Slow pyrolysis of bamboo: an approach on quality of charcoal and greenhouse gases emission

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ABSTRACT: Bamboo is a grass known worldwide for its versatility, fast growth and short rotation. The combination of these characteristics makes the species a potential source of biomass for energy use, especially when submitted to a thermochemical conversion treatment, such as pyrolysis. However, the environment aspects of the pyrolysis should be observed, like the emission of greenhouse gases. In this context, the aim of this study was to characterize the proprieties the charcoal and the emission of greenhouse gases of Dendrocalamus asper (Schult f.) Backer ex Heyne, in different pyrolysis temperature (400, 550, 700 °C). The charcoal properties are influenced by the pyrolysis temperature. The increase in the final pyrolysis temperature resulted in a reduction of around 24,5% in the values of charcoal yield and caused an increase in the emission of greenhouse gases (CO₂, CO, CH₄, and H₂). Despite the advantages of performing pyrolysis as a thermal treatment, ways to mitigate such emissions are one aspect that has to be evaluated.

Key words: Dendrocalamus asper; gravimetric yield; methane; pyrolysis

Pirólise lenta de bambu: uma abordagem sobre a qualidade de carvão e emissão de gases de efeito estufa

RESUMO: O bambu é uma gramínea conhecida mundialmente pela sua versatilidade, crescimento rápido e curta rotação. A combinação destas caraterísticas faz com que a espécie seja uma fonte potencial de biomassa para uso energético, principalmente quando submetidos a tratamentos termoquímicos, como a pirólise. No entanto, os aspectos ambientais referentes a pirólise do bambu devem ser levados em consideração, como a emissão de gases de efeito estufa no processo. Neste contexto, o objetivo do estudo foi caracterizar as propriedades do carvão vegetal e emissão de gases de Dendrocalamus asper (Schult f.) Backer ex Heyne, em diferentes temperaturas finais de carbonização (400, 550 e 700 °C). As propriedades do carvão vegetal foram influenciadas pela temperatura de carbonização. O aumento da temperatura final de carbonização resultou em uma redução de cerca de 24,5% no rendimento de carvão vegetal, e o aumento na emissão de gases do efeito estufa (CO₂, CO, CH₄, e H₂). Apesar das vantagens em realizar a pirólise como um tratamento térmico, formas de mitigar essas emissões são um aspecto a ser avaliado.

Palavras-chave: Dendrocalamus asper; rendimento gravimétrico; metano, pirólise
Introduction

Rapid growth, short cutting cycle, versatility and production capacity make bamboo a potential biomass source for energy use. In a global context of insecurities about climate change and dependence on fossil fuels, the use of renewable energy resources is a key factor for sustainability of a nation’s energy matrix (Verma et al., 2017). However, the use of raw biomass may present some disadvantages to energetic use, such as high heterogeneity, high moisture content, low calorific value and low grindability (Yip et al., 2009). An alternative to reduce such characteristics is the biomass thermochemical conversion, such as pyrolysis. The slow pyrolysis is a type of thermal degradation in which the biomass is heated at a slow heating rate in a non-oxidizing atmosphere that has, as its main product, a high carbon solid (charcoal), gases and condensable organic vapors.

The carbonization process is influenced by the characteristics of the raw material and the process parameters, such as the heating rate and pyrolysis temperature (Pereira et al., 2013). Pyrolysis temperature is an important parameter to define the quality of the solid fuel, since it affects the yields, as well as the physical, chemical, anatomical and mechanical properties of charcoal (Dhyani & Bhaskar, 2018). Among the charcoal properties that vary according to the pyrolysis temperature, we can cite the apparent density, friability, high heating value, energetic density, fixed carbon content, volatile matter and ashes (Somerville & Jahanshahi, 2015).

The main gases produced during pyrolysis are CO₂ (carbon dioxide) and O₂ (oxygen), considered inert gases, and CO (carbon monoxide), CH₄ (methane) and H₂ (hydrogen), classified as combustible gases. From the environmental point of view, CH₄ presents a high potential for global warming when compared to other gases, whereas CO inhalation is associated with respiratory problems. Thus, such gases are considered harmful, which requires process and practices that mitigates it (Pereira et al., 2017).

The analysis of the bamboo’s potential in the charcoal production, together with the evaluation of the environmental aspects related to this production is fundamental for a sustainable manufacture of this product. Giving the above, the present research had the objective of characterizing the charcoal properties and emission of gases of *Dendrocalamus asper* (Schult f.) Backer ex Heyne, at different pyrolysis temperatures.

Material and Methods

The bamboo stems of the species *Dendrocalamus asper* (Schult f.) Backer ex Heyne were collected on a production farm located in the interior of the state of Minas Gerais. The stems were selected that presented adequate phytosanitary conditions, harvested 60 months after planting. After the material was collected, they were processed and homogenized, forming a composite sample for each stem, in a laboratory chip mill. To carry out the pyrolysis, the samples were processed into chips with average size of 25 mm. The characterization of the of raw biomass is presented Table 1. The values of ultimate analysis, component analysis, specific gravity and high heating value were provided by the company.

| Properties                | Bamboo |
|---------------------------|--------|
| Ultimate analysis (%)     |        |
| C                         | 47.91  |
| H                         | 5.57   |
| N                         | 0.77   |
| S                         | 0.05   |
| O                         | 44.35  |
| Component analysis (%)    |        |
| Extractives               | 14     |
| Lignin                    | 27.9   |
| Holocelluloses            | 56.80  |
| Ash                       | 1.35   |
| Specific gravity (g.cm⁻³) | 0.525  |
| High heating value (MJ.kg⁻¹) | 19.17  |

Charcoal production and characterization

The pyrolysis was conducted in a laboratory electric oven using a metal container with approximately 0.003 m³. The temperature control of the oven was performed manually, with increments of 50 °C every 30 minutes, which corresponds to a heating rate of 1.67 °C.min⁻¹. Three final pyrolysis temperatures, 400, 550 and 700 °C, were analyzed.

To determine the amount of bio-oil produced during the pyrolysis process, the gases were conducted at the outlet of the oven to a bio-oil recovery system. This system consists of a water cooler tubular condenser coupled to a collecting vessel. The bio-oil was collected in this recovery system and weighed to obtain its yield. After the end of the process, the charcoal and the bio-oil produced were weighed to determine the gravimetric yield in charcoal, bio-oil and gas by gravimetry.

To perform the gas characterization, such product, after passing through the bio-oil recovery system, was directed to an on-line gas analyzer (Gasboard 3100 Wuhan CUBIC Optoelectronics Co. LTDA.). The amount of CO, CO₂ and CH₄ produced throughout the process was measured.

The contents of volatile matter and ashes of charcoal were determined according to ASTM D3175-89a (ASTM, 1997) and ASTM D3174-04 (ASTM, 2006). The fixed carbon content was calculated by difference. The higher heating value of the charcoal was determined using an adiabatic calorimeter IKA300, according to the methodology described by ASTM D240-02 (ASTM, 2007).

The apparent density of charcoal was performed by the mercury immersion, using the hydrostatic method, according to Pereira et al. (2013). The friability was determined using a sample of approximately 20 grams. This sample was rotated at 35 rpm for 15 minutes using an electronic friability tester (MA-791). After this process, the remaining sample was weighed, and the friability calculated according to formula (Eq. 1).
Statistical analysis

The experiment was carried out according to a completely randomized design, with three treatments (pyrolysis temperatures), and three replicates. Linear and nonlinear models were adjusted to verify the effect of final carbonization temperature on pyrolysis yields, charcoal properties and emitted gases.

The model that fitted better to the dispersion of data was \( Y = \beta_0 \cdot \exp\left(\frac{b}{x}\right) \), used, therefore, in the verification of the effect of the final pyrolysis temperature. However, for the charcoal’s friability the model that adequate better to the data dispersion was \( Y = e^{(\beta_0+\beta_1/X+\beta_2\ln(X))} \). To verify the significance of the parameters of the adjusted equation, Student’s t-test was performed. The criterion used to determine the quality of the fit of the model to the experimental data was the residual standard error (s_y.x) and coefficient of determination \( (R^2) \). The analyzes were performed using the R software.

Results and Discussion

The Table 2 show the adjustments of the equations referring to the model that fitted better to the data dispersion. In general, it is observed that the equations presented good adjustments for all the charcoal properties analyzed.

The adjusted curves for the gravimetric yields and for each charcoal property, using the final pyrolysis temperature as the independent variable are shown in Figure 1. The increase in

\[
\text{Friability (\%) = } \left(\frac{\text{Inicial weight} - \text{Final weight}}{\text{Inicial weight}}\right) \times 100 \quad (1)
\]

Table 2. Model fit for gravimetric yields and charcoal properties, significance of parameter estimates and precision measurements of equations.

| Properties                          | Parameters | Estimation of parameters | p-value | \( R^2 \) | Sy.x |
|-------------------------------------|------------|--------------------------|---------|----------|------|
| Charcoal gravimetric yield (%)      | \( \beta_0 \) | 24.96                    | <0.001  | 98.01    | 0.47 |
|                                     | \( \beta_1 \) | 201.14                   | <0.001  |          |      |
| Gravimetric yield in bio-oil (%)    | \( \beta_0 \) | 43.49                    | <0.001  | 94.47    | 0.30 |
|                                     | \( \beta_1 \) | -74.55                   | <0.001  |          |      |
| Gravimetric gas yield (%)           | \( \beta_0 \) | 37.35                    | <0.001  | 93.87    | 0.57 |
|                                     | \( \beta_1 \) | -200.19                  | <0.001  |          |      |
| Apparent relative density (g/cm³)  | \( \beta_0 \) | 0.31                     | <0.001  | 92.94    | 0.01 |
|                                     | \( \beta_1 \) | -28.84                   | <0.001  |          |      |
| Volatile materials (%)              | \( \beta_0 \) | 0.01                     | <0.001  | 99.72    | 0.43 |
|                                     | \( \beta_1 \) | 900.81                   | <0.001  |          |      |
| Ash (%)                             | \( \beta_0 \) | 9.35                     | <0.001  | 95.29    | 0.16 |
|                                     | \( \beta_1 \) | -345.81                  | <0.001  |          |      |
| Fixed carbon (%)                    | \( \beta_0 \) | 114.54                   | <0.001  | 95.91    | 1.51 |
|                                     | \( \beta_1 \) | -222.32                  | <0.001  |          |      |
| Higher Heating Value (MJ/Kg)        | \( \beta_0 \) | 980.72                   | <0.001  | 97.43    | 0.41 |
|                                     | \( \beta_1 \) | -216.92                  | <0.001  |          |      |
|                                     | \( \beta_2 \) | 80.93                    | <0.001  |          |      |
| Friability (%)                      | \( \beta_1 \) | -5784.00                 | <0.001  | 91.66    | 0.97 |
|                                     | \( \beta_2 \) | -10.70                   | <0.001  |          |      |

Legend: CY = Charcoal Yield; BY = Bio-oil Yield; GY = Gas Yield; VM = Volatile materials; FC = Fixed carbono; HHV = High Heating Value; AD = Apparent relative density.

Figure 1. Data dispersion and model fit for gravimetric yields and charcoal properties.
the temperature from 400 to 700 °C resulted in a reduction of around 24.5% in the values of gravimetric yield in charcoal, a contrary result was observed for the gravimetric yield in bio-oil and non-condensable gases that increased 7.5 and 19.4%, respectively.

The thermal decomposition of wood components by volatilization of organic matter results in the reduction of the solid fraction, while there is an increase in the gas and oil fractions (Rowell & Le Van-Green, 2005). The charcoal yield observed for bamboo is higher than the wood species commonly used for charcoal production in Brazil, such as the genus Eucalyptus (Santos et al., 2016).

The high yield of charcoal found for bamboo is related to the low content of holocelluloses observed in its stem. Holocelluloses have low resistance to thermal degradation when compared to lignin, that presents greater numbers of C-C and C=C bonds (Haykiri-Acma et al., 2010). Furthermore, the extractive content is another factor that can contribute to the increase of the charcoal yield. Some chemical constituents present in the extractives, especially those of an aromatic nature, that have greater stability to the thermal degradation, thus increasing the charcoal yield (Silva et al., 2017).

The content of volatile matter reduced about 158.6%, while the fixed carbon content increased approximately 21% with the pyrolysis temperature increase from 400 °C to 700 °C. The increase in the temperature leads to a higher degradation of the wood components, thus reducing the amount of volatile materials present in charcoal, accompanied by the increase of the fixed carbon content (Ghodke & Mandapati, 2019). This fact is due to the reduction of the hydrogen and oxygen contents, which results in the carbon concentration in the solid residue (Pimenta et al., 2018).

The ash content increased 30.8%, in function of the final pyrolysis temperature increase. This effect is relative, because as the organic matter is being volatilized, there is the concentration in the inorganic fraction in the charcoal. The high ash content of a material can be detrimental to its use as biofuel, since the inorganic elements do not participate in the combustion process. High ash content in a fuel favors the increase of the inorganic elements in the charcoal, thus contributing to reduce the friability of charcoal (Silva et al., 2017). Materials that present a basic carbon in its constitution, when submitted to pyrolysis temperatures higher than 500 °C, have a characteristic to connect the carbons, resulting in structures with more organization. This fact, associated with the reduction in the volatilization of organic matter and the increase of the apparent relative density, greater mechanical resistance of the charcoal, thus contributing to reduce the friability of charcoal at a temperature of 700 °C (Somerville & Jahanshahi, 2015).

Table 3 shows the adjustments of the equations referring to the model that best fitted to the data dispersion. In general, it is observed that the equations presented good adjustments for all the charcoal properties analyzed.

An effect of final pyrolysis temperature was observed in the emission of gases. The final temperature increase results in a greater thermal degradation of the biomass, which favors a larger formation of gases. The behavior of the gases production during pyrolysis is related to the chemical composition of the biomass used and the reactions that occur in parallel, consecutively and competitively during the process (Turner et al., 2010).

Hemicelluloses are the first components of the biomass to be degraded during pyrolysis, and a part of these constituents is degraded in the temperature range of 200 to 300°C. In

| Table 3. Adjustment of the model for the greenhouse gas emissions and for the calorific power of the gas, significance of the parameter estimates and precision measurements of the equations. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Propieties | Parameters | Estimation of parameters | p-value | R² | s_{yx} |
| Carbon dioxide (Kg of gas / ton of bamboo) | β₀ | 190.48 | <0.001 | 91.55 | 2.07 |
| | β₁ | -98.55 | <0.001 | | |
| Carbon monoxide (Kg of gas / ton of bamboo) | β₀ | 106.95 | <0.001 | 95.42 | 1.26 |
| | β₁ | -171.08 | <0.001 | | |
| Methane (Kg of gas / ton of bamboo) | β₀ | 179.440 | <0.001 | 99.40 | 0.74 |
| | β₁ | -1203.750 | <0.001 | | |
| Calorific value of gas (MJ/Kg of gas) | β₀ | 9359.70 | <0.001 | 99.37 | 55.56 |
this temperature range the main gases emitted are carbon monoxide and carbon dioxide, which are the result of decarboxylation reactions and secondary carbon reactions. At approximately 380 °C a peak of CO₂, CO and CH₄ release occurs due to the thermal degradation of cellulose present in the biomass (Yang et al., 2007). These reactions are mainly responsible for the emission of greenhouse gases during pyrolysis at temperatures below 400 °C.

A second peak of gas emission occurs at temperatures close to 500°C, and a significant amount of CO₂, CO and CH₄ is released, mainly from the final degradation of the hemicelluloses (Yang et al., 2007). This degradation is mainly responsible for the increase in greenhouse gas emissions observed for the final temperature of 550 °C. At temperatures above 600 °C the secondary pyrolysis is initiated, characterized by thermal cracking reactions of tar in charcoal. At this temperature a lignin degradation peak occurs which is characterized by the emission of CO₂, CO and CH₄. This degradation is mainly responsible for the increase in greenhouse gas emissions observed for the final temperature of 700 °C.

The origin of the gases produced during the pyrolysis, the release of CO₂ is mainly due to cracking and reforming reactions of carboxyl (C=O) and COOH functional groups. The release of CO occurs mainly with the cracking of carbonyl (C-O-C) and carboxyl. The release of CH₄, in turn, can be caused mainly by the breakdown of functional groups methoxy (R-O-CH₃) (Yang et al., 2007).

The gases produced during the pyrolysis of the biomass, if emitted directly into the atmosphere, represent an important environmental impact for the charcoal sector. In this context, ways of mitigating these gases are necessary to contribute to the sustainability of this sector. An interesting alternative for the transformation of this impact into a by-product of the industry is the burning these gases. By burning, thermal energy is produced, which in turn can be directed for use in biomass dryers or for use in the electric energy production (Pereira et al., 2017).

Conclusions

The increase in the final pyrolysis temperature results in an increase in the gravimetric yield in gases and bio-oil, in detriment to the charcoal yield. Furthermore, the charcoal properties are influenced by the pyrolysis final temperature. It is recommended the final carbonization temperature between 400 °C and 500 °C. In this range a balance between charcoal yield, quality parameter and gas emission are found.

In relation to the gases emitted during the carbonization, the increase in the final temperature causes an increase in the emission of greenhouse gases. Therefore, despite the advantages of performing pyrolysis as a thermal treatment, ways to mitigate such emissions are one aspect that has to be evaluated.

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