Improvement of The Energy Density of Rice Husk Using Chemical Treated Torrefaction

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Abstract- *The main objective of this present study was to investigate the Torrefaction process of lignocellulose biomass rice husk produced in Ethiopia through chemical treated Torrefaction. Torrefaction is a technology that a partial pyrolysis of biomass which is carried out under atmospheric pressure in a narrow temperature range of 200-300°C and under an inert environment which yields higher solid yield than pyrolysis. Three different torrefaction temperatures 230, 255 and 2800C with three different holding times 20, 40 and 60 minutes were considered. The result showed that a net reduction of the volatiles content, mass yield, moisture content, bulk density and atomic oxygen content correlate with increasing torrefaction temperature and reaction time, while atomic carbon content, higher heating value(HHV),fixed carbon content and energy density increase with higher torrefaction temperatures .So, torrefaction temperature and holding time had a significant effect on torrefaction process of rice husk. Based on the findings of this study, temperature of 280 with a residence time of 40 min for chemical treated torrefaction could be suggested for an effective and proper torrefaction process to recycle the agricultural biomass. The energy density of chemical torrefaction was enhanced by 127.4%. Therefore, the torrefied biomass becomes fuel sources which can be applied to replace with fossil fuel.*

Keywords- Rice husk biomass, Torre faction, higher heating value, fixed carbon content, energy density.

I. INTRODUCTION

Biomass is expected to play a major role in the transition to renewable or sustainable energy production [1-4]. Woody and herbaceous biomasses are regarded as lignocellulose biomass, because their major organic mass fraction consists of cellulose, hemicellulose and lignin[5].Bioenergy can be generated in different ways. It can be converted to a value-added liquids and gaseous products such as ethanol, synthesis gas, or bio-oil, or it can generate electricity via direct combustion, or gasification. Bioenergy is produced from organic materials, which are any form of biomass such as food crops, organic wastes, and forestry products[6]. Ethiopia has an abundance of forest resources, and these resources can provide a considerable amount bio-based energy; however, utilizing these sources presents problems. Existing is either adapting this infrastructure to accommodate lower quality Biomass fuel, infrastructure for generating energy uses low moisture and oxygen content fuels, such as coal. The major challenge which can be very costly, or creating a biomass product that can be utilized in a current steam generation or gasification plant. It is for this reason that methods to upgrade the biomass are being explored. The method being researched in this study is torrefaction. Torrefaction is a treatment process for biomass meant to reduce oxygen content and moisture absorption, which increases the energy content. Torrefaction is a thermo-chemical pretreatment process using biomass within a narrow temperature ranging from 200℃ to 300℃[7]. Torrefaction process provides an alternative bioenergy resource since it increases energy density and reduces transport cost. This treatment is carried out under atmosphere conditions in a non-oxidizing environment and for a relatively long residence time[8]. A longer residence time up to an hour and higher temperatures increase the percentage of CO in non-condensable product gas [9- 10].Many researchers have observed regarding different types of biomass (bamboo, rice husk, or wood) with the similar result that mass yield decreases with longer residence time.[11-12].Repellin et al[13] simulated the weight loss by calculating element contents of wood chips at torrefaction time and observed similar results In this study, selected biomass feed stock typical lignocellulose biomass ricehusk produced in Ethiopia was torrefied. The effect of chemical treated torrefaction pretreatment on the fuel properties of biomass was examined. In this study, selected biomass feed stock typical lignocellulose biomass ricehusk produced in Ethiopia was torrefied. The effect of chemical treated torrefaction pretreatment on the fuel properties of biomasswasexamined.

II. MATERIALS AND METHODS

1. Biomass Preparation:

Rice husk obtained from local farmers was air dried to a moisture content of 10-15 % (w.b). The husk was then fractionated to remove the large (>4mm) and smaller chippes (<2mm) with the use of vibrating screen separator. After screening, the husk was kept in dry atmosphere for further analysis. The raw and fractionated rice husk is shown in figure. 1.

Figure 1. Raw and fractionated rice husk

2. Raw Material Characterization:

Rice husk from rice producing farmers was selected as feedstock for this study since it is the main agricultural crops in Ethiopia. The selection aims among others to utilize these available resources potential by improving the energy density using method. i.e. chemical torrefaction. Proximate analyses of the raw feedstock and the torrefied rice husks were performed according to ASTM standards: ASTM E871, ASTM E872, and ASTM D1102 for moisture content, volatile matter, and ash content, respectively.

3. Experimental Setup and Description:

All experiments were carried out in a tubular reactor equipped with a hot plate heater (AM-5250A), nitrogen cylinder, a thermocouple and a pressure gauge. A thermocouple for monitoring the reaction temperature(temperature of the sample and the reactor) is connected to the reactor by which the electrical duty of the heater is controlled manually. The reactor is connected to a nitrogen (99.99% purity) cylinder via a valve to create inert atmosphere. After the samples were placed inside the tubular reactor, it was completely purged with nitrogen gas to remove all oxygen. The furnace/torrefied reactor was preheated to the desired temperature set point. Treatment time was said to begin when the furnace reached the desired set point. At the end of the treatment time, the biomass samples were pulled from the furnace and immediately placed in desiccators to prevent from moisture exposer and for further treatment and combustion. Once the crucible cooled to room temperature, the samples were weighed and analyzed with the respective test. The experimental set up for the torrefaction experiments are shown in figure 2 and figure 3 and the general experimental frame work are shown in Figure 4.

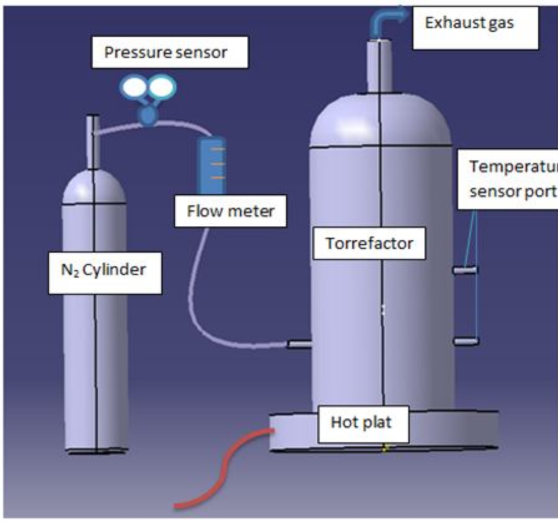

Figure 2. The theoretical experimental set up of torrefaction process.

Figure 3. The actual experimental set up for torrefaction process.

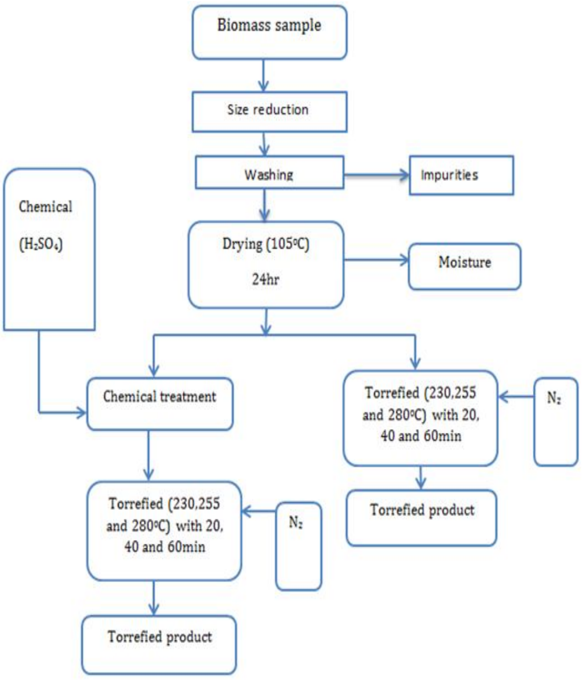

Figure 4: General experimental procedure for torrefaction process.

Proximate Analysis: Proximate analysis which is a standardized procedure that gives an idea of the bulk components that make upgrade a fuel was done to determine the average of the percentage volatile matter content, percentage ash content, moisture content and percentage content of fixed carbon of the rice husk obtained from three replicates. The contents were found according to ASTM standards.

Mass yield: Mass yield can be calculated from the ratio of torrefied to raw solids [14]. The mass yield was calculated using the following equations eq.1

$$\text{Mass yield} = \left(\frac{Mf}{Mi}\right)x100\% \quad (1)$$

Where: Mf is the final mass of biomass after torrefaction; Mi is initial mass of biomass before torrefaction (raw biomass).

MoistureContent: Moisture content of each sample was found using oven drier. That is drying in the oven at 1050C for 24 hours and taken a mass difference before and after drying to the mass before drying.

$$MC\% = \frac{(mi - mf)}{mi}x100 \quad (2)$$

Where:MC% moisture content of sample, mi is initial mass of sample and mf is final mass of sample after oven dry.

VolatileContent: The percentage volatile matter (VM%) was determined by weighing of the dry rice husk sample in a crucible and placing it in an oven until a constant weight was obtained. The sample were then kept in a furnace at a temperature of 550°C for 10min and weighed after cooling in a desiccator. The percentage volatile matter was then calculated using the Equation 3

$$\%Vol = \frac{[mi\ ]-[mf\ ]}{[mi]}\ x100 \quad (3)$$

Where: %Vol is percentage of volatile content, mi is initial mass of sample and mf is final mass of sample.

Ash Content: Ash is the inorganic solid residue left after the fuel is completely burned. Its primary ingredients are silica, aluminum, iron, and calcium; small amounts of magnesium, titanium, sodium, and potassium may also be present. Ash content is determined by ASTM test protocol D-1102 for wood, E-1755-01 for other biomass, and D-3174 for coal.A 2-g sample in a standard condition was placed in a muffle furnace with the lid of the crucible removed. Temperature of the furnace is raised slowly from 550 to 575 0C to avoid flaming for 3hrs. Following this, the temperature is increased to 575 °C and kept there until all the carbon is burnt. After that the sample was cooled and weighed. The percentage ash content was determined using the Equation 4

$$\%Ash = \frac{[\,Mash]}{[\,Mi]}x100 \quad (4)$$

Where: % Ash is the percentage of Ash content, Mash is ash mass; Mi is initial mass of sample.

Fixedcarboncontent: The percentage fixed carbon (%FC) was computed by subtracting the sum of %VM and %AC from 100 as shown in the Equation5

$$FC\% = 100\% - Ash(dry)\% - Volatile\% \quad (5)$$

Each test was performed in triplicate, and the average was reported. Results were given on a dry basis.

Elemental Analysis (Ultimate composition): Elemental analysis of the biomass samples was performed using an elemental analyzer an “EA 1112 Flash CHNS-O- analyzer” at Addis Ababa University (AAU) Chemistry department. Conditions for the ultimate analysis were: Carrier gas flow rate of 120 ml/min, reference flow rate 100 ml/min, oxygen flow rate 250 ml/min; furnace temperature of 9000C and oven temperature of 750C.A small sample was placed in the analyzer, and results for carbon, hydrogen, and nitrogen content were returned by the analyzer. Helium was used as a carrier gas. Rice husk samples with two repetitions were analyzed for each set of treatment and reported only the average values on a dry basis. Results were corrected for moisture content and reported on a dry basis. Oxygen was calculated by difference:

$$\text{Oxygen\%} = 100\% \quad \text{carbon\%} \quad \text{hydrogen\%} \quad \text{nitrogen\%} \quad \text{as (6)}$$

Energy Content: Energy content can be described by using higher heating value (HHV) and Lower heating value (LHV). HHV is the most commonly used way of describing energy contents. The HHV from ultimate and proximate analysis of torrefied biomass was determined by using unified correlation proposed by (Daya Ram Nhuchhen and Muhammad T. Afzal, 2017).

$$HHV = 0.1846VM + 0.3525FC \qquad (7)$$

Where:VM is volatile matter and FC is fixed carbon contents

$$HHV = 32.7934 + 0.0053C^2 - 0.5321C - 2.8769H + 0.0608CH - 0.2401N \quad (8)$$

EnergyDensity: Energy yield and Mass yield were used to calculate an energy density for the biomass samples. Torrefaction should be performed after transport to ensure the maximum amount of energy is moved per load. Biomass volume can change and be modeled as a function of moisture content[15].

$$ED = \frac{Yenergy\,(\%)}{Ymass\,(\%)} \qquad (9)$$

Where: ED is the energy density, %Ymass is the percentage mass yield

Hydrophobic properties: The equilibrium moisture content (EMC) of a material surrounded at least partially by air is the moisture content at which the material is neither gaining nor losing moisture. The value of the EMC depends on the material and the relative humidity and temperature of the air with which it is in contact. The speed at which it is approached depends on the properties of the material and the speed with which humidity is carried away or towards the material (e.g. diffusion in stagnant air or convection in moving air).Equilibrium moisture content (EMC) can be used as an indicator of the hydrophobicity of a solid[16]. Hydrophobic property of torrefied biomass is examined by water immersion test or by equilibrium moisture contents (EMC) studies[17]. Both water immersion and equilibrium moisture content test was performed in the study for hydrophobicity analysis. The equilibrium moisture content was analyzed by equilibrium moisture content analyzer.

Figure 5. Equilibrium Moisture content analyzer

Equilibrium Moisture Content (EMC), showing the amount of moisture that biomass has absorbed at a specific temperature, pressure and humidity. And the equilibrium moisture content analyzer calculates the EMC using equation 10:

$$EMC\% = \frac{(Me - Md)}{Md} x100 \qquad (10)$$

Where Me is the mass of the sample at equilibrium with a humid atmosphere and Md is the mass of dry sample. The sample was measured at 79% relative humidity (RH) and temperature of 250C.

Bulk density: Bulk density is the ratio of the mass of a material to its volume, and it plays a crucial role in the economic analysis of a bioenergy supply chain. It can be calculated by emersion of a known quantity (mass) of biomass to a known volume of water in graduated cylinder. And, the ratio of mass of biomass to the volume of water displaced is bulk density.

$$\rho = \frac{m}{V} \qquad (11)$$

Where:ρ is the density of biomass, m is mass of sample and V is the volume of water displaced

Thermo gravimetric analysis: Thermal gravimetric analysis (TGA) is a method of thermal analysis in which change in physical and chemical properties of materials measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The TGA instrument (BJ HENVEN Analysis (ATAT2012)) as seen in, it continuously weighs and measure the sample as it was heated up to 10000C. The systems consist of a combustor and balance connected to a computer in order to record automatically every 30 second and a thermal meter records data every 1 second. Two samples (raw rice husk, and 2800C and 40min treated) having 5mg weight for each sample were loaded separately.Once the 5-mg sample was loaded to the balance, 10ml/min nitrogen gas was purged to the sample port to create inert atmosphere, the temperature rise was set to 100C/min, and the final temperature was set to 10000C and finally the sample was analyzed.The information that was obtained from TGA is in order to precede further investigation on the effect of torrefaction temperature on the thermal decompositions of the biomass raw materials to observe the torrefaction peaks or to clearly identify thermal degradations of raw biomasses.

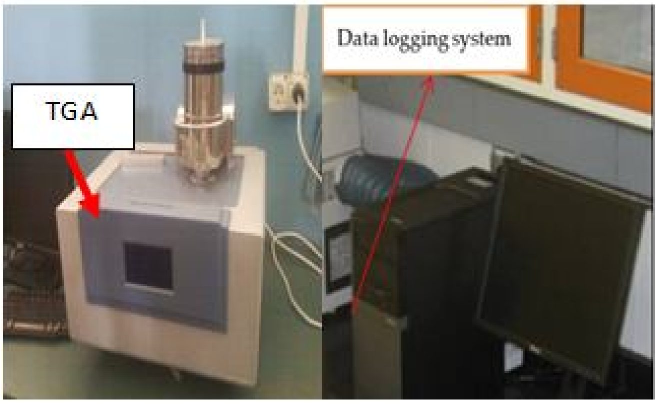

Figure 6. Thermo gravimetric Analyzer (TGA)

III. RESULTS AND DISCUSSION

1) **Preliminary Qualitative Assessment:**

Figure 7 shows, the surface morphology of chemical treated and torrefied rice husk. As can be seen in the figure, the color had changed gradually from yellow to red and then turned to brown due to oxidation within the environment, finally after torrefaction, changed to deep black. As it has been discuss previously, this is due to the oxidation of phenolic compounds and the presence of sugars and amino acids during torrefaction. Since chemical treatment modifies the fiber structure, and dilute sulfuric acid is better used for surface modification, the fiber strictly modified for better carbonization that was the reason for its deep black after torrefaction.

Raw Rice Husk

2.5% H_2SO_4 treatedce husk

2800C and 40min

Figure 7. Effect of Torrefaction temperature on surface morphology of chemical treated torrefied rice husk sample.

2) **Mass yield:**

Figure 8 shows the effect of torrefaction temperature and time on the solid yield of rice husk for chemical treated torrefaction. From the result, it can be concluded that temperature had significant effect on mass yield than residence time. Torrefaction temperature and torrefaction time had significant effect on mass yield. When the torrefaction temperature. was 2300C and 20 min, the solid yield was 87.87 % for chemical treated .As the torrefaction temperature increased the solid yield decreased . When torrefaction temperature is higher than 2550C, most of hemicellulose was decomposed, and the cellulose started to decompose, so the solid yield decreased quickly, at 2800C and 40 min solid yield became 70.1 for chemical treated torrefaction. Increasing torrefaction temperature from 230 to 2800C, the mass yield dropped gradually at the respective treatment time. This illustrates the effect of torrefaction temperature and holding time on the mass yield. This is in compliance with the expected results, since torrefaction involves the loss of both moisture and volatile matter fromthesampleofbiomass.

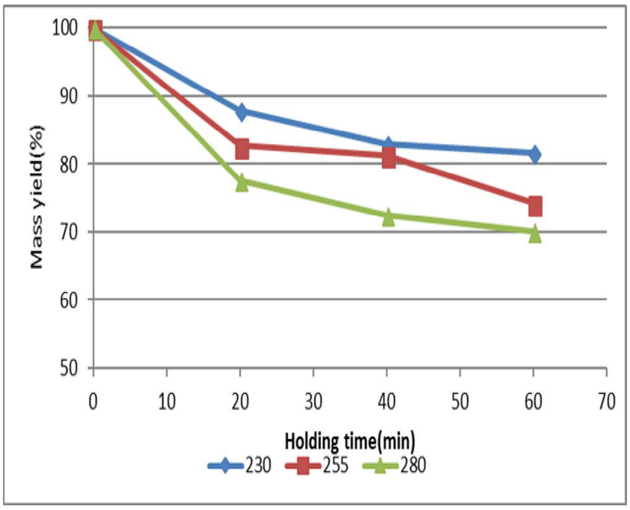

Figure 8. Effect of torrefaction temperature and holding time on mass yield of chemical treated torrefied rice husk .

3) Fixed carbon:

Figure9 presents the changes in the fixed carbon content in the rice husk torrefied at different temperatures and residence times for chemical treated torrefaction. The chemical torrefaction, increasing the temperature to 230, 255, 280 C for 40-min residence time increased the fixed carbon content to about 33.57%, 38.30%, and 37.77% (an increase of 142%, 176.33% and 172.51% from its original value) and torrefaction treatment at 2800C and 40 min, the fixed carbon content became 43.73(an increase of 215.5% from its original value). Therefore, chemical treated torrefaction increases the fixed carbon content even for the lower residence time.A higher temperature and a longer residence time increased the composition of fixed carbon in torrefied rice husk. The weight percentage of fixed carbon increases significantly with increasing torrefaction temperature due to the carbonization process. The reason behind is that during torrefaction at different temperature, the moisture content and volatile matter removed. So, the composition remained is purely ash and fixed carbon.

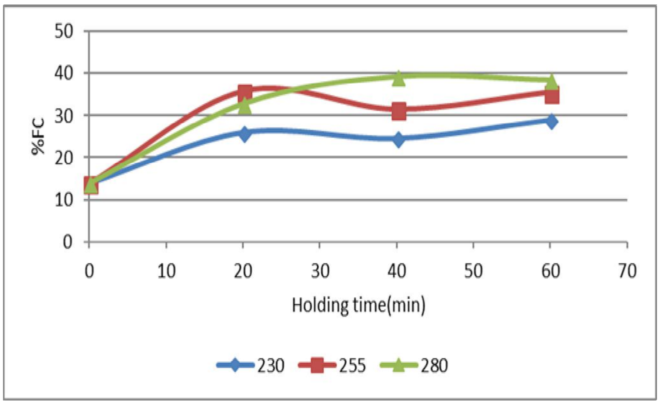

Figure 9. Effect of torrefaction temperature (0C) and reaction time on fixed carbon yield of chemical treated torrefaction

4) Bulk density:

During torrefaction, the bulk density decreases due to the decrease in mass (moisture and volatile matter). The same results were obtained as expected in torrefaction of rice husk at different torrefaction temperature and time. Figure10 shows increasing the torrefaction temperature and holding time, results a decrease in bulk density of rice husk for chemical treated torrefaction.

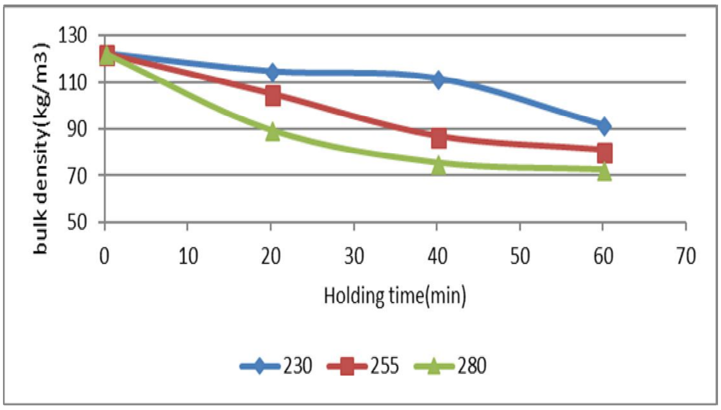

Figure 10. Effect of torrefaction temperature and residence time on bulk density of chemical treated torrefied rice husk.

5) Higher heating Value (MJ/kg):

Figure11, the HHV of torrefied rice husk noticeably increased with increasing torrefaction temperature and time for chemical treated torrefaction. The increase in heating values of rice husk during torrefaction was comparable with other similar studies for agricultural residues (wheat straw and cotton gin waste and rice husk) [18]. More moisture and high oxygen content are the primary reasons for the low quality of biomass. The decrease in moisture content and increase in the carbon to oxygen ratio improves the HHV of the torrefied rice husk compared to the raw rice husk, which will also help enhance the value of rice husk as a raw material for thermochemical conversion. So, temperature and time had significant effect on the HHV of rice husk. The increments of chemical treated (2800C and 40min) was 27.63% compared to the original biomass.

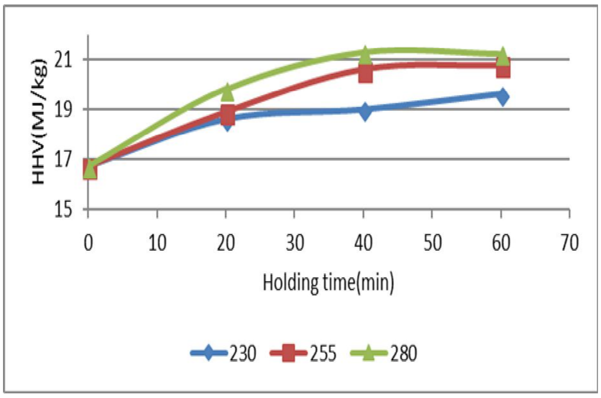

Figure 11. Effect of torrefaction temperature and holding time on HHV of chemical treated rice husk

6) Energy density:

Figure12 showed that the energy density was determined from the ratio of HHV of torrefied product to raw biomass. In line with HHV results, energy density increases for the torrefied biomass according to the increase in temperatures and residence time. The highest energy density yield was obtained with a resident time of 40min and 2600C for chemical treated torrefaction. At those conditions, the energy densityofchemicaltreatedtorrefiedricehuskwas127.4%.

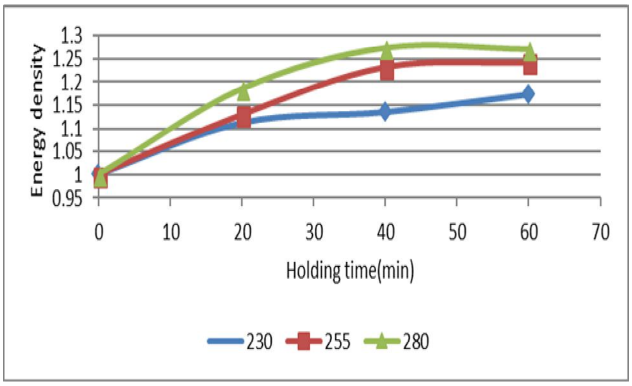

Figure12. Effect of torrefaction temperature and holding time on energy density of chemical treated torrefied rice husk.

IV. CONCLUSIONS

chemical treated torrefaction of rice husk was performed to enhance the energy contents or the bioenergy property. A mild torrefaction treatment of 2800C at 40 min is found to be the optimal torrefaction conditions for improving the heating value, energy density and hydrophobicity characteristics of rice husk. Torrefied rice husk became brittle and fragile, and showing gradual shrinking volume and turning from yellow to brown and then black in chemical treated torrefaction . The chemical treated torrefaction yields better result to enhance the energy density. The energy density of chemical treated torrefaction was enhanced to 127.4%.

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