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Research paper

Evaluation and classification of eucalypt charcoal quality by near infrared spectroscopy

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ABSTRACT

The objective of this study was to establish multivariate models to estimate gravimetric carbonization yield (GCY), apparent relative density (ARD) and final carbonization temperature (FCT) of Eucalyptus charcoal by NIR spectroscopy. Eucalyptus clones from commercial plantations managed for energy purposes and pulp and paper production were used. Wood prismatic specimens with nominal dimensions of 25 mm x 25 mm x 80 mm were carbonized at final temperatures of 400° C, 500° C, 600° C, and 700° C. NIR spectra measured directly on 160 charcoal specimens were correlated with GCY and ARD values obtained through conventional laboratory analyzes. Principal component analysis (PCA), partial least squares regression (PLS-R) and partial least squares discriminant analysis (PLS-DA) were utilized based on spectral and experimental information. The NIRS technique associated with PLS-R was able to predict FCT and GCY presenting cross-validation coefficients (R^2cv) between reference and estimated data of 0.96 and 0.85, respectively. It was not possible to predict ARD based on charcoal spectral signature. Cross- and independent validations presented similar statistics, confirming the capacity of NIR spectroscopy coupled with multivariate analyses for monitoring charcoal quality. Specimen classifications into carbonization temperature groups through PLS-DA obtained 100% correct classification, except for the 500° C temperature (97.5%). These models are able to reliably estimate the gravimetric yield and final pyrolysis temperature of charcoal, an important parameter that can be used as a quality criterion for industrial applications. This work will serve as a reference for the development of new studies and applications of the NIR technique in the assessment of charcoal quality.

1. Introduction

In the context of the post-Kyoto protocol, the iron and steel industry faces new environmental challenges in reducing CO_2 emissions [1]. One possible solution is replacing top coke by charcoal in blast furnaces.

According to Faostat [2], Brazil is the major producer of charcoal producing 7.24 million tons per year. Part of this production (4.6 million tons in 2015) is destined for the domestic market, of which 82% was produced from planted trees [3]. In steel mills, charcoal is used as a source of energy, reducing agent and support of the iron ore load, besides allowing gaseous percolation through the bed [4,5]. Iron ore is an essential raw material for the production of pig iron, which in turn is used in the production of steel [6]. The quality of charcoal for iron and steel purposes is controlled by factors related to the pyrolysis process and the variation of raw material [1,7,8].

The industries that use the charcoal in the productive processes need to monitor the properties of the carbonaceous material so that its products have uniform quality. However, according to Andrade et al. [9] the characterization of the materials performed through conventional laboratory methods are often expensive and time-consuming. Near infrared (NIR) spectroscopy has been pointed out as a fundamental tool for managing and making decisions in productive processes, since it allows real-time analysis in a fast and reliable way [10]. It is a non-destructive technique that has been applied successfully to estimate the characteristics of organic materials containing C-H, O-H, N-H or S-H molecules [11], which is the case of charcoal.

Few studies have applied NIR spectroscopy for evaluating charcoal. In relation to the qualitative analyzes of charcoal based on NIR technology, few studies have shown that it was possible to discriminate the raw material and the productive process of the charcoal. For example, Labbé et al. [12] have discriminated charcoal produced from four wood species used for the manufacture of distilled beverages using mid infrared. Monteiro et al. [13] have used this technique to distinguish the pyrolysis process and charcoal origin (*Eucalyptus* and native species). Devrieux et al. [14] have discriminated Ipê (*Tabebuia serratifolia (Vahl)* Nichols) and Eucalypt (*Eucalyptus grandis* Hill ex Maiden) wood and

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charcoal powders. Nisgoski et al. [15] have distinguished four species belonging to two families. Muñiz et al. [16] have differentiated species of wood and charcoal marketed as angelim. Ramalho et al. [17] have differentiated charcoal produced from wood coming from planted (legal) and native forest (illegal) produced at different temperatures. In regard to quantitative analysis, there are only two studies: Labbé et al. [12] estimated the carbonization temperature and Andrade et al. [9] estimated the fixed carbon content, volatile material content and gravimetric yield of *Eucalyptus* charcoal based on NIR spectra.

Therefore, the aim of this study was to establish multivariate models for estimating the final temperature, apparent density and gravimetric yield of *Eucalyptus* charcoal and for classifying the charcoals as a function of the final carbonization temperature based on the near infrared spectra. Since the final temperature can be used as a qualitative parameter, being able to quickly and reliably predict the final temperature can be useful for monitoring charcoal quality in iron and steel industries.

2. Material and methods

2.1. Biological material

The biological material used were *Eucalyptus* clones from commercial plantations of two companies: Vallourec (clones of hybrids of *Eucalyptus grandis* × *E. urophylla*, 6.5 years old) located at Paraopeba (19°16′S, 44°24′W), state of Minas Gerais, Brazil, focused on the production of charcoal for energy and Cenibra Nipo-Brasileira S.A. (clones of hybrids of *Eucalyptus grandis* × *E. urophylla*, 6 years old) managed in Belo Oriente (19°17′S, 42°23′W) state of Minas Gerais, Brazil, for pulp.

2.2. Sample preparation

Central boards were removed from the first log and 160 specimens (80 from Cenibra and 80 from Vallourec) were produced with nominal dimensions of 25 × 25 × 80 mm (R × T × L), defects free. All specimens were properly identified using a copying pencil, labeling did not disappear after pyrolysis). Before the pyrolysis, specimens were previously oven-dried at 103 ± 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) according to procedure described in Trugilho and Silva [8]. The pyrolysis conditions were:

- Initial temperature: 100 °C.
- Heating rate: 1.67 °C min^{-1}.
- Final temperature: 400 °C, 500 °C, 600 °C, and 700 °C.
- Residence time at the final pyrolysis temperature: 30 min.
- Cooling period by natural convection: 16 h.

The wood specimens were carbonized within a carbonization capsule placed inside the muffle furnace. The carbonization capsule was connected to a water-cooled condenser coupled to a receiver flask of condensable gases. The charcoal specimens were produced at 400, 500, 600 and 700 °C to simulate the temperature range adopted in real situations in most Brazilian industries.

2.4. Recording NIR spectra

A Bruker FT-NIR (model MPA, Bruker Optik GmbH, Ettlingen, Germany) was used in diffuse reflectance mode. This Fourier transform spectrometer is designed for reflectance analysis of solids with an integrating sphere that measures the diffuse reflected infrared energy from a 150 mm^2 spot. Spectral analysis was performed within the 12,500–3600 cm^{-1} range at 8 cm^{-1} resolution (each spectrum consisted of 2307 absorption values), according to the procedure described in Ramalho et al. [17].

The spectra of each sample was obtained by means of a mean of 16 scans performed at two different points on the specimen, a reading obtained on the radial face (Rd), a reading on the tangential face (Tg), that is, 2 × 16 scans per samples. The readings were carried out on the specimen surfaces, avoiding the regions with cracks and other defects. The spectrometer was connected to a computer that stored the spectra data collected through the OPUS program, Version 7.5.

Before NIR recordings, charcoal specimens were kept in acclimatized room at a temperature around 20 °C and relative humidity around 65%. Under these conditions, the charcoal specimens reached equilibrium moisture of approximately 6%.

2.5. Characterization of charcoal

The gravimetric yield of charcoal was determined after each carbonization by dividing the mass of charcoal by the mass of oven-dried wood, in percentage. The apparent relative density of charcoal was performed by the hydrostatic method, based on water immersion, as described in standard ABNT NBR 11941 [18] with adaptations for charcoal.

2.6. Multivariate data analysis

The software, The Unscrambler® (CAMO AS, Oslo, Norway, v. 9.7), was used for the multivariate analysis of the data.

Principal component analysis (PCA) was carried out in order to previously explore the data and to evaluate the dependence of the data by means of clusters. The analysis was calculated with the maximum number of eight principal components (PC).

Partial least squares regression (PLS-R) were adjusted based on NIR spectra (matrix X, independent variables) and gravimetric carbonization yield (GCY), apparent relative density (ARD) and final carbonization temperature (FCT) values, creating the Y matrix as dependent variables.

In short, the analyses rely on developing a calibration that relates the spectra of a large number of charcoal specimens to their known characteristics such as GCY or FCT. This calibration is then used to predict the GCY or FCTof further samples based on their NIR spectrum. It is implicit in this technique that the “training” sets on which the calibrations are based contain the whole range of variation in the samples to be analyzed.

The calibrations were validated by full cross validation (leave one out) and test set validation. Cross-validation was performed using eight segments with twenty samples chosen at random while the external validation was based on two data sets composed of 100 samples in the calibration lot and 60 samples in the validation lot.The number of latent variables was determined based on the minimization of the standard error of the validation and maximization of the coefficient of determination of the validation.

The models were adjusted from original spectra and after the following mathematical: first derivative (13-point filter and a second order polynomial), second derivative (25-point filter and a second order polynomial), normalization and normal standard variate (SNV). For developing charcoal apparent density models, only wavelengths from 9000 to 4000 cm^{-1} were used for calibrations and the Martens uncertainty test [19] was applied for selecting significant wavenumbers to improve the signal-to-noise ratio. Outliers were detected by means of the student x leverage residuals graph and removed from the models.

The selection of models were based on the following statistics: coefficient of determination of cross validation (R^2cv) and test set validation (R^2p); root mean standard of cross-validation error (RMSECV) and test set error (RMSECV); standard deviation from performance ratio (RPD) and number of latent variables used in the models (LV).

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