

CHARACTERIZATION OF BAMBOO BIOMASS AND PYROLYSIS PRODUCTS AIMING TO ENERGY APPLICATIONS

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Abstract. Biomass is becoming increasingly important as a modern energy resource due to its potential as alternative fuel to the fossil ones. Bamboo has multiple uses, varying from applications in furniture to energy generation. It is a promising biomass due to its very fast growing, when compared to others biomasses, which makes it attractive for energy conversion processes. This work aimed to study the giant bamboo specie (Dendrocalamus giganteus) to verify its potential to pyrolysis process in fluidized beds. Characterization has been made for grinded bamboo involving sieving, shape, particle and bed density analysis, proximate analysis and high heating value. Additionally, pyrolysis tests were conducted in a fixed bed bench scale reactor to obtain the products yields at 500°C operating temperature. Results allowed the determination of important data to design fluidized bed systems using bamboo as solid fuel. The pyrolysis products exhibited a diverse range of potentially beneficial properties, which allows their use as bio-oil or bio-coal in many industrial applications.

Keywords:Biomass characterization, energy generation, pyrolysis, bamboo specie Dendrocalamus giganteus, fluidized beds.

1. INTRODUCTION

The interest in biomass as an energy source replacement to fossil-based fuels has received much attention in recent years. There is a need in the world for identifying the sustainable energy options without polluting the environment. Biomass is of great potential importance worldwide with respect to energy conversion processes, it is clean, abundant and a renewable energy source with many ecological advantages.

Thermo-chemical processes such as pyrolysis, gasification and combustion are technologies that can convert biomass into valuable products. These different processing techniques define the different mechanism by which biomass is converted to primary products or to final products depending on the process involved (Balat *et al.*, 2009). Many of these processes are based on fluidization. Advantages of fluidized bed include: high heat transfer; uniform and easy control of bed temperatures; high gas-solid contacting and ability to handle a wide variety of particulate materials (Cui and Grace, 2007). Depending on their specific objectives, thermal conversion processes employ solid particle mixtures with two or more particulate material. Biomass and a second fluidization medium, typically an inert material (silica, sand, aluminum oxide, and CFB cinder) can be used to facilitate the fluidization of biomass, as well as to act as a good heat transfer medium in the reactor. Thus, understanding the fluidizing characteristics of biomass and inert particle mixtures is important for the optimal design and operation of a fluidized bed reactor/device. The minimum fluidization velocity is one of the most important parameters needed when designing a fluidized bed system. It sets a lower limit on the flow rate needed for fluidization and it must be known when the modeling of a fluidized process is required (Paudel *and Gang*, 2013).

According to Balat *et al.* (2003) and Bridgwater (2003), pyrolysis of biomass is a promising route for the production of solid (char), liquid (tar or hydrocarbon liquids and water) and gaseous products (CH₄, CO₂, CO, H₂, etc.).

Pyrolysis products yields depends on reactor's atmosphere and temperature, particle properties, heating rate, reactor type and geometry (Apaydin-Varol *et al.*, 2007). The proportion of gas, liquid and solid products depends very much on the pyrolysis technique used and on the reaction parameters. Lower process temperature and longer vapor residence times favor the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapor residence time are optimum for producing liquids (Bridgwater, 1999 and 2003). Depending on vapor residence time, the pyrolysis processes may be classified as slow pyrolysis or fast pyrolysis. They differ from each other in terms of chemistry, overall yields and products properties. Slow pyrolysis provides the conversion of biomass into more useful and valuable solid products to energetic applications (Karaosmanoglu *et al.*, 1999).

Nowadays, the majority of pyrolysis processes is focused on liquid production. The produced pyrolytic oilmay be stored and easily transported allowing, with little expenses, to be used far from the process plant. The pyrolytic oil product may be useful as a fuel, or may be upgraded to refined fuels, or added to petroleum refinery feedstock or even

may be used as a source of chemicals for industries. In addition, the solid products can be used as a fuel either directly as briquettes or it can be used as feedstocks to prepare active carbons.

The pyrolytic gas presents a high calorific value and may also be used for the total energy requirements of a biomass pyrolysis plant or as a fuel (Apaydin-Varol *et al.*,2007).

Bamboo is a member of a taxonomic group of woody grass (subfamily Bambusoideae) which consists of about 1250 species within 75 genera worldwide, most of which are relatively fast-growing, attaining stand maturity within five years. Dwarf bamboos may be as little as 10 cm in height, but tall species may reach 15-20 m, and the largest known (Dendrocalamus giganteus) grows up to 40 m in height and 30 cm in culm (stem) diameter. According to the experimental plantation of Dendrocalamous Giganteus bamboo species developed in Sao Paulo State University (UNESP/Bauru), the average productivity of this species is about 56 m³/ha.year, the yield is bases on 225 stems/ha. When compared to wood, bamboo shows great potential as a biomass material, given that average productivity of Pine and Eucalyptus plantations was of about 40.1 and 40.7 m³/ha.year respectively for 2012 (ABRAF, 2013). Furthermore it possesses many advantages such as easy propagation, fast growth, low ash content and high productivity (SCURLOCK et al., 2000). As a reforesting crop, compared to wood, bamboo plantations can be quickly established. While the establishment time for a giant bamboo plantation to come to maturity takes no longer than 10 years, wood's may take around 15 years for Eucalyptus (VOGTLANDER et al., 2010). Utilization of biomass requires various steps: harvesting, transportation, drying, cutting or comminution, sorting or screening, feeding into processing vessels, processing and separation. Most of these operations require that the biomass material be subjected to two or threephase flow, usually in air or water. For effective utilization of biomass fuel, the knowledge of their characterization is essential. The biomass particles are commonly nonstandard, have peculiar shapes, sizes and densities. These differences are often critical, making difficult to handle, feed or process biomass particles. (Cui and Grace, 2007). Thermochemical characterization of biomass is one of the methods required in assessing the viability of available feedstock for use in biomass pyrolysis processing (Greenhalf et al., 2012). Therefore, the knowledge of the characteristics of a particular biomass will be useful in selecting a suitable reactor operating condition for optimization and viability of the overall process (Odetoye et al., 2013). Hence their multiphase hydrodynamics characteristics are of special interest. Understanding and managing multiphase flow are critical to the success of new energy-related processes for biomass, and to improve existing biomass processes (Cui and Grace, 2007).

The objective of this study are:(i) characterization of bamboo particles by physical and themo-chemical analysis; (ii) hydrodynamic study of bamboo-sand mixtures (0 to 10 wt% of biomass in the bed) involving the minimum fluidizing velocity measurement for each binary mixture; (iii) development of experimental tests in a bench scale slow pyrolysis reactor to obtain products yields from bamboo pyrolysis at 500°C; and (iv) characterization of pyrolysis products (solid and liquid) in order to verify its potential to energy applications.

2. MATERIAL AND METHODS

2.1 Solid particles

This experimental work uses bamboo (*Dendrocalamus giganteus*) as feedstock and sand particles as inert material regarding hydrodynamic studies.

The culms of bamboo were harvested at University of Campinas. The mature stems were gathered after 5 years old from plantation. Culms were split into pieces of about 1 m and cut into blocks about 10 cm long to facilitate milling. All the feedstock was air-dried to remove moisture. Raw biomass were ground in a hammer mill and, after that, the particles were sieved by a vibrating screen, before the experiments were carried out. Particle chosen for this research were that between 10 and 42 Tyler (i.e., opening sieve area from 178 to 1700 μ m) as they presented an average diameter around the one obtained for sand particles.

2.2 Particles characterization

In our study, the physical characteristics of the biomass and sand were determined. The methods used to determine the physical characteristics of the particles, alongside its results, are shown in Table.1.

Both particles were classified as group B concerning Geldart (1973) classification.

The high heating value of bamboo particles was measured by using a bomb calorimeter (Model: IKA 2000 Basic). This value defines the energy content of a biomass fuel.

The proximate analysis was performed to measure moisture, volatiles matter, fixed carbon and ash content, following the ASTM standard methods, E1756-08, E872-06, E870, respectively. A muffle furnace and an analytical balance (OHAUS- GA200)was used for this analysis. For moisture content calculation, 1 g of bamboo sample was weighed and then heated at 110 ± 2 °C until the weight becomes constant. In determining the ash content, the bamboo sample was heated in a muffle furnace from250 °C to 575 ±25°Cwhich final temperature was kept constant for 3 h. The volatile matter was measured by weighting loss calculation after a bamboo sample was maintained at 900°C for 6 min in

a muffle furnace. The fixed carbon was determined by difference. The tests were carried out in duplicates and the mean averages reported.

Thermogravimetric analysis (TGA) of bamboo was performed in a Shimadzu 51H thermogravimetric analyzer (accuracy $\pm 1\%$ of Measuring Range). The bamboo samples were heated to 700 °C using nitrogen gas as the carrier gas at fixed flow rate of 100 mL/ min. Sample sizes of about 10 mg in weight were used for the analysis and heating rate of 20 °C/min was selected for this test. The analyses were performed in duplicate. This study was conducted to observe the decomposition of hemicellulose, cellulose and lignin and thermal stability of bamboo biomass.

Property	Methodology	Number of repetitions	Additional Information	Res Sand	ults Bamboo
Mean Sauter Diameter*	Sieving, following the ABNT NBR 6508 norm.	2	$\bar{d}_p = \frac{1}{\sum \frac{x_i}{d_{pi}}}$	466± 1 μm	669± 1 μm
Apparent Particle Density*	Liquid pycnometer method, checking the amount of water dislodged.	2	$\rho_{\rm p} = \frac{M_s}{V_s}$	$2602 \pm 5 \text{ kg/m}^3$	$\begin{array}{c} 1273\pm258\\ kg/m^3 \end{array}$
Bulk Density*	The material is weighed while naturally packed inside a measuring cylinder.	2	$\rho_b = \frac{M_s}{V_b}$	$\begin{array}{c} 1598 \pm 18 \\ kg/m^3 \end{array}$	$\frac{103 \pm 13}{\text{kg/m}^3}$
Sphericity	Images of the biomass were treated by the software UTHSCSA ImageTool 3.0, to retrieve the longest (h) and shortest (d) measures of each particle analysed. The geometry of the bamboo biomass is approximated by a cylinder.	100 (particles)	$\Phi = = \left(\frac{3}{2} \cdot h\right)^{\frac{2}{3}} \cdot \left(\frac{d^{\frac{1}{3}}}{h + \frac{d}{2}}\right)$	0.83 ± 0.09	0.64 ± 0.12

Table 1. Physical characterization of particles and methods employed

*An OHAUS-GA200 analytical balance (4 digits) was used to do the weighing.

2.3 Experimental set-up for hydrodynamics tests in a fluidized bed containing bamboo-sand mixtures

Hydrodynamics tests were conducted in a laboratory-scale fluidized bed system located at Thermal Process and Environmental Engineering Laboratory at School of Mechanical Engineering - UNICAMP. It is composed mainly by plenum, gas distributor (porous plate type), main column or riser (0.10 m internal diameter, 2.5 m height) and cyclone (Lapple type 0.12 m internal diameter). A Roots-type supercharger supplies the air to the system and an orifice meter provides the measurement of the air flow rate into the system. Air temperature is measured by a thermocouple (J-type) located between the orifice meter and the plenum, and the pressure drops by pressure transmitters (Smar-LD301-D2). Figure 1 (a) shows the photography of the experimental system and Fig.1(b) shows a schematic view of the main loop. The system was made of glass, acrylic and carbon steel sections allowing visual observation of the gas-solid flow.

Tests were performed in order to obtain the minimum fluidizing velocity (Umf) for five different bamboo-sand blending ratios (0.0, 2.5, 5.0, 7.5 and 10.0 wt% of biomass inside the bed).

The insertion of sand was done first, followed by the bamboo particles, forming two segregated columns. The height of the columns combined was 0.1m prior to fluidization.



(a)Image of the experimental set

(b) Schematics of the experimental set up

Figure 1. Fluidized Bed experimental set up

Air injection allowed the particles to reach complete fluidization (bubbling condition), which was then stabilized in a fixed bed by gradual reduction of the gas flow. For each reduction, the average gas flow and pressure drop ΔP (using 500 data points) were determined. From this value the pressure drop in the porous plate distributor, previously determined using an empty bed, was subtracted in order to yield the pressure drop in the fluidized bed. The plot of this data is expected to behave as in Figure 2.



Figure 2. Typical curve of pressure drop versus superficial velocity for mixtures

As evidenced, the minimum fluidization velocity (U_{mf}) is determined through the intersection of the lines tangent to the first and second parts of the graph (fixed bed and fully fluidized bed, respectively). Figure 2 also shows the initial fluidizing velocity for the fine particles (Umf,i) and the complete fluidizing velocity for the mixture (Umf,c).

2.4 Pyrolysis reactor

Pyrolysis experiments were carried out in a fixed bed reactor designed by BiowareTecnologia, which was heated indirectly by four electrical heaters. Figure 3 shows the main components of the fixed bed pyrolysis reactor. The reactor was made of a carbon steel tube presenting 230 mm height and 115 mm inner diameter. There were two K-type

thermocouples at different positions in the reactor. The reaction temperature was considered as the average value taken from these thermocouples. The cooling water temperature in the condenser ($T_{w,I}$ at inlet and $T_{w,o}$ at outlet) were also measured in order to control the vapor condensing process. In this study, the condensation temperature was about 24°C. In each test, 200 g of sample was heated from room temperature to a final temperature of 500 °C. The heating rate was ranged from 10 to 20 °C/min. The average particle size of the bamboo in these experiments was 669 ± 0.1 µm.



Figure 3. Fixed bed pyrolysis system.

2.5 Product analysis

Pyrolysis products yields were determined gravimetrically by weighing. The liquid product was heterogeneous and consisted of aqueous and oil phases. It was collected in an Erlenmeyer and after liquid yield determination, it was separated into two phases by a centrifugal separator. Solid product was removed from the reactor after it reaches room temperature and weighed. The gas yield was calculated by difference. Both liquid and solid fractions were analyzed.

2.5.1 Pyrolysis liquid and solid characterization

Physical and chemical analyses were conducted to characterize the liquid and solid products. The analytical methods for char characterization were proximate analysis and heating value determination. Regarding the pylolytic liquid characterization, pH analysis and heating value were obtained. The analyses were performed in duplicate.

The Proximate analysis of the char; moisture, volatile matter and ash contents were determined according to ASTM standard methods, D3172. In brief, 1 g of the sample was heated in a porcelain crucible and the sample weight difference was determined between before and after the specified heating process for each component. Regarding moisture content, samples were dried at 105 °C for 2 h; for volatile matter, samples were heated to 950 °C for 11 min (in a covered crucible) and for ash content, samples were heated to 700-750 °C for a minimum of 2 h (in an uncovered crucible). The weight of the original sample, subtracted by its moisture content, ash content and volatile matter content corresponds to the stable carbon fraction of that sample and hence, this fraction is termed the fixed carbon content.

The HHV (Higher heating value) of products pyrolysis were determined using a IKA C2000 basic Oxygen Bomb Calorimeter following the ASTM D4809-00 Standard method.

The pH was measured with a digital pH meter (Digimed DM 20).

3. RESULTS AND DISCUSSION

3.1 Characterization of bamboo particles

The high heating value and proximate analysis for bamboo are shown in Tab. 2 with their respectively standard deviation. The heating value was similar in comparison with biomass from woods 17.8 MJ/kg for oak tree and 16.5 MJ/kg for eucalyptus (Kim *et al.*, 2013). Values of proximate analysis are in agreement with reported in the literature for different bamboo samples. Scurlock *et al.*, (2000) reported analyses for nine bamboo samples. The moisture content

of their samples ranged from 8% to 23%, the ash content were 1% or less, the volatiles content ranged from 63 to 75%, the fixed carbon ranged from 12 to 17%. Their high content of volatile matter and low amount of ash are particular desirable in biomass feedstock for pyrolysis.

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Table 2.	Properties	of bamboo	Dendrocal	amusgiganteus
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Property	Value
High heating value (MJ/kg)	17.235±0.143
Proximate analysis (% wet basis)	
Moisture	10.43 ± 0.68
Fixed carbon	16.27±5.4
Volatile	72.33±5.35
Ash	0.97 ± 0.2

3.2 Minimum Fluidizing Velocity

The data obtained in the experimental setup was used to plot the pressure drop versus superficial velocity of the gas for each mixture, given in Fig. 4 for each tested blending ratio.



Figure 4. Pressure drop versus superficial velocity of bamboo-sand mixtures

The experimental minimum fluidizing velocities (U_{mf}) values obtained for each tested blending ratio (weight fraction of biomass in the bed) are given in Tab. 3. From this table it is observed that U_{mf} increases with the increasing weight fraction of biomass in the mixture.

Blending ratio	Umf
(wt % *)	(m/s)
0.0	0.14
2.5	0.15
5.0	0.20
7.5	0.22
10.0	0.33

Table 3. Experimental minimum fluidizing velocities.

*mass of bamboo / mass of the mixture

As listed, the value of the U_{mf} grows as the fraction of biomass is increased. This behavior was also observed by Nascimento *et al.* (2001) in a study of maize/sand mixture in similar conditions.

By studying the curves from Figure 4, we see how similarly the curves behave, except for 10% bamboo mass. In each curve it is possible to notice a gap of data points. The reason for this gap is due to our trying to avoid spending long periods of time making adjustments on the gas velocity, from the bubbling to the fixed bed regime which creates great segregation of the two material inside the bed. The more biomass added to the bed, the more difficult it was to avoid segregation; at 10%, it was virtually impossible to avoid segregation of the particles, causing the curve to differ from the others. Therefore, it is safe to say that mixtures containing up to 7.5% can be controlled to avoid bed segregation.

3.3 Thermogravimetric analysis

Thermogravimetrical analysis (TGA) was used to determine the thermal degradation of the bamboo in slow rate. As shown in Fig.5, the pyrolysis process included three steps. In the first step of 25 at 100 °C occurs the weight loss of about 2,85%, which meant the moisture was moved out from bamboo. In the second step, the main reaction was carried out at 250-450 °C and most of the volatile materials decomposed within these temperatures, the degradation of cellulose, hemicellulose e partial lignin happened in this step, there is only one weight loss peak in the differential thermogravimetric (DTG) curve and the maximum decomposition rate appears at about 368.7°C, which indicates that the pyrolysis of cellulose is completed. A small shoulder at nearly 300°C indicates the decomposition of hemicelluloses. In the third step, the degradation temperature was from 450 °C to 700°C, the weight loss was about 17.32% and decreased slowly. In general, the observed thermaldegradation of bamboo is similar to those reported by others authors for the pyrolysis degradation of ligno-cellulosic biomass (Wang *et al.*, 2007).



Figure 5. The TG curve of bamboo pyrolysis

3.4 Pyrolysis yields and products characterization

The product distribution of bamboo pyrolysis at 500 °C is presented in Tab. 4.

	Table 4.	Pyrolysis	operational	conditions and	products	yields
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Operational Conditions	
Amount of bamboo (g)	200
Temperature (°C)	500
Temperature increasing rate (°C/min)	20
Pyrolysis products	
Liquid yield	38.1 ± 3
Aqueous phase (%wt)	24.1±1.72
Bio-oil phase(%wt)	14.0 ± 1.30
Char yield (%wt)	34.5 ± 3.1
Gas yield (%wt)	27.4 ± 2.7

The yield of liquid products was 38.1 %, the product solid was about 34.5% and gas was 27.4%. These results differe from others reported in the literature for slow pyrolysis of wood at 500 °C. Williams *et al.* (1996) reported that the char yield from wood pyrolysis was about 8% less, the liquid yield was about 12% higher and the gas yield was about 7% less than present work results. According with other studies, yields depend on the biomass feedstock type, as shown by Phan *et al.* (2008) who pyrolysed waste wood , cardboard and textile at different temperatures. They obtained the highest amount of product liquid at around 500 °C but the yields were instable, however, the yields were relatively stable at temperature between 500 and 600 °C. The char yield gradually decreased with increasing final pyrolysis temperature and the gas yield increase with increasing final temperature for all three feedstock. According with others analyses involving fast pyrolysis in a fluidized bed reactor at constant reactor temperature, the yield of bio-oil ranged from 59 to 65% and the char yield ranged from 13 to 15% (Kim et al., 2013). It is well known that different pyrolysis techniques caused difference on product quantity.

3.5 Products characterization

The liquid product collected presented a heterogeneous color, which an aqueous phase as lighter liquid of low molecular weight and a bio-oil phase as a dark viscous liquid of heavier molecules. Generally the heavier part is mainly aromatics components which may be suitable as a substitute for fossil diesel fuel. The aqueous phase mainly consists of chemicals such as acetic acid and hydroxyl cetone, which emit an unpleasant odor and present a low flash point (Hossain *et al.*, 2013). Thus, the bio-oil phase obtained in this work was characterized by measuring the heating value of the oil phase and the pH of the liquid phase. The results are summarized in Table 5.

Table 5	Pν	rolvti	ic lic	mid	properties	s
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Property	Value
Phase oil	
Higher heating value (MJ/kg)	17.8 (±0.3)
Phase liquid	
рН	3.42
Phase liquid pH	3.42

The solid product was characterized and the results are summarized in Tab. 6. The volatile matter content is about 8 % and the ash content of 3,9% are lower than others reported in the literature. Xiao *et al.*, 2007 reported, for fast pyrolysis of bamboo, values of 20.65 % and 6.53% for volatile content and ash content, respectively. As seen from Tab. 4 heating value of char obtained from slow pyrolysis has higher energy content and is comparable to most heating value of wood biochars which have approximately 31 MJ/kg, a value comparable to coal (Kim *et al.*, 2013).

Table	e 6.	Char	pro	perties
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Property	Value
High heating value (MJ/kg)	$30.865 \pm 0,187$
Proximate analysis (%)	
Moisture	6.5 ± 1.0
Fixed carbon	81.5±0.4
Volatile	8.10 ± 1.7
Ash	3.9 ± 0.4

4. CONCLUSION

In this study, bamboo pyrolysis in a fixed bed reactor was conducted and the pyrolytic products were characterized. The liquid fractions of the products pyrolysis consist of two phases: an aqueous phase presenting low molecular weight with high pH and a non-aqueous phase containing high molecular weight and high heating value. Characterization of the solid product have showed that the produced char, have a high fixed carbon content, little ash content and high heating value showing potential to be used as a solid fuel.

Hydrodynamics studies of bamboo-sand mixtures showed that the minimum fluidizing velocities increases with the increment in the weight fraction of biomass in the mixture. Mixtures containing up to 7.5 wt% of bamboo present a stable behavior in fluidized beds and segregation can be avoided by gas velocity control.

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