

A comparative study on pyrolysis characteristic Indonesia biomass and low grade coal

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Abstract. A comparative study on pyrolysis of biomass and low grade coal was conducted using a thermogravimetric analyzer. Each kind of biomass and coal has a characteristic pyrolysis behavior which is explained based on its individual component characteristics. All fuels experienced a small weight loss as temperatures approached 450K because of moisture evaporation. The coal had smallest total weight loss compared to biomass due to its high content of fixed carbon, suggesting that coal would produce high amounts of char and small amounts of volatile matter (*e.g.*, tar and gas). The biomass exhibits similar tendency regarding the decomposition process which is the hemicelluloses break down first at temperatures of 470 to 530K, cellulose follows in the temperature range 510 to 620K, and lignin is the last component to pyrolyze at temperatures of 550 to 770K. The thermal decomposition of biomass consisted of two predominant peaks corresponding first to the decomposition of cellulose and, second, to the decomposition of lignin. Meanwhile, the coal exhibited only single peak because these fuels were predominantly composed of carbon. Based on the kinetic analysis, coal have the smaller activation energy (55.32kJ/mol) compared to biomass (range from 89.80-172.86 kJ/mol). Pyrolysis process also created more pore material in the solid product. These results were important for the optimization of energy conversion from those solid fuels. Biomass resulted lower solid product and higher tar product, thus would be suitable for liquid and gas energy production.

1. Introduction

Indonesia produce 147.7 million tons of biomass per year, equivalent to about 470 GJ/year. Biomass is a renewable energy source[1]. Indonesian biomass spread all over the country such as rice residue, wood, and oil palm residue. Biomass is a solution to substitute the excessive demand of non-renewable energy like fossil fuel. Burning fossil fuels release large amount of carbon dioxide into atmosphere causing environmental problem. Therefore, if biomass is used as an alternative fuel it will reduce the consumption of fossil fuel and also reduce the environmental pollution of greenhouse[2,3].

The energy source within the biomass can be obtained either through biological or thermochemical conversion. Biological conversion involves the usage of microorganisms such as anaerobic digestion and fermentation. Thermochemical conversion involves the application of heat and chemicals in the production of energy. Thermochemical conversion can be divided into combustion, gasification and



pyrolysis. Among the thermochemical conversion, pyrolysis is considered the most efficient process due to its high feed to fuel ratio in comparison to combustion and gasification process[4].

Biomass pyrolysis can be converted into bio-fuels, adsorbent bio-char, and other useful chemicals. Kinetic is very important to understand reaction mechanism, predict the conversion and design reactor. TGA measure the amount and rate of change in the weight of tested material as a function of temperature or time in atmospheric pressure. Various weight loss processes determined during the TGA reflect the physical and chemical structure changes during the conversion. Differential thermogravimetry (DTG) shows thermal behavior of material and also the optimum operating condition of the material pyrolysis. The kinetics of these thermal events has been determined by the application of the Arrhenius equation corresponding to the separate slopes of constant mass degradation[5,6].

Nomenclature

A: pre-exponential factor (min^{-1})	t: heating time (minute)
B: heating rate (K min^{-1})	X: conversion of sampe (-)
E_a : activation energy (J mol^{-1})	W: weight of sample (mg)
K: rate constant (min^{-1})	
n: order of reaction (-)	Subscript
R: universal gas constant ($=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)	i: initial state (at 105°C)
T: temperature (K)	f: final state (at 800°C)

2. Material and experiment method

2.1. Material

The biomass residues of rice huck and ulin wood were obtained from agricultural residue in Bantul Yogyakarta while low grade coal was obtained from Kalimantan. The proximate analysis of the samples was shown in table 1. To avoid the effect of particle size, the sample were crushed and sieved to a granular size.

Table 1: Proximate analysis of solid fuels

Sample	Proximate analysis (%mass)		
	Fixed C	Volatile	Ash
Low grade coal	47.77	31.05	1.47
Rice husk	21.14	55.23	15.75
Palm kernel shell	30.78	57.52	2.21
Ulin wood	22.83	74.32	2.85

2.2. Thermogravimetric analysis (TGA)

The pyrolysis characteristics of the samples were examined using a thermogravimetric analyzer (TG\DTA). Sample was placed inside the TG where the weight was constantly measured. The functions of the TG were to measure and record the dynamics of sample weight loss with increasing temperature or time. Sample use for TG analysis is 11.788 mg for palm kernel shell, 8.541 mg rice husk, and 10.40 mg ulin wood. Heating rate was controlled at 10°C/min , temperature range used in this experiment was $25 - 800^\circ\text{C}$. Once the heating temperature reached 105°C , it was held for 30 min

to completely remove moisture and provide a basis for analysis. Nitrogen was used as the carrier gas in the TG, so that the sample was paralyzed in an inert environment without oxygen.

2.3. Pyrolysis Kinetics

The non-isothermal kinetics for solid decomposition is usually written as follows:

$$\frac{dX}{dt} = kf(X) \quad (1)$$

where X is fuel conversion, and is given

$$X = \frac{W_i - W}{W_i - W_f} \quad (2)$$

In the above equation, W, W_i , and W_f represent the instantaneous, initial (at 105°C), and final (at 800°C) weights of the sample. The reaction rate constant k is expressed in terms of the Arrhenius equation as

$$K = A. \exp\left(\frac{-Ea}{RT}\right) \quad (3)$$

and the function f(X) can be written as

$$f(X) = (1 - X)^n \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (1) gives

$$\frac{dX}{dt} = A. \exp\left(\frac{-Ea}{RT}\right) (1 - X)^n \quad (5)$$

For a constant heating rate $\beta = \frac{dT}{dt}$, Eq.(5) can be rearranged to the following equation

$$\frac{dX}{dT} = \left(\frac{1}{\beta}\right) A. \exp\left(\frac{-Ea}{RT}\right) (1 - X)^n \quad (6)$$

The integral method based on Coats and Redfern (CR) equation[7,8,9] is used in this work, and the approximate integration of Eq. (6) gives

$$\ln \left[\frac{-\ln(1-X)}{T^2} \right] = \ln \frac{AR}{\beta Ea} \left[1 - \frac{2RT}{E} \right] - \frac{Ea}{RT}, \text{ if } n = 1 \quad (7)$$

or

$$\ln \left[\frac{-\ln(1-X)^{1-n}}{(1-n)T^2} \right] = \ln \frac{AR}{\beta Ea} \left[1 - \frac{2RT}{E} \right] - \frac{Ea}{RT}, \text{ if } n \neq 1 \quad (8)$$

For most reactions, the value of $\frac{2RT}{E}$ is very small (i.e. $\frac{2RT}{E} < 1$), and thus the preceding two equations can be approximated by

$$\ln \left[\frac{-\ln(1-X)}{T^2} \right] = \ln \frac{AR}{\beta Ea} - \frac{Ea}{RT}, \text{ if } n = 1 \quad (9)$$

or

$$\ln \left[\frac{-\ln(1-X)^{1-n}}{(1-n)T^2} \right] = \ln \frac{AR}{\beta Ea} - \frac{Ea}{RT}, \text{ if } n \neq 1 \quad (10)$$

The plot of $\ln \left[\frac{-\ln(1-X)}{T^2} \right]$ versus $\frac{1}{T}$ becomes a linear line for $n = 1$; the plot of $\ln \left[\frac{-\ln(1-X)^{1-n}}{(1-n)T^2} \right]$ versus $\frac{1}{T}$ is also a linear line for $n \neq 1$. Accordingly, the apparent activation energy (E_a) and the apparent frequency factor (A) can be determined from the slope and intercept of the regression line, respectively

3. Result and Discussion

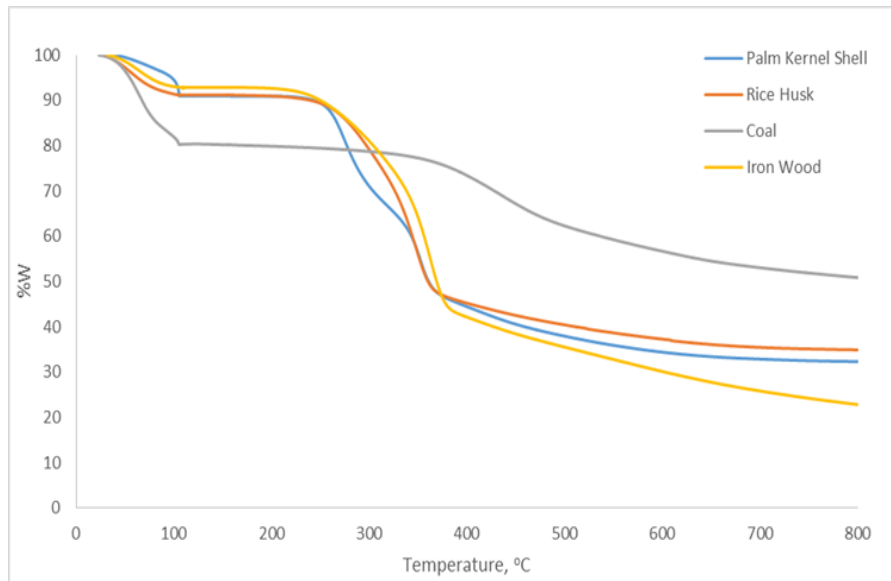


Figure 1. TGA Curves for Palm Kernel Shell, Rice Husk, Coal, and Ulin wood

For pyrolysis of palm kernel shell, rice husk, ulin wood, and coal, the percent weight change curves are shown in Fig. 1. It can be seen that the percent weight change of all samples are decreased with the increasing temperature. Ulin wood have the most percent weight loss from all the biomass sample and coal was the least. The remaining ulin wood after pyrolysis is 16.88% from the initial mass and coal is 35.87%. It indicating all sample are undergo thermal degradation and decomposition. Derivative of TG curve are shown in figure 2. Biomass shown slightly same curve pattern. It has 2 peak curve while coal only have one. The study of lignocellulose compounds is relevant to pyrolysis because decomposition these components occurs at different temperatures. The pyrolysis process divided into three main region: Moisture content removal ($<105^\circ\text{C}$); degradation of hemicellulose ($200 - 320^\circ\text{C}$); lignin and cellulose decomposition ($320 - 400^\circ\text{C}$). Since coal doesn't have cellulose, hemicellulose and lignin the DTG curve only have one peak and have different pattern with biomass. Pyrolysis reaction end when the percent weight loss have horizontal pattern. Rice husk and palm kernel shell end at 600°C , coal at 700°C and Ulin wood at 750°C .

Maximum decomposition hemicellulose temperature at $10^\circ\text{C}/\text{min}$ for rice husk is 295°C , palm kernel shell 278.38°C , and ulin wood 276.65°C . Maximum decomposition cellulose and lignin temperature at $10^\circ\text{C}/\text{min}$ 349.47°C for rice husk, 353.61°C palm kernel shell, Ulin wood 362.82°C .

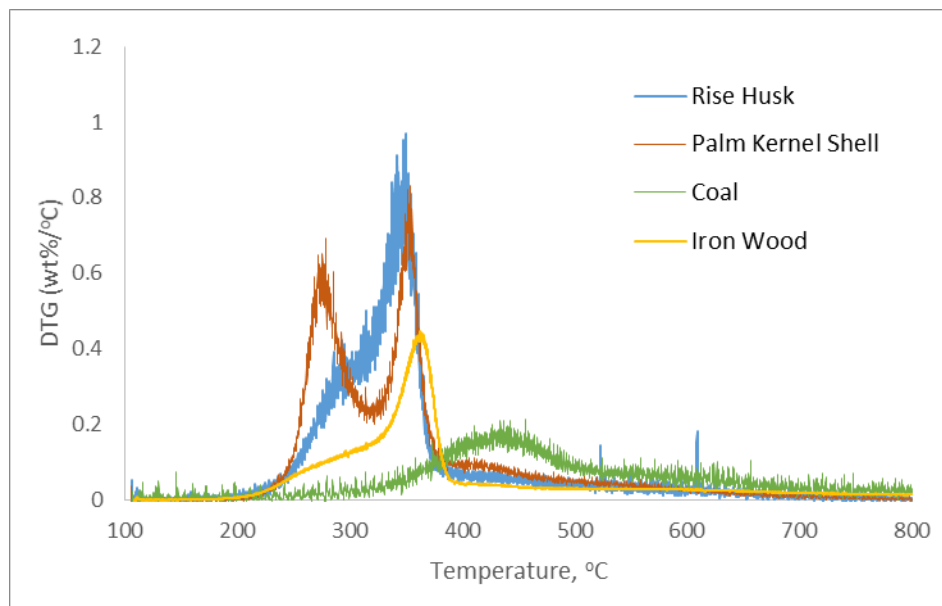


Figure 2. DTG Curves for Palm Kernel Shell, Rice Husk, Coal, and Ulin wood

Table 2 show the result of kinetic parameter obtained from the Arrhenius method for rice husk, palm kernel shell, ulin wood, and coal. All the data obtained at different value of n are fitted and the best-fit regression line that has highest value of correlation R^2 was shown in each figure. Coal has pyrolysis range from 594 – 779 °C activation energy 55.32 kJ/mol $A = 610$ R and the best-fitted regression $n = 2.6$ with correlation coefficient $R = 0.99$. Palm kernel shell the decomposition divided into two stage with activation energy value for the first region is 172.86 kJ/mol second stage 164.23 A for first stage and second stage is 5275810276075090.00 and 141694773043700.00 best-fitted regression $n = 7$ for first stage and $n = 4$ for the second stage which give coefficient correlation (R) 0.99 and 0.97. Rice husk activation energy for first and second stage is 89.80 and 108.5226 A for first and second stage 11963597.96 and 688935605.9 and the best-fitted regression $n = 2.2$ and 2.5 which give coefficient correlation 0.99 and 0.97. Ulin wood activation energy for first and second stage is 85.42635 and 135.0692 A for first and second stage 3745831.323 and 88315997175 and the best-fitted regression $n = 3$ and 4 which give coefficient correlation 0.98 and 0.97. Coal give least energy activation and ulin wood give most value of activation energy. It mean that coal is still a material which easiest to burn. Calculation using Arrhenius method shown that value of activation energy for ulin wood in first stage is the least among the other biomass.

Table 2: Kinetic parameters and characteristic temperatures for pyrolysis of biomass and coal

Sample	Pyrolysis range		Order	Ea (kJ/mol)	R^2
	T_i (°C)	T_f			
Low grade coal	594	778	2.6	55.32	0.99
Rice husk	200	302	2.2	89.90	0.99
	302	385	2.5	108.52	0.97
Palm kernel shell	200	322	7	172.86	0.99
	322	384	4	164.23	0.97
Ulin wood	180	328	3	85.42	0.98
	328	400	4	135.06	0.97

As examples, the linear regresion for low grade coal and rice husk can be shown in the below

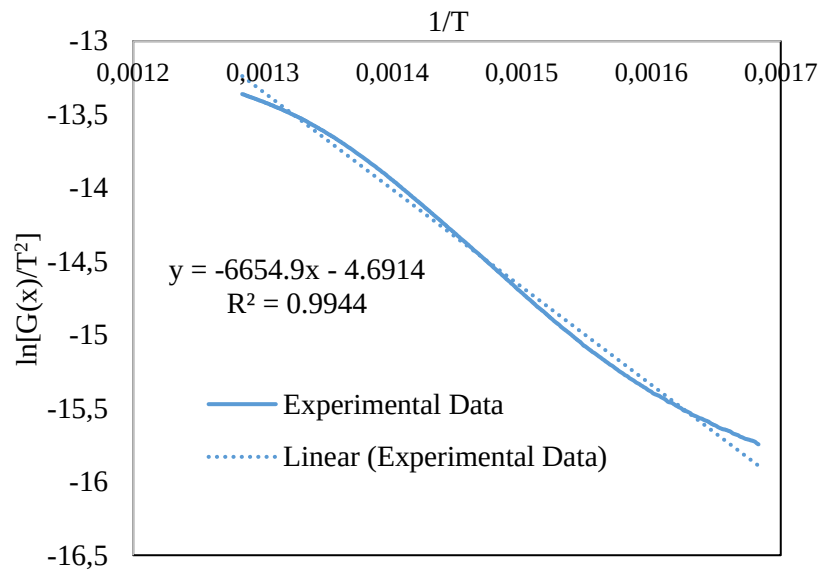


Figure 3. The linear regression of coal for calculation of activation energy

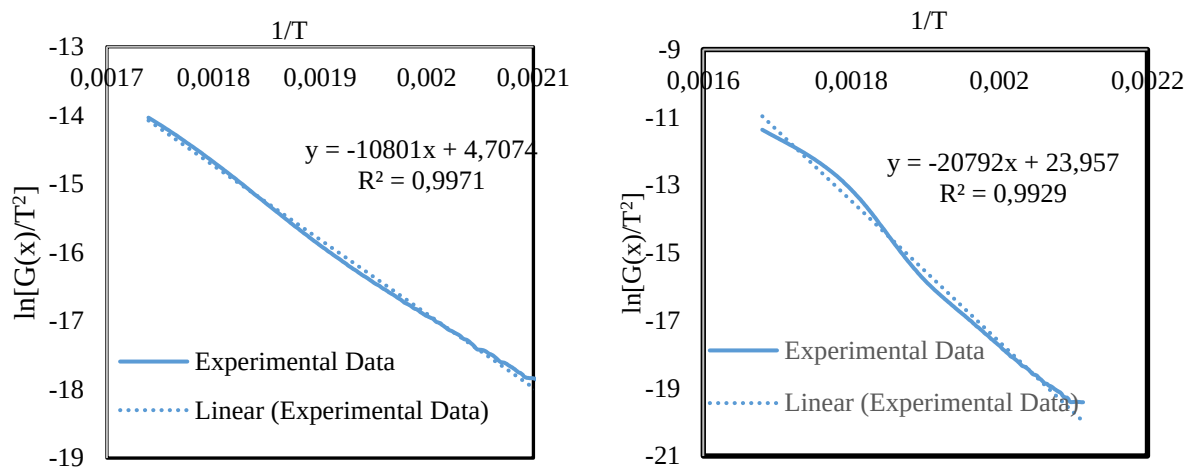


Figure 4. The linear regression of rice husk for calculation of activation energy

Figure 5 shows the comparison of SEM (Scanning Electron Microscopic) image between raw ulin wood residues before pyrolysis process and char products after pyrolysis process. It is seen that raw ulin wood there are no visible pores, while char products has visible pores.

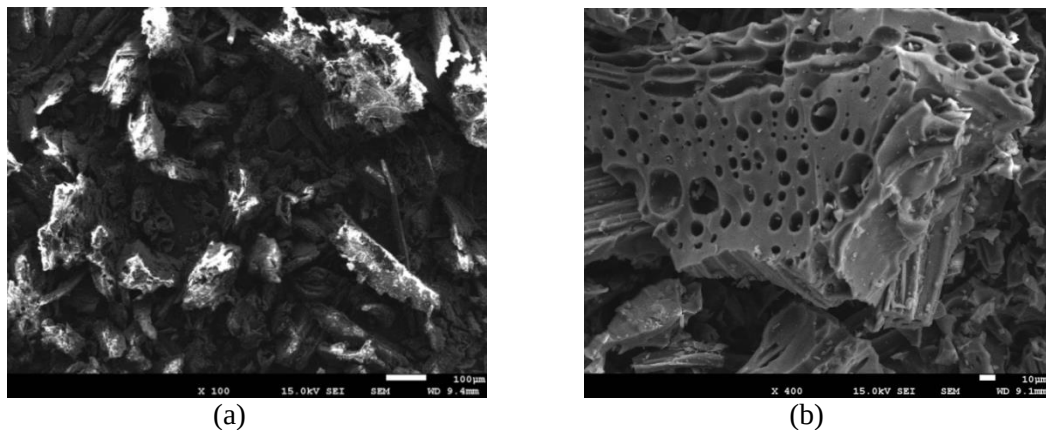


Figure 5. The effect of the pyrolysis process on the SEM image of the ulin wood.

4. Conclusion

Based on TG-DTG analyses found that the biomass pyrolysis process occurs in two stages, the decomposition of hemicellulose and lignin decomposition while coal pyrolysis occurs only in one stage. This happens due to differences between the composition of biomass and coal. As a whole, coal have the smaller activation energy (55.32kJ/mol) compared to biomass (range from 89.80-172.86 kJ/mol).

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