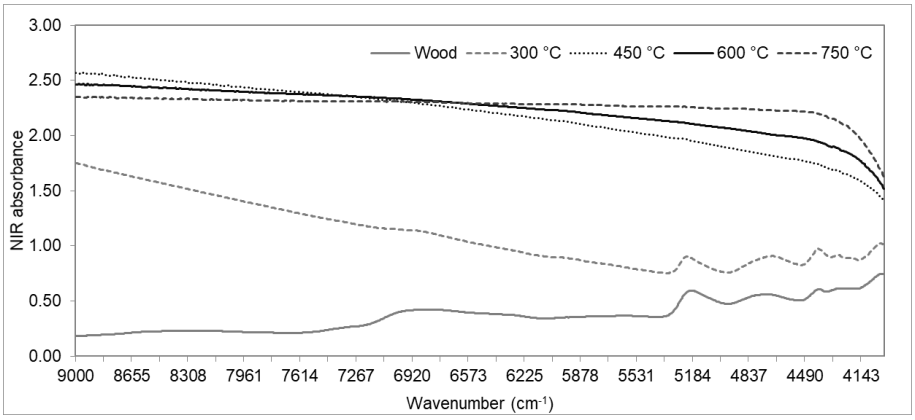

Figure 1. NIR spectra collected in wood and charcoal produced at final pyrolysis temperatures of 300, 450, 600 and 750°C.

Materials submitted to thermal treatment have different spectral signatures than those obtained by wood. Despite difference in absorbance caused by temperature, it is possible to observe similarity in absorbance curves of wood and treatment at 300°C. With a greater number of absorption regions especially below 5250 cm^{-1}, region attributed to the polymers inherent to the vegetal material, which suffered little or no degradation at temperature of 300°C.

Charcoals produced at temperature at 450, 600 and 750°C exhibit similar behaviour, with low absorbance compared to wood, consistent with that found in literature (Davrieux et al., 2010, Muñiz et al., 2016). Low interaction between equipment radiation and chemical constituents of material probably due to the burning of wood polymers (Trugilho and Silva, 2001; Costa et al., 2018). This phenomenon can be interpreted as homogenization of charcoal caused by pyrolysis temperature. Wood samples pyrolyzed at high final temperatures result in more homogeneous charcoal and have a higher concentration of carbon in their composition (Andrade et al., 2012; Ramalho et al., 2017).

Behaviour of wood and treated material at 300°C observed in this study are similar to observed by Ramalho et al. (2016), where interaction with molecules of different materials exhibits different absorbances (Pasquini, 2003), suggesting a difference in chemical composition of wood and charcoal (Andrade et al., 2012; Costa et al., 2017; Barcelos, 2007).

3.2 Principal Component Analysis (PCA)

Figure 2 shows the scores of PCA carried out from wood of different vegetal materials analysed (thermally untreated).

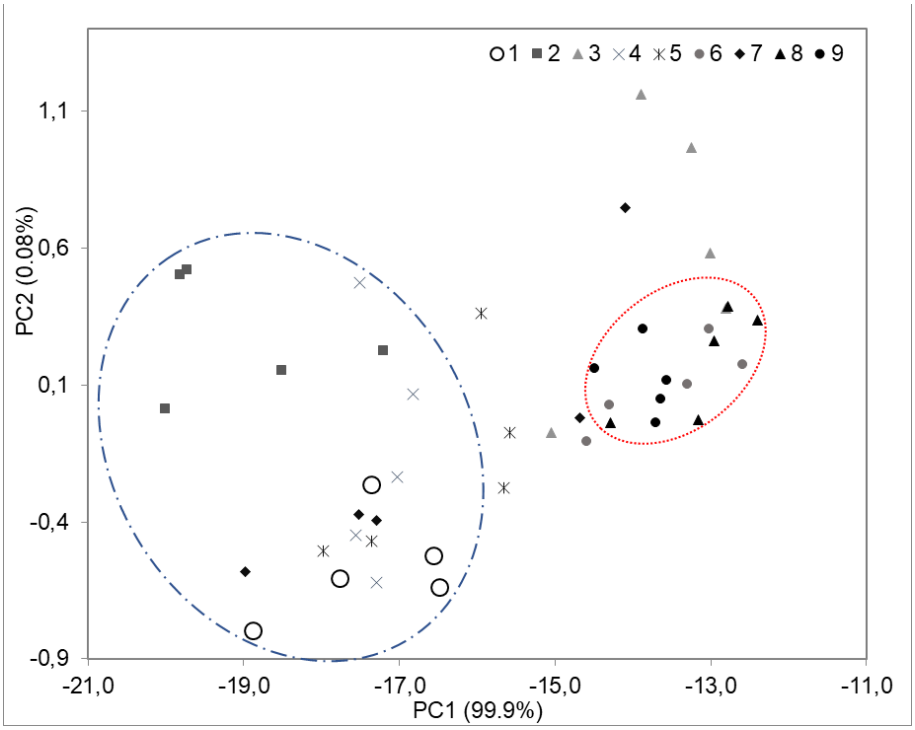

Figure 2. NIR spectra principal component analysis of different wood.

There are many variations among woods, even among same genetic material (Figure 2). It was difficult to distinguish groups of genetic material. However, it was possible to observe two materials groups, first is composed of materials presented highest values of wood dynamic hardness, *C. citriodora* (Code 2), *E. deglupta* (Code 4) and other group composed of materials presented lower values, *E. urophylla* × *E. grandis* 6.0 (Code 6) e *E. dunnii* (Code 8). This result indicating that the NIR is capable of detecting difference between wood species and can infer about the mechanical properties.

First principal component (PC1) accounts for 99,9% of the variability of analysed data, while second component (PC2) accounts for 0,08%, totalling 100% of explanation of variance.

Figure 3 shows the scores of PCA carried out from submitted samples at heat treatment.

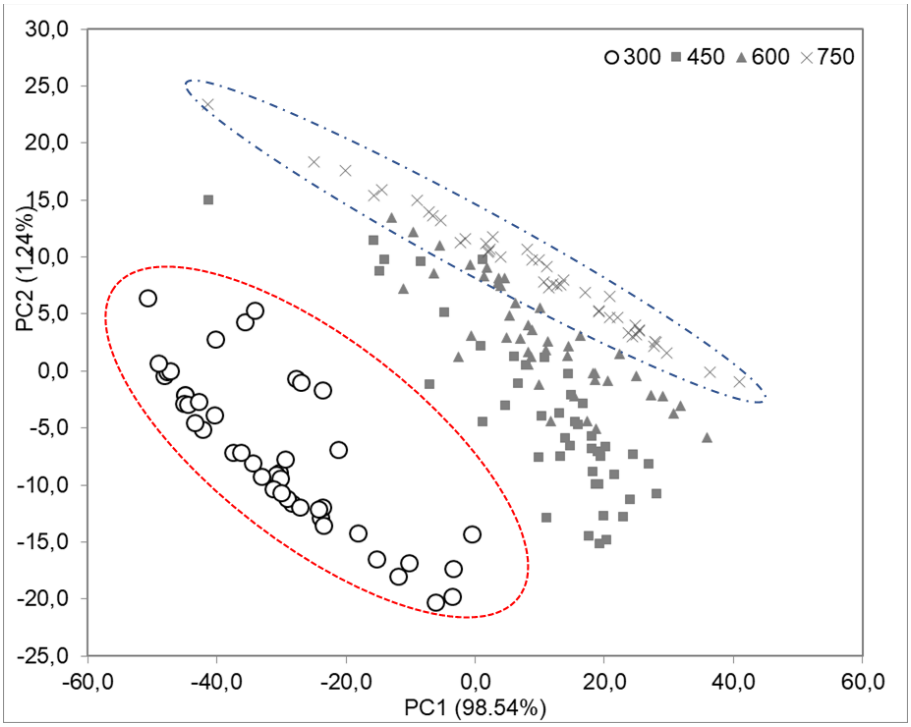

Figure 3. NIR spectra Principal Component analysed of samples thermally treated at 300, 450, 600 and 700°C.

Figure 3 shows distinct groups form by heat treatments, there was a visible difference between treatments of 300 and 750°C, it can also be observed material treated at 300°C shows greater variability when compared to pyrolysis at 750°C. Therefore, NIR is able to detect parameters of charcoal pyrolysis process, such as final temperature. The PC1 accounts for 98.54% of the variability of analysed data while PC2 accounts for 1.24%, totalling 100% of explanation of variance (Figure 3).

Ramalho et al. (2016) observed samples produced at 300°C distributed more heterogeneously, compared to charcoals produced at temperatures of 500 and 700°C. Costa et al. (2018) observed more defined grouping for charcoals produced at 700°C, the same authors could not observe distinction in samples produced at 400, 500 and 600°C.

3.3 Partial least squares regression analysis (PLS-R)

The Table 2 shows the statistic associated to PLS-R calibration and cross validations to estimate density and hardness of wood.

Table 2. Statistic associated to PLS-R calibration and cross-validations for estimating density and hardness of the wood.

Properties	Mathematical treatment	R^2c	RMSEc	R^2cv	RMSEcv	LV
Density	-	0.900	0.059	0.788	0.087	6
	normalization	0.885	0.063	0.798	0.084	6
	1d	0.924	0.051	0.737	0.098	4
	snv	0.917	0.054	0.823	0.079	7
Hardness	-	0.821	4.730	0.731	5.844	4
	normalization	0.819	4.762	0.735	5.813	4
	1d	0.900	3.542	0.643	6.881	4
	snv	0.810	4.877	0.706	6.236	4

R^2c: Coefficient of determination for calibration. $RMSE_C$: Mean quadratic error for calibration. R^2cv: Coefficient of determination for cross validation. $RMSE_{CV}$: Mean square error for cross validation. LV: Latent variables.

Density data set treated with Standard Normal Variate (SNV) showed better result (Table 2). Low error value for the calibration (RMSEc), lowest Mean square error for cross validation (RMSEcv), higher coefficient of determination for calibration (R^2c) and higher coefficient of determination for cross validation (R^2cv) make this model the most robust for analysis of wood density.

Set of dynamic hardness data treated with mathematical 'normalization' treatment presented similar results with data without mathematical treatment. Both with low error for calibration (RMSEc), lower Mean square error for cross validation (RMSEcv), higher coefficient of determination for calibration (R^2c) and higher coefficient of determination for cross-validation (R^2cv), therefore, are the most robust models for analysis of wood density.

The Table 3 shows Statistics associated with PLS calibration and cross-validations to estimate apparent relative density and hardness of the charcoals produced at different temperatures.

Table 3. Statistic associated to PLS-R calibration and cross-validations for estimating density and hardness of pyrolyzed materials.

Property	Temperature	Mathematical treatment	R^2c	RMSEc	R^2cv	RMSEcv	LV
Density	All	-	0.568	0.110	0.368	0.133	6
	300	-	0.676	0.106	0.492	0.134	5
	450	-	0.895	0.061	0.487	0.134	4
	600	-	0.732	0.096	0.399	0.149	4
	750	-	0.748	0.094	0.246	0.163	4
Hardness	All	Normalization	0.507	3.179	0.427	3.439	4
	300	Normalization	0.383	4.103	0.129	5.058	4
	450	-	0.185	1.630	0.078	1.758	2
	600	-	0.836	1.051	0.390	2.031	4
	750	snv	0.912	0.844	0.242	3.909	4

R^2c, Coefficient of determination for calibration; $RMSE_C$, root-mean-square error for calibration; $R^2(cv)$, coefficient of determination for Coefficient of determination for cross-validation; $RMSE_{CV}$, Mean squared error for cross validation; LV, latent variables.

The Table 3 presents density of analysed samples, it is possible to observe charcoal pyrolyzed at 450°C presented model with highest coefficient of determination (R^2c) and smaller mean square error, both for calibration ($RMSE_C$) and for validation ($RMSE_{CV}$), followed by models of pyrolyzed materials at 300°C and 'All' spectra together.

Density data do not use mathematical treatment in any of final pyrolysis temperatures analysed. With these results it can be affirmed the NIR is an efficient equipment to estimate charcoal density by PLS-R model. Analysing the dynamic hardness, the samples of charcoal produced at 750°C presented the most robust model.

Contrary to our results, Costa et al. (2018) did not find models with satisfactory correlations for apparent density of charcoals produced at temperatures between 400 and 700°C, even after applying mathematical treatments, the model did not show statistical improvement.

3.4 Thermally treated materials

Figure 4 shows the scores PCA carried from results of thermally treated samples. Pyrolyzed samples data at 300 and 450°C did not receive mathematical treatment (Figure 4 - A and B).

Samples at 600 and 750°C received mathematical treatment from Mean Center (Figure 4 - C and D).

In all these cases, PC1 explained 99.9% of the variability of analysed data while PC2 accounted for 0.08% of remaining data variability, totalling 100% of explanation of variance (Figure 4).

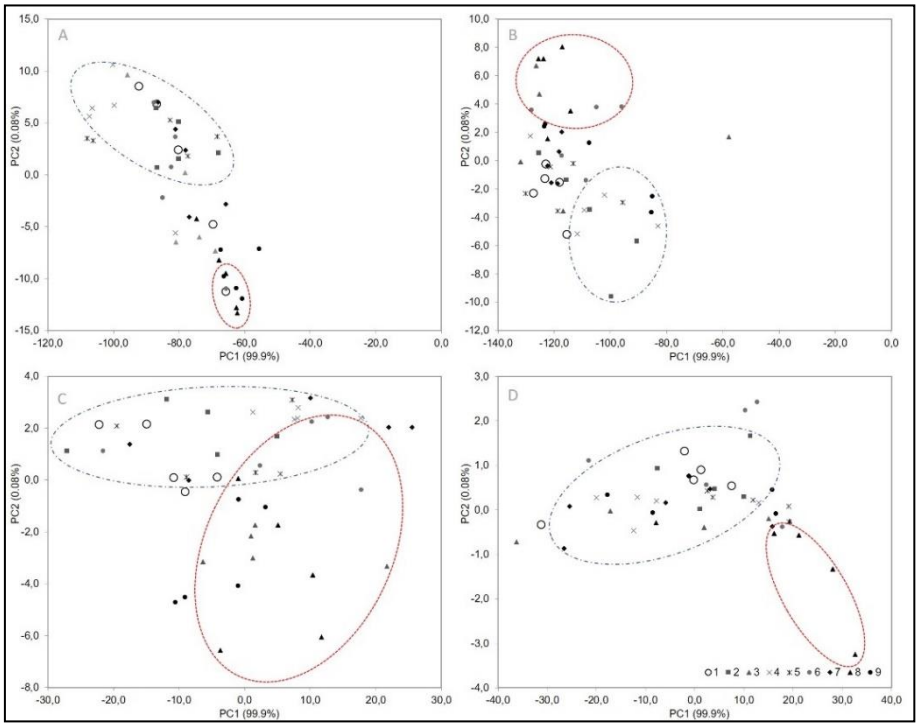

Figure 4. Scores of specimens submitted to final pyrolysis temperature of 300 (A), 450 (B), 600 (C) and 700°C (D).

Materials thermal treatments at 300 and 450°C formed different groups, it was possible to separate vegetal materials presented higher values of hardness and density of those presented lower values for these properties, with no mathematical treatment (Figure 9 – A and B).

Charcoals produced at temperature of 600 and 750°C formed groups less distinguishable, being necessary a mathematical treatment (Mean center) to promote separation of genetic materials with higher values of dynamic hardness of the lower values (Figure 9 – C e D). Delwiche and Reeves (2004) have demonstrated application of pre-treatments on NIR spectra helps to optimize

NIR information and derive models from them. Monteiro et al. (2010) also had difficulty separating charcoal of twenty-seven species of wood, but the authors were successful in separating samples on final temperature of pyrolysis using PCA of NIR spectra.

4 CONCLUSIONS

Materials submitted to thermal treatment have different spectral signatures than those obtained by the wood. Wood and treatment at 300°C shows similarity in absorbance curves, with a greater number of absorption regions in NIR. While charcoals produced at temperature 450, 600 and 750°C exhibit similar behaviour, with low absorbance compared to wood, suggesting a homogenization of charcoal caused by pyrolysis temperature.

NIR spectroscopy was able to detect: a) Pyrolysis final temperature, there was a visible difference between treatments, especially between 300 and 750°C. b) Density and c) Dynamic hardness, it was possible to observe materials groups, composed of materials presented highest values of dynamic hardness, and other group composed of materials presented lower values.

Charcoal pyrolyzed at 450°C presented model with highest coefficient of determination and smaller mean square error. PC1 accounts for 99.9% of the variability of analysed data while PC2 accounted for 0.08% of the remaining data variability, totalling 100% of the explanation of variance, for all pyrolyzed samples data.

With these results it can be affirmed NIR spectroscopy is an efficient equipment to estimate density and hardness of charcoal.

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CHAPTER 4:

Effect of final temperature on charcoal stiffness and its correlation with wood density and hardness

Paper submitted to: *Wood Science and Technology*

ABSTRACT

Charcoal quality depends on the characteristics of vegetal material. However, variations in pyrolysis process may strongly affect charcoal properties. Many studies have been dealt to correlation between wood and charcoal properties, but relationships among density, stiffness and hardness of charcoal as a function of carbonization temperature is still poorly understood. Therefore, the aim of this study was to evaluate density, stiffness and hardness of wood and charcoal using non-destructive devices, for establishing correlation among these properties and to determine their variation according to the pyrolysis temperature. Wood specimens from nine forest species including six *Eucalyptus* species, two *Eucalyptus* hybrids from commercial plantations and *Corymbia citriodora* were carbonized at different final temperatures (300°C, 450°C, 600°C and 750°C). Stiffness of wood and charcoal were determined by ultrasound with flat-faced piezoelectric transducers with frequency 45 kHz. Dynamic hardness of wood and charcoal were determined by an automated portable hardness tester. There is a tendency of a decreasing stiffness with increasing temperature. Compared to wood, pyrolysis at 450°C reduces charcoal stiffness by approximately 30%. Wood presents a greater dynamic hardness, 29 MPa. Pyrolysis temperature of 450°C decreases material hardness to approximately 3 MPa. Considering the genetic materials, highest values of wood stiffness were presented by *C. citriodora* and *E. deglupta*, same materials presented highest density, confirming high positive correlation between wood properties. Correlation between density and stiffness was R^2=0.87, for charcoal R^2=0.99, regardless of final pyrolysis temperature. Correlation between density and dynamic hardness was R^2=0.93, for charcoal R^2=0.69. Correlation between stiffness and dynamic hardness of wood was R^2=0.79, final pyrolysis temperature negatively affects correlation between these properties.

Keywords: Pyrolysis, rigidity, specific gravity, ultrasound, carbonaceous materials, charcoal mechanics.

1 INTRODUCTION

Pyrolysis process causes physical, anatomical and mechanical changes. It can influence charcoal characteristics and affect quality of product in use. Pyrolysis temperature changes cellular composition and causes degradation of components, changing the fibrous wood into carbonized material composed mainly of graphitic carbon (Xu et al., 2017), changing charcoal quality and charcoal stiffness (Veiga et al., 2018). Charcoal quality depends on the characteristics of vegetal material (Dufourny et al., 2008). Among the most important characteristics of origin biomass, one can highlight the wood density (Brito and Barrichello 1977, Santos et al., 2011, Nones et al., 2015), stiffness, (Babich et al., 2010, Castro et al., 2016) and hardness (Hirata et al., 2001). These factors will influence density (Trugilho and Silva, 2001), stiffness (Veiga et al., 2018) and hardness (Zickler et al., 2006) of charcoal.

Correlation between hardness and density of wood is well known (Zickler et al., 2006, Swaczyna et al., 2011); as well as the high correlation between density and stiffness (Ballarin and Nogueira, 2005, Almeida et al., 2012). However, due to variations occurring in pyrolysis process, the characteristics of charcoal and wood of origin are different. As far as we know, there is no specific methodology to evaluate hardness and stiffness of charcoal. In view of the fact that Brazil is one of the few countries in the world to use large-scale charcoal for blast furnaces, the development of new techniques is important to correctly classify it.

Veiga et al. (2018) evaluated mechanical strength of charcoal and reported the lack of a methodology for charcoal makes it difficult to standardize the tests. Therefore, new solutions are necessary to evaluate the stiffness and hardness of charcoal, and non-destructive equipment can be effective in this demand.

In this study, two equipment already successfully tested for wood evaluations were applied to charcoal specimens: 1) the portable durometer - an equipment developed to measure dynamic hardness of wood (Assis et al., 2017), and 2) ultrasound - an effective tool in the inference of physical and mechanical properties of wood, allows indirectly to estimate material elastic constants (Ballarin and Nogueira, 2005). The ultrasonic method was efficient to evaluate wood quality, with a quickly estimating mechanical parameters such as modulus of elasticity and rupture (Stangerlin et al., 2010). The portable durometer presented reliable results in evaluation of dynamic hardness of woods (Assis et al., 2017) and charcoal produced at different temperatures (Abreu et al., 2018).

These results suggest the equipment can be used as a reference for mechanical classification charcoal quality in steel industry.

There are studies on the correlations between mechanical properties of wood and resulting charcoal quality. However, the relationship among density, stiffness and hardness of charcoal as a function of final pyrolysis temperature is still unknown.

Therefore, the aim of this study was to evaluate stiffness and hardness of wood and charcoal using ultrasound and automated portable hardness tester to establish the correlation between these properties and the density, in addition to determine to what extent they are influenced by final pyrolysis temperature.

2 MATERIALS AND METHODS

2.1 Vegetal material

Woods from nine different trees were studied – one *Corymbia citriodora*, six *Eucalyptus* species, and two *Eucalyptus* hybrids from commercial plantations, as described in Table 1.

Table 1. Description of the species, ages and origins of the studied trees.

Code	Vegetal material	Age (years)	Source
1	*E. saligna*	37	Progeny test
2	*C.citriodora*	37	Progeny test
3	*E. pilulares*	37	Progeny test
4	*E. deglupta*	37	Progeny test
5	*E. cloesiana*	37	Progeny test
6	*E. urophylla* × *E. grandis*	6.0	Commercial planting
7	*E. microcorys*	37	Progeny test
8	*E. dunnii*	37	Progeny test
9	*E. urophylla* × *E. grandis*	6.5	Commercial planting

Samples with nominal dimensions of 25 × 25 × 40 mm (R × T × L) were prepared, 25 samples of each plant material were produced, totalling 225 specimens. These were kept in a room with the temperature controlled at 20ºC ± 1°C and 65% ± 3% relative humidity until the humidity was stabilized.

2.2 Pyrolysis of the material

Four pyrolysis were performed with varying the final temperatures: 300°C, 450°C, 600°C and 750°C. Initial temperature was 100°C, heating rate was 1.67°C min^{-1}, and residence time at final pyrolysis temperature was 30 minutes.

Five specimens of each of nine genetic material (considered as repetitions), totalling 180 samples, were pyrolysed in an electric furnace (muffle). These were then placed inside a carbonization capsule and pyrolysed inside electric muffle furnace.

2.3 Apparent density of wood

Wood apparent density was determined according to standard NBR 14984 (ABNT).

2.4 Density of charcoal

Charcoal apparent relative density was determined according to hydrostatic method, by immersion in water.

2.5 Dynamic hardness

Portable Hardness Tester - Third Generation (DPM3) was used to evaluate the dynamic hardness (DH) of wood and charcoal, according to procedure described by Assis et al. (2017) e Abreu Neto et al. (2018).

2.6 Stiffness by ultrasound

Stiffness of wood and charcoal was determined by a *Steinkamp* brand ultrasound device, model BP-5, from Department of Rural Engineering, School of Agricultural Sciences, Sao Paulo State University (UNESP), Botucatu - SP - Brazil. Device has two equivalent flat piezoelectric transducers – one for emission and another for reception of ultrasound waves, frequency 45 kHz. Stiffness (GPa) in longitudinal direction was determined from ultrasound wave propagation speed (dry contact; without gel), as performed by Ballarin and Nogueira (2005).

A total of 45 measurements were performed on the wood samples, with five replicates for each of nine genetic materials analysed. In addition, five samples of each genetic material, which

were produced under four different temperatures, were measured for charcoal, totalling 180 charcoal specimens. Thus, a total of 225 samples of wood and charcoal were analysed.

3 RESULTS AND DISCUSSION

3.1 Wood stiffness by ultrasound

The average wood stiffness was 3.920 MPa and the average wood density was 0.791 g.cm^{-3}(Figure 1). Highest values were presented by *C. citriodora* (Code 2) and *E. deglupta* (Code 4), same materials present highest density, suggesting high positive correlation between this wood properties. Lowest values were observed by *E. pilulares* (Code 3), *E. urophylla* × *E. grandis* 6.0 (Code 6), *E. dunnii* (Code 8) and *E. urophylla* × *E. grandis* 6.5 (Code 9).

Almeida et al. (2012) studied *Dinizia excelsa* Ducke and found stiffness of approximately 23,919 MPa. The authors found a low correlation with modulus of elasticity and static bending and attributed this outcome to influence of samples moisture. Stangerlin et al. (2010) used an ultrasound device to evaluate wood from *Peltophorum dubium* (Spreng.) Taub. With 41 cm in length and found elastic constants close to 7,800 MPa; the authors mention morphological and anatomical properties may have influenced results. The authors observed dynamic constant is 1.3 times greater than modulus of elasticity due to the viscoelastic behavior of wood. Ballarin and Nogueira (2005) performed ultrasonic stiffness measurements to evaluate juvenile wood and adult wood of *Pinus taeda* L. and found values of 11,816 and 17,914 MPa, respectively.

The stiffness in literature is greater than observed in this study. Samples size used in this study may have influenced this result, since ultrasonic stiffness is measured as a function of distance travelled by wave.

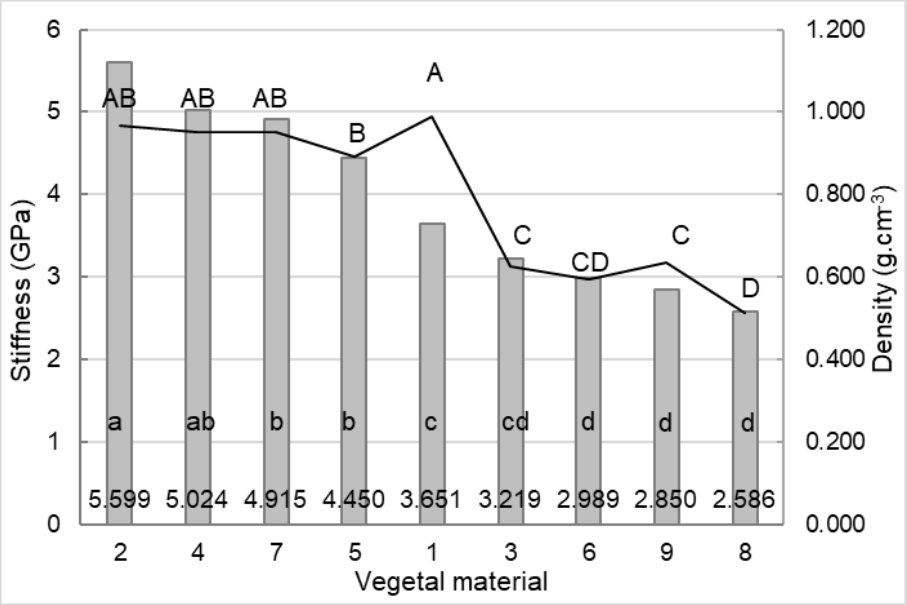

Figure 1. Ultrasonic stiffness (MPa) by genetic material in longitudinal direction (bar) and apparent density ($g.cm^{-3}$) (line). Means followed by the same lower-case letters in a column and capital letters on the lines did not differ significantly by Tukey test at 5% significance.

3.2 Stiffness of genetic material as a function of final pyrolysis temperature

Figure 2 shows stiffness and density results of different genetic materials at temperatures of 300, 450, 600 and 750°C.

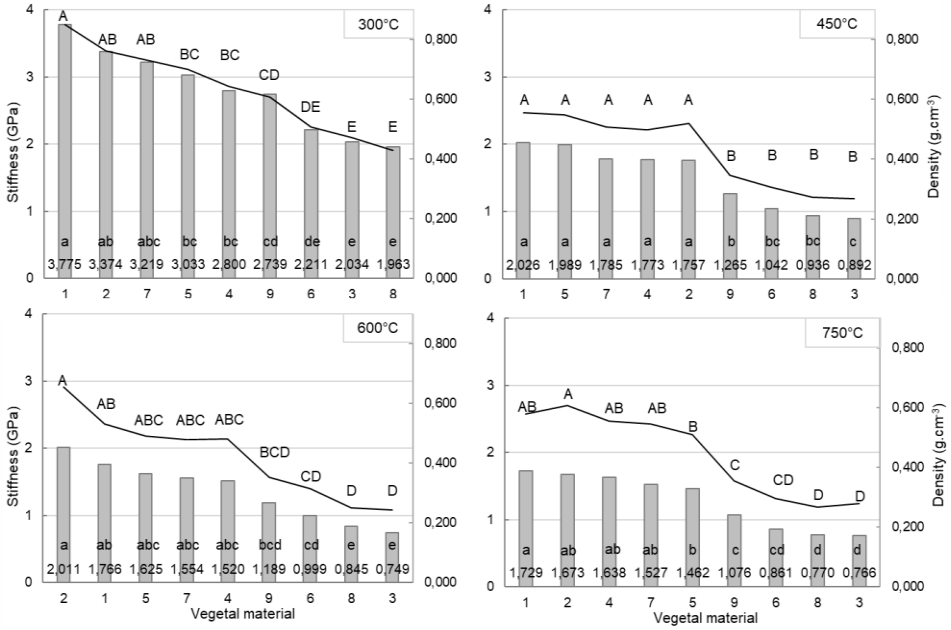

Figure 2. Stiffness and density of materials produced at final temperatures of 300, 450, 600 and 750°C. Means followed by the same lower-case letters in a column and capital letters on the lines did not differ significantly by Tukey test at 5% significance.

In general, the genetic materials *E. saligna* (Code 1), *C. citriodora* (Code 2), and *E. microcorys* (Code 7) had highest stiffness values, concomitantly, these materials presented highest values of density, regardless of thermal treatment used (Figure 2). The lowest values of stiffness and density were observed for *E. pilulares* (Code 3), *E. urophylla* × *E. grandis* 6.0 (Code 6) and *E. dunnii* (Code 8), regardless of thermal treatment used.

Veiga et al. (2018) observed that *C. citriodora* presented higher stiffness, 1.585 MPa, compared to *E. urophylla*, around 900 MPa, the first one is also more resistant, 5 MPa and 3 MPa, respectively. Poncsak et al. (2006) observed birch wood (*Betula papyrifera*) MOE is around 1.500 MPa, and decreases to approximately 1.200 with thermal treatment near 120°C. The authors observed a maximum peak in the MOE value at a temperature of 160°C. The authors observed a maximum peak in the MOE value at 160°C, and MOE decreases with increasing temperature. It was also observed exothermic chemical reactions start between 150 and 160°C. Probably due to the dismemberment of hemicelluloses and cellulose polymers. This behavior appears almost constant under experimental conditions, until the temperature of 250°C.

3.3 Physico-mechanical properties of charcoal as function of final pyrolysis temperature

Increase in final pyrolysis temperature reduces material stiffness (Table 2). Wood stiffness, 3,920 MPa, is greater compared to the heat-treated material at 300°C, 2,794 MPa. The decreasing trend continues with increase in temperature to 450°C. Temperatures of 450, 600 and 750°C produced charcoal with statistically equal stiffness.

Veiga et al. (2018) in a study with *C. citriodora* and *E. urophylla* also observed higher stiffness of wood, an average of 7,552 MPa, compared to charcoal produced at 450°C, average of 1,115 MPa. The authors performed mechanical tests in a universal test machine, in accordance with BS-373 (BS, 1957) for wood, and adapted the methodology for analysis of charcoal stiffness. The authors concluded wood is eighteen times stiffer and seventeen times more resistant than charcoal.

Table 2. Density, stiffness in longitudinal direction and dynamic hardness of wood and charcoal at different final pyrolysis temperatures.

Final temperature (°C)	Density ($g.cm^{-3}$)	Dynamic hardness (MPa)	Stiffness (MPa)
Control	0.791 a	29.82 a	3,920 a
300	0.634 b	10.72 b	2,794 b
450	0.425 c	3.25 c	1,496 c
600	0.423 c	3.59 c	1,362 c
750	0.444 c	4.63 c	1,278 c

Same letter in the column, do not differ statistically by the tukey test at 5% of significance.

Temperature decreases the density of material (Table 2). Control sample presents higher density than thermally treated materials. Temperatures of 450, 600 and 750°C produce charcoals with a statistically equal density.

This behavior corroborates with results found in literature, Coutinho and Ferraz (1988) observed a reduction in density, from 0.31 to 0,18 g/cm^{-3}, with increasing temperature from 400 to 1000°C. Trugilho and Silva (2001) observed decrease of apparent relative density with increase of

final pyrolysis temperature of 300 to 700°C. The authors concluded there is a minimum density point in carbonized materials at 660°C, above this temperature, for instance 900°C, density increases

Wood presented a higher dynamic hardness (Table 2) compared to charcoal, approximately 29 MPa. Pyrolysis temperature decreases material hardness, and so the charcoal presents a lower hardness compared to the wood. Temperature of 300°C decreases dynamic hardness to approximately 10 MPa, i.e., 1/3 of hardness of source material. Dynamic hardness tends to decrease with increase of final temperature to 450°C. Above this temperature (600 and 750°C), hardness remains statistically equivalent, with values close to 3.5 and 4.6 MPa.

Poncsak et al. (2006) investigated mechanical properties of birch and observed that there is a maximum hardness at about 160°C, values close to 22 and 28 MPa for samples analysed radially and transversely, respectively. The authors observed reduction of birch hardness with increase of holding time at the maximum temperature 220°C, due to a greater structural degradation. The values found are very close to those found in this study. According to Veiga et al. (2016) the reduction observed can be explained by the formation of cracks during carbonization process.

Variation of stiffness decreases with heat treatment (Figure 3). Control treatment presents amplitude of variation around 3,013 MPa. Final pyrolysis temperature of 300°C produced material with a range of variation of approximately 1,334 MPa. At temperature of 750°C variation is 963 MPa. Compared with wood variation, pyrolysis temperature of 750°C produces charcoal with variation approximately 3 times lower.

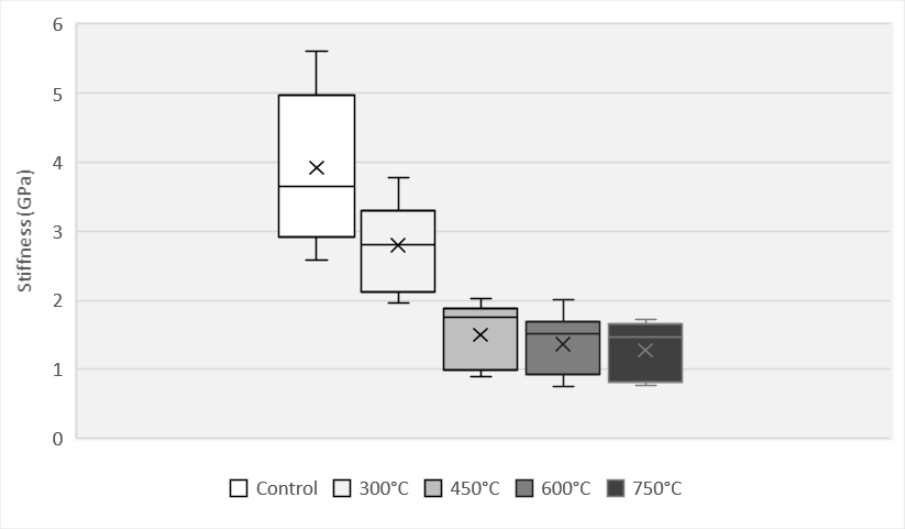

Figure 3. Variation of stiffness as a function of final pyrolysis temperature.

3.4 Correlations among physic-mechanical properties of wood and charcoal

There was high correlation ($R^2 = 0,87$) between wood density and stiffness (Figure 4), this correlation increases with application of heat treatment, for all temperatures (Figure 5 – A). Therefore, charcoal correlation is higher than found in wood, regardless of final pyrolysis temperature (Figure 4). These results were consistent with those found in literature (Couto et al., 2015; Andrade et al., 2018).

It is possible to observe high correlation ($R^2 = 0.93$) between density and dynamic hardness (DH) of wood (Figure 4). Final pyrolysis temperature negatively affects the correlation between these properties, the correlation decreases to $R^2 = 0.69$ (Figure 5 – B).

Correlation between stiffness × dynamic hardness of wood shows high, $R^2 = 0.79$ (Figure 4). The correlation of thermally treated material is lower compared to Control material (Figure 5 - C).

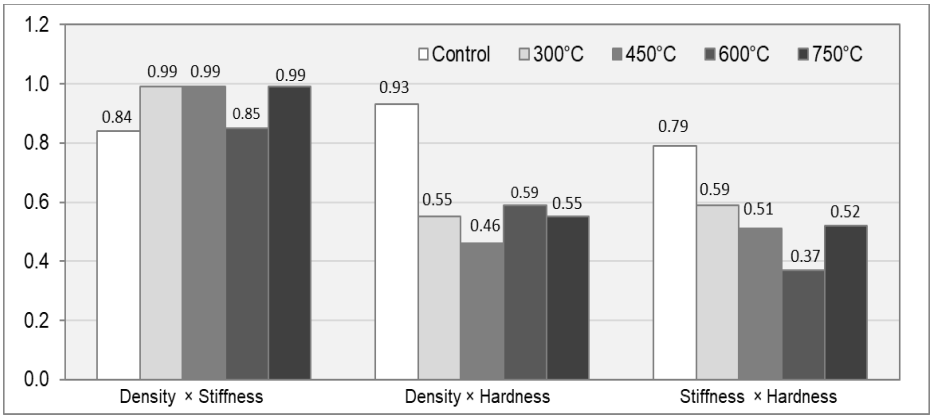

Figure 4. Correlations among physic-mechanical properties of wood and charcoal produced at different final temperature.

It is known the mechanical properties of wood correlate well with density (Andrade et al., 2018). For charcoal, Couto et al. (2015) observed a higher relative apparent density and greater stiffness. The authors observed rearrangement and greater organization of carbon chains under higher final carbonization temperature, producing charcoal with higher stiffness.

Veiga et al. (2018) found a high correlation between basic wood density and stiffness ($r = 0.732$). In addition to these results, same authors observed a high correlation between wood strength and wood stiffness ($r = 0.898$) but found a lower correlation for strength and stiffness of charcoal ($r = 0.607$).

A high correlation between hardness and density is in agreement with findings of Antal et al. (1990) and Chrzazvez et al. (2014), who evaluated relationship between density and mechanical strength. According to data found in literature, there are positive correlation between basic wood density, modulus of elasticity, gravimetric yield and density of charcoal (Moutinho et al., 2017; Doat et al., 1975).

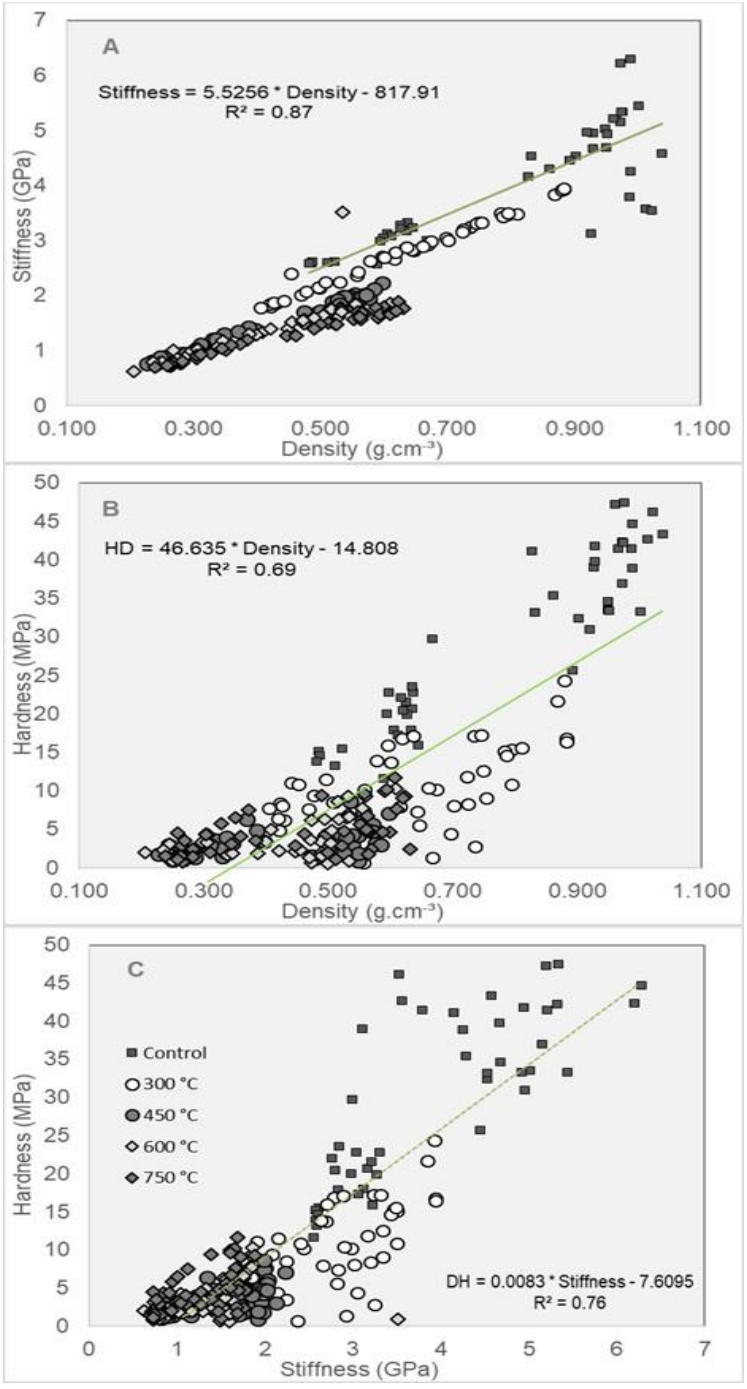

Figure 5. Correlations between density × stiffness (A), density × dynamic hardness (B) and stiffness × dynamic hardness (C) for all final pyrolysis temperatures.

4 CONCLUSIONS

There was a tendency of a decreasing stiffness with the increasing temperature, compared to wood, pyrolysis at 750°C reduces charcoal stiffness by approximately 30%. Wood presents a greater dynamic hardness, 29 MPa. Pyrolysis temperature of 450°C decreases material hardness to approximately 3 MPa.

Considering the genetic materials, highest values of wood stiffness were presented by *C. citriodora* and *E. deglupta*, same materials presented highest density, confirming high positive correlation between wood properties. The correlation between density and stiffness was $R^2 = 0.87$, charcoal correlation is higher than found in wood, $R^2 = 0.95$Correlation between density and dynamic hardness of wood was $R^2 = 0.93$, there was correlation reducing with pyrolysis temperature increase, $R^2 = 0.69$. Correlation between stiffness and dynamic hardness of wood was $R^2 = 0.79$. Final pyrolysis temperature negatively affects correlation between these properties.

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CHAPTER 5:

Área superficial e cristalinidade do carvão vegetal produzido sob diferentes temperaturas

RESUMO

Carvão vegetal utilizado em indústrias siderúrgicas deve permitir que o ar quente circule com liberdade dentro do alto forno, levando a frente de carbonização a toda matéria-prima nele contida, proporcionando uma pirolise homogênea. Dentro do alto-forno, a permeabilidade promove reações mais eficientes na redução do minério de ferro. Existem estudos que abordam a porosidade do carvão vegetal, porém, a influência da temperatura de pirólise na área superficial ainda é pouco conhecida. Além disso, não se sabe ao certo qual a influência da área superficial e cristalinidade na qualidade mecânica do carvão vegetal. Portanto o objetivo deste estudo foi avaliar área superficial e cristalinidade do carvão vegetal de uso siderúrgico. Para isso, nove árvores diferentes foram investigadas. As amostras foram pirolisadas em forno elétrico (mufla) em quatro temperaturas finais pirólise, 300°C, 450°C, 600°C e 750°C.Posteriormente, amostras foram moídas e, cerca de 5g do pó, analisadas no *Micromeritics TriStar* II Plus para determinação da área superficial por adsorção/dessorção de nitrogênio a 77,35K. A determinação da cristalinidade do carvão vegetal foi realizada no Difractômetro de Raios X D8 Discover (XRD), Bruker. Os valores de área superficial BET dos materiais tratados a temperatura de 300°C foram próximos de zero. Amostras pirolisadas a 300 e 450°C apresentaram pouca adsorção de gás N_2, com aumento da temperatura a adsorção é estatisticamente superior, com valores entre 97 e 130 cm^2/g, e entre 90 e 117 cm^2/g para amostras carbonizadas a 600 e 750°C, respectivamente. As curvas adsorção/dessorção de nitrogênio se mostram semelhantes, independentemente das espécies analisadas, com comportamento típico de materiais micro poroso. Espectros obtidos por difração de raio X dos materiais pirolisados a 300°C apresentam picos característicos de material que se tornou cristalino, porém ainda não está totalmente ordenado. Com o aumento da temperatura de pirólise para 750°C, as amostras apresentam mudança no padrão espectral, com picos associados a fase mineral do grafite. A similaridade dos espectros obtidos por difração de raio X e das curvas de adsorção de N_2 das diferentes espécies indicam a eficiência do processo de pirólise na homogeneização do carvão.

Palavras-chave: Difractômetro de Raios X (XRD), pirólise, BET, adsorção/dessorção de nitrogênio

1 INTRODUÇÃO

Indústrias produtoras de ferro-gusa, aço e ferro-ligas são as principais consumidoras de carvão vegetal do Brasil. Para este setor, além de suportar a carga de minério de ferro e gerar calor, o carvão vegetal utilizado deve permitir que o ar quente circule com liberdade dentro do alto forno, levando a frente de carbonização a toda matéria-prima nele contida. Dentro do alto-forno, a reatividade é influenciada pela porosidade do carvão vegetal, onde a permeabilidade promove reações mais eficientes na redução do minério de ferro e proporciona reações mais homogêneas. A área superficial do carvão influencia no processo de produção do aço e altera a qualidade do produto final.

Existem poucos estudos sobre adsorção/dessorção de carvão vegetal disponíveis na literatura. Área superficial tem sido comumente estudada em carvão ativado (Bansal et al., 1988), onde o carbono poroso apresenta estrutura para impregnação aplicada como filtros, adsorventes, eletrodos e suportes de catalisadores (Byrne e Nagle, 1997). Para materiais porosos, como madeira, essa propriedade apresenta forte correlação com densidade e influencia na higroscopicidade e reatividade do material (Assis, 2008). Para o carvão vegetal, influencia nas características físicas e no comportamento do produto em uso. A porosidade no carvão vegetal pode chegar a 80% (Barcellos, 2007), sendo os micros poros os principais responsáveis pela redutibilidade do minério de ferro (Bhagat, 2006).

Sabe-se que a temperatura influencia a área superficial do carvão ativado (Zanzi et al., 2001; Herzog et al., 2006). Para o carvão vegetal, a porosidade total aumenta com o aumento da temperatura final (Assis et al., 2016). Durante a produção do carvão vegetal a temperatura de pirólise causa perda de massa (Beall et al., 1974), altera as dimensões da madeira, destrói a parede celular e torna o material mais amorfo (McGinnes et al., 1971). Tushar et al., (2012) observaram que o grau de porosidade e grafitização aumentaram com o aumento da temperatura de pirólise, os autores observaram diminuição do carbono amorfo e aumento da quantidade do carbono grafítico, indicando melhor cristalização e aumento do tamanho dos cristalitos do carvão.

A cristalinidade influencia significativamente as propriedades mecânicas da madeira, Zhao et al. (2016) utilizaram difração de raios X para analisar a estrutura cristalina dos polímeros de madeira em baixa temperatura, inferindo no desempenho do produto, observando a estabilidade e propriedades mecânica da madeira em baixas temperaturas. O difractometro de raio X pode ser

usado para correlacionar a intensidade dos picos obtidos com a quantidade de cristalitos de carbono do carvão, os dados gerados permitem elaboração de gráficos onde as áreas sob o pico estão relacionadas com a quantidade de cada fase. Já a área superficial do carvão vegetal pode ser determinada pelo método BET, descrito por Brunauer, Emmett e Teller, (1938). Essa técnica mede o fenômeno de adsorção e dessorção do material, os resultados podem ser correlacionados com propriedades físicas como distribuição do tamanho dos poros e porosidade.

Existem estudos que abordam a porosidade e sua correlação com as propriedades do carvão vegetal (Trugilho, 1995), mas a influência da temperatura de pirólise na cristalinidade do carvão vegetal é pouco conhecida. Além disso, não se sabe ao certo qual a influência da porosidade e cristalinidade na qualidade mecânica do carvão. Portanto o objetivo deste estudo foi avaliar área superficial e cristalinidade do carvão vegetal de uso siderúrgico.

2 MATERIAL E MÉTODOS

2.1 Material vegetal

Foram investigadas madeiras de nove árvores diferentes, sendo um *Corymbia citriodora*, seis espécies de *Eucalyptus* e dois híbridos de *Eucalyptus* provenientes de plantios comerciais, para que o material genético seja um fator de variação (Tabela 1).

Tabela 1. Descrição das espécies, idades e origens das árvores estudadas.

Material vegetal		Idade (anos)	Origem
1	*Eucalyptus saligna*	37	Teste de progênie
2	*Corymbia citriodora*	37	Teste de progênie
3	*Eucalyptus pilulares*	37	Teste de progênie
4	*Eucalyptus deglupta*	37	Teste de progênie
5	*Eucalyptus cloesiana*	37	Teste de progênie
6	*E. urophylla* × *E. grandis*	6.0	Plantio comercial
7	*Eucalyptus microcorys*	37	Teste de progênie
8	*Eucalyptus dunnii*	37	Teste de progênie
9	*E. urophylla* × *E. grandis*	6.5	Plantio comercial

As árvores do teste de progênies foram cortadas de plantio florestal localizado na Universidade Federal de Lavras, Lavras, Brasil (densidade de espaçamento: 400 plantas/ha) com 37 anos de idade. Os testes de progênie estão localizados a uma altitude média de 900 metros, em uma zona de transição entre os biomas Cerrado e Mata Atlântica (21°14'S e 45°00'W), e o clima local se enquadra na categoria Cwb. Classificação de Köppen.

2.2 Preparação das amostras

Foram confeccionadas peças com dimensões nominais de 25 × 25 × 40 mm (R × T × L), foram produzidos quatro corpos-de-prova de cada material vegetal, totalizando trinta e seis amostras, estas foram mantidos em sala climatizada até a estabilização da umidade.

2.3 Pirólise do material

As amostras foram pirolisadas em forno elétrico (mufla), para isso as amostras de madeira foram colocadas dentro de uma cápsula metálica de carbonização, e depois, dentro do forno elétrico mufla, nas seguintes condições de pirólise: temperatura inicial de 100°C, taxa de aquecimento de 1,67°C min^{-1}, tempo de 30 minutos de permanência na temperatura final de pirólise, 16 horas de período de resfriamento por convecção natural. Quatro tratamentos, variando a temperatura finai pirólise, foram realizados, sendo 300°C, 450°C, 600°C e 750°C.

Após a preparação do carvão vegetal, as amostras foram moídas e parte do pó, cerca de 5g, forame levado em cápsulas e utilizado para caracterização tecnológica do material.

2.4 Determinação da área superficial

A área superficial foi determinada por adsorção/dessorção de nitrogênio (N_2) a 77,35K (-195,8°C), usando aparelho *Micromeritics TriStar* II Plus (Figura 1). As análises foram realizadas na Université de Lille 1, Lille - França.

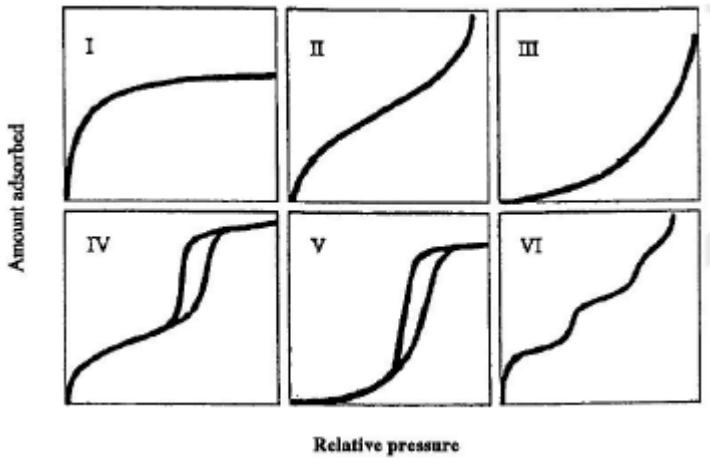
Foram investigados materiais pirolisados oriundos de seis árvores de diferentes materiais vegetais, sendo: *E. saligna (1), E. deglupta (4), E. urophylla × E. grandis 6.0 (6), E. microcorys (7), E. dunnii(8)* e *E. urophylla × E. grandis(9).*A desgaseificação preliminar das amostras foi realizada a vácuo com temperatura de 75°C durante 60 minutos, depois a temperatura foi aumentada para 150°C durante 4 horas. Esse procedimento é necessário para garantir que não exista

umidade, outro gás ou outro poluente no interior da amostra (Tushar et al., 2012). Em seguida, a adsorção-dessorção com nitrogênio líquido foi realizada (Figura 1-A). O modelo BET foi utilizado para calcular a área superficial específica dos catalisadores e a isoterma de dessorção do modelo BJH foi utilizada para determinar o diâmetro do poro e o volume do poro, baseado em Silvester (2013).

Figura 1. (A) Equipamento *Micromeritics TriStar* II Plus. (B) e Difractômetro de Raios-X (XRD) HotBird Bruker-AXS, modelo D8 *Discover.*

A classificação dos poros foi realizada com relação a adsorção de N_2, a 77 K, segundo método Brunauer et al. (1938).

Figura 2. Classificação dos poros segundo Brunauer et al. (1938).



Fonte: Brunauer et al. (1938).

Em que:

- Tipo I: Típica superfície exposta quase exclusivamente de micros poros, os quais, uma vez preenchidos, deixam pouca ou nenhuma superfície externa para posterior adsorção.
- Tipo II: Frequentemente encontrado quando ocorre adsorção de materiais não porosos ou com diâmetros superiores a micro poros. O ponto de inflexão ocorre perto da conclusão da primeira monocamada adsorvida.
- Tipo III: Caracterizada por calor de adsorção menor que o adsorbato de liquefação,
- Tipo IV: Ocorrem em adsorventes porosos, com poros na faixa de 1,5 – 100 nm. Em pressões mais altas, a inclinação mostra aumento da absorção à medida que os poros ficam cheios, o ponto de inflexão ocorre tipicamente perto da conclusão da primeira monocamada
- Tipo V: São observados onde há pequenos potenciais adsorventes de interação absorvente (semelhante ao tipo III), e também estão associados com poros na faixa de 1,5 a 100 nm.
- Tipo VI: ocorre em superfícies uniformes não porosas e representa adsorção camada por camada.

Fonte: Brunauer et al. (1938).

2.5 Determinação da cristalinidade do carvão vegetal

A determinação da cristalinidade do carvão vegetal foi realizada no Difractômetro de Raios X D8 Discover (XRD), *Bruker*(Figura 1-B).Com tubo de raios-X anticátodo em radiação de cobre (Kα, λ = 1,538 Å), em suporte de tubo fixo e o ângulo de abertura do feixe incidente de 0.5°. O

detector 2Dpermite observação simultânea da difração em ampla faixa de espaço, com ângulo de difração 2θ na faixa de 10-70° com passos de 0,02° por segundo. A interpretação do espectro de XRD foi feita a partir do software *Diffrac Eva* e a identificação da fase cristalina a partir de padrões de referência.

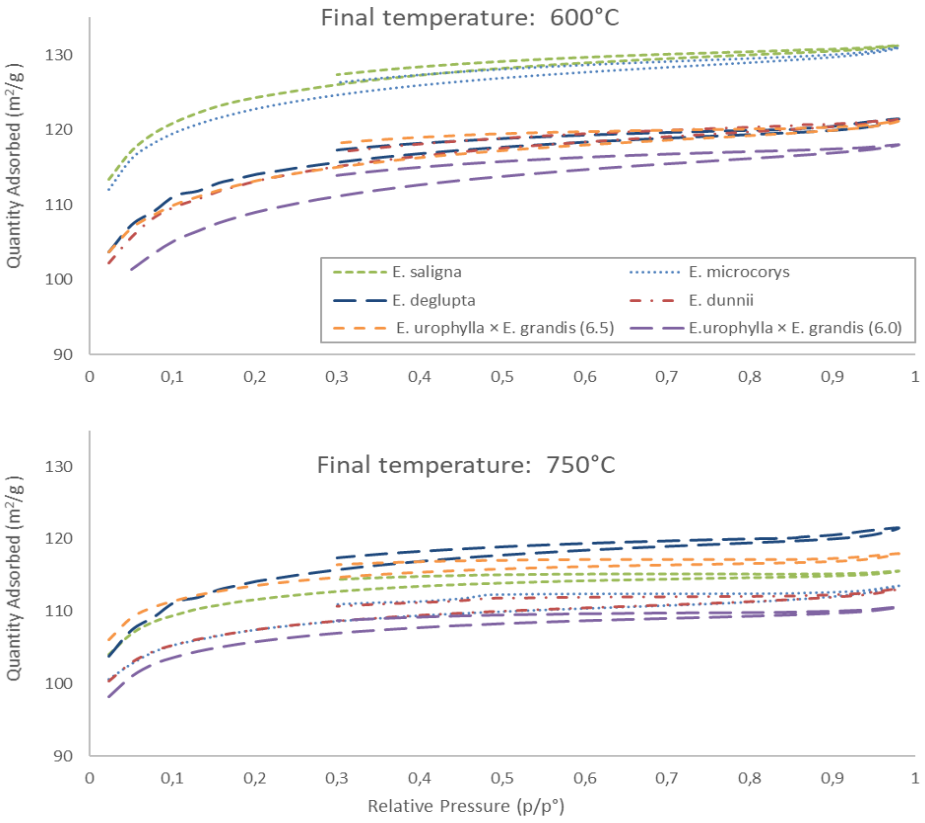
Amostras de carvão vegetal de cada um dos nove (9) materiais vegetais produzidos sob quatro (4) temperaturas de pirólise (300, 450, 600, 750°C) foram analisadas, totalizando trinta e seis (36) amostras analisadas.

3 RESULTADOS E DISCUSSÃO

3.1 Isotermas de adsorção e dessorção de N_2

Na Figura 3estão apresentadas as isotermas de adsorção e dessorção de N_2, a 77 K (-196,15°C), dos carvões oriundos de diferentes espécies pirolisados a temperatura de 600 e 750°C.

Figura 3. Isotermas de adsorção/dessorção de nitrogênio (77 K) para o carvão vegetal produzido a temperatura final de 600 e 750°C.



Os valores de adsorção para as amostras pirolisadas a temperatura de 600°C variaram entre 97 e 130 cm^2/g, e entre 90 e 117 cm^2/g para amostras carbonizadas a 750°C. As curvas adsorção/dessorção de nitrogênio se mostram semelhantes, independentemente das espécies analisadas (Figura3). Esse fenômeno pode ser interpretado como a eficiência do processo de pirólise na homogeneização do carvão vegetal.

Observa-se uma elevada adsorção do gás a baixas pressões relativas, variando pouco com o aumento desta, comportamento típico de materiais micro porosos. Esse fenômeno ocorre quando os micros poros adsorvem o gás e, uma vez preenchidos, deixam pouca ou nenhuma superfície externa para posterior adsorção (Brunauer et al., 1938).

Não foi possível observar as isotermas das amostras de madeira, em outros estudos com madeira, fez-se necessário um pré-tratamento para estabilização da amostra antes da realização do

teste de área superficial. As amostras carbonizadas a 300 e 450°C apresentaram valores próximos de zero, inferiores a 1 $m^2.g^{-1}$, com baixa adsorção e alta instabilidade, semelhante ao da madeira sem tratamento.

Avelar (2008), em estudo com carvão ativado, observou que a Piaçava sem tratamento apresentou menor volume de adsorção comparado ao carvão ativado, os valores foram próximo de zero. Ehrburger et al. (1981) em estudo com Beechwood (*Fagus Sylvatica*), em ciclo completo com amostras pirolisadas a aproximadamente 460°C observaram adsorção/dessorção lenta para madeira, e área superficial inferior a 1 $m^2.g^{-1}$. classificando-as como isotermas do tipo I, com enchimento de micro poros a baixa pressão relativa. Os autores, utilizando microscopia eletrônica de varredura e porosimetria de mercúrio, observaram que a temperatura de pirolise não altera a o tipo de poros, mantendo a meso e macro porosidade observada para a madeira original. Os autores concluíram que a temperatura de pirólise não forma novos tipos de poros, porém, observaram que o tratamento térmico causa diminuição do peso e encolhimento da amostra.

Villegas et al. (2006) caracterizaram quatro carvões comerciais fabricados a partir de madeira de azinheira (holm-oak) e *Eucalyptus*, variando o tipo de carbonização. Os autores concluíram que o carvão oriundo da madeira é um material de carbono poroso, na faixa de micro a macro poros, a características dos carvões dependem da madeira utilizada e também do sistema de carbonização. Keech et al. (2005) estudaram carvão vegetal de oito espécies de plantas lenhosas boreais, produzidos a partir galhos, pirolisados em mufla a temperatura de 450°C. A capacidade de adsorção do carvão vegetal foi testada pela técnica de bioensaios, a porosidade do carvão vegetal foi estimada e a distribuição do tamanho dos poros foi calculada para relacionar as características anatômicas da madeira com a capacidade de adsorção. Os autores encontraram porosidade transversal total variando entre 47 e 67% entre as espécies, e os materiais com maior quantidade relativa de macro poros apresentam maior capacidade de adsorção.

Existem poucos dados na literatura sobre adsorção/dessorção de carvão vegetal, o estudo da porosidade do carvão ativado é mais comum (Bansal et al., 1988) devido à sua grande área superficial é considerado um adsorvente versátil, basicamente micro poroso. Comparando valores com carvão ativado, Zou e Han, (2001) estudaram isotermas de dois carbonos ativados oriundos da China. Os autores observaram que em geral, temperaturas de ativação mais altas resultam em maiores capacidades de adsorção e menores rendimentos de carvão ativado.

O carvão vegetal pirolisado à temperatura de 600°C apresentou maior adsorção, em torno de 130 cm^2/g, enquanto o carvão produzido a 750°C apresentou valor máximo de adsorção próximo de 117 cm^2/g (Figura 4). Pode-se observar que a curva é do tipo I em ambas temperaturas de pirólises (600 e 750°C), indicando presença predominante de micro poros.

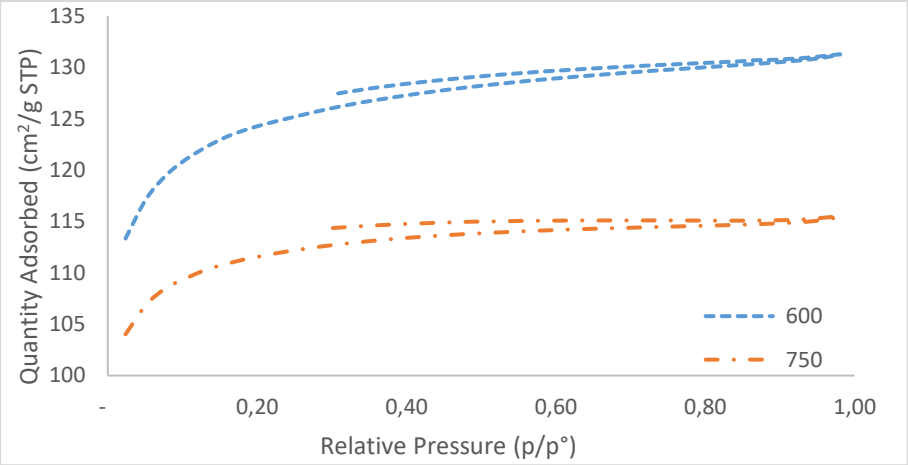


Figura 4. Isotermas média de adsorção/dessorção de nitrogênio (77k) para o carvão vegetal de produzido a 600 e 750°C.

Resultado contrário ao encontrado na literatura que aponta maior adsorção em materiais pirolisados sob temperatura mais alta (Chang et al., 2000; Treusch et al., 2004). Chang et al. (2000) observaram que quanto maior a temperatura de pirólise, maior a porosidade do material. Os autores estudaram carvão ativado produzidos em temperaturas próximas de 800 e 900°C, e encontraram valores de área superficial próximas de 91 e 54 $m^2.g^{-1}$, respectivamente. Os mesmos inferiram que temperaturas mais altas formam uma estrutura de poros mais desenvolvida, com o aumento da área superficial do carvão ativado, concluiu-se que esse fenômeno ocorria devido ao aumento da micro porosidade e também ao alargamento dos micros poros, os micros poros originais são transformados em meso poros nas reações de cristalitos. Salientando que os autores trabalharam com carvão ativado e, portanto, as comparações com os resultados desse estudo devem ser feitas com cautela.

3.2 Área superficial BET e caracterização dos poros

A Tabela 2 apresenta valores de área superficial BET, adsorção, dessorção, volume de poros e tamanho de poros.

Tabela 2. Valores de área superficial - BET, adsorção e dessorção de N_2, volume e tamanho de poros nos carvões produzidos em diferentes temperaturas.

Final Temperature	Surface Area ($m^2.g^{-1}$)	Adsorption cumulative ($m^2.g^{-1}$)	Desorption cumulative ($m^2.g^{-1}$)	Pore Volume ($cm^3.g^{-1}$)
300°C	0.84	0.45	0.46	0.0022
450°C	2.41	0.33	0.10	0.0008
600°C	358.25	38.60	8.84	0.0113
750°C	327.01	25.18	3.98	0.0070

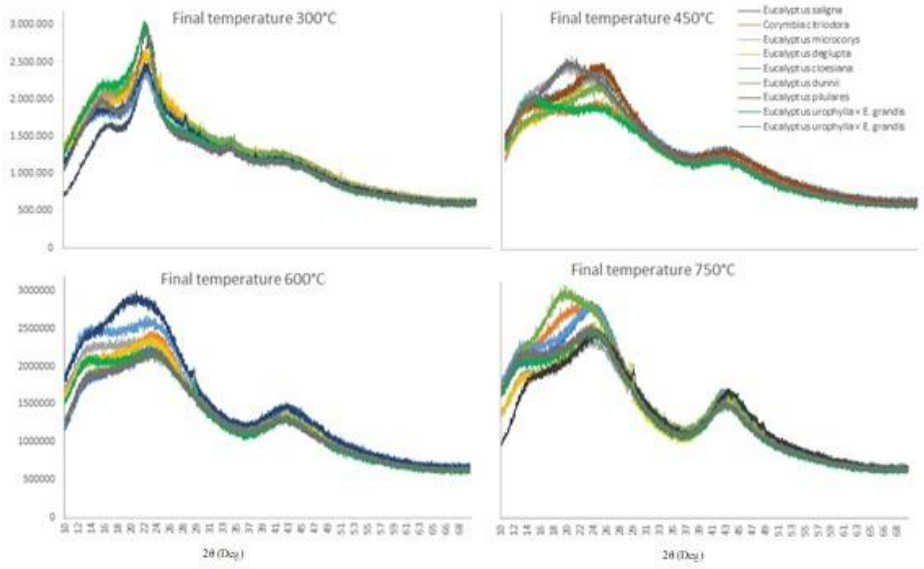
Os valores de área superficial BET não são representativos a temperatura de 300°C, com valor próximo de zero (Tabela 2). Provavelmente a temperatura desses tratamentos é insuficientes para alterar algumas características da madeira. O material carbonizado a 450°C apresentou área superficial inferior. Nas temperaturas de 600 e 750°C a área superficial é de 358 e 327 m²/g, respectivamente(Tabela 2),a degradação dos componentes internos do material pode liberar espaços e aumentar a porosidade do material. Neste estudo, a área superficial é mais alta a temperatura de 600°C e apresenta um ligeiro decréscimo a temperatura de 750°C.

Treusch et al. (2004) estudaram seis tipos de partículas e fibras para produção de painéis produzidos a 180°C e carbonizados de 500 a 900°C. Os autores observaram que a área superficial específica aumenta com o aumento das temperaturas de carbonização, com um máximo de 262 m²/g a temperatura de 700°C. Os autores concluem que, dentre outros fatores, as características da madeira têm efeito na área superficial dos materiais de carbono. Apesar da perda de massa e diminuição das dimensões com o aumento da temperatura, a estrutura original da madeira é retida no material de carbono poroso durante a carbonização.

3.3 Espectros obtidos por difração de raio X

Todas as bandas apresentam dois picos máximos próximos ao ângulo de 2θ, em torno de 23º e 45º (Figura 5), estes picos podem ser associados a fase mineral do grafite (Lopes et al., 2013), característicos do material semicristalinos (Klemm et al., 2005, Teixeira et al., 2010).

Figura 5. Espectros obtidos por difração de raio X de diferentes espécies de *Eucalyptus* e *Corymbia* em função da temperatura final de pirólise.



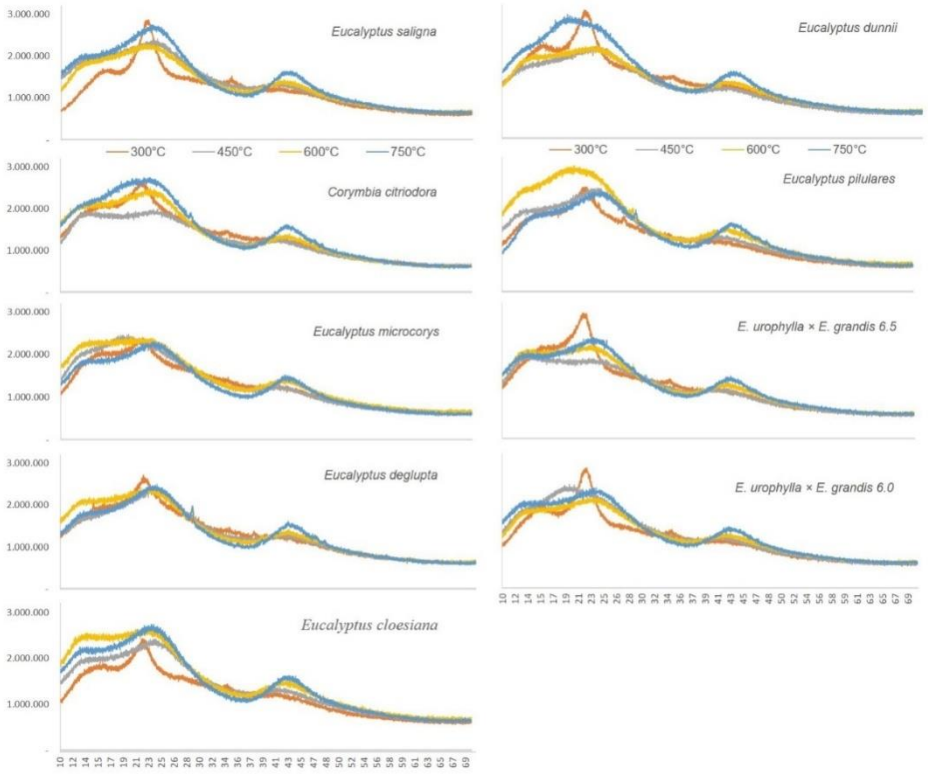
As análises de XRD apresentam principais picos na escala de 2θ a 16,8° e 22,8°, atribuídos aos planos de (101) e (002), respectivamente. Esses dois picos não mostraram mudança de posição em diferentes temperaturas, indicando que a estrutura cristalina dos polímeros de madeira não foi influenciada pela baixa temperatura. Isto é confirmado pelas ligeiras mudanças de grau de cristalinidade que variaram de 40,2 a 40,7%.

Os materiais pirolisados a 300°C apresentam dois picos distintos que ocorrem próximos a região 2θ de 14° e 23° (Figura 5), com o primeiro pico largo amorfo e o segundo pico mais intenso. Este, entre 20 e 25°, é característico de um material que se tornou cristalino, porém ainda não está totalmente ordenado (Lee et al., 2018). Observa-se também, um pico na região de 2θ de 42°, semelhante ao observado por Tsubouchi et al. (2003).

Com o aumento da temperatura final de pirólise as amostras apresentam mudança no padrão espectral (Figura 5). Na temperatura de 450°C observa-se, na região 2θ entre 14° e 23°, picos mais suaves que os dois descritos a 300°C. Na temperatura de 600°C, os picos próximos a região 2θ de 14° e 23° se tornam indistintos. Observa-se também, uma curva suave próxima aos 45° com o aumento da temperatura, a temperatura final de 750°C confirma essa tendência, com duas curvas próximas a região 2θ de 14° e 23° e, um pico intenso em 45°. A similaridade das curvas dos espectros das diferentes espécies de *Eucalyptus* e *Corymbia* demonstra a eficiência do processo de pirólise na homogeneização dos materiais pirolisados. Com o aumento da temperatura de pirólise, aumenta a formação de cristais de grafite provocados por mudanças na estrutura do carbono durante a produção de carvão.

Jesus (2014), observou que os picos característicos do carvão vegetal, se tornam menos evidentes com o processo de ativação do carvão, porém, ainda apresentam características dos compostos provenientes do material precursor. Tushar et al. (2012) observaram que o grau de cristalização e teor de carbono grafítico aumentou o com aumento da temperatura de pirólise e tempo de permanência, indicando aumento do tamanho dos cristalitos.

Figura 6. Espectros obtidos por difração de raio X das nove espécies de *Eucalyptus* e *Corymbia* em quatro diferentes temperaturas finais de pirólise.



Na Figura 6 pode-se observar a influência da temperatura nos espectros de raio x dos materiais genéticos analisados. Os materiais genéticos pirolisados a 300°C apresentam dois picos distintos que ocorrem próximos a região 2θ de 14° e 23°, independente da espécie. A pirólise a 750°C exibe um pico próximo a 45°, para todas as espécies. As temperaturas de 450 e 600°C parecem suavizar as curvas espectrais das espécies de *Eucalyptus* e *Corymbia*.

4 CONCLUSÃO

Os valores de área superficial BET dos materiais tratados a temperatura de 300°Cforam próximos de zero. Estes apresentaram comportamento característico de material que se tornou cristalino, porém ainda não está totalmente ordenado. Amostras pirolisadas a 300 e 450°C apresentaram pouca adsorção de gás N_2. Com aumento da temperatura a adsorção é estatisticamente superior, com valores entre 97 e 130 cm^2/g, e entre 90 e 117 cm^2/g para amostras

carbonizadas a 600 e 750°C, respectivamente. Com o aumento da temperatura de pirólise para 750°C, aumenta a formação de cristais de grafite e o carvão apresentam mudança no padrão espectral.

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CHAPTER 6:

General conclusion

Heat treatment at 450°C decreases hardness, stiffness and apparent density of wood. Increasing final pyrolysis temperature to 750°C does not alter these properties in charcoal. Final pyrolysis temperature of 650°C increases charcoal surface area. Charcoal crystallinity increases until at temperature of 750°C.

Controlling carbonization processes is more important than selecting vegetal material, at least for mechanical performance of charcoal into blast furnaces. Final pyrolysis temperature produces more homogeneous product, reducing influence of origin wood on charcoal mechanical properties.

There is a high positive correlation between density, stiffness and hardness in wood and charcoal. Increase final temperature increase stiffness correlation. For density and hardness, final pyrolysis temperature negatively affects these correlations.

Ultrasound and portable hardness tester were able to analyse charcoal mechanical properties. With these results it can be affirmed these are an efficient equipment to estimate density, hardness and stiffness of charcoal. Hardness and stiffness can be used as a new criterion for classifying quality of charcoal in terms of mechanical performance in blast furnaces.

NIR spectroscopy models were successfully developed for estimating pyrolysis final temperature, charcoal density and its dynamic hardness. The statistics of the models indicate that NIR spectroscopy is an efficient solution to quickly estimate density and hardness of charcoal.

This study can serve as a reference for the mechanical classification of charcoal quality.