Production of Solid Fuel From Rice Straw Through Torrefaction Process

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Abstract- Torrefaction tests were carried out on rice straw samples in order to understand the changes in chemical composition at temperatures of 200–300°C and residence times of 30 and 60 minutes. The raw material chemical composition has moisture content of 14.75%, carbon (C) 48.70%, hydrogen (H) 6.59%, nitrogen (N) 1.39%, sulphur (S) 0.36%, volatiles (V) 17.13%, and calorific value (CV) 19639.3 KJ/kg. The raw biomass also has a bulk density of 73 kg/m3. Torrefaction at temperatures of 250°C and residence time of 30 minutes resulted in a significant decrease in moisture by about 83.94%, but the other components, C, H, N, O, S, and V changed only marginally. Increasing the torrefaction temperature to 300°C and residence time to 60 minutes further reduced the moisture to a final value of 0.00% (a 100% reduction compared to original) and also resulted in a decrease in the other components, H, S, and O by 23.07%, 75.00%, and 22.32%, respectively. The carbon content at 300°C and 60 minutes increased by about 12.55% while N content increased by 91.37%. The calorific values increased by about 6.25% at 250°C and 30 minutes, whereas at 300°C and 60 minutes, the increase was higher (about 11.11%) and resulted in a maximum degree of carbonization of 1.111. The H/C ratio decreased with increase in torrefaction temperature, where a minimum value of 0.093 was observed at 300°C and 60 minute while bulk density decreased with increase in temperature with the lowest value of 66 kg/m3which represents 9.59% decrease at 300°C and 60 minutes residence time.

Keywords- *Rice straw; Torrefaction temperature; time; calorific value.*

I. INTRODUCTION

Biomass is the term used to refer to all organic matter which can be traced back to photosynthesis as their source. Plants, vegetable oil, wood, manure and sewage are examples of biomass. Though, the availability and sustainability of this biomass as solid fuel differs, their reception by the public differs too. Biomass is readily available source of fuel which is neutral to the environment as the CO_2 emitted to the atmosphere is being absorbed with the implementation of re-planting plant. Due to its large potentials, it has the capability to be a leading energy source in the nearest future. These potentials include Agricultural and forestry sector growth, rural development, sustainable energy, heat generation and a clean environment as well. Several scenarios for the future predict a strong increase in the use of biofuels between 2025 and 2050 [1].

Crop residue to complement dedicated energy crops is an option as a raw material supply for bioenergy. Paddy rice is one of the major crops grown for food and livestock feed production in Nigeria. The grain is encapsulated in a husk that hangs on a straw. The grain is harvested while the straw is either set aside for animal grazing or used as thatched roof for local houses. A survey was carried out on rice production in Nigeria and five states were found to produce rice relatively at constant rate. These states include Niger, Kaduna, Ekiti, Taraba and Benue with average rice yield of 3.1, 1.6, 2.3, 1.1 and 1.1 metric ton paddy per hectare [2]. This indicates that rice straw is available renewably after rain fed and irrigated farming seasons. High moisture content and low energy density are part of the undesired properties of biomass [3,4]. Rice straw is particularly more tenacious than coal due to its lignocellulose structure thus, it is difficult to grind. These disadvantages can be removed by pre-treatment by Torrefaction process before cofiring with coal in pulverised coal power plants.

Torrefaction is a mild pyrolysis process that takes place within the temperature range of 225-300°C in the absence of oxygen which decomposes the lignocellulose structure and the highly reactive hemicellulose fraction to increase energy density of biofuel. Torrefaction is a thermal treatment that occurs in an inert atmosphere [5]. The products formed during the process are solid char, gases and aqueous compounds [5]. Solid fuel is a better feedstock for entrained flow gasification and can also be cofired with coal for power generation. For woody biomass, energy density increase as approximately 70% while biomass remains with 90% of its original energy content [4]. Gases from the torrefaction process can be used to operate the process auto-thermally to minimize energy consumption by the process. One of the most prominent differences between torrefied biomass and coal is the lower heat value (LHV). While the LHV of coal is typically in the range of 25 to 30 MJ kg-1 (dry basis), it is within the range of 18 to 23 MJ kg-1

(dry basis) for biomass depending on the torrefaction conditions [6]. Despite the attention torrefaction has received in the last two decades, it is yet to become a commercial process. The majority of research has focused on the proximate, ultimate analysis, mass and energy yields. Agricultural wastes such as rice straw have received little attention, and there is still a need for comprehensive understanding of the optimum torrefaction conditions.

II. MATERIAL AND METHOD

A. Sample Acquisition and Preparation

An agricultural residue namely rice straw which is classified as herbaceous biomass suitable for thermochemical conversion process in UK standard was grown by the National Cereals Research Institute, Baddegi, Niger state, Nigeria and obtained for torrefaction process carried out in this experiment. This sample was pre-treated to remove sand particles and foreign materials and as well sun dried to reduce moisture content.

B. Torrefaction Procedure

A Gallenkamp electric muffle hotspot furnace was used to perform torrefaction experiments at laboratory scale while volatile torrefaction products were flared. Rice straw was resized to 100 mm from their original sizes and 8 g of resized straw was weighed out into crucibles of known weights. Samples were charged into the furnace at subsequent temperatures and residence times as shown in table 1.

TABLE I.   TEMPERATURE, RESIDENCE TIME AND HEATING RATE OF TORREFACTION PROCESS

Temperature (^{o}C)	Residence time (min)	Heating rate (^{o}C min^{-1})
200	30	06.667
200	60	03.333
250	30	08.333
250	60	04.167
300	30	10.000
300	60	05.000

1) Process Product Yield

8 g of sample was weighed into crucibles of known weights before torrefaction. Samples were reweighed after torrefaction.

2) Bulk density

Measurements to determine the density of the biomass samples were attempted using the water displacement method in accordance to the wood density protocol. Rice straw samples were oven-dried overnight and weighed prior to the experiment. Several beakers were filled with deionised water in accordance to the number of samples and placed on a weighing balance. The balance was tared and the sample was introduced quickly to the centre of the beaker till it is fully submerged in water, making sure that the entirety of the straw was below the meniscus and not touching the sides of the beaker. The mass of water displaced by the wood is equivalent to the fresh volume of the sample, assuming that the density of water is equal to 1 g/cm^3 [7].

3) Proximate Analysis

Proximate analysis carried out on raw and torrefied samples include moisture, ash and volatile matter content determination. These experiments were carried out six (6) times and mean values of these analyses were recorded.

4) Moisture Content Determination

The Gallenkamp oven, the sensitive weigh balance, the desiccator and the crucible were used to determine moisture content. Crucible was weighed empty and the weight recorded. 4 g of sample was added into the crucible and this was weighed to the nearest 0.001 g.

The sample containing crucible was heated in the oven at (96 ± 2) ºC and then, removed every 30 minutes to cool in a desiccator before reweighing. This was repeated until a constant weight over two successive weighing was obtained.

5) Ash Content Determination

Empty crucible was weighed to the nearest 0.001 g. 1 g of sample was added into empty crucible before it was reweighed and heated into a muffle furnace set to the temperature of (650 ± 10) ^{o}C. After a residence time of one hour thirty minutes, the crucible and its content were removed and allowed to cool in a desiccator and then weighed.

6) Volatile Content Determination

Empty crucible was weighed to the nearest 0.001 g with the aid of a sensitive weigh balance. 1 g of sample was added into the crucible before it was placed in a furnace set to the temperature of (900 ± 10) ^{o}C. After seven minutes, the crucible was removed and placed in a desiccator to cool at room temperature before it was weighed.

7) Fixed Carbon Content Determination

The fixed carbon content was determined by computing the difference between 100 and the sum of the moisture, volatile matter and Ash contents of the samples.

C. Ultimate Analysis

Ultimate analysis carried out on raw and torrefied samples include Nitrogen content, Carbon and hydrogen content, sulphur content, oxygen content and calorific value determination respectively.

1) Nitrogen Content Determination

1 g of sample was weighed into a digestion tube with the aid of a sensitive weighing balance. Into the digestion tube containing sample, 0.5 g of catalyst (mercuric oxide + potassium sulphate) was added as well as 2 ml of concentrated H_2SO_4. The digestion tube was installed into a kjeldatherm digestion block for three hours at 350 ^{0}C. The sample was allowed to cool before making up to 100 ml with distilled water using a volumetric flask. 10 ml of the digested sample in addition to 10 ml of 40 % Sodium hydroxide was ingested into the reaction chamber of Markham distillation unit while 2 % boric acid was measured into 250 ml beaker into which three drops of indicator (bromo cresol green + methyl red) were added. This 250 ml beaker was the receiving flask placed under the tip of the condenser as the sample was allowed to

distil until 50 ml of the distillate was obtained. Sample was then removed and titrated against 0.01 N Hydrochloric acid (Mohammed *et al*, 2004).

2) Carbon and Hydrogen Contents Determination

Carbon and hydrogen contents of biomass were determined simultaneously. 1 g of sample was weighed and placed with the aid of 60-mesh/250 μm sieve in a closed system containing stream of dry oxygen to combust. Known weights of cupric oxide and sodium hydroxide were used as absorbents to absorb water and carbon dioxide respectively. The amounts of water and carbon dioxide were determined from the difference between the initial and final weight of respective absorbents.

3) Sulphur Content Determination

1 g of sample was weighed out into crucible of known weight and thoroughly mixed with 3 g of Eschka mixture (magnesium oxide + anhydrous sodium hydroxide). The porcelain containing sample was covered and placed in a muffle furnace heated to a temperature of (800 ± 25) °C until oxidation is complete. The sulphur compound evolved during combustion reacts with Eschka mixture under oxidising condition to form sodium sulphate and magnesium sulphate in the residue. The sulphate in the residue was extracted and determined gravimetrically using 10ml $BaCl_2$ as titrant. Solution obtained after titration was decanted to retrieve precipitate of $BaCl_2$ formed. Precipitate obtained was weighed.

4) Oxygen Content Determination

The oxygen content was determined by computing the difference between 100 and the sum of the Nitrogen, Sulphur, Carbon and Hydrogen of the samples.

5) Calorific Value Determination

A method using an equation to calculate HHV (dry basis) based on C, H and N contents was used in determination of calorific value of sample. Friedl *et al* (2005) developed the model by finding the average between the equation of an ordinary least squares regression (OLS) and the equation of a partial least squares regression (PLS) method as displayed in Equation (1) and (3).

$$HHV\ (OLS) = 1.87C^2 - 144C - 2802H + 63.8CH + 129N + 20147 \tag{1}$$

$$HHV\ (PLS) = 5.22\ C^2 - 319C - 1647H + 38.6CH + 133N + 21028 \tag{2}$$

The final model for the determination of the calorific value of biomass gave a standard error of calibration of 337 KJ/Kg and R^2 of 0.943 as equated in Equation (3):

$$HHV = 3.55C2 - 232C - 2230H + 51.2CH + 131N + 20600 \tag{3}$$

III. RESULT AND DISCUSSION

Figure 1 shows that torrefaction temperature and residence time has a great effect on moisture content. The lowest value of 0 % moisture content was obtained at the temperature of 300 °C and time of 30 minutes and 60 minutes respectively. A substantial reduction in moisture content of about 83.94 % was noted at 200 °C and 30 minutes. Increasing the temperature

from 250°C to 300°C has reduced the moisture content by 99.97 % and 100 % respectively.
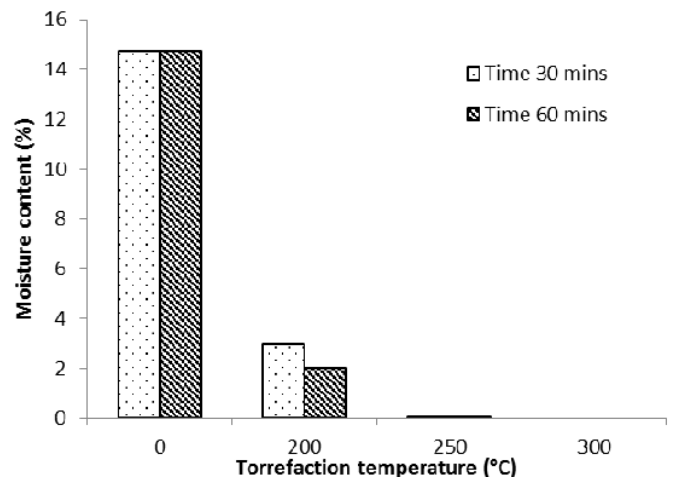

Figure 1. Moisture content of raw and torrefied rice straw

Figure 1 also indicates that the effect of residence time on moisture content is minimal as increase in residence time from 30 minutes to 60 minutes at 200 °C resulted into moisture loss of 83.94 % and 86.46 % respectively while residence time has no effect at 300 °C as moisture loss of 100 % was recorded at 30minutes and 60 minutes. The influence of the torrefaction temperature as shown in the Figure 1 is in the direction of that reported by Sadaka *et al.* [7] in their studies on the torrefaction of rice straws in which a moisture content of 85.82% was loss. The torrefaction process was done at a temperature of 200 to 315 °C with residence time with residence time between 60 and 180 minutes.

Change in the carbon content of the rice straw samples as a result of torrefaction temperature and time is shown in Figure 3. Slight increase in carbon content of 2.2 % was observed at 200 °C and residence time of 30 minutes which increased to 8.81 % at 300 °C and time of 30 minutes. However, further increase in residence time to 60 minutes at the temperatures of 200 °C and 300 °C increased the carbon content to 4.91 % and 12.55 % respectively as shown in Figure 2. This indicate an increase in carbon content of more than 2.2 % over the previous residence time of 30 minutes for every torrefaction temperature investigated. Figure 2 clearly indicates that carbon content was at its peak of 54.81 % at temperature 300 °C and residence time 60 minutes which represent a 12.55 % increase in carbon content compared to the value of 48.7 % obtained without torrefaction of rice straw.
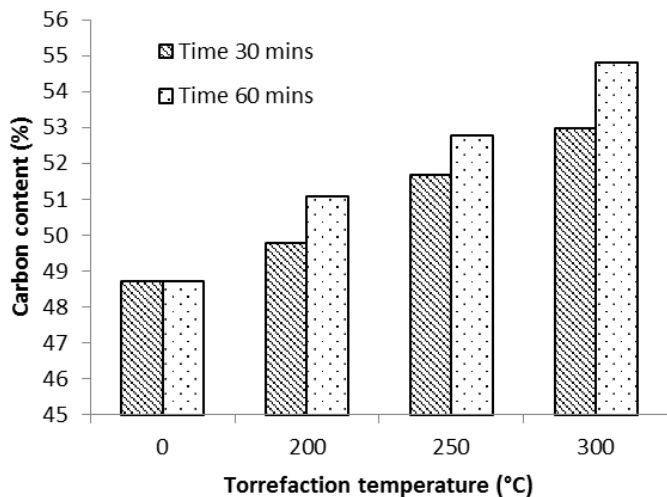
Figure 2.   Carbon content of raw and torrefied rice straw

Figure 4 Show the influence of temperature and time on the volatile content of torrefied rice straw. Volatile content at the residence time of 30 minutes increased from 2.74 % to more than 100% at 200 °C to 300 °C while at 60 minutes residence time, it increased from 1.34 % to 93 % at the temperature of 200 °C to 300 °C minutes as shown in figure 4. The highest value of 36.25 % which represent over 100% increase compared to untreated rice straw was observed at the temperature of 300 °C and residence time of 30 minutes.

Figure 3 indicate the effect of torrefaction temperature and residence time on the hydrogen content of the torrefied rice straw. Hydrogen content at torrefaction temperature of 200 °C decreased insignificantly by 0.3 % compared to 8.35 % decrease recorded at 250°C and 16.84 % at 300 °C considering the residence time of 30 minutes. However from the surface plot in Figure 4.6, decrease in hydrogen content was more pronounced at the increase in time to 60 minutes with percentage decrease of 2.28 % to 23.06 % at the temperature of 200 °C to 300 °C. The decrease was large at 250 °C (20.18 %) but was most significant at temperature of 300 °C (23.06 %). A low hydrogen content value of 5.07 % was observed at torrefaction temperature of 300 °C and residence time of 60 minutes as shown in Table 3.
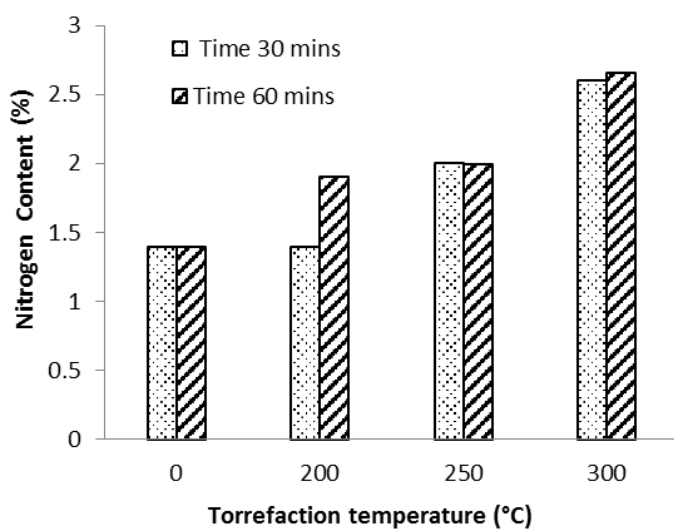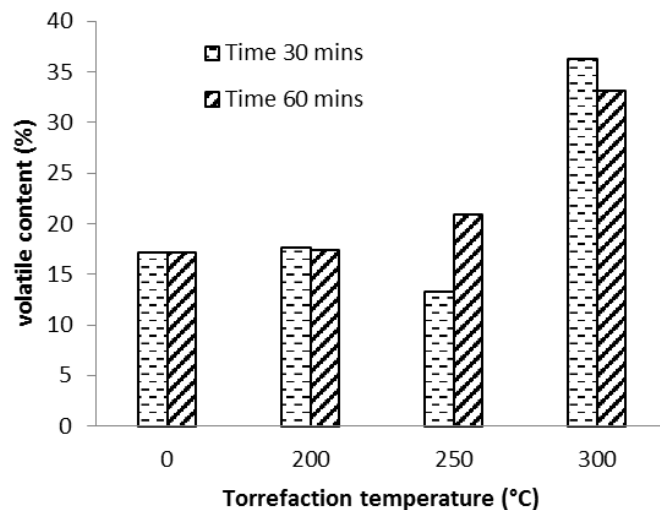

Figure 4.   Volatile content of raw and torrefied rice straw

Figure 5 indicate the influence of temperature and time on higher heating value of torrefied rice straw. Increasing the temperature to 200 °C at the residence time of 30 minutes resulted to increase in heating value from 19639.3 KJ/Kg to 20119.7 KJ/Kg (2.45 %) as shown in Table 4.3. Further increase in temperature from 250 °C to 300 °C for 30 minutes time increased the heating value by 6.25 % and 8.26 %. Figure 4.12 shows that increasing the time from 30 minutes to 60 minutes increased the heating value to 20746.8, 20981.3 and 21818.9 KJ/Kg at 200 °C, 250 °C and 300 °C respectively. These represent an increase of 5.64%, 6.83% and 11.11% increase in higher heating value compared to untreated rice straw. The highest value of 21818.9 KJ/Kg was noted at 300 °C and residence time of 60 minutes as clearly shown in Figure 5.

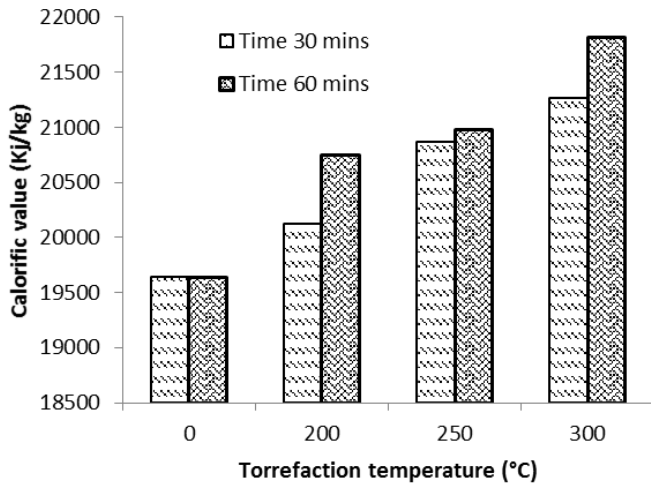Figure 3.   Nitrogen content of raw and torrefied rice straw

Figure 5. Calorific value of raw and torrefied rice straw

H/C ratio decreased significantly as a result of torrefaction temperature as well as residence time as shown in Figure 6. The percentage decrease at 200 ^{0}C to 300 °C for 30 minutes was 2.2 % to 23.7 %, whereas at 60 minutes the decrease was about was 6.67 % to 31.11 % at the temperatures of 200 °C to 300 °C as clearly shown in Figure 6. The lowest H/C ratio of 0.093 which represent 31.11 % decrease compared to untreated rice straw was observed at the temperature of 300 °C and residence time of 30 minutes as show in Figure 6.
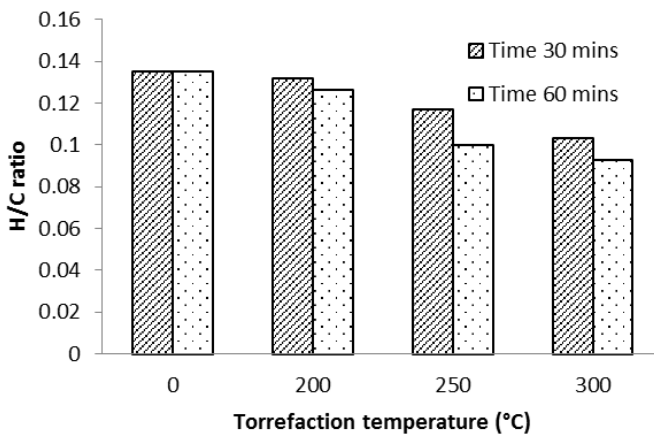

Figure 6. H/C ratio compared to untreated rice straw

The ratio of the calorific value of torrefied biomass to raw biomass is referred to as the degree of carbonization. From figure 7, the influence of torrefaction temperature and time on degree of carbonization (DC) values is noticeable as increase in temperature from 200 °C to 300 °C resulted into DC values of 1.024 to 1.083. These represents 2.4 % to 8.3 % increase in degree of carbonization. Figure 7 shows increase in residence time to 60 minutes resulted into increase of DC values from 5.6

% to 11.1 % at 200 °C to 300 °C. Degree of carbonization was most significant at the highest temperature and residence time with the value of 1.11 at 300 °C and 60 minutes which represents 11.1 % increase compared to untreated rice straw.
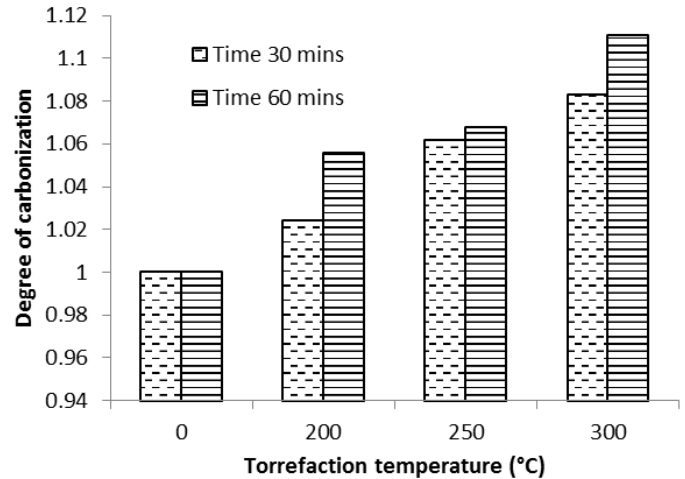

Figure 7. Degree of carbonization of torrefied rice straw

IV. CONLUSION

From the research carried out, the following conclusions are drawn: (i) Increase in torrefaction temperature and residence time above 250 °C and 30 minutes effectively decreased the H/C ratio, bulk density, moisture content and hydrogen content which may be attributed to decomposition of hemicellulose and cellulose to release volatiles. (ii) Increase in torrefaction temperature and residence time above 250 °C and 30 minutes decreased the oxygen and hydrogen content while carbon content increased simultaneously, which be attributed to higher proportions of hydrogen and oxygen in liberated compounds than carbon. (iii) The degree of carbonization and calorific value increased with increase in torrefaction temperature and time, which might be attributed to effective removal of moisture and reduction in H/C ratio. (iv) Increase in torrefaction temperature and residence time above 250 ^{0}C and 30 minutes drastically reduced process product yield without significant increase in calorific value which implies reduced conversion efficiency of the process.

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