



Characterization of biochar from hydrothermal carbonization of bamboo

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Abstract

This paper presents a preliminary investigation on producing biochar from bamboo using a technique of hydrothermal carbonization. Laboratory scale experimentation to produce carbonaceous materials was carried out. The suspended biomass samples in water were subjected to hydrothermal carbonization at 220°C, 2.2 MPa in a closed vessel for six hours. The resulting products were in solid and liquid phase. The coal-like biochar was found to have rough surface and porous structure. The aqueous solution was found to contain a high concentration of nutrients, especially nitrogen, phosphorus, and potassium. The study shows that bamboo is an interesting and adequate biomass for the production of biochar with several applications including carbon sequestration.

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1. Introduction

With the global warming in the centre of international concern and discussions, a profound review in energy policy is being conducted. In this arena, ideas for alternatives to ever-decreasing reserves of fossil fuels as well as measures to decelerate or reduce the CO₂ emissions are urgently required. The efficient management of biomass, for instance to produce biofuels, is one of the most interesting aspects under investigation in order to achieve an environmentally-clean and CO₂-neutral solution.

A possible method to convert biomass into a biofuel is hydrothermal carbonization, also known as HTC. The first experiments involving the HTC process were already performed during the first half of the twentieth century and were aimed at understanding the mechanism of natural coalification [1, 2] although it was not until recently that this mechanism was proposed for the production of biofuels [3]. The HTC process is relatively simple, requiring mainly a closed vessel that contains the wet biomass and that is heated to temperatures between 170 and 250°C over a period ranging from a few hours to a day [4]. The hydrothermal carbonization process includes several reaction mechanisms, such as hydrolysis, dehydration, decarboxylation, polymerization and aromatization, although the detailed reactions have been only well characterized for a few types of biomass, such as cellulose [5]. The process takes place effectively only in water and is exothermic. The products of the HTC are a solid phase or “HTC-coal” and a liquid phase, referred as process water. A small amount of gas is also produced.

In the field of biofuel research, most attention has been paid to the liquid and gaseous products, while the solid phase or char did not receive much consideration, partially explained by the fact that its energy

density is lower than for most of the liquid and gaseous energy carriers. However, other characteristics, such as a relatively simple production process, also applicable in remote or low-industrialized areas, and its amenability for storage, thus allowing an efficient management of energy demand, make char an interesting focus in the biofuel development. Apart from its use as an energy carrier, HTC-coal has also potential applications as a soil conditioner, in mechanisms of CO₂ sequestration and storage, as a part of an integrative solution for biomass management and in the production of synthetic carbon-based materials with a variety of applications [3, 4, 6, 7].

The raw material used for the hydrothermal carbonization is preferably plant biomass with high content of lignin, cellulose and hemicellulose, e.g. agricultural waste or wood material [4] although a broad range of materials have been tested and effectively carbonized, such as microalgae, wastewater sludge or whey [4, 8]. One of the significant advantages of the HTC is that the biomass does not need to be dried. Biomass with water content up to 96% has been effectively carbonized. One of the key questions, therefore, is to find out which level of biomass dry weight is optimal for the carbonization of biomass in order to keep a reasonable energy balance.

In this study, bamboo was selected as a representative of biomass. Bamboo is the common term applied to a broad group of woody grasses (family Poaceae, subfamily Bambusoideae) ranging from 100 mm to 40 m in height. It encompasses 1250 species within 75 genera. It is distributed mostly in the tropics, comprising natural stands of native species. Bamboo has several interesting aspects for the HTC. It is a fast-growing plant that can grow on slopes and other areas where cultivation of wood is not possible [9]. Typical water content values are 10.4% at harvest and 2.9% after drying [10], which make it a suitable material for HTC. Thailand is abundant in lignocellulosic materials which are largely untapped, such as bamboo. Bamboo has been used for handicrafts, paper-making and construction materials as well as cultivated for edible shoots. Nowadays, it is used mostly for fiber and food within Asia. It has been suggested that non-fuel applications of bamboo biomass might be actually more profitable than energy recovery [10]. Actually, the heating value of bamboo is higher than most agriculture wastes but it is lower than most woody products. However, HTC process offers the possibility of increasing the energy density of bamboo by means of a basically exothermic and relatively simple process.

The principal objective of the present work was to investigate the amenability of bamboo for hydrothermal carbonization and to obtain biochar that is a solid energy carrier with a good process energy balance. The HTC process as well as the characteristics of the obtained char and the process water were the focus of this experimental study.

2. Methodology

2.1 Raw materials

Bamboo (*Dendrocalamus asper*) was collected from a local bamboo furniture factory. The raw material was cut, milled and sieved to particle sizes below 300 µm. It was subsequently air dried to low moisture content (< 10 %). All of the materials were stored in plastic bags at room temperature until being used in the experimentation. Its properties obtained from chemical analysis in a previous study [11] are shown in Table 1.

Table 1. Chemical analysis of bamboo

| Property | Unit | Bamboo |
|----------------------|---------|--------|
| Moisture | [%] | 5.7 |
| Volatile | [%] | 74.7 |
| Fixed carbon | [%] | 14.1 |
| Ash | [%] | 5.5 |
| Carbon | [%] | 45.7 |
| Hydrogen | [%] | 4.3 |
| Oxygen | [%] | 49.7 |
| Nitrogen | [%] | 0.3 |
| Higher heating value | [MJ/kg] | 16.8 |

2.2 HTC reactor and test procedure

Experimental runs on HTC of the bamboo were performed in a batch reactor, as shown in Figure 1. The HTC reactor was 0.6 m high and inside diameter of 50 mm. It was made of stainless steel cylinder, surrounded by a 2-kW electric heater coil, thick insulating wool, and a 3 mm thick steel sheet. It had a 30

mm thick steel cover, equipped with temperature and pressure sensors, as well as pressure relieve valve. Prior to the test, pre-weighed batches of bamboo materials (10 g) were dispersed in distilled water (300 mL) and stirred for 4 h. The mixture was then loaded into the autoclave. The cover was put in place, checking that the reactor was air tight. The closed reactor was then heated to 220°C, 2.2 MPa. The reaction time of six hours after reaching 220°C was used, before cooling down to room temperature. Reaction temperatures were measured by a thermocouple inserted through its cover. The temperature and pressure were recorded manually at a regular interval of 10 min. At the end of each experiment, the solid chars and process water were collected and weighed to determine the mass balance. The chars were filtered, followed by drying in an oven at 105°C for 4 h.

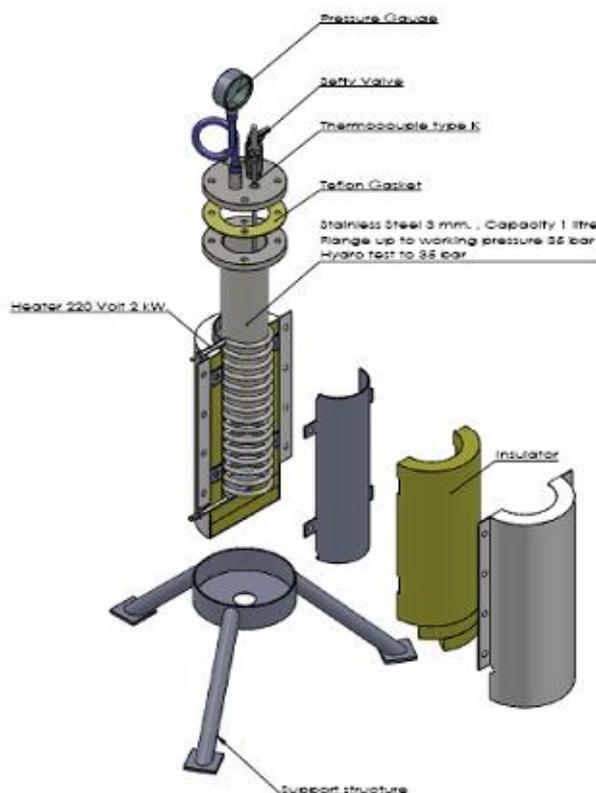


Figure 1. Schematic drawing of the HTC reactor setup

2.3 Analytical methods

The surface morphology was studied by scanning electron microscopy. Char imaging was carried out using a JEOL JSM-6335F Field Emission Scanning Electron Microscope. During the SEM analysis, char samples were selected and imaged randomly to minimize bias. Magnifications between 500X and 1,000X were typically used. Additionally, the heating value of the dried bamboo, and the resulting char were determined using a Parr bomb calorimeter. It is reported as gross heat of combustion at constant volume.

Atomic absorption analysis was used to determine the nutrient content of the process water. The target elements in this study were N, P, and K. Exactly 25 mL of each sample were used for analysis. Each sample was directly heated in crucible until all carbonaceous matter was removed. The ash was then allowed to cool down, and later transferred to a flask. The ash was treated with 10 mL of concentrated HNO₃ and 30 mL of concentrated HCl. All the reagents used were of analytical grade. The mixture was digested at 60°C for at least 2-3 hours or until the mixture appeared to have no residue. Digested samples were filtered and their volume adjusted to 100 mL by adding solution of 1.0% HNO₃ in deionized double distilled water. High purity of standard stock solutions of 1000 ppm (mg/L) were prepared for different metals. The atomic absorption determinations were measured with a Perkin-Elmer Corporation AA analyst 100 instrument and all data were sampled and processed automatically via a personal computer using AA Win/Lab software. The spectrometer was operated in the absorption mode (absorbance readings), using standard solutions for calibration. For each element determination, the recommended wavelengths were set and burner position as well as flame conditions (C₂H₂, air, N₂O) were optimized

using a standard solution. Deionized water was atomized after each reading of standard or sample. The calibration curves were prepared by plotting the absorbance versus concentration for each standard. From calibration graphs, concentrations of a sample were calculated by comparing the absorbance of the sample solution with that of the standard solution. All analytical determinations were performed in triplicate and average results are presented.

3. Results and discussion

3.1 HTC process conditions

A temperature measurement was possible using a thermocouple inserted directly into the closed reaction chamber. Temperature and the corresponding pressure profiles are illustrated in Figure 2, which shows that the heating arrangement was able to provide the reaction temperature rapidly (less than 50 min), and maintain at the controlled HTC temperature and pressure within a small degree of fluctuation throughout the test runs.

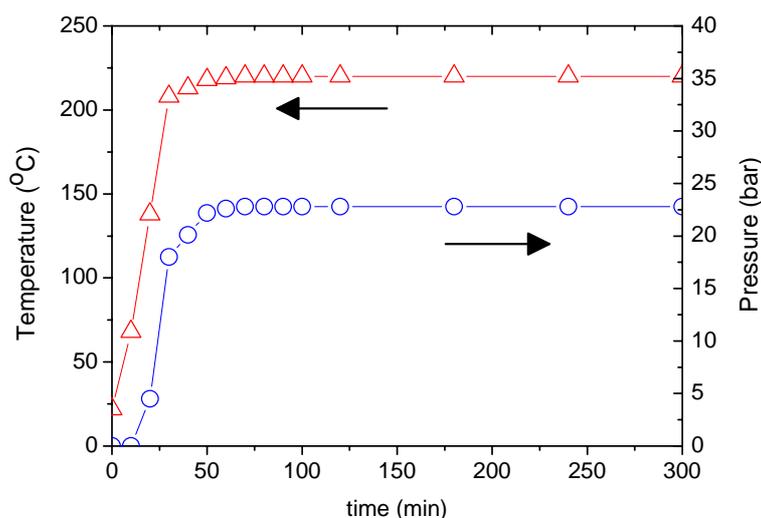


Figure 2. Evolution of reaction temperature (Δ) and pressure (\circ) inside the HTC reactor

3.2 Characteristics of biochar

Hydrothermal treatment of biomass leads to the formation of solid char particles, potentially a coal-like fuel. In this work, about 45% of original raw bamboo mass was recovered as HTC char. Images of raw bamboo and HTC char are shown in Figure 3. The surface property is important for char activity. From the SEM results, it was observed that the HTC char had rougher surface than the raw bamboo. Porous structures were formed on the surface. The HTC char was observed to contain more porous structure than the original bamboo samples.

Analysis of biochar energetic content showed an average heating value of 28.7 MJ/kg, which is similar to that of lignite coal. With respect to energy conversion efficiency, defined as a ratio between energy content in the biochar divided by that in the raw bamboo, it was calculated to be 76.9%. Further analysis for carbon in all HTC products should be carried out to evaluate carbon conversion efficiency of the process.

3.3 Nutrients in process water

It is generally known that water plays a significant role as a solvent and reactant in the HTC process. The liquid phase is expected to contain a high load of organics and inorganics. Atomic absorption analysis of the process water from bamboo carbonization was carried out. Results are shown in the second column in Table 2. A drop in pH of the process water was observed after HTC reaction. It is noted here that original pH of deionized water was at neutral. The liquid phase was found to be acidic which can be explained by the formation of a variety of organic acids that typically occur during the HTC process [5].

The nutrient content of the process water was analyzed in order to inspect its value as a useful fertilizer. The liquid phase was found to contain high values of potassium and nitrogen, while the phosphorus was relatively low. Also shown in Table 2, results from HTC of various biomass materials at similar conditions are compared with this work. The raw materials are cheese whey, biogas digestate, and sewage sludge.

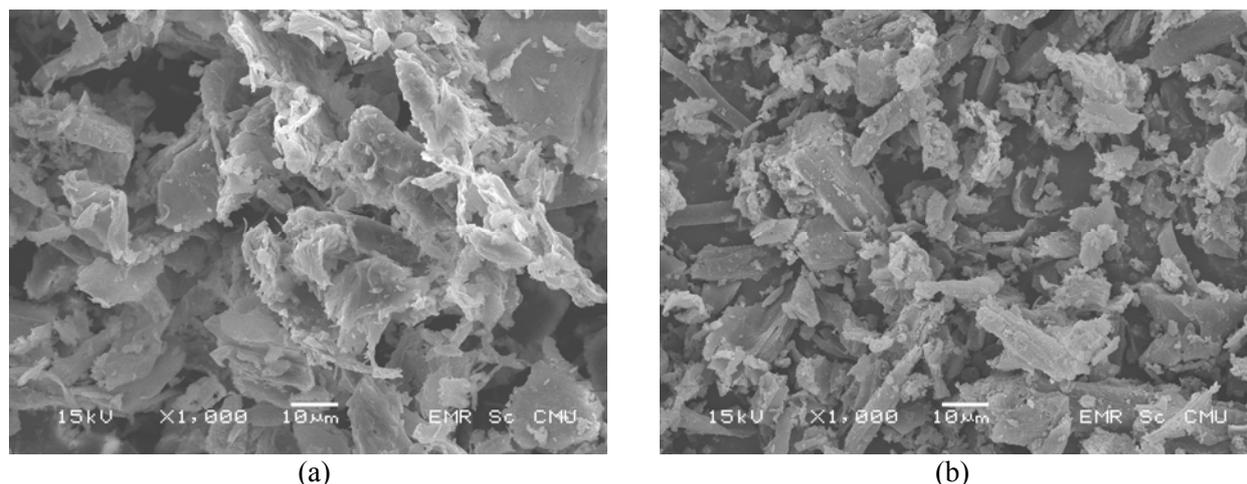


Figure 3. SEM images of (a) raw bamboo and (b) biochar from HTC of bamboo

Table 2. Comparison with other biomass materials

| | This work | Escala et al. [8] | Escala M. [12] | Koller C. [13] |
|-------------------------------------|-----------|-------------------|------------------|----------------|
| Raw materials | Bamboo | Whey | Biogas digestate | Sewage sludge |
| Carbonization temp. (°C) | 220 | 205 | 205 | 205 |
| time (h) | 6 | 6 | 6 | 5 |
| Char heating value (MJ/kg) | 28.7 | 27.1 | 16.4 | - |
| Process water total nitrogen (mg/L) | 100 | 511 | 2342 | 1230 |
| phosphorus (mg/L) | 52 | 226 | 6.4 | 10 |
| potassium (mg/L) | 1642 | 1387 | 6213 | 446 |
| pH | 3.4 | 3.9 | 9.3 | 5.0 |

4. Conclusion

In this study, carbonaceous samples have been prepared by hydrothermal carbonization of bamboo. Preliminary study has shown that a thorough carbonization process can take place during hydrothermal treatment at relatively mild conditions, evidenced by the stark change in the heating value of the samples, which is a consequence of the rearrangement of the chemical bounds, especially those between carbon, oxygen and hydrogen. The HTC treatment can develop rough surface and porous structure of the obtained biochar. The coal-like solid particles produced during the treatment may be used as fuels, or alternatively suitable for adsorption purposes because of its structure. Additionally, limited analysis of the process water suggested there may be a vast amounts of compounds dissolved in the liquid phase. The liquid phase contained nutrients that may be useful as fertilizer.

From this preliminary work, HTC appeared to be a conversion technology that is worth serious attention due to potential of its possible applications.

Acknowledgements

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