The Valorization of Rice Waste via Torrefaction Method

Kwo W. Teh and Saidatul S. Jamari

***Abstract*—Biomass plays a crucial role as the source of renewable carbon which can be utilised in the production of biofuels. However, the raw biomass itself has some undesirable properties such as high moisture content, low energy density and deterioration after a short duration of storing period. Hence, a thermochemical process, known as torrefaction is normally used to preliminary treat the biomass to enhance its physical properties. This study focus on the characterization of the physical properties of the torrefied rice biomass which are rice husk and rice straw under three different temperatures of 220 ℃, 250 ℃ and 280 ℃ with residence time of 30 min.The heating rate was set as 15 ℃/min after the temperature profile study on the customized reactor was investigated. From the experimental results, it is noticeable that torrefaction enhances the calorific value of the biomass by 3-17% for rice husk and 4-20% for rice straw. The torrefied rice-based biomass also helps to remove the moisture content of raw rice husk and rice straw by 6.5% and 8.3% respectively. The mass yield of the torrefied rice-based biomass is between the range of 78-91% for rice husk and 82-90% for rice straw. Meanwhile, the energy yield for rice husk is in the range of 92-94% and 93-98% for rice straw after torrefaction. This study concludes that 250 ℃ is the optimum torrefaction temperature for the conversion of rice waste into valuable biofuel.**

***Index Terms*—Biomass, torrefaction, rice husk, rice straw.**

I. Introduction

Rice is an essential food grain for two thirds of the world's population. The demand towards the rice will increase as the population grows. Malaysia as one of the top 25 rice producing countries in the world solely has an annual production of 2.75million metric tons. According to Kadam *et al*. [1], 1.35 tons of rice waste is produced in order to obtain one ton of rice. Thus, the advantages of using rice waste as a study material is due to its availability from agricultural sector in Malaysia. The concept of using the biomass as an energy carrier has been proposed since past few decades [2], [3]. However, the implementation foresees a defect in the supply chain and commercializing purpose due to the expensive logistics cost [4]-[6].

Previous studies towards torrefaction technology were predicted as a significant leap stone in pushing the biomass energy sector to the peak as it transforms the biomass into rich energy carrier [7], [8]. Although Eseltine *et al*. [9], Medic *et al*. [10], Uemura *et al*. [11], Van der Stelt *et al*. [12], Deng *et al*. [13], and Bergman *et al.* [14] proposed that the energy intensification and mass loss of biomass are proportional to the heating temperature of 200-300 ℃ but they are all tinged with uncertainty as the temperature range is too wide and does not specify a precise effect of different torrefaction temperature towards particular biomass. Hence, the objective of this study is to investigate effect of torrefaction on the physical characteristics of the rice waste at different temperature. Characterizations of physical properties are evaluated by using TGA, DTG and FTIR analyses.

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II. Material and Methods

A. Materials

The rice husk was obtained from Kilang Beras Rakyat Sekinchan Sdn. Bhd. Sekinchan, Selangor whereas the rice straw was collected from a village in Tanjong Karang, Selangor, Malaysia.

B. Sample Preparation

The rice straw was grinded into approximate length of 2 cm. While to perform the physical properties testing, for example calorific value with bomb calorimeter, the rice husk and straw was pulverized into powder form by using a 400 W blender. The pulverized biomass was sieved to segregate and acquire a uniform size of powder particles.

C. Torrefaction Process

The torrefaction began by inserting 2 grams of the raw material into the reactor. Glass wool was then placed on top of the supporting ring in the tubular reactor. Next, the raw biomass (rice husk or 2 cm long of rice straw) was inserted into the tubular reactor. After that, the tubular reactor was fixed at a position where its center supporting ring is located at the correct position in the furnace.

Nitrogen gas at pressure of 1 atm was then flushed into the reactor for 15 minutes in order to eliminate the oxygen inside. This was followed by selecting the required pattern which was first at temperature of 220 ℃ with a constant heating rate of 15 ℃/min, heated by an electric furnace surrounding the reactor. During the process, the exit gas was trapped in a cold bath to prevent emission of harmful gas to the atmosphere. After 30 minutes of residence time, the heater was turned off and the reactor was left to cool down to ambient temperature. The torrefied sample was collected, weighed and kept in an air tight sample bottle prior to characterization. The previous procedures were repeated 3 times to obtain the mean value before starting out with the next temperature of 250 ℃ and 280 ℃.

Moisture content, heating value, mass and energy yield, thermogravimetric analysis and fourier transform infrared spectroscopy (FTIR) were carried out to determine the characteristics of the torrefied samples.

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III. Result and Discussion

A. Raw Material Properties

In the experiment, prior investigation on the physical properties of the raw rice husk and rice straw were performed and the results obtained are tabulated in Table I. This was aimed to compare between the particular properties of raw and torrefied materials and thus a good interpretation on the results can be achieved.

TABLE I: Physical Properties of Raw Materials

Sample	Moisture content (wt%)		Calorific Value (MJ/kg)	
	Experimental	Literature	Experimental	Literature
Rice husk	6.53	6.44 [15]	18.32	17.40 [15], [16]
Rice straw	8.29	13.61 [17], [18]	17.67	16.35 [17], [18]

B. Heating Value

Fig. 1 depicts the calorific value (HHV) of rice waste at different torrefaction temperature. After torrefaction, it can be seen that an apparent improvement in the calorific value of rice husk and rice straw. The trend of HHV has increased simultaneously with the torrefaction temperature. In brief, the HHV of the raw materials has risen from the range of 17.67-18.32 MJ/kg to 18.44-21.46 MJ/kg.

From Table I, it is noticeable that the calorific value of raw rice straw is lower than the of raw rice husk. The calorific value gap between these two materials continue to exist after performing the torrefaction at the temperature of 220 ℃ in which the calorific value of torrefied rice husk (18.78 MJ/kg) was slightly higher than that of rice straw (18.44 MJ/kg). However, by comparing the calorific value curve of rice husk and rice straw, the HHV of rice straw soared up significantly to 20.12 MJ/kg and exceeded the HHV value of rice husk (19.79 MJ/kg) when both raw materials were torrefied at the temperature of 250 ℃. At 280 ℃, a more significant increase in calorific value was observed for rice husk.

Next, the HHV of torrefied rice husk increased up to 21.46 MJ/kg whereas for torrefied rice straw, the HHV is 21.14 MJ/kg at the temperature of 280 ℃. In concise, the HHV ratio of rice straw has increased by 4-20% while the HHV ratio of rice husk has elevated by 3-17%.

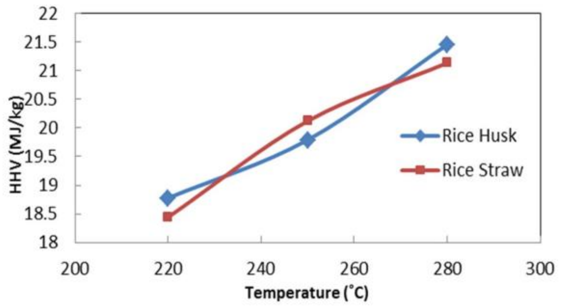


Fig. 1. Calorific value of torrefied rice waste.

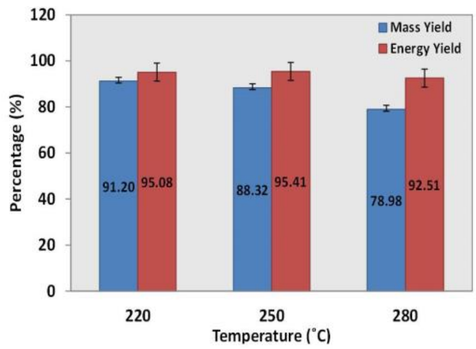
C. Mass and Energy Yield

The effect of temperature on mass and energy yields of the corresponding rice wastes is illustrated in Fig. 2. The mass yields of both rice straw and rice husk were significantly decreased with the increment of torrefaction temperature. However, among these two raw materials, rice straw appeared to be degrading at a faster rate during torrefaction contributing to a lower mass yield at the three different respective temperatures (220 ℃, 250 ℃, and 280 ℃).

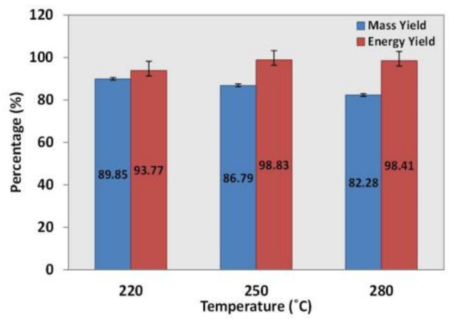
Mass loss during torrefaction was due to the loss of moisture content, volatile organic compounds and also degradation of lignocellulosic components [19]. Thus, the mass yield was expected to dwindle by the increase of torrefaction temperature due to the decomposition of hemicellulose and cellulose at high temperature [15].

The energy yield of the torrefied rice husk was remarkably peaked at 250 ℃ which is 95.41.% compared to the the energy yields at 220 ℃ and 280 ℃ that are relatively similar (93.47% and 92.51% respectively). For the case of rice straw, the average energy yields are 93.77% at 220 ℃, 98.83% at 250 ℃ and 98.41% at 280 ℃. The energy yields of the torrefied rice straw at 250 ℃ and 280 ℃ are almost equivalent due to the extent of which increase of calorific value is balanced by the mass loss.

In summary, the increase in energy yield is observed when the increase in calorific value surpassed the mass loss at specific torrefaction temperature. Thus, from this study, the optimum temperature to acquire the maximum energy yield is at 250 ℃ for both rice husk and rice straw.



(a) Rice Husk



(b) Rice Straw

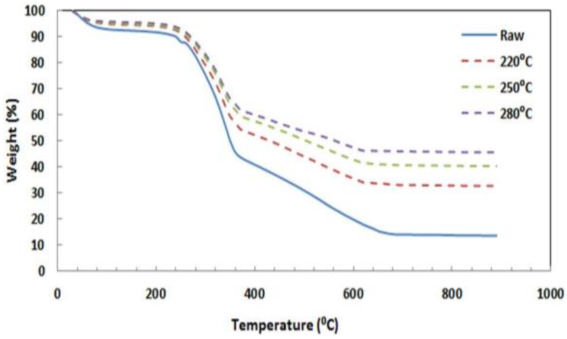
Fig. 2. Mass and energy yield of torrefied (a) rice husk, (b) rice straw

D. Thermal Analysis

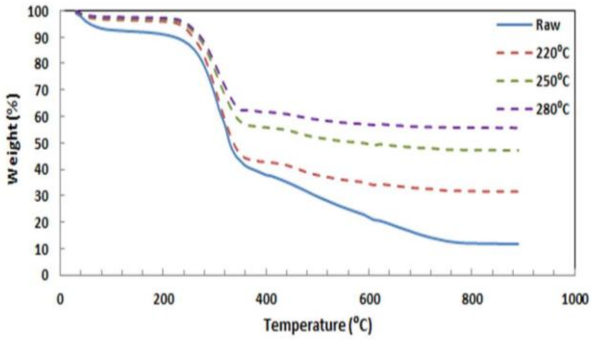
Thermogravimetric analysis (TGA) and Derivative Thermogravimetric (DTG) analysis are efficient methods to evaluate the weight loss of biomass as a function of temperature. From the TGA distribution (Fig. 3), both materials showed a decreasing step change in weight with increasing temperature. When the temperature is between 25 and 110 ℃, the weight drop of the raw materials is more pronounced than the torrefied rice based-biomass. This is an evidence of water removal to achieve the hydrophobic behaviour in torrefied biomass which is later proven by FTIR analysis (Fig. 4).

The apparent distinguishable pattern of the TGA distribution between raw and torrefied rice biomass arises with higher torrefaction temperature. Drastic thermal decomposition of rice husk and rice straw, which marks the oxidation of hemicellulose, cellulose and lignin take place at the temperature ranges of 240-360 ℃ and it resembles the findings by Chen *et al*. [16].

The DTG results shown in Fig. 5, inferred that the lignocelluloses of the biomass are degraded during torrefaction as both peaks representing hemicellulose and cellulose respectively significantly shrunk after being torrefied. Hemicellulose was the first component to degrade followed by cellulose at torrefaction temperature, 220 ℃. Lignin was the most complex components to decompose as it slightly decomposition recorded even at the temperature of 280 ℃. Hence, the cellulose is the main contributor for energy yield while lignin plays an auxiliary intensification role to increase the energy density.

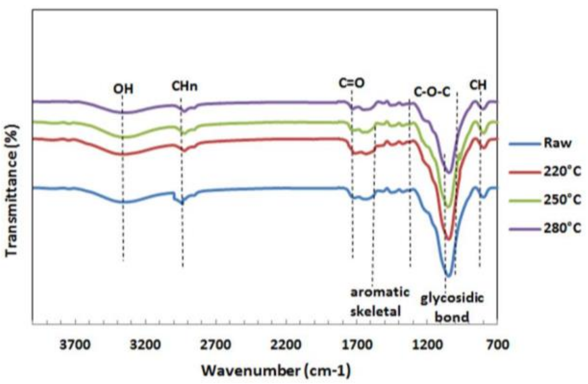


(a) Rice husk

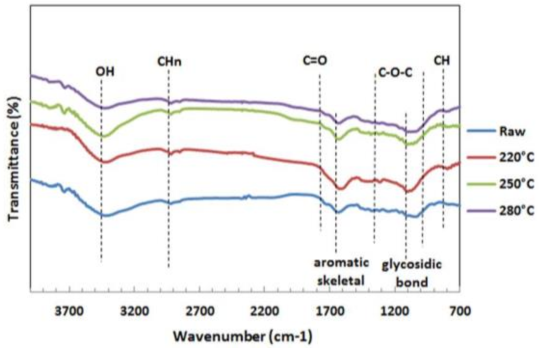


(b) Rice Straw

Fig. 3. Distribution of TGA of raw and torrefied (a) rice husk and (b) rice straw.

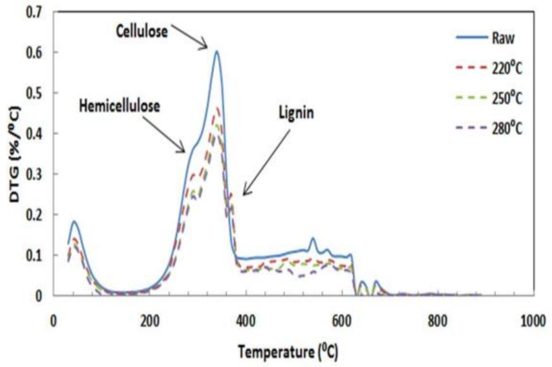


(a) Rice Husk

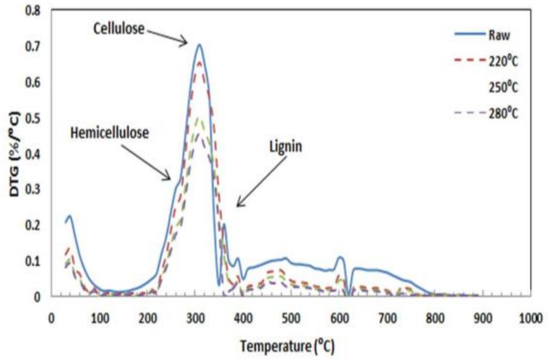


(b) Rice Straw

Fig. 4. FTIR spectra of raw and torrefied (a) rice husk and (b) rice straw



(a) Rice husk



(b) Rice Straw

Fig. 5. Distribution of DTG of raw and torrefied (a) rice husk and (b) rice straw.

E. Fourier Transform Infrared (FTIR) Spectra

In Fig. 4, the stretching of H-bonded OH groups (~3360cm^{-1}) has shown the most prominent decrease in intensity at elevated temperature. This explained the loss of moisture and the acquired of hydrophobic behavior by the torrefied biomass.

During torrefaction, long aliphatic carbon chains, CH_n were broken down and this led to the lower intensity at the peak of 2986 cm^{-1}. Meanwhile, C-H bond of aromatic ring represents by the 809 cm^{-1} peak remained intact and a small shrinkage of intensity is detected only at the temperature of 280 ℃. The transmittance peaks shoulder between the wave number of 890-1131 cm^{-1} is attributed to C-O-C stretching whereas the indicative peak at 1080cm^{-1} is related to the ß-glycosidic bond or linkages [20]. This region is associated with the typical hemicellulose decomposition and the distinguished peak of 1080cm^{-1} described the cellulosic degradation [16], [21].

Next, the carbonyl group, C=O stretching vibrations is represented by the peak of 1715 cm^{-1}. The occurrence of the peak at 1715cm^{-1} suggests that the hemicellulose associated with the lignin fraction are rich in acetyl, hydroxycinnamate or ester groups [22], [23]. Meanwhile, the decrease in intensity for aromatic skeletal vibrations at ~1602 cm^{-1} depicts the lignin decomposition [22], [23].

In brief, the TGA results are supported by the FTIR analysis. The discussion regarding the inferior temperature resistant of hemicellulosic structure was proven by the FTIR spectra. Lignin as expected, do not easily degrade and no remarkable changes or shrinkage in the peak was observed. Hence, it can be concluded that the hemicellulose was the first to decompose and significant oxidation is noticed at the temperature of 220 ℃ while cellulose only starts to show obvious disappearance starting from the temperature of 250 ℃ and above.

IV. Conclusion

It can be observed that the energy yields for all the torrefied rice husk and rice straw exceed 90%. Only a small fluctuation in energy yield is detected across the torrefaction temperature of 220 ℃, 250 ℃ and 280 ℃.This trend implying that the torrefied biomass is able to withstand the mass loss during torrefaction process by increment of 3-20% in calorific ratio. Besides the high promising energy yield, the torrefied rice biomass is also happened to exhibit the hydrophobic behavior as discussed in the TGA and FTIR analyses. In concise, torrefaction is able to convert rice husk and rice straw into valuable biofuel especially at the temperature of 250 ℃ where the highest energy yield is remarked for both materials.

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