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Solid fuel characterization of torrefied coconut shells in an oxidative environment

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Abstract

Torrefaction is a thermo-chemical treatment to address problems in use of biomass as a fuel especially for combustion; it is usually done between 200-300 ℃ in an inert or low oxygen environment. This study investigated the properties of local Coconut Shell chips that were torrefied using a batch reactor in an oxidative environment at torrefaction temperatures of 250 ℃ and 300 ℃, and torrefaction time of 30 minutes and 60 minutes. Analysis of solid products included Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Proximate Analysis, Higher Heating Value (HHV) determination, and Equilibrium Moisture Content (EMC). Overall, the results in the solid product showed changes in composition and on the thermal degradation curve; also improvement of fuel properties in terms of HHV, Fixed Carbon Content, and EMC. Among the settings, the 300 ℃ and 30 minutes setting is recommended with significant improvement of the solid fuel.

Keywords: Biomass, coconut shell, oxidative torrefaction, solid fuel

1. Introduction

Biomass can be a source of fuel in the promotion of the use of renewable energy. Some of its major advantages pointed out by Basu are renewability, environmental and socio-political benefits [1]. Renewability since the biomass materials can be replaced over a period of time. Environmental because biomass is considered carbon-neutral in which the release of gases is not considered having an effect the balance of green house gases (GHG). For the socio-political benefits since biomass material are found locally; development of local communities and reduction of imported fossil fuels are more likely to happen.

In the Philippines, coconut trees (*Cocos nucifera)* are a potential source of biomass materials [2]. Some reasons are because the coconut trees are readily and abundantly available in the country. Other positive characteristics of the coconut tree as a resource are described by Banzon such as; non-disturbance on the food crops, no need for replanting since only the fruit and leaves can be harvested, can last up to 70 years with regular production of nuts and leaves, and it can offer both fuel and food. Also, the possible energy sources are obtained from the nut is the husks, shell and the oil [2]. Focusing on the coconut shell, it is part of the lingo-cellulosic biomass, in which it contains majority of cellulose, hemicelluloses and lignin. In terms of mass yield, the weight of the coconut shell (0.193 kg/nut) is lower than the coconut husk (0.242 kg/nut) however the energy content of the coconut shell (4.44 MJ/nut) is higher than the coconut husk (4.04 MJ/nut) [3].

Using raw solid biomass as fuel poses problems such as low calorific value, high moisture, hygroscopic in nature, and the high energy of grinding needed; these problems result to additional cost in transporting, handling and grinding [1]. Biomass conversions, such as thermo-chemical processes, are

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done to improve the state of biomass. Torrefaction is a thermo-chemical pre-treatment for biomass to address these problems in the use of biomass fuel and it is usually done between 200 -300 ℃ under inert or low oxygen environment [4]; recently many studies were about torrefaction focusing on its effect on different biomass and or its reaction mechanisms[5]-[9]. Another sub-category of torrefaction is oxidative torrefaction which is done in air environment for cost reduction[4, 8-9].

Oxidative torrefaction is a new method of improving solid biomass properties, however it is material dependent [9]. With no oxidative torrefaction studies focusing on the local biomass materials such as coconut shells, this study aims to produce torrefied coconut shells using a batch reactor in oxidative environment with varying process temperature and residence time. Also the objectives are to characterize the raw and solid product in terms of Thermogravimetric Analysis (TGA), Fourier Transform (FTIR) Spectroscopy, Proximate Analysis, higher heating value (HHV), and Equilibrium Moisture Content (EMC).

2. Materials and Methods

Coconut shell samples were obtained from Camalig, Albay, Philippines. The shells were by-products of the coconut oil production; hence the samples are dry, half shell size and coconut meat- free. Then the samples were fed into a Chipmunk Crusher to reduce the size into chips. The chips were then sieved passing 1½ inch and over ½ inch screen.

For torrefaction temperature, the low value was set at 250 ℃ and the high value was set to 300 ℃. While the torrefaction time, the low value was set at 30 minutes and the high value was set to 60 minutes.

Torrefaction of samples were conducted in an air tight stainless steel tubular batch reactor. It has an outlet for volatiles connected to a condenser with a liquid storage, then to a series of gas scrubbers before the exhaust seen in Fig. 1. The temperature controller used consists of thermocouple, data logger, laptop, and a micro-controller setup.

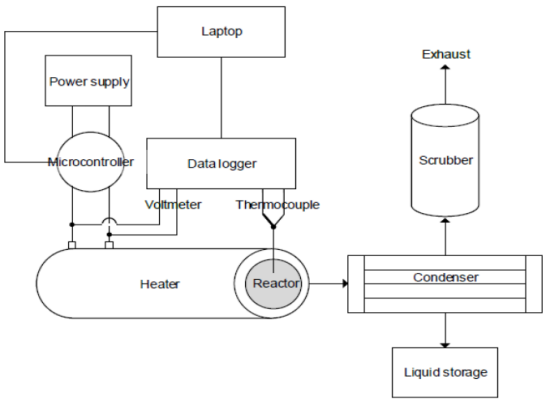

Fig. 1. A schematic diagram of the torrefaction reactor setup.

For the TGA and DTG characterization, samples were analyzed using a TA instruments TGA Q500 with the procedure was according to Chen & Kuo [10] and the results were processed in TA Universal Analysis Software. Samples were heated under nitrogen gas to 800 ℃ with a ramp rate of 20 ℃ per minute. The change in weight data was used to obtain the TGA and DTG graphs.

For the FTIR characterization, dried samples were analyzed using a THERMO SCIENTIFIC NICOLET 6700 FT-IR with wave number of 4000 to 400 cm^{-1}. The results were processed using Essential FTIR software.

For the Proximate Analysis samples were analyzed in a TGA Q500 with the procedure from Compositional Analysis by Thermogravimetry, ASTM E1131 - 08 [11] and the results were processed using the TA Universal Analysis Software.

For the HHV analysis, samples were analyzed in a Parr 6200 Calorimeter to determine the Higher Heating Value (HHV) value (MJ/kg).

Lastly for the EMC, Moisture of the raw and solid products was first obtained following the Chemical Analysis for Wood Charcoal, ASTM D1762 -84[12]. One gram of samples were placed in crucibles and were heated at 105 ℃ for 2 hours. The samples were then cooled in a dessicator for 1 hour and were weighed after. The samples were then heated, cooled and weighed until the differences of weight, individually is less than 0.005 grams. Exposure tests were done to determine the additional increase in moisture of the samples during storage. An air-tight box with a salt solution to maintain the relative humidity of 98% at 30 ℃ was used. The salt solution of saturated Potassium Sulfate was based on Maintaining Constant Relative Humidity by Means of Aqueous Solutions, ASTM E104-02 [13].

3. Results and Discussion

Images of raw and torrefied biomass samples indicate changes in color, particularly darker color samples at a higher time and a higher temperature, as shown in Fig. 2.

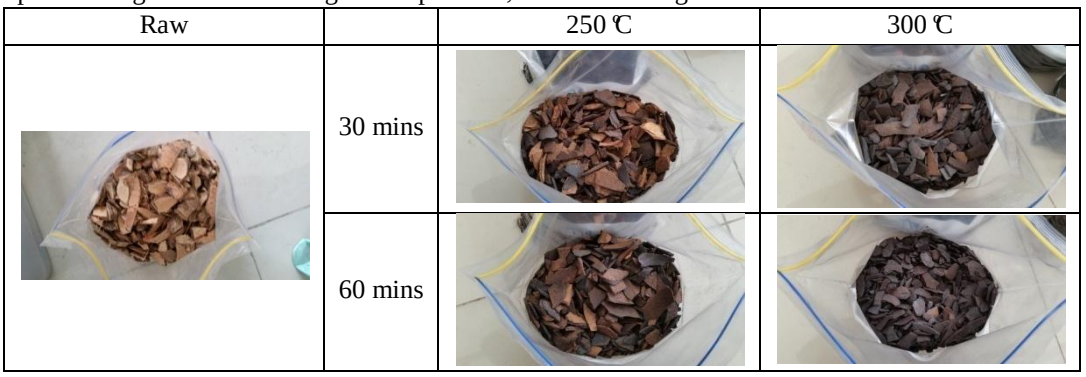

Fig. 2. Images of raw and torrefied coconut shells.

The TG curves of the raw and torrefied solid biomass samples in Fig. 3 shows the percent weight change as the temperature increase. Decrease in percent weight loss was observed while increasing the torrefaction temperature and time since the samples were thermally treated and the moisture and volatiles were previously removed. Similarly there is a horizontal shift of the significant decrease in weight as the torrefaction temperature and time are increased because of the nature of components remaining in the sample. The residence time at the higher temperature had no effect on the weight loss because the intended materials seemed to have been degraded at the shorter period of time following the fast oxidative reactions according to Chen et al., [4].

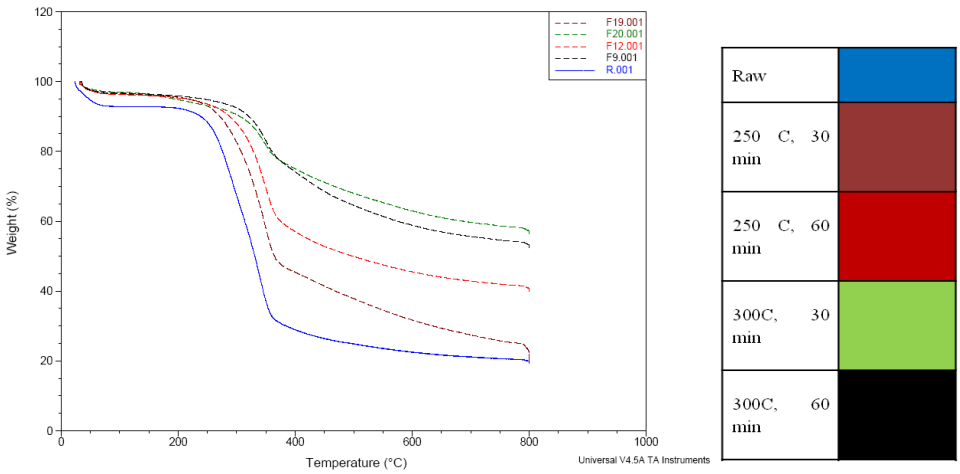

Fig. 3. TGA Curve of raw and torrefied coconut shells.

The DTG curve in Fig. 4 shows the rate of change of the mass sample as the temperature increases. Using the same method as of Chen et al., [10] the peaks of hemicelluloses and cellulose were observed for the raw coconut shell at 291 ℃ and at 340 ℃ respectively. Comparing the DTG curve of the processed product it can be observed that the curve in the range of hemicelluloses decreased at 250 ℃ and 30 min and further decreased at 250 ℃ and 60 min setting, while a horizontal portion at the 300 ℃ setting may mean that hemicelluloses was significantly degraded. A shift also happened in the peak that indicates the cellulose degradation relating to the greater thermal stability of the retained crystalline structure of cellulose [14]. The results from the Thermogravimetric analysis suggest that the hemicellulose was significantly degraded and slight degradation for cellulose which were the objective of torrefaction [1].

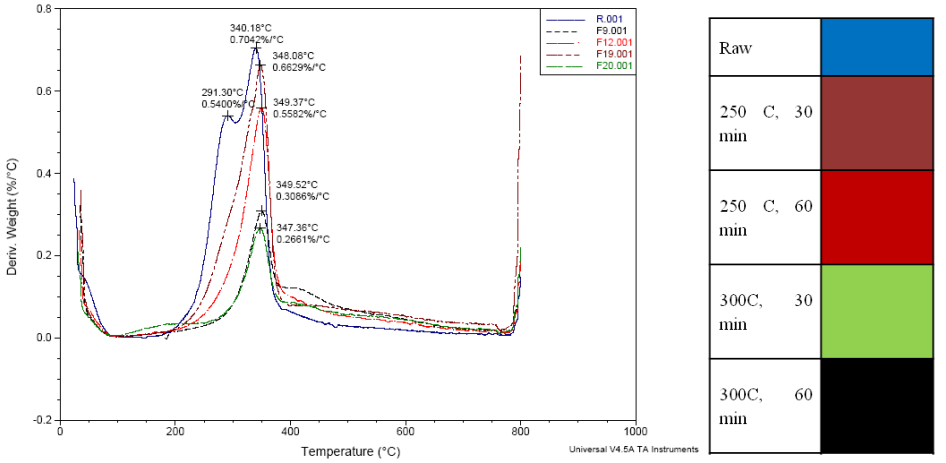

Fig. 4 DTG Curve of raw and torrefied coconut shells.

FTIR Analysis was also used to determine changes in the chemical structure between the raw sample and the torrefied product samples [15]. In Fig. 5, it was observe that at 250 ℃ torrefaction temperature the intensities and peak locations were similar to the raw sample while significant differences occurred at the 300 ℃ torrefaction temperature setting. The decrease in intensity is observed at 3350 cm^{-1} related to O-H band is due to partial dehydration [16]. While at 300 ℃ the absence of peak the 1732 $cm^{-1}$and new peak at 1700 cm^{-1} were similar to the previous study of Shang et al., and they concluded that these were due to the removal of carboxylic group in hemicelluloses and the formation of a product band [17] . Decrease was also observed at the 1240 cm^{-1} and 1030 cm^{-1} which is related to hemicellulose and cellulose respectively [18]. Decrease at the 2900 cm^{-1} peak related to the C-H functional group is also noticed. Observed changes were on hemicellulose and cellulose, which is the target to be removed or decreased at higher temperature consistent with the TGA and DTG findings.

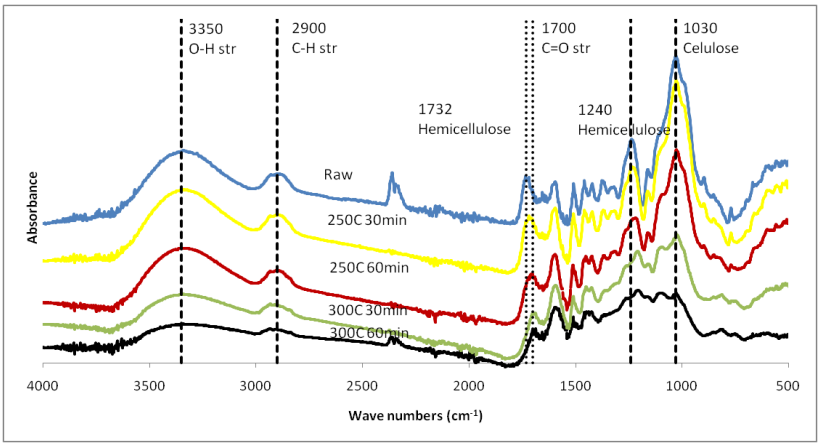

Fig. 5. FTIR Spectra of raw and torrefied coconut shells.

Proximate Analysis of the raw and solid products follows the trend in Fig. 6 with decreased percent volatile matter and increased percent fixed carbon with increasing temperature due to evolved moisture and volatiles. For fuels the increased in the percentage of fixed carbon mean a higher heating value. At the 300 ℃ level the values for the Fixed Carbon and Volatile Matter are similar at the different time; this may mean that the amount of volatiles were released around or before 30 minutes supported by the claims of Chen et al., that oxidative reactions can occur at shorter time [4].

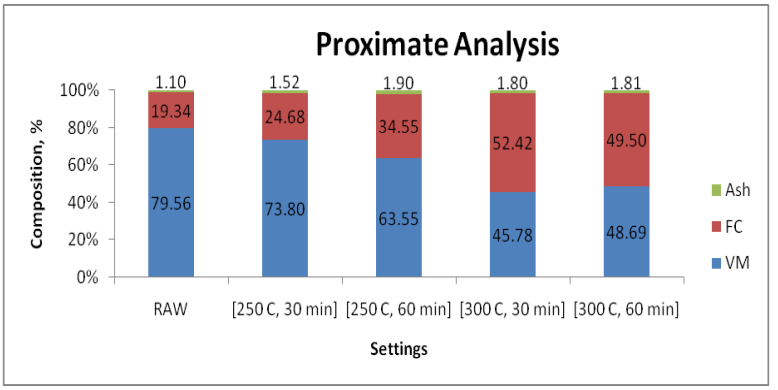

Fig. 6. Proximate Analysis of raw and torrefied coconut shells.

In Fig. 7, overall there is an increase up to 41% in Higher Heating Value (HHV) of the torrefied sample compared from the raw biomass (19.58MJ/kg). HHV is also proportional on the amount of Fixed Carbon, in which high values occur also at the 300 ℃. The highest HHV of the torrefied coconut shell chips at around 27.58 MJ/kg is in the range of those of coal and traditional coconut shell charcoal values found [2,4].

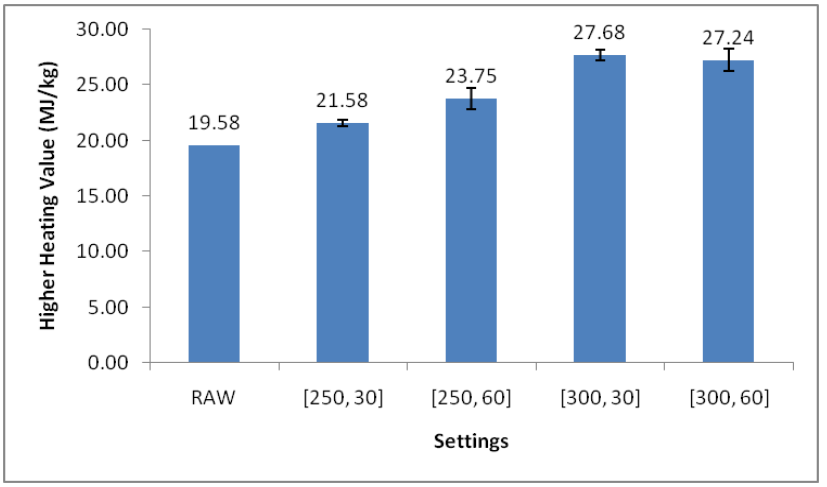

Fig. 7. HHV of raw and torrefied coconut shells.

Exposing the raw and solid products to 98% relative humidity at around 30 ℃ environment, increased the weight of the samples due to moisture absorption. In Fig. 8, the highest weight gained is on the raw material with 15.03% compared to the torrefied product at around 7.22 to 9.03%. There is a decrease up to 52% comparing the raw to the torrefied samples. At higher torrefaction temperature a lower increase in moisture was observed. Also similar values were found at 300 ℃ for both time setting due to the degradation of hemicelluloses which has the highest moisture absorption capacity [1,4].

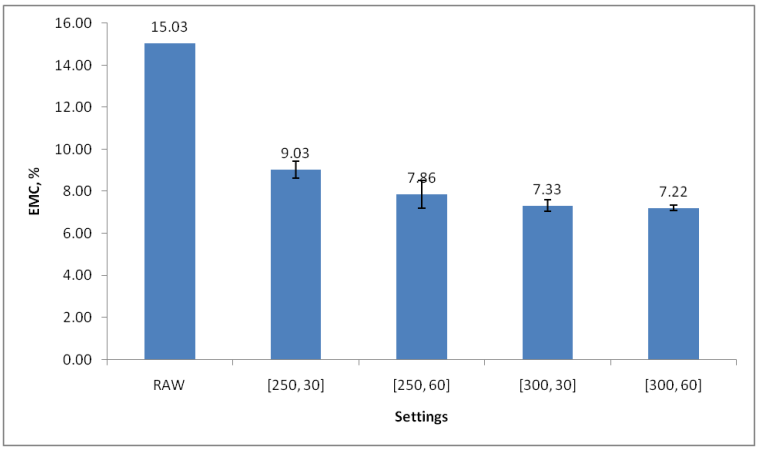

Fig. 8. EMC of raw and torrefied coconut shells.

4. Conclusion

Torrefied coconut shells were produced under oxidative environment at varied torrefaction temperature and time. The solid products were characterized in terms of TGA, DTG, FTIR, Proximate Analysis, HHV, and equilibrium moisture content. Changes in the solid composition are more on the decrease of volatiles, hemicelluloses and cellulose structure. Oxidative torrefaction improved the fuel characteristics of the solid fuel in terms of higher heating value of the solid up to 41% and lessen the equilibrium moisture content up to 52%. For the solid fuel product it is recommended to be processed at 300 ℃ and 30 minutes, since no significant difference between the two time settings at the higher temperature in terms of fuel characteristics.

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