






Influence of Particles Size on NIR Spectroscopic Estimations of Charcoal Properties

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ABSTRACT

The objective of this study was to evaluate the influence of particle size of charcoal samples on the predictive model statistics of charcoal chemical composition based on the NIR spectroscopy. Spectra of *Acacia* and of *Eucalyptus* charcoal were collected in the 100, 60 and 40 mesh granulometry, besides the powder remaining at the bottom of the sieves sets. They were subjected to principal component analysis and partial least square regression in order to estimate of volatile material (VMC), ash (AC) and fixed carbon content (FCC) values. The estimation of the FCC, VMC and AC of *Eucalyptus* based on NIR was more accurate using spectra of lower-particle-size powder. The models for *Acacia* charcoal were better using spectra measured at 40 mesh to predict FCC, 100 mesh for AC, and smaller size for VMC. NIR spectroscopy was efficient in estimating the immediate chemical composition of charcoal, except for AC.

Keywords: wood pyrolysis, NIR, proximate chemical analysis, forest biomass.

1. INTRODUCTION

Charcoal is an alternative to add value to wood by turning it into a highly energetic and carbon-rich product. Carbonization increases the calorific value and the fixed carbon content of the wood, making the product a more energy-intensive material when compared to the raw material from which it originated (Trugilho et al., 2001). During the carbonization process, the wood is subjected to the action of high temperatures in the transformation process in which its chemical components are extensively modified (Akhtar et al., 2018).

Variation in the chemical composition of charcoal influences its performance in industrial use (Vilela et al., 2014). Therefore the study of the chemical properties of charcoal is of great interest for a more rational use of this key input by most Brazilian steelmakers (Protásio et al., 2011). The fixed carbon content, volatile materials and ash content has a considerable influence on the energetic use of the biofuel, since they have significant correlation with the calorific value of charcoal (Majumder et al., 2008; Parikh et al., 2005).

In general, fuels with high fixed carbon content burn more slowly, resulting in longer residence times in the furnace, compared to materials with low fixed carbon content (Vale et al., 2001). Moreover, the fixed carbon of charcoal affects the pig iron production process: the higher the fixed carbon content the greater the mass quantity of this compound inside the blast furnace, improving the use of its internal space during the thermoreduction (Barbieri et al., 2016).

Assessing and monitoring the quality of charcoal is a challenge for companies that use charcoal in their production process, such as steel industries. Charcoal properties are commonly determined by conventional methods, but are time-consuming and require sample preparation. In order to obtain greater agility and precision, near infrared (NIR) spectroscopy has been successfully applied to analyze the properties of a large number of materials. The technology makes it possible to save reagents to determine various properties, besides reducing cost and time spent in routine laboratory analyses (Diesel et al., 2014; Pasquini, 2018).

NIR spectroscopy has been used in charcoal evaluations by means of qualitative analyses, such as the differentiation of carbonization processes (Monteiro et al., 2010) and the distinction of charcoals

produced by different forest species (Davrieux et al., 2010; Muniz et al., 2013; Nisgoski et al., 2015a; Ramalho et al., 2017). Moreover, the technique can be used in quantitative approaches for predicting several charcoal properties such as moisture content, volatile matter content, fixed carbon content, ash content (Barbosa et al., 2013), apparent relative density and gravimetric yield (Costa et al., 2018). However, the influence of the charcoal granulometry on the accuracy of chemical properties estimates based on near infrared radiation is unknown. Therefore, the objective of this study was to evaluate the effect of powder granulometry on the performance of chemical properties predictive models based on the near infrared spectra of charcoal.

2. MATERIAL AND METHODS

2.1. Origin of material

Twenty samples of *Acacia mangium* and twenty samples of *Eucalyptus urophylla* × *E. grandis* hybrid with 54 months of age from the municipality of Montes Claros, northern region of the state of Minas Gerais, Brazil (16°44'06" south and 43°51'43" west) were investigated in this study. Wood discs (thickness: 30 mm) were collected at 0% of the commercial height of the trees and divided into 4 wedges passing through the pith. Two opposing wedges (defect free) were used for charcoal production.

2.2. Carbonization of wood

Wood carbonization was carried out in a muffle-type laboratory electric oven connected to a water-cooled condenser, which is coupled to the non-condensable gas collecting flask. Before carbonization the wood samples were oven dried at 103 °C ± 2 °C and introduced into a cylindrical metal reactor (length: 30 cm and diameter: 12 cm). The total pyrolysis time was approximately 4 hours with a heating rate of 1.67 °C/min. The pyrolysis started at 100 °C and ran up to the final temperature of 450 °C, with a residence time of 30 minutes.

2.3. Charcoal characterization and sample preparation

Proximate chemical analysis was carried out in order to determine the volatile material content (VMC) and ash contents (AC). The fixed carbon content (FCC) was

calculated by difference according to the procedure described in ASTM D1762-84 (ASTM, 2007).

Charcoal pieces were reduced to particles with granulometries of 40, 60 and 100 mesh by the use of vibrating sieves. The finest material remaining in the sieve was also collected.

2.4. NIR spectra acquisition

Near infrared (NIR) spectra were recorded on charcoal samples of different granulometries using a Fourier transformed NIR spectrometer (Bruker Optik GmbH, model: MPA, Ettlingen, Germany) using an integrating sphere. NIR spectra acquisition was performed on the charcoal samples of different particle sizes in glass containers (vials) by means of OPUS version 7.5 software. The spectral range of 12500 to 4000 cm^{-1} was used, with a resolution of 8 cm^{-1} in diffuse reflection mode.

2.5. Multivariate statistical analyses of data

Statistical analyses were performed using Chemoface v.1.61 software (Nunes et al., 2012). Principal component analysis (PCA) was performed with the purpose of previously exploring the data dependence. Partial least squares (PLS) regression was adjusted based on the NIR spectra (matrix X) and the fixed carbon, ash and volatile material content values as dependent variables (matrix Y). The models were adjusted from untreated spectra data and after mathematical treatments such as first derivative (13-point filter and a second order polynomial), normalization and standard normal

variate (SNV). PLS regression models were evaluated by the mean square error (RMSE) and the coefficient of determination (R^2) between laboratory determined and NIR predicted values.

3. RESULTS AND DISCUSSION

3.1. NIR spectra on charcoal

The mean untreated NIR spectral signature of *Acacia* and *Eucalyptus* charcoal samples of different particle sizes (40, 60, 100 mesh and fine) is shown in Figure 1. As the particle size reduces, the average NIR absorbance also decreases; however the absorption bands are the same, independent of particle size. This behavior was previously reported by Nisgoski et al. (2015b), who investigated the effect of granulometry on NIR absorbance in *Salix* sp.

NIR spectra ranging from 12500 to 9000 cm^{-1} presented high noise (Figure 1). Costa et al. (2018) have studied *Eucalyptus* charcoal through NIR and also observed this tendency. The spectra plot does not allow verifying if there are differences between the charcoals according to the granulometry. That is why it is necessary to use multivariate statistical analysis to identify such possible differences.

3.2. Multivariate analyses

Principal component analyses (PCA) was performed separately for the two species: the first two PC together accounted for 99.99% of the data variation for *Acacia* and 99.90% for *Eucalyptus*. PCA scores of the *Acacia*

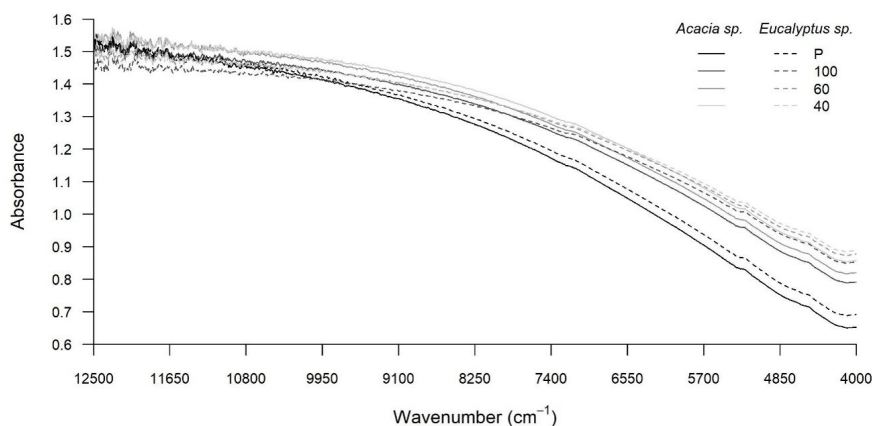


Figure 1. Diffuse reflection spectra shown as original data for *Eucalyptus* and *Acacia* charcoal milled at 100, 60, 40 mesh and fine powder (P).

(Figure 2A) and *Eucalyptus* (Figure 2B) charcoal spectra in different granulometries were not clearly divided into groups according to the particle size of samples because the chemical composition of charcoal is the same within each species. However, the scores containing information on the fine powder spectra

(P) showed a tendency to separate from the others. Fahey et al. (2018) reported that although there is influence of particle size on NIR acquisition, the effect of this variable is small. Thus, it is difficult to observe the grouping of samples in function of this characteristic.

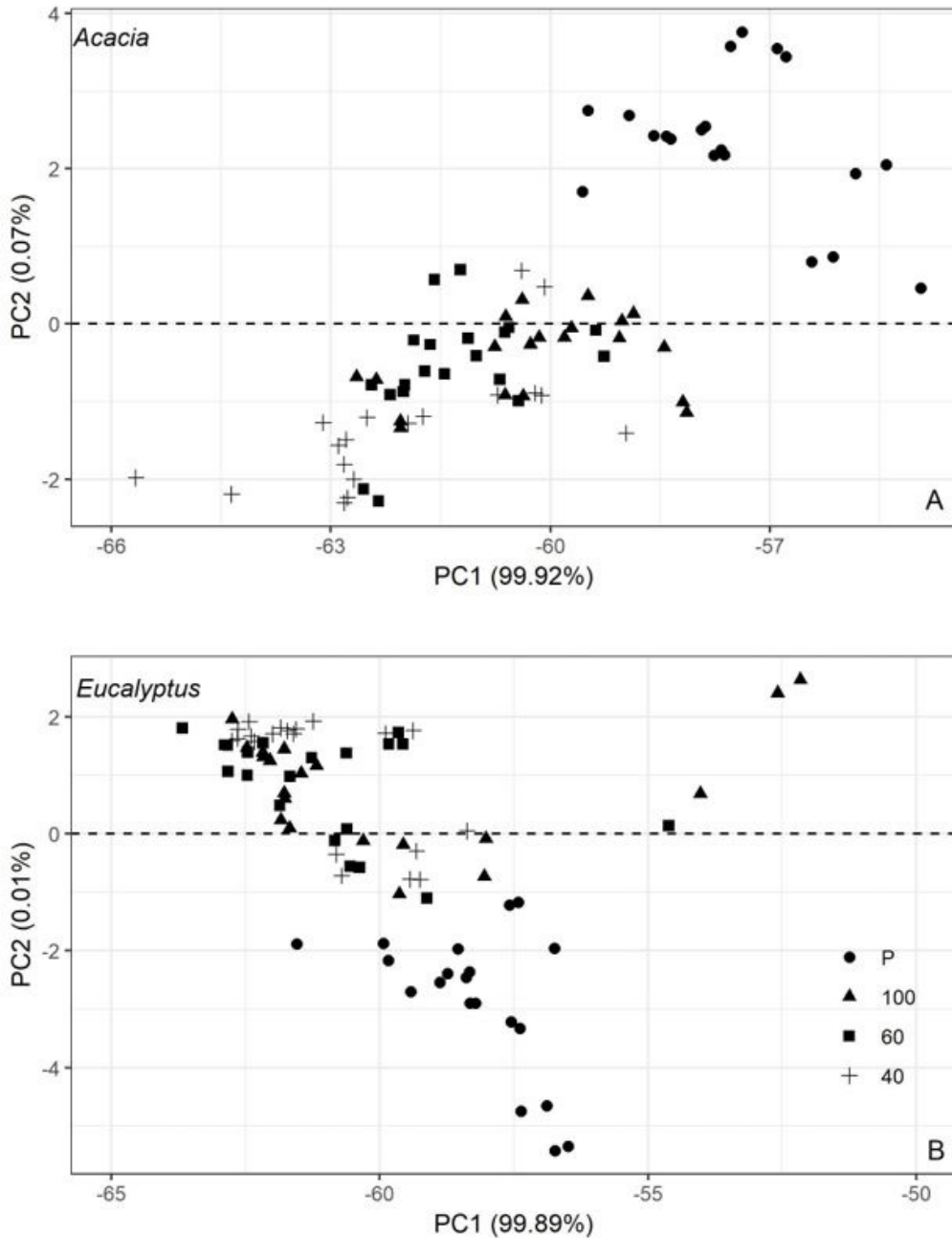


Figure 2. Scores of PCA applied to NIR spectra recorded on charcoal powder milled at 100, 60, 40 mesh and fine powder (P) for *Acacia* (A) and *Eucalyptus* (B) charcoal.

The statistics of PLS regressions for estimating volatile matter (VMC), ash (AC) and fixed carbon (FCC) content according to the species and particle size are presented in Table 1. The coefficient of determination for the calibration (R^2c) was over 0.99 in all models. Root mean square error for calibration (RMSEc) ranged from 0.000 to 0.046, whereas the variation was broader for cross validation. The R^2cv values ranged from 0.032 to 0.842, with the RMSEcv ranging from 0.058 to 1706 in the cross-validations. The model based on charcoal spectra from the fine powder (P) showed the highest R^2cv . However, these statistics are lower than those reported by Costa et al.

(2018), which presented an R^2cv of 0.96 in calibrations using untreated NIR spectra of *Eucalyptus* charcoal.

The PLS-R model for estimating ash content that yielded the best coefficient of determination was obtained in the finer grain size for *Euclyptus* (R^2cv of 0.375), whereas the 100 mesh powdered spectra resulted in higher correlation (R^2cv of 0.353) for *Acacia*. However, all parameters of the Ash models did not obtain satisfactory values. Ash is composed of inorganic materials such as minerals and the near infrared spectroscopy is indicated only for organic materials.

In order to estimate the volatile material content (VMC), the PLS-R models with higher R^2cv were obtained

Table 1. Statistics for volatile matter (VMC), ash (AC) and fixed carbon (FCC) content models developed from NIR spectra recorded on charcoal powder milled at 100, 60 and 40 mesh and fine powder (P) for *Acacia* and *Eucalyptus* charcoal.

Statistics	<i>Acacia</i>			<i>Eucalyptus</i>		
	VMC	AC	FCC	VMC	AC	FCC
Fine Powder						
Treat	Raw	Norm	Raw	Norm	Raw	Norm
LV	6	6	7	6	5	6
RMSEc	0.013	0.001	0.003	0.005	0.002	0.005
R^2cal	1.000	1.000	1.000	1.000	0.999	1.000
RMSEcv	0.946	0.191	0.945	0.885	0.058	0.904
R^2cv	0.682	0.215	0.640	0.842	0.375	0.828
Powder 100 mesh						
Treat	Norm	1d	Norm	Raw	1d	Raw
LV	6	8	4	6	6	6
RMSEc	0.004	0.000	0.034	0.017	0.002	0.046
R^2cal	1.000	1.000	1.000	1.000	0.999	1.000
RMSEcv	1.174	0.170	1.021	1.706	0.096	1.290
R^2cv	0.507	0.353	0.573	0.451	0.070	0.650
Powder 60 mesh						
Treat	Norm	Raw	Norm	Norm	1d	Norm
LV	7	7	7	5	6	7
RMSEc	0.001	0.000	0.001	0.017	0.002	0.002
R^2cal	1.000	1.000	1.000	1.000	0.999	1.000
RMSEcv	1.138	0.215	1.031	1.706	0.096	1.651
R^2cv	0.468	0.032	0.524	0.451	0.070	0.461
Powder 40 mesh						
Treat	Norm	Raw	Norm	Norm	1d	Norm
LV	6	6	6	5	6	6
RMSEc	0.009	0.005	0.004	0.028	0.002	0.010
R^2cal	1.000	1.000	1.000	1.000	1.000	1.000
RMSEcv	1.022	0.319	0.839	1.453	0.069	1.402
R^2cv	0.627	0.171	0.725	0.583	0.129	0.596

LV: Latent Variables; RMSEc: Mean square error for calibration; R^2cal : Coefficient of determination for calibration; RMSEcv: Mean square error for cross validation; R^2cv : Coefficient of determination for cross validation; Raw: Untreated spectra data; 1d: first derivative; Norm: Normalization.

using NIR spectra recorded on the fine powder, either in *Eucalyptus* (R^2_{cv} of 0.842) or *Acacia* (R^2_{cv} of 0.682) charcoal. The PLS-R models for fixed carbon content from spectra of the fine powder also presented higher R^2_{cv} (0.828) for *Eucalyptus*. Andrade et al. (2012) presented R^2_{cv} values in the prediction of the fixed carbon content and content of volatile materials for *Eucalyptus* between 0.86 and 0.91, respectively. In regard to *Acacia* models, NIR spectra taken from 40-mesh charcoal generated the highest R^2_{cv} model (0.725), as shown in Table 1. These findings showed the same trend probably because the values of volatile material content were used for the calculation of the fixed carbon content. To sum up, our findings suggest that charcoal milled at finer particle size is indicated for NIR spectral acquisition and prediction of this property.

PLS-R models developed from NIR spectra mathematically treated by normalization yielded better results, followed by models from untreated

spectra. Most models were better using normalization for predicting FCC and VMC while estimates of AC should be performed from models based on untreated signal or spectra treated by first derivative. Andrade et al. (2012) reported higher R^2 values for prediction of the FCC, VMC and gravimetric charcoal yield (GCY) using untreated NIR spectra of *Eucalyptus*. Costa et al. (2018) also found better statistics for estimating GCY, apparent relative density and final temperature carbonization of solid charcoal specimens using untreated NIR signals.

The lab-measured and NIR-predicted values plot (Figure 3) for the fixed carbon content according to particle size allows one to observe that there was no strong association between the values for the *Eucalyptus* and *Acacia* samples. Leave-one-out cross-validated PLS-R models for FCC in *Acacia* charcoal based on NIR spectra recorded on charcoal milled at 60 mesh presented the worst statistics ($R^2_{cv} = 0.461$).

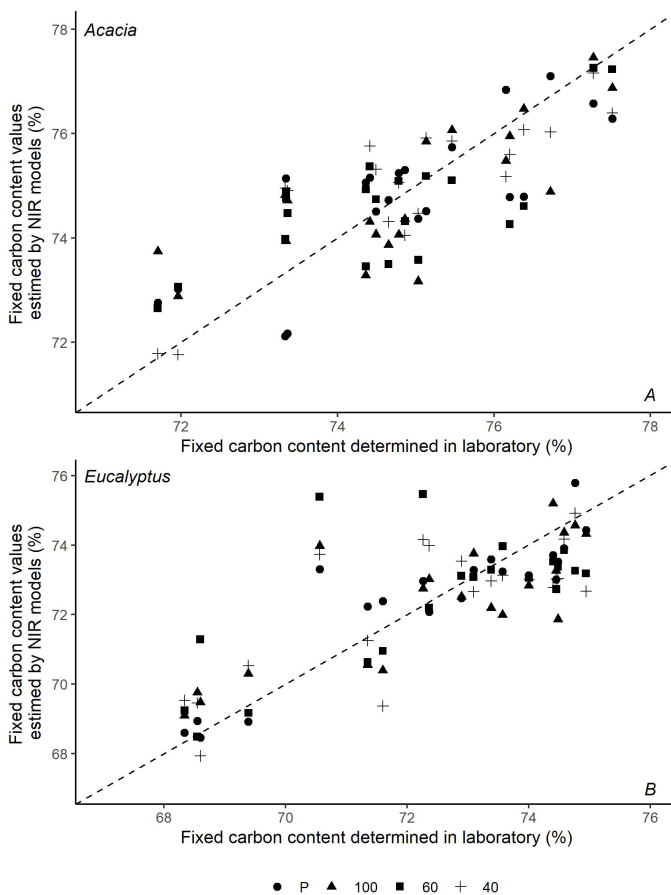


Figure 3. Fixed carbon content values determined in the laboratory and estimated by models based on spectra obtained on powder milled at 100, 60 and 40 mesh and fine powder for *Acacia* (A) and *Eucalyptus* (B).

4. CONCLUSION

The estimation of the fixed carbon content, volatile content and ash content of *Eucalyptus* based on NIR is more accurate when spectra are recorded in powder of lower particle size. On the other hand, the predictive models for *Acacia* charcoal were obtained from spectra measured in powders of 40 mesh to predict the fixed carbon content, 100 mesh for the ash content and the lowest grain size for the volatile material content.

NIR spectroscopy proved to be efficient in estimating the chemical composition of charcoal, except for ash content. In short, the PLS-R models reported in this paper are able to satisfactorily provide estimates in unknown charcoal samples.

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