Grindability and Kinetic Study During Pyrolysis of Raw and Torrefied *Leucaena Leucocephala*

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Abstract—**Malaysia is a country that is highly dependent on fossil fuel energy as the main energy source. This has been a problem for the country because for a fact, fossil fuel is an energy source that is not renewable and will be depleted over the years. Biomass is one of the potential alternatives for fossil fuel replacement due to its traits being renewable. The reason Malaysia does not fully utilize its renewable energy resource because Malaysia is lacking in biomass conversion technology and its application. Malaysia is still comfortable with the usage of fossil fuel resource because of their lack of awareness. Direct combustion of biomass is the most promising method to exploit biomass to produce energy. However, one of the method's drawbacks is the difficulty to grind the product to obtain fine particles. To improve the properties of raw biomass, torrefaction or mild pyrolysis is considered. Therefore, for this research, the grindability and kinetics study during pyrolysis need to be carried out to obtain the best way to produce high quality bioenergy feedstock. Biomass chosen for this research project, *Leucaena Leucocephala* (LL) as a type of potential energy crop, was chosen as the raw material. The torrefaction was done under the temperature range from 200ºC to 300ºC. Torrefied biomass pellet was compared to its raw pellet in terms of its grindability and its kinetics parameter through Coats-Redfern, chemical non-isothermal kinetic method. From the results obtained, pyrolysis of biomass does increase the grindability properties of the biomass pellets and its activation energy (E_a) significantly. As the temperature of torrefaction increases, comparing the raw pellets and pellets that is torrefied at 300ºC, the weight percentage of particle size below 100 µm of grinded pellets increases from 26.94% to 62.31%. Meanwhile for the activation energy (E_a), the value decreases as the torrefaction temperature was increased. It means that the higher temperature of torrefied pellets requires less activation energy thus improving the kinetics properties of the torrefied pellets as the value of activation energy of raw pellets is 119.8 kJ/mol meanwhile for pellets that is torrefied at 300ºC is 82.9 kJ/mol. It is found that during pyrolysis, raw *Leucaena Leucocephala* (LL) followed Third Order (F3) reaction mechanism.**

Keywords— ***Activation Energy, Biomass, Coats-Redfern, Grindability, Leucaena Leucocephala, Pyrolysis, Torrefaction.***

I. INTRODUCTION

There are many alternatives in producing energy other than exploiting fossil fuel energy. The most popular alternative is producing energy through biomass. In Malaysia, at least 168 million tons of biomass produced yearly that include waste from timber, oil palm, rice husks, coconuts, sugarcanes and municipal waste. According to World Energy Market Observatory (WEMO) 2017 report [1], Malaysia's renewable energy usage is predicted to have increment by 4.8% by the year 2030. Renewable Energy Act was introduced in year 2011 to provide establishment and implementation of a special tariff system to catalyze the generation of renewable energy. This act will help to increase the renewable energy contribution in Malaysia, and this shows that the Malaysian government fully supports the idea of biomass utilization of energy. In comparison with other developed countries such as Germany, the country's development in biomass energy industry increased 10 times higher since 2000 [2]. In 2015 their biomass energy contributed the largest share that is a solid 88% to their country energy usage [2]. The reason energy crop was chosen as a solid biomass fuel is to prevent rapid release of carbon dioxide and greenhouse gas emissions due to global use of fossil fuels (coal, oil and gas) and Malaysia should use the energy crop as solid biomass fuel due to emissions of carbon dioxide and greenhouse gas is growing rapidly [3].

LL is one of the woody plants that can be used as an energy crop. It is also known as the "Miracle Tree" in some parts of the world where it is heavily utilized due to its long lifespan, and highly nutritious forage tree used to produce firewood, timber, human food, green manure, shade and also to control erosion [4]. LL has a good growth rate and it is very likely to live in Malaysia's weather and geographic conditions.

The focus of this research is to convert this potential energy crop into solid bioenergy product. Comparing to past studies, the differences between this research is the method used in analyzing the kinetics parameters. The objectives of this research are to study the effect of torrefaction on grindability of LL pellets and to perform a non-isothermal kinetics study of LL during pyrolysis via Coats-Redfern method.

II. METHODOLOGY

A. Materials

The raw materials are collected from the open areas around Shah Alam province, Selangor, Malaysia. Bulky LL stem samples were cut, chipped and ground and dried to reach moisture content of less than 15 wt%. The pelletization was done in Forest Research Institute of Malaysia (FRIM) using a pellet machine with a diameter or 8 mm and length between 1 to 6 cm.

B. Torrefaction Experiment

Nitrogen was be purged in to the system before the torrefaction process with a flow rate of 10 cc/min for ten to fifteen minutes to make sure there is no excess air inside the system. Then the nitrogen flow rate was lowered to 2 cc/min. The temperature and its respective holding time were set so the torrefaction process can be initialized.

The temperature chosen for this study are 200, 250 and 300ºC with holding times of 30 and 60 minutes. After the torrefaction process is completed, the temperature of the furnace must be made sure to reduce to 75 to 100ºC to avoid cracking in the glass tube due to spike of different temperature of the tube and the surroundings during opening the tube. The samples were taken out, weighed and stored in air-tight containers.

C. *Grindability of Pellets*

Two equipments used for the grindability process were grinder and sieve analyzer. Each pellets of the different temperature and with different holding time underwent grindability study. Grindability process is conducted in order to observe any change or improvement of the torrefied biomass by evaluating the particle size distribution [5]. Treated samples with mass of 50 g of each temperature and its respective holding time will be grinded using a grinder and the grinded samples will be sieved using sieving trays with different size of sieving mesh that are 50, 75, 125 and 150 µm [5].

The mass of sieved samples will be collected and recorded by calculating its percentage i.e. each mass of sieved sample over total mass. Particle size distribution and cumulative particle size distribution of each sample were plotted to determine which sample has the smallest particle size that is below than 50 µm.

D. *Kinetic Study*

This research utilizes the Coats-Redfern method with reaction mechanism up to seven type that is First Order (F1), Second Order (F2), Third Order (F3), One-Dimensional Diffusion (D1), Two-Dimensional Diffusion (D2), Three-Dimensional Fusion-Jander (D3) and Three-Dimensional Diffusion-GB (D4). Data from the Thermogravimetric Analyser (TGA), were analyzed and model-fitting of Coats-Redfern was chosen to fit the data to measure the kinetic parameters. After TGA was conducted, the data will be fit into the simplified equation of Coats-Redfern method. Equation (1):

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\frac{AR}{\beta E}\left(1 - 2\frac{R\bar{T}}{E}\right) - \frac{E}{RT} \qquad (1)$$

The chosen model, represented by g(α) were F1, F2, F3, D1, D2, D3 and D4 yields approximately straight lines. Each of g(α) expression for each chosen model are represented in Table 1.

Table 1: Expressions for g(α) based on various reaction mechanisms

Mechanisms	Symbol	g(α)
First Order	F1	$-\ln(1-\alpha)$
Second Order	F2	$(1-\alpha)^{-1} - 1$
Third Order	F3	$[(1-\alpha)^{-2} - 1]/2$
One-Dimensional Diffusion	D1	α^2
Two-Dimensional Diffusion	D2	$[(1-\alpha)x\ln(1-\alpha)] + x$
Three-Dimensional Diffusion-Jander	D3	$[1-(1-\alpha)^{1/3}]^2$
Three-Dimensional Diffusion-GB	D4	$1 - \frac{2\alpha}{3} - (1-\alpha)^{2/3}$

E_a is estimated from the slope of the line having best fit to the experimental data. This model has been used extensively for estimation of kinetics of solid fuel's reaction [6].

III. RESULTS AND DISCUSSION

A. *Grindability*

Fig. 1 shows the graphical presentations of weight percentage of the grinded samples of each size distribution. As the temperature of the torrefaction increases, the percentage of the biggest size distribution, ≥150 µm decreases as the percentage of the smallest size distribution, ≤50 µm increases. Comparing raw samples with torrefied samples with the highest temperature, the percentage of particle with size distribution of ≥150 µm for raw pellets is 69.30% while for torrefied samples at 300ºC is 33.59%. There is a significant drop in weight percentage of the samples as the increase of the temperature of torrefaction helps to break down the molecular composition of the pellets and makes it easier to grind and break down into smaller particle size.

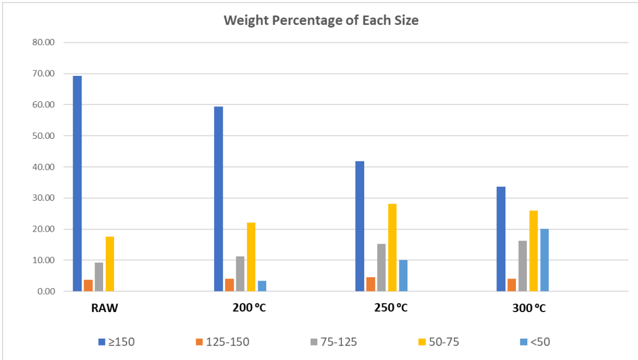
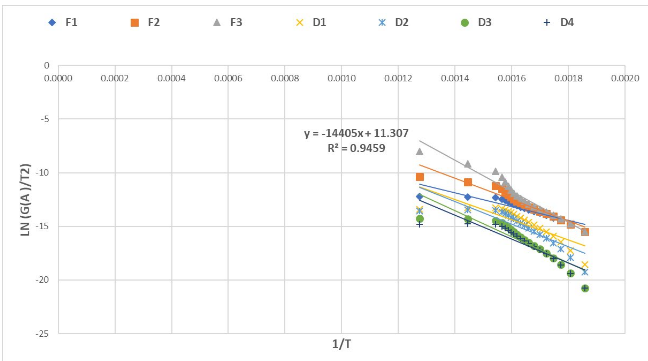


Fig. 1: Weight percentage of samples at different condition with respective size distribution class.

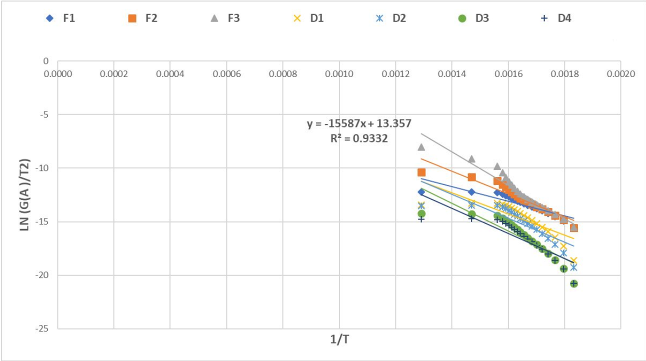
In comparison with past studies that has been conducted by M. V. Gil et al. [5], the untreated and torrefied samples shows the same trend in terms of grindability properties. The torrefied samples has a greater proportion in particle size fractions that is smaller than 710 µm compared to the untreated samples and it also make the grinding of samples process easier. As the temperature for the torrefaction increases, the proportion in particle size fractions that is smaller than 710 µm increases.

B. *Kinetic Analysis*

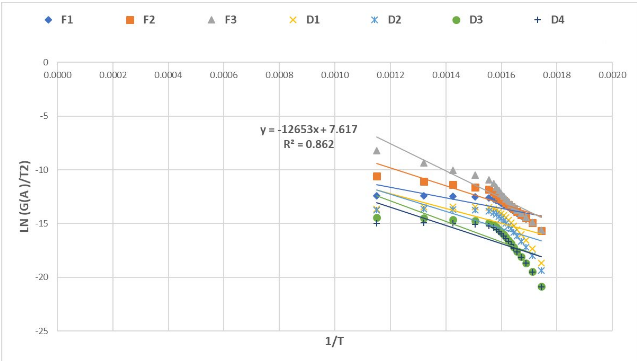
By utilizing the non-isothermal method Coats-Redfern, the kinetic parameter E_a of the raw and torrefied LL pellets under pyrolysis with the range of temperature from 200 to 300ºC were calculated and presented in the Table 1.



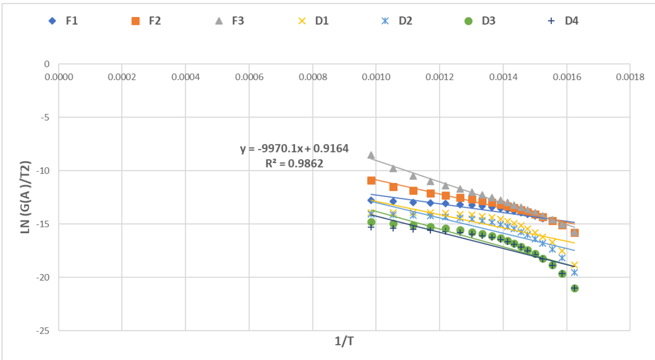
(a)



(b)



(c)



(d)

Fig. 2: (a) Raw LL (b) LL torrefied at 200ºC (c) LL torrefied at 250ºC (d) LL torrefied at 300ºC

The calculation values are from the values of R^2 based on the best fit of reaction mechanism and the value of slope from the graph of the best fit reaction mechanism. Fig. 2 below shows the plotted data of each reaction mechanism, F1, F2, F3, D1, D2, D3 and D4 against 1/T for each condition of samples. It is found out that the best reaction mechanism is F3, i.e. Third Order reaction mechanism. E_a values were calculated based on the slope of best fit reaction model.

Table 2: Activation energy (E_a) and coefficient of correlation (R^2) for raw and torrefied samples for 3rd order reaction mechanism.

Sample	E_a (kJ/mol)	R^2
RAW LLP	119.8	0.9459
TLLP 200	129.6	0.9332
TLLP 250	105.2	0.862
TLLP 300	82.9	0.9862

As the temperature of torrefaction increase, the value of E_a decreases. As can be seen from Table 2, sample that was torrefied at 300ºC (highest temperature chosen for torrefaction), has the lowest value of E_a, that is 82.9 kJ/mol. This implies that torrefaction treatment on LL samples has successfully reduces E_a, which means the torrefied samples will be easier to be combusted as compared to its raw form. From the obtained values of E_a, the calculated value of maximum reduction is 31%. By comparing with the past studies conducted by S. Matali et al. [7], torrefied LL can be regarded as more thermally stable compared to it's raw conditioned LL when subjected to heating at higher temperature and this is crucial in relation to auto ignition during storage and transportation.

IV. Conclusion

Solid biofuel of *Leucaena Leucocephala* that is obtained from the process of torrefaction has been analyzed thoroughly for its properties of grindability and kinetic parameters. From the results, it indicates that the grindability properties of the torrefied samples improved significantly as the torrefaction temperature increases. This is due to the loss of composition of the hemicellulose due its breakdown of the high temperature. As for the analysis of the kinetics, reaction mechanism of Third Order has the best fit of data compared to the other reaction mechanism with the highest value of R^2. As the temperature of torrefaction increases, the value of E_a decreases. This proves that treating of LL pellets by torrefaction can give advantage to the rate of burning of solid biofuel thus increase the efficiency of the solid biofuel product. In conclusion, temperature has a big impact on the torrefaction process in enhancing its grindability properties and its activation energy. This finding may be further validated by optimization of torrefaction parameter.

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