

Investigation of Biomass Carbonization by using Different Temperature on Corncob

Aye Aye Naing¹, Zhifeng Zheng^{2*}

*Corresponding Author: zhifeng.zheng@xmu.edu.cn.

Abstract

Large quantities of plant wastes and agricultural by-products are produced annually. Meanwhile, excellent renewable raw materials for adsorbent production can be prepared. The carbonization stage may be decisive in charcoal production even though it is not the most expensive one. Thus, in this study, carbonization of corncob and the energy properties of the prepared biochar are reported. The preparation involved carbonizing in the furnace with the variation temperature of 500°C, 600°C, and 700°C at 5°C min⁻¹. The prepared biochar were characterized using elemental (C,H,N,O,S) analyzer, Bomb Calorimeter, Fourier transform infrared spectroscopy, X-ray diffractometer, and Nitrogen sorption measurement. The results show that increased carbon content and higher grade carbon as the increasing temperature.

Key words: Carbonization, elemental analyzer, bomb calorimeter, Fourier transform infrared spectroscopy, X-ray diffractometer, nitrogen sorption measurement.

Introduction

With the continuing concern over global warming due to CO₂ emissions, more attentions are turning to renewable energies. Compared with other carbon-based fossil fuels, biomass is a carbon neutral renewable energy source (**Bioresource Technology 100, 2009, 1428–1434**).

The use of cheap, fast and different environmentally friendly strategies for the preparation of carbon materials from renewable resources has been on the increase in recent times in the areas of environmental science and technology. This is because of the vital roles these materials play in different applications, such as adsorbents, catalyst supports, energy storage materials, electrode materials, and stationary phases in liquid chromatography (**Sunday E. Elaigwu, Gillian M. Greenway. 2016**).

¹ Dr., Lecturer, Department of Botany, University of Yangon, Myanmar

²Dr., Professor, Xiamen Key Laboratory of High-valued Conversion Technology of Agricultural Biomass; Fujian Engineering and Research Center of Clean and High-valued Technologies for Biomass; College of Energy, Xiamen University, Xiamen 361102, P.R. China;

National-Local Joint Engineering Research Center for Highly-Efficient Utilization Technology of Forest Biomass Resources; Key Laboratory for Highly-Efficient Utilization of Forest Biomass Resources in the Southwest China, National Forestry and Grassland Administration; Yunnan Provincial International Joint Research Center for Bioenergy, Southwest Forestry University, Kunming 650224, P.R. China.

Waste lignocellulosic material, which is easily available, inexpensive, and renewable, represents a kind of significant cellulosic biomass as raw material to produce fuel ethanol with many advantages in bioethanol conversion. Corncob residue (CCR) is a kind of waste lignocellulosic material (**Lingxi Bu, Yang Xing, Hailong Yu, Yuxia Gao and Jianxin Jiang. 2012, 5:87**).

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Each year, more than 40 million tons of inedible plant material, including wheat stems, corn stover (the stalks and leaves) and wood shavings from logging, are produced-much of which is thrown away(**Sherif S. Z. Hindi. 2012, Vol. 2, Issue. 3, pp-1386-1394, ISSN: 2249-6645**).

This practice does not help in building an eco-friendly economy. A better approach to this is to convert them to more useful energy products by the use of thermochemical technologies. The products obtained have higher energy values than the biomass and because of their abundance; they can continue to serve as feedstock for the production of bio-oil and bio-char (**Joseph K. Ogunjobi and LabunmiLajide. 2013**).

Agricultural and food industries create various waste matters that need to be utilized and convert in value added product. Carbonaceous materials such as coconut shell, palm shell, saw duct and tropical wood are some of the most common agricultural wastes shells used to produce activated carbon (**Patil Pragya1, Singh Sripal1 and YenkieMaheshkumar. 2013, Vol. 3(12), 12-15.**).

The aim of this work was to investigate carbonization of biomass especially on corncob commonly found in China, to test the quality and characterize the biochar of these biomass.

Experiment

Preparation

The samples were dried and grinded. The grinded powders were sieved with 50 mesh to get the fine powders. The powders were dried in the oven at 105°C temperature for 24 hours to remove the moisture. The samples were used in the carbonization and the obtained biochars were investigated by characterization techniques.

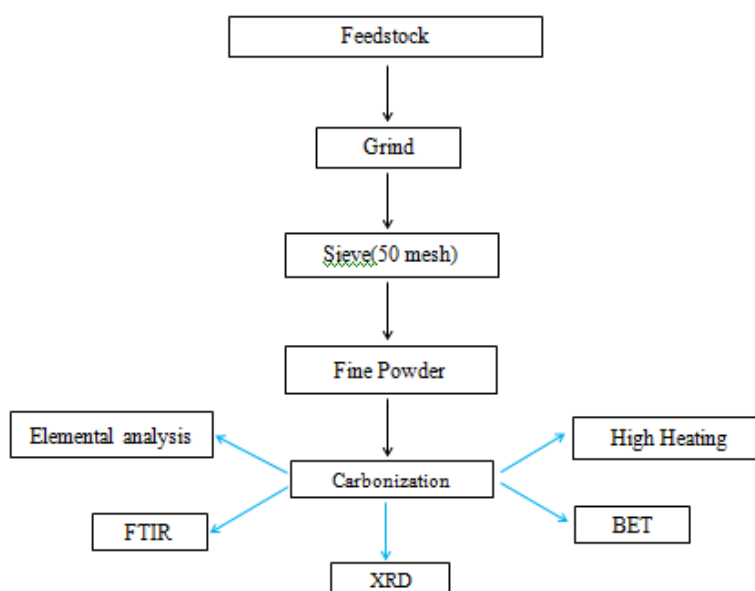


Figure 1. Flow diagram for procedure

Carbonization process

Carbonization was conducted in a tube furnace 1200°C (Tianjin Zhonghuan Experiment Electric Furnace Co., Ltd) with the temperature arrange 500°C, 600°C, 700°C and the following was the heating procedure: (1) temperature was increased from room temperature to 500°C, 600°C, and 700°C at 5°C min⁻¹; (2) temperature was held at 500°C, 600°C, and 700°C for 1 hr; and (3) sample was cooled down to room temperature. A constant nitrogen flow was maintained through the tube during the carbonization.

Elemental analysis

The elemental analysis was carried out with an elemental analyzer (model: vario SOLID Sampler, Germany) to detect the percentage of nitrogen, carbon, hydrogen, sulphur and oxygen.

Higher Heating Value (HHV) analysis

Determination of higher heating value for biomass and charcoal was performed using Bomb Calorimeter (model: Parr 6400 Calorimeter, item No. A587M, USA) by burning about 0.5 g of biomass in the calorimeter with oxygen level regulated to 3000 Kpa.

XRD analysis

The X-ray diffraction (XRD) was also used to analyze the structure of the samples on Rigaku Ultima Plus X-ray diffractometer. The samples were ground into the fine powder, weighed and placed on the plate for analysis. An accelerating voltage of 40 kV was used at 40 mA. The X-ray diffraction (XRD) grams were obtained at the scanning rate of 2.0°/min within the range $2\theta = 10.0^{\circ}$ – 80.0° .

FTIR analysis

The sample was mixed with KBr at an approximate ratio of 1:150 and ground in an agate mortar to prepare the transparent KBr pellets. FT-IR spectra were recorded on Thermo Scientific Nicolet is50 FT-IR and each sample was investigated in wavenumber range of 4000-400 cm^{-1} .

BET analysis

The specific surface areas of carbonized samples were determined by the Brunauer-Emmett-Teller (BET) method using N_2 adsorption-desorption (ASAP2020 Plus HD88, Micromeritics Co., Ltd., USA) at -196°C . Before the analysis, samples were degassed under nitrogen atmosphere at 200°C for 5h. The pore size distribution was obtained from the adsorption branches of isotherms by density functional theory (DFT) method.

Results and Discussion

Effect of Temperature on the carbonization of biomass

The effect of temperature on the process is presented in Table 1. As the processing temperature was increased from 500°C to 700°C , the mass yield were decreased for the biochars; reason being that increase in temperature favors gasification reactions, which results in part of the carbon being lost in form of volatile compounds. Otherwise lower yield of charcoal give the higher grade.

Carbonization temperature ($^\circ\text{C}$)	Charcoal Yield (%)
500	33.6
600	29.1
700	26.9

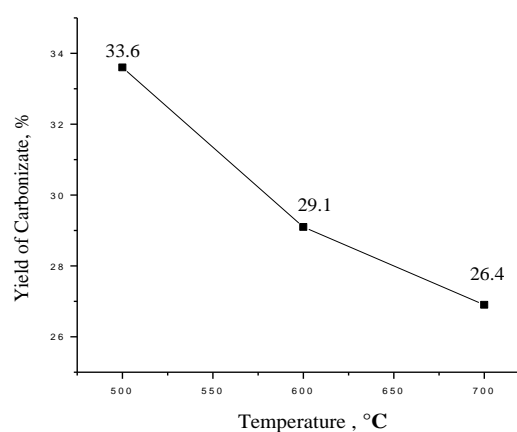


Figure 2. Dependence of the carbonized charcoal yield on the final heating temperature

Elemental composition of the biochar

The elemental compositions (N, C, H, S and O) of the starting material (biomass) and different biochar samples are listed in Table 2. It was observed that carbon contents increased from 42.1% in the starting materials of corncob to about 65.11%, 71% and 73.1% in the biochar samples on 500°C , 600°C and 700°C respectively. The hydrogen, Sulphur and oxygen contents of the biochar reduced at the same time. The gradual increase in carbon content, and the decrease in hydrogen, Sulphur and oxygen contents of the biochars, with increase in processing time is due

to deoxygenating, dehydration and decarboxylation reactions that occurred during the carbonization process.

Table 2. Elemental compositions of biomass and biochar of corncob

Component	Biomass	Biochar (%)		
	(%)	500°C	600°C	700°C
N	0.7	1.08	1.01	1.22
C	42.1	65.11	71	73.1
H	5.6	3.252	2.31	1.55
S	0.1	0.114	0.1	0.13
O	51.5	30.44	25.6	24

Higher Heating Value (HHV) analysis

An important parameter to test the quality of biochar is their higher heating value (HHV). It provides information about the quality of energy present in the biochar. The calculated HHV increased as increase in temperature from 28.9444 MJ/kg in 500°C to 31.0157 MJ/kg in 600°C, and 31.1701 MJ/kg in 700°C of corncob were presented in (Table 3). The highest HHV in this study showed an increase of 2% when compared to that of the starting material for Corncob.

Table 3. Comparison for Higher Heating Values (HHV) of biomass and biochar

Higher heating values of Corncob (MJ/Kg)			
Biomass	Biochar		
	500°C	600°C	700°C
18.173	28.9442	31.0157	31.1701

FT-IR analysis

The FT-IR spectra gave further insight into changes in the chemical composition of biochar during the process of variation temperature. Road peak between 3500 and 3000 cm^{-1} (section 1) corresponds to stretching vibration of aliphatic O-H (hydroxyl and carboxyl), while the peaks between 3000 and 2800 cm^{-1} (section 2) due to stretching vibration of aliphatic C-H bonds, indicate the presence of aliphatic structures. The appearance of peaks between 1650 and 1500 cm^{-1} (section 3) due to C=C vibration, while the peaks between 1500 and 1000 cm^{-1} (section 4) correspond to C-O stretching vibration from esters, ether, phenols and aliphatic alcohols and well-defined peak below 1000 cm^{-1} (section 5) from deformation of C-H out of plane bending vibrations in aromatic compounds.

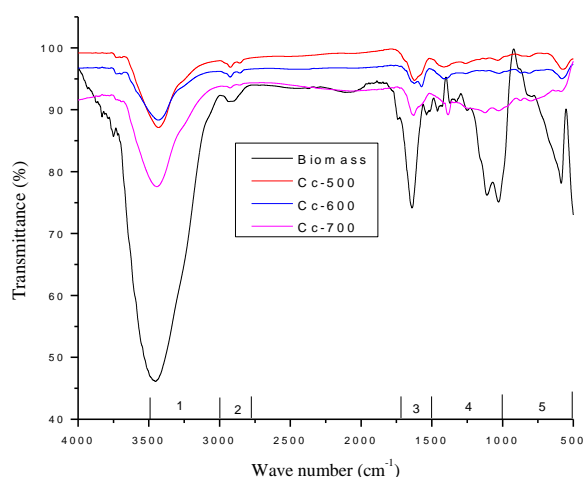


Figure 3. FT-IR spectrum of biochar derived from corncob at temperature 500°C, 600°C, and 700°C

XRD analysis

XRD analysis was used to characterize the degree of graphitization of biochars during the carbonization process. As presented in Fig. 6 two broad reflections located at the $2\theta \sim 23^\circ$ (major) and $\sim 44^\circ$ (minor) were observed for each of the carbonized samples, which are assigned to typical crystallographic plane of (002) and (100) in graphitic carbon. The height and peak width at half height of the two peaks correlated with the degree of graphitization of the biochars. Analysis of the (002) reflection gives the average interplaner spacing $d(002)$, calculated by the Bragg Equation of 0.260, 0.254 and 0.253 nm for corncob with increasing carbonization temperatures from 500, 600 and 700°C, respectively. In addition, a broad band at about 43° (100) is apparently observed in 700°C while weakly observed in 600°C and 500°C, which indicative disordered state, amorphous carbonaceous interlayers with a very low amount of crystalline phases at the low carbonization temperature and believed to be a result of the precursor used here follows a different mechanism for structure formation.

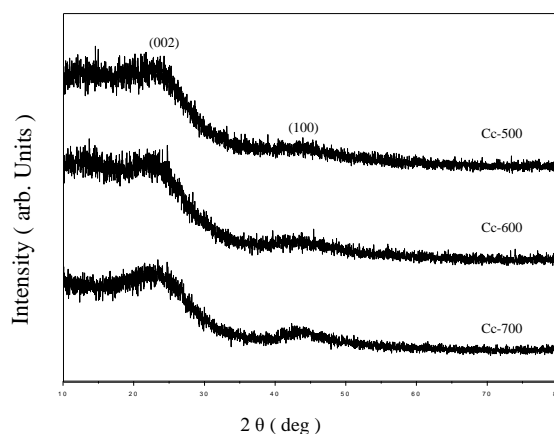


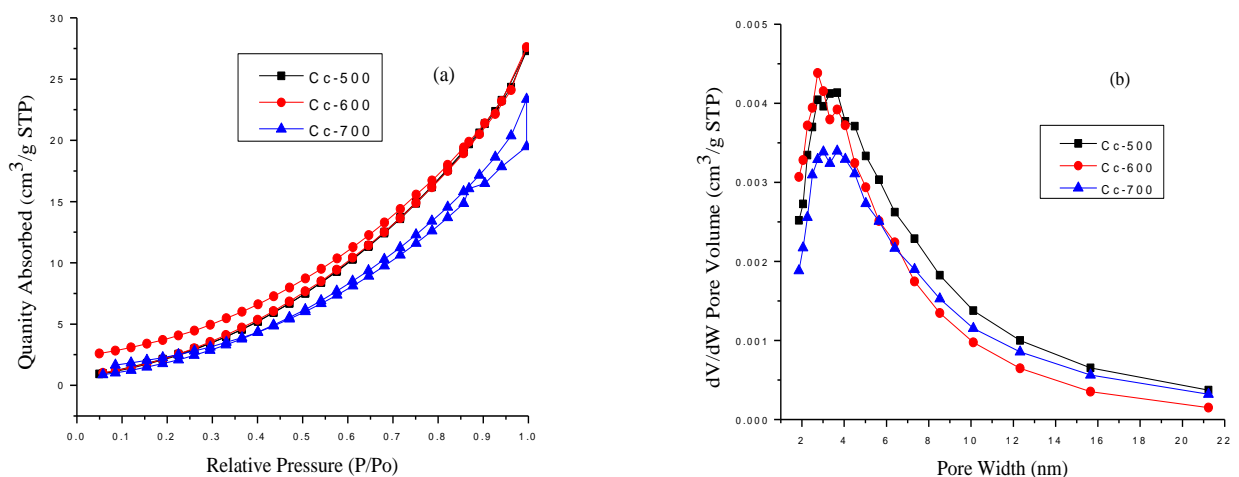
Figure 6. XRD patterns of biochar derived 500, 600 and 700°C

BET analysis

The BET specific surface area and the DFT pore size distribution of carbonized biomass were characterized using nitrogen adsorption/desorption analysis at -196°C . As shown in (figure 7), the isotherm of the Cc-500, 600, and 700 exhibited type II N_2 adsorption isotherms, typical of nonporous and macroporous materials with weak affinities to nitrogen. The adsorption behavior sharply increased in low relative pressure and approached a plateau at high relative pressure, which can be ascribed to N_2 adsorption in more microspores. In Table 4, although the largest BET surface area of $15.13 \text{ m}^2 \text{ g}$ shows in Cc 600°C all of the samples are non-porous materials. It is, therefore, not surprising that the biochar has a very small BET surface area of $11.72 - 15.13 \text{ m}^2 \text{ g}$, due to poor porosity. Similarly, the pore volume of temperature 600°C shows the highest. While carbonization temperature increased and decreased to 700°C and 500°C , the velocity of this process increase, thus leading to the decrease in pore volume. Conversely, the average pore width of temperature 700°C and 500°C more increased than 600°C , it seems meaningless because of their very small specific area.

Table 4. Porous structure parameter of biochar

	BET SSA ($\text{m}^2 \text{ g}$)	Total pore volume ($\text{cm}^3 \text{ g}$)	Average pore size (nm)
Cc 500°C	14.79	0.036	9.85
Cc 600°C	15.13	0.036	9.54
Cc 700°C	11.72	0.03	10.38



Conclusion

In summary, the obtained results have shown the influence of the major carbonization factors on the yield. Possibilities of corncob application as raw material for activated carbon production have been studied.

Further studies are considered to investigate the carbonization process of corncob, in order to find technological criteria to determine the optimum conditions of the carbonization process for activated carbon production. The activated carbon production can be the solution of the problem of annual waste utilization as well as provide the market with large quantity of renewable raw materials.

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