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Slow Pyrolysis of Bamboo Biomass: Analysis of Biochar Properties

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Due to the issue of deforestation and the pressure to avoid use of native forest resources for production of char, there is increasing requirement for the use of renewable materials and development of additional sustainable processes. Bamboo, a biomass that presents the property of fast growth, is an alternative to native or reforested wood. In this work the slow pyrolysis of a woody bamboo (species Dendrocalamus giganteus Munro) was studied, aiming the determination of biochar properties. The process was conducted in a fixed bed reactor at temperatures ranging from 300 to 600 °C and at a 10 °C/min heating rate. The thermal degradation behaviour of bamboo was investigated through thermogravimetric analysis (TGA/DTG). The bamboo biomass and the biochar were characterized by physical-chemical analysis in order to investigate the main changes caused by the pyrolysis process on biochar properties. The surface morphology of bamboo biomass and biochar was determined using scanning electron microscopy (SEM). Additionally, a discussion about the advantages and disadvantages of biochar production by slow pyrolysis is presented, taking into account the applied conventional methods in the process. Results revealed the advantage of pyrolysis process due to simultaneous biochar and bio-oil production. The bamboo biochar presents suitable properties for its use as energy source and for agricultural applications. Its high porosity and carbon content suggest its application as activated carbon after physical or chemical activation.

1. Introduction

Brazil is the largest producer of charcoal in the world, with nearly half of the woody biomass harvested for energy in Brazil being transformed into charcoal, mostly from eucalyptus plantations derived either from natural or planted forests. The primary use of charcoal has been as a source of heat and carbon in massive processing and metallurgical industries which are among the top wood fuel users (Bailis et al., 2013). Brazil has abundant biomass sources, presenting the greatest bamboo diversity in America. Dwarf bamboos may be as little as 10 cm in height, but tall species may reach 15-20 m, and the largest known species (Dendrocalamus giganteus) grows up to 40 m in height and 30 cm in culm (stem) diameter. According to an experimental plantation of Dendrocalamous giganteus species developed in Sao Paulo State University (UNESP/Bauru), its average productivity is about 56 m³/ha/y, with 225 stems/ha/y in wet basis (Pereira and Beraldo, 2007). However, the productivity of bamboo plantations varies considerably depending on species, management and location. Very productive species may yield around 30 t/ha/y (dry material). Well-managed bamboo plantations yield in average 25 t/ha/y (dry material), according to NL agency (2013). Bamboo, as a kind of wood, is mainly composted of hemicelluloses, cellulose and lignin that can produce higher value-added products by pyrolysis processes. Furthermore, it possesses many other advantages such as easy propagation, fast growth and low ash content (Scurlock et al., 2000).
In Brazil, charcoal production takes place primarily through small earthen kilns and traditional “hot-tail” kilns. The efficiency of these kilns in producing charcoal can be 10-20 % (dry basis) for the earthen kilns and 25-30 % for “hot tail” kilns, leading to losses around 60-70 % of the input energy and consequently, release of high amounts of gases and other unburned hydrocarbons into the atmosphere (Bailis et al., 2013). In order to reduce the environmental impact of charcoal using these traditional kilns, new alternatives can be implemented to convert biomass into valuable products. Slow pyrolysis is a

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thermochemical decomposition process that takes place in the absence of oxygen and at a slow heating rate (approximately 10 °C/min) to produce a liquid phase (tar or hydrocarbon liquids and water), a carbon-rich solid phase (charcoal) and non-condensable gases (CH_4, CO_2, CO, H_2, etc.), as discussed in Demirbas (2004) and Balat et al. (2009).This slow heating rate leads to higher char yield than liquid and gaseous ones. Therefore, it is a recommended technology for biochar production (Bahng et al., 2009).
Biochar originating from biomass is typically 20-40 % of dry lignocellulosic biomass. However, the yield and chemical properties of the pyrolysis products are strongly influenced by operating conditions during pyrolysis such as temperature, heating rate, holding times, particle size, atmosphere and feedstock (Lee et al., 2013a). Depending on the final use of biochar, the required properties of the material may be different. The primary use has been as fuel (charcoal) for heat production, for cooking and for heating (Lee et al., 2013b). Biochar has a large microscopic surface area due to the micro pores developed during pyrolysis, and may be used as a soil amendment improving water infiltration, ion exchange capacity, nutrients retention and adsorption of pollutant (Thies and Rillig, 2009). Zhao et al. (2013) showed that both feedstock properties and production conditions affected the yield and properties of biochar. Enders et al. (2012) verified that biochars have widely varying properties, requiring more than proximate analysis for characterization. A combination of thermogravimetric analysis, pH and elemental (ultimate) analysis are necessary but not sufficient on their own to predict behavior of biochars in soils.
This paper presents an experimental research of the slow pyrolysis of bamboo D. giganteus Munro aiming to determine biochar yield as a function of the final reactor temperature. Additionally, physical-chemical properties of the biochar produced at 500 °C are presented in order to verify its main characteristics and applications.

2. Experimental

2.1 Biomass samples

The bamboo D. giganteus Munro was harvested at University of Campinas in Brazil. Tests were carried out using mature stem samples of 5 y age. Before the experiments, the sample was split into pieces of about 1 m and cut into blocks about 10 cm long to facilitate the milling process. All the feedstock was air-dried until final moisture about 10 %. Raw biomass was ground in a hammer mill and then the particles were sieved by a vibrating screen and dried before the experiments were carried out. Table 1 shows the main characteristics of the studied biomass.

Table 1: Characteristics of the bamboo biomass

Property	Value
Particle diameter (μm)	669 ± 1
Particle density (kg/m^3)	1,400 ± 10
Bulk density (kg/m^3)	146 ± 4
High heating value (MJ/kg)	17.235 ± 0.143
Proximate analysis (% wet basis)	
Moisture	9.37 ± 0.80
Fixed carbon	17.75 ± 0.40
Volatile	70.31 ± 0.44
Ash	2.57 ± 0.41
Elemental Analysis (%dry basis)	
C	39 ± 3
H	6.1± 0.2
N	0.6 ± 0.3
S	0.018± 0.006
O[a]	54±3
Structural Composition (% dry basis)	
Cellulose	47.5 ±0.4
Hemicellulose	15.35 ±0.42
Lignin	26.25±0.07
Extractives	4.90 ±0.14
Silica	0.7±0.0

[a] By difference

The proximate analysis of raw biomass was based on the ASTM standards methods (ASTM E871-82, ASTM E1755-01, ASTM E872-82). The structural composition was determined according to standards of the Technical Association of the Pulp and Paper Industry (TAPPI 264 cm-97, TAPPI 222 and TAPPI UM 250). Thermogravimetric and differential thermogravimetric analysis (TGA/DTG) were carried out using (10.0±0.5) mg of raw biomass samples. The experiments were performed at a constant heating rate of 10 °C/min, from room temperature up to 700 °C, using a Shimadzu analyzer, TGA-50H, in inert atmosphere (pure nitrogen) with a flow rate of 100 mL/min. TGA/DTG results in Figure 1 showed the thermal degradation of bamboo.

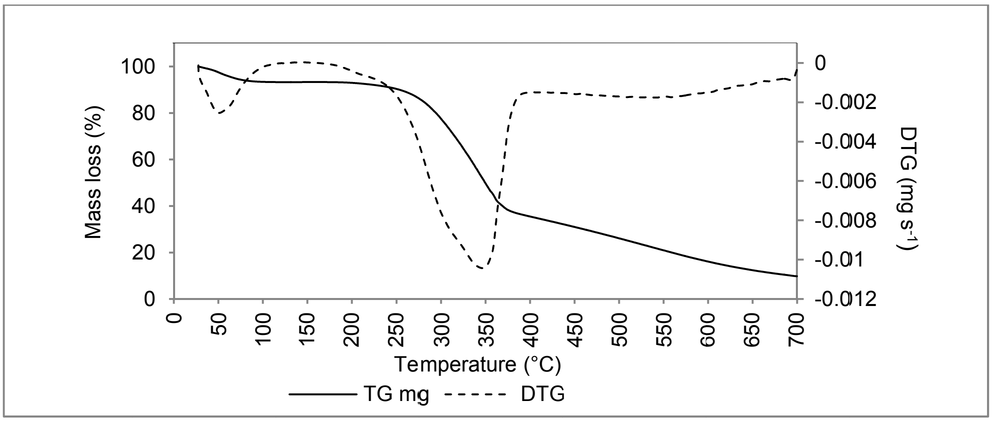

Figure 1: TGA and DTG curves of bamboo in N_2 atmosphere

TGA results showed that at 500 °C the thermal decomposition of bamboo is almost complete. The first mass loss (50 < T < 150 °C) is due to moisture and some extractives compounds evaporation. The second one (200 < T < 360 °C) is mainly related to hemicelluloses and cellulose thermal degradation. The maximum of the DTG curves is attributed to cellulose complete degradation. Lignin is a more stable component presenting a large range of thermal degradation (from 250 to 500 °C or even higher temperatures, depending on biomass), and in this way the third degradation step (360 < T < 600 °C) is attributed to lignin degradation.

2.2 Slow pyrolysis tests

Pyrolysis experiments were carried out in a fixed bed reactor designed by Bioware Technology, which is located in Campinas, Brazil. The reactor was heated indirectly by four electrical heaters of 800 W capacity each. Figure 2 shows the main components of the fixed bed pyrolysis reactor.

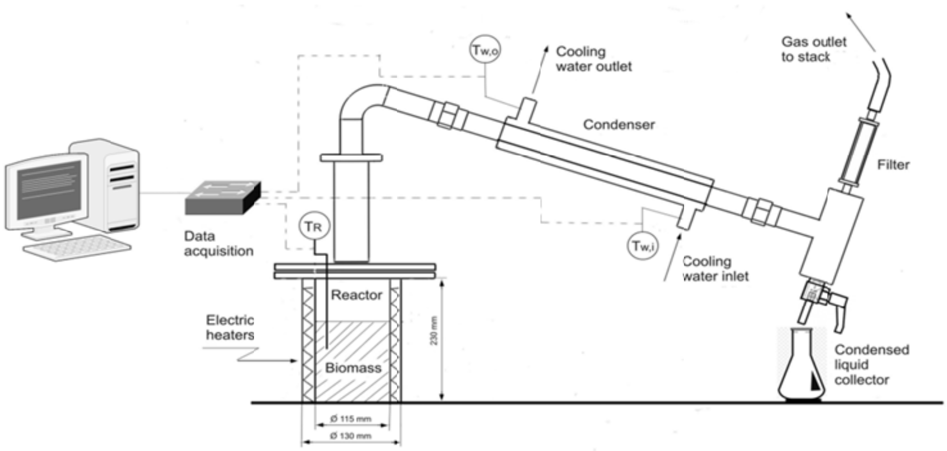

Figure 2: Fixed bed pyrolysis system

The reactor is made of a carbon steel tube presenting 230 mm height and 115 mm inner diameter. There were two K-type thermocouples at different positions inside the bed material near the reactor wall. The reactor temperature was considered as the average value taken from these thermocouples which presented a maximum variation of 10 °C between them. The temperatures of the cooling water in the condenser ($T_{w,i}$ at inlet and $T_{w,o}$ at outlet) were also measured in order to control the vapour condensing process. In each test a sample of 200 g of bamboo particles was heated from room temperature to a final reactor temperature from 300 to 600 °C. The heating rate was 10 °C/min. The holding time at each tested final temperature was 15 min, thus the total time of each experiment varied from 42 min (300 °C) to 72 min (600 °C). The differences in heating times among tests at different temperatures were neglected as previous work of Aylon et al. (2006) showed that the final reactor temperature is the main factor on the fixed bed pyrolysis process. After each test bio-char and bio-oil were collected from the reactor. The yield of the recovery biochar was determined gravimetrically by weighing, after reaching room temperature. The bio-oil product was heterogeneous and consisted of an aqueous and an oil phase. The gas yield was calculated by difference (mass balance in the system).

2.3 Analysis of biochar

Physical and chemical analyses were conducted for the biochar product generated at final reactor temperature of 500 °C. The density of biochar particles was measured by liquid picnometry using water as the displacement fluid. The bulk density of the loosely packed bed was measured by weighting the mass of char introduced in a calibrated volume.

The analytical methods applied for char characterization were proximate analysis, high heating value (HHV) determination and elemental analysis. The analyses were performed in duplicate using standard methods. The proximate analysis was determined according to ASTM D1762-84 standard method. The HHV was determined using an IKA C2000 basic Oxygen Bomb Calorimeter following the ASTM D4809-00 standard method. The elemental analysis (CHN) was performed in duplicate using an Elemental Analyser (Perkin Elmer-Series II 2400).

Morphological changes of biomass samples before and after pyrolysis process were observed by scanning electron microscopy (SEM).

3. Result and discussion

3.1 Pyrolysis product yields

Previous studies have shown that the temperature of pyrolysis plays an important role on the yields of the liquid, gas and char products. The effect of the final reactor temperature on the production of bio-oil, biochar and gases from bamboo pyrolysis is shown in Figure 3, where it can be observed that bio-oil and char are the main products in the pyrolysis process.

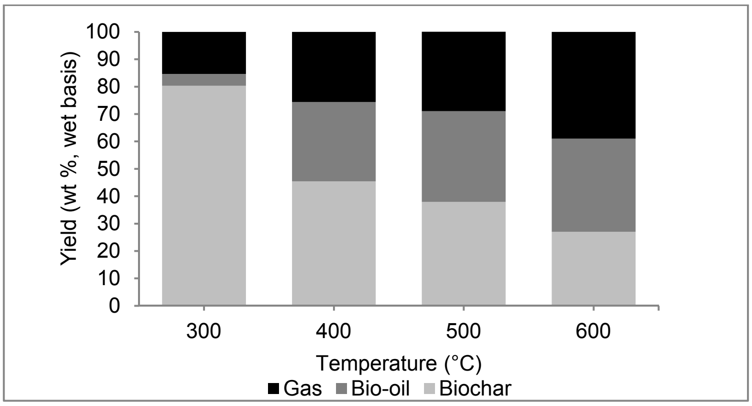

Figure 3: Pyrolysis products yield vs reactor operating temperature

The yield of char decreases as the temperature gets higher due to increased thermal degradation rate. A maximum biochar yield of 80 % was attained at 300 °C. The bio-oil yield increased until 500 °C, remaining practically constant after that. Secondary reactions of volatile compounds are also favored with the temperature increment resulting in a high gas yield.

3.2 Bamboo char characterization

The present study focuses on the properties of the biochar produced at final pyrolysis temperature of 500 °C, considered the best condition regarding the liquid and the solid yields. Pyrolysis at lower temperatures would result in a large amount of char, but properties such as pore structures are sufficiently developed at around 500 °C by the complete thermal decomposition of cellulose and hemicelluloses (Lee et al., 2013b). Table 2 shows the bamboo biochar properties.

Table 2: Properties of bamboo biochar produced at 500 °C

Property	Value
Particle density (kg/m^3)	1740 ± 10
Bulk density (kg/m^3)	105.1 ± 1.8
High heating value (MJ/kg)	30.865 ± 0.187
Proximate analysis (% wet basis)	
Moisture	6.5 ± 1.0
Fixed carbon	81.5 ± 0.4
Volatile	8.10 ± 1.70
Ash	3.9 ± 0.4
Elemental Analysis (% dry basis)	
C	82.1 ± 0.6
H	2.72 ± 0.02
N	0.54 ± 0.05
S	0.00116 ± 0.00004
O[a]	14.6 ± 0.6

[a] By difference

The bamboo biochar presents a higher particle density and a lower bulk density than the particles of raw biomass. A subsequent compression and pelletisation of biochar is indicated for energy densification. Its HHV is above 30 MJ/kg, which is as high as anthracite's HHV. The char produced at 500 °C contained about 68 % of the energy content in the raw material.
The ash content of biochar was smaller compared with sugar cane biochar which contains 8.57 % according to Lee et al. (2013b). An additional analysis of the ash composition is required to determine the presence of elements like K, Na and Cl that can cause operational problems in combustors.
The ultimate analysis shows that bamboo biochar is highly carbonaceous, with a carbon content of 82.1%.The high carbon content of biochar is advantageous in terms of maximizing the amount of carbon storage and could be used as an energy resource or for soil adsorption of pollutants (Lee et al., 2013b).
Two SEM images of the char produced at final reactor temperature of 500 °C are shown in Figure 4.

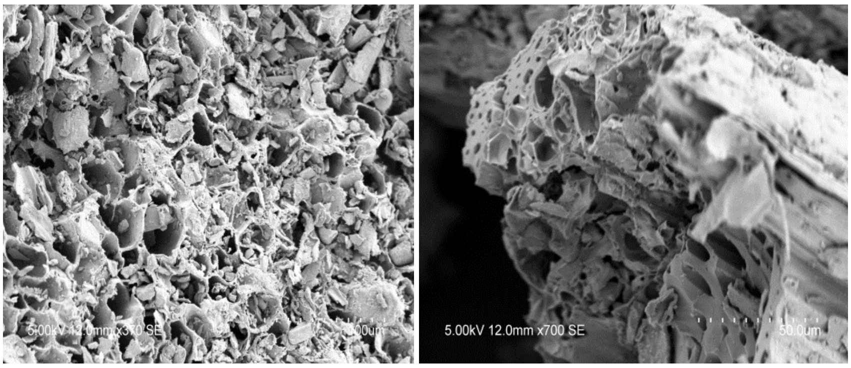

Figure 4: SEM pictures of the bamboo biochar obtained at 500 °C

The biochar from bamboo developed high porosity, presenting longitudinal pores with sizes ranging from micro to macro pores (10-200 μm). The large pores are originated from the vascular bundles of the raw biomass and they are important for improving the soil quality as it can provide habitats for symbiotic microorganisms (Thies and Rilling, 2009). They can also act as release routes of pyrolytic vapors generated in the process (Lee et al., 2013b). Tan et al. (2011) reported that bamboo biochar presents good performance as adsorbent for elemental mercury removal from coal combustion, which can be improved using physical or chemical activation processes.

4. Conclusions

In this study slow pyrolysis of bamboo Dendrocalamus giganteus Munro was conducted and the products' yields as a function of the final reactor temperature were determined. Additionally, physical and chemical properties of the bamboo biochar produced at 500 °C were characterized in order to verify the main characteristics and applications of this product. The characterization of the biochar showed a high carbon content. The heating value of the biochar obtained from slow pyrolysis is comparable to most heating values of wood biochars and could therefore be applied as energy source in gasification or combustion reactors. Its high porosity and carbon content suggest its application as activated carbon after physical or chemical activation.

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