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Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product

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ABSTRACT

Torrefaction is a thermal treatment used to improve the properties of biomass in relation to thermo-chemical processing techniques for energy generation. It is a thermo-chemical treatment method primarily characterized by an operating temperature within the 200–300 °C range. It is carried out under conditions of atmospheric pressure and in the presence of a minimum amount of oxygen in order to avoid spontaneous combustion. The aim of this study was to evaluate the combined effect of the temperature (240 and 280 °C) and oxygen concentration (2, 6, 10 and 21%) on the physical and chemical properties of large particles of *Eucalyptus grandis*. A statistical analysis was carried out. The different oxygen concentrations did not significantly affect the composition of the solid by-product for low temperatures. At 280 °C, the high oxygen concentration affected some of the properties studied.

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1. Introduction

The global problems associated with the intensive use of fossil fuels have increased interest in the use of renewable fuels worldwide, mainly in countries like Brazil, where biomass is widely available at low cost. However, a pre-treatment process is required to convert biomass into a hydrophobic solid product with an increased energy density [1]. One way to achieve that goal is to apply torrefaction, which is considered as a biomass feedstock pre-treatment, particularly for thermal conversion. It is gaining attention as an important pre-processing step for improving biomass quality in terms of physical properties and chemical composition [2,3]. Torrefaction involves the slow heating of biomass in an inert environment or reduced O_2 content to a maximum temperature of approximately 300 °C. Torrefaction can also be defined as a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–280 °C [4,5]. The yields and properties of torrefaction by-products are influenced by several parameters, including biomass composition, particle size, processing temperature and time, heating rate and the composition of the working atmosphere [6,7]. Much work has been done to study how these operating parameters influence torrefaction [8,9], but there still remains a need to study the influence of different oxygen concentrations on the thermal reactivity of large biomass particles during torrefaction, as well as their effect on the physical and chemical properties of torrefied biomass.

The thermal decomposition of lignocellulosic materials involves a complex series of chemical reactions and heat and mass transfer processes [10–12]. An oxidizing atmosphere can promote the oxidative degradation of the material and the subsequent oxidation of the volatile matter released during such degradation, in addition to promoting the combustion of the char residue. Studies to evaluate the thermal behaviour of biomass in both oxidizing and inert atmospheres have been carried out by several authors [13,14]. Most of them showed that when oxygen is present, the thermal reactivity of biomass (especially cellulose) is greatly enhanced due to the acceleration of mass loss in the first stage of pyrolysis. Analysing the influence of the initial solid weight and the sample shape on solid conversion for different oxygen concentrations, Bilbao [15] proposed a simple model. He showed that the influence of oxygen concentrations on mass loss depends on the weight of the sample and the temperature at which the process occurs. More recently, Shen and his co-authors [16] used a DAEM method and global kinetic model in both inert and oxidative atmospheres to examine the mechanisms involved in the thermal decomposition of wood. The apparent activation energy of pyrolysis and combustion varied linearly with oxygen concentration [17]. However, these studies were carried out at high temperatures using small samples. For temperature lower to 250 °C, the mass losses rates of wood were similar. Thus, it is important to evaluate the effect of different oxygen concentrations in the working atmosphere using larger samples, closer to the true conditions of use, and at the low temperatures of torrefaction process.

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This study investigated the thermal reactivity of *Eucalyptus grandis* during torrefaction under different oxygen concentrations by examining the relationship between mass loss and the physical and chemical properties of the solid by-product.

2. Material and methods

2.1. Materials

The raw material was *Eucalyptus grandis* wood obtained from a 31-year-old plantation at an experimental station administered by the Forestry Science Department of the University of São Paulo/ESALQ, in the municipality of Piracicaba (Brazil) [6]. Three trees were felled and planks were cut to make samples, each measuring 10 mm × 40 mm × 80 mm, respectively the thickness, the width and the length. The samples were previously dried to a constant weight at 105 °C. The proximate and ultimate analyses and the gross calorific value of Eucalyptus *grandis* wood are shown in Table 1.

2.2. Torrefaction device

The experimental system (Fig. 1) consists of a precisely controlled temperature batch reactor. A programmable PID (proportional-integral-derivative) controller was used to control the temperatures and heating rate of the reactor thank to three thermocouples: one in the base (near the electric heater), one inserted through the lid of the reactor (at the top of the reactor) and the last one inside the sample to monitor its temperature. A nitrogen source is used to control the oxygen content; the oxygen, carbon monoxide and carbon dioxide contents inside the reactor are measured with a gas analyser. Two samples were tested in each trial run, one coupled to a precision balance to monitor mass loss (sample 2) and another with a thermocouple to monitor the internal temperature (sample 1).

The temperature of the reactor was raised to the selected temperature (240 or 280 °C) by a linear heating rate of 4 °C min^{-1}, and held for 60 min at that temperature. Nitrogen was introduced into the system in order to perform experiments with oxygen percentages in the atmosphere of 2, 6, 10 and 21%. The chosen oxygen rate was maintained during sample cooling. The system provided continuous acquisition of the temperature, oxygen level and sample mass. The data were recorded every minute during thermal decomposition. All experiments were performed twice.

The thermal decomposition of wood was also evaluated in terms of conversion rate, which was calculated over time for all treatments. The conversion rate, α, was defined as:

$$\alpha = \frac{M_0 - M_t}{M_0}, \quad (1)$$

where M_0 is the initial solid mass (dry basis) and M_t is the solid mass at time t.

2.3. Solid analysis

Proximate and ultimate analyses were performed on torrefied samples, as well as the gross calorific value. Proximate analyses (volatile matter, ash and fixed carbon contents) were conducted according to the procedure of the Brazilian Association of Technical Standards – ABNT NBR 8112 (ABNT, 1986). The ultimate analysis (C, H, N, O contents) was carried out with a Vario Macro CHN elemental analyser, according to the European procedure XP CEN/TS 15104. The oxygen content was calculated by difference. The gross calorific value was measured in a Parr 6200 isoperibol oxygen bomber calorimeter in accordance with the European procedure XP CEN/TS 14918. The lignin content of the torrefied samples was measured according to the standard method NREL LAP-003, for acid-insoluble lignin, and NREL LAP-004 for acid-soluble lignin. All the analytical characterizations were carried out on extractive-free milled samples. The solvent for extraction was ethanol–toluene.

2.4. Statistical analysis

Sixteen assays were conducted, corresponding to 8 treatments and two replicates. We used a modular statistical software, XLSTAT (addinsoft), to enhance the analytical capabilities of Excel. It handles models relating one or more continuous dependent variables to one or more independent variables. Ten variables in response to the experiments were analysed and discussed: the mass loss (W_t%), the fixed carbon content (FC%), the volatile matter content (VM%), the ash content (Ash%), the carbon content (C%), the hydrogen content (H%), the nitrogen content (N%), the oxygen content (O%), the lignin content (L%) and the gross calorific value (GCV). The values for the oxygen concentration in the reactor (O_2%) and the temperature (T) parameters were defined in accordance with earlier work [9,18]. The general model for variance analysis was that described by the following equation:

$$Y_{ij} = \beta_0 + [O_{2i} + T_j + (O_2 \times T)_{ij}] + \varepsilon_{ij} \quad (2)$$

where Y_{ij} is the value observed for the dependent variable for observation ij, O_2 is the oxygen concentration in the reactor, T the temperature and ε_{ij} is the error of the model. β_0 is a constant.

3. Results and discussion

3.1. Proximate and ultimate analyses

The results of the ultimate and proximate analyses and gross calorific value of all the torrefied samples, as well as the final conversion and summary statistics for the experimental factorial design performed, are shown in Table 1. We carried out an analysis of variance (ANOVA) of the means obtained, taking into account possible interactions between the two explanatory variables: oxygen rate and temperature.

The results show that there were globally no significant differences between the means obtained with the different oxygen rates, whereas the temperature significantly impacted on mass loss, lignin rate and carbon and oxygen rates. It was found that the volatile matter rate displayed a significant difference between 240 °C/21% and 280 °C/6% with 80.59 and 71.20% respectively. Whilst the GCV was greatly linked to the lignin content, we found that, despite a significant increase in the relative lignin content due to the cellulose and hemicelluloses degradation [18], the gross calorific value showed a tendency to increase, though not significantly. These observations are only valid in the case where we used the model with level 2 interactions ($O_2 \times T$). We modelled these means without taking into account interactions between the explanatory variables; the results confirmed the absence of any significant impact of the oxygen concentration in the reactor whilst the temperature had a significant impact on 8 of the 10 variables observed. These observations corroborated several studies focusing on the effects of torrefaction parameters on end-product quality [19].

From the model described previously (Eq. (2)), we performed type III sum of squares to analyse which parameters significantly interfered ($\alpha = 0.05$) with the ten response variables, along with the effect of second order interactions on the quality of the torrefied biomass produced. Of the parameters studied, the temperature was the factor with the greatest impact on 8 of the 10 response variables. The oxygen content in the reactor and the second order

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