

Kinetic Study of Pyrolysis of *Ulin* Wood Residue using Thermogravimetric Analysis

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Abstract— Biomass as a renewable and sustainable energy source is expected to solve the energy crisis problem. *Ulin* wood residues as a biomass source could be converted into bioenergy utilizing the pyrolysis process since its primary component is a hydrocarbon. Pyrolysis process has received many interests for bioenergy production from biomass, elevating the importance of the kinetic study of pyrolysis. The kinetic study of pyrolysis is related to the beginning stage behavior of gasification and combustion process. The kinetic mechanism of pyrolysis is analyzed using Thermogravimetry Analysis (TGA), by estimating the mass decomposition at solid-state that shows TG and DTG curve. The TG and DTG curves were analyzed to see the effect of heating rate on decomposition temperature. This experiment was performed by heating 10 mg of *Ulin* wood sawdust from ambient temperature to 1473 K utilizing 100 mL/min of nitrogen (N₂) gas as carrier gas at various heating rate: 5, 10, 20, and 50 K/min. The kinetic parameters were determined by applying the iso-conversional methods, the Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) methods, and then compared the results with the non iso-conversional method, using Kissinger method. The average value of activation energy calculated using the KAS and FWO methods are 253.5514 and 245.2512 kJ/mol, with the average value of constant coefficient square (R²) of 0.9848 and 0.9859, respectively, whereas the calculated activation energy and R² using the Kissinger method are 237.4478 kJ/mol and 0.8520, respectively.

Keywords— *ulin* wood residues; pyrolysis; thermogravimetric analysis; iso-conversional method; kinetic parameters.

I. INTRODUCTION

Concern about the depletion of energy from fossil fuels, some researchers have found out new and renewable energy sources [1], [2]. In order to create a more sustainable society, biomass is one of the prominent renewable energy sources in the future [3]. Biomass is an organic matter formed from living species, such as wood [4], agricultural crop residues [5], animal waste [6], municipal solid waste [7], algae [8], and some kind of organic waste. Indonesian biomass from the forestry sector has the potency to be developed as a bioenergy source [9], one of which is *Ulin* wood. Generally, *Ulin* wood is used as a raw material in the furniture industry, construction material, and vessel material that producing biomass residue. The major component of this residue is a hydrocarbon which can be converted into biofuel.

The conversion of biomass into bioenergy is categorized by two methods: biochemical and thermochemical conversions. Biochemical conversion generally produces ethanol as the main product of fermentation [10].

Thermochemical conversion usually can be executed by the pyrolysis and gasification process [11]. Pyrolysis is a thermal decomposition process with limited or without oxygen [12]. Slow and fast pyrolysis can categorize pyrolysis. They depend on various factors, such as heating rate, temperature, and residence time [13]. Wood, such as *Ulin* wood residue, is well pyrolyzed due to the high content of hydrocarbon and the small content of moisture. Moreover, biochar, as a side-product of pyrolysis, also can be transformed to be a more valuable product, such as bio-briquette [14] and catalyst support [15] since pyrolysis has received many interests for the bioenergy production from biomass so that the kinetic study of pyrolysis is useful to be investigated.

Existing studies have investigated the kinetics of biomass pyrolysis. One of the considered methods is thermogravimetry analysis (TGA). This method defines the kinetics of biomass pyrolysis by weight loss due to the devolatilization process. Devolatilization is the first decomposition process in which volatile matter started to

released from the raw material [16]. For non-isothermal solid-state kinetic, model-fitting and model-free can be applied to analyze the phenomena [17]. Model fitting is a method that is fitting a few models on data of TGA, which give the best fit. The model that gives the best linearization from the data of TGA to choose. By using model-fitting, we only need one curve of TGA data at one heating rate. However, the possibility of more than one model will fit the same data is high. Therefore, to choose the best kinetic model is quite hard. The example of the non-isothermal model-fitting solid kinetic model is differential, Freeman-Carrol, and Coats-Redfern method.

Another method is model-free, using several data curves at the different heating rates to obtain the kinetics parameters. The calculation obtained the kinetics parameters as a function of conversion, or we called it as iso-conversional. The reaction model can be assumed that is similar for each conversion within the different heating rate. This method is quite simple to determine the kinetics parameters. However, this method only can be performed for the same mass of the sample and the flow of inert gas at different heating rates. The example of a model-free iso-conversional method is Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), Vyazovkin, Vyazovkin AIC, Friedman, and Starink method. In contrast, Kissinger model is one of model-free but not an iso-conversional method because the kinetics parameters is assumed to be constant.

Previously, Mishra and Mohanty [18] studied about pyrolysis kinetic of pine sawdust, sal sawdust, and areca nut sawdust. They compared the result of kinetic parameters using Kissinger-Akahira-Sunose (KAS), Coats-Redfern, Flynn-Wall-Ozawa (FWO), Friedman, and Distributed Activation Energy Model (DAEM) methods. Xu et al. [19] compared the iso-conversional kinetic methods of single-step and Distributed Activation Energy Model (DAEM) for pyrolysis of biomass-pyrolysis-derived-tar. Dhyani et al. [20] studied about kinetic pyrolysis of sorghum straw by comparing with a different method. They used seven models to calculate the kinetic parameters: Kissinger-Akahira-Sunose (KAS), Friedman, Flynn-Wall-Ozawa (FWO), Starink, Chai & Chen Iterative method, Li & Tang equation, and Vyazovkin AIC method,

The mechanism of solid-state processes, which is multi-step processes with different rates, is quite complex to be approached by the simple kinetic model [21]. This work presents the kinetic study of *Ulin* wood residues pyrolysis. To simplify the process mechanism, iso-conversional method is proposed to depict the kinetic phenomena in a solid-state process. This method allows us to approach the kinetic parameters without assuming the reaction model. The fundamental idea of this method is the rate of decomposition affected by temperature and conversion. In this work,

Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) were proposed as iso-conversional methods to determine the kinetic parameters of *Ulin* wood residue pyrolysis. For comparison, the Kissinger method was also investigated.

II. MATERIALS AND METHOD

A. Materials

Ulin wood residues, in sawdust form, were obtained from the furniture industry located in Kalimantan, Indonesia. The proximate and ultimate analysis of *Ulin* wood, which was compared with pine wood and sub-bituminous coal, as presented in Table 1. From Table 1, *Ulin* wood residue had quite good quality to be converted into bioenergy as biomass. *Ulin* wood is a hardwood that had a higher carbon content compared with pine wood, which was a softwood, even though still under the sub-bituminous coal. From the ultimate analysis, the carbon content approached half of the components. The ash content was also low compared with pine wood.

B. Method

1) *Experiment*: Pyrolysis was performed using thermogravimetric analysis (TGA) Mettler Toledo. Nitrogen (N₂), as a carrier gas, was flowed at 100 mL/min. All samples were then heated at a temperature range of 298-1473 K and varied heating rates of 5, 10, 20, and 50 K/min. The morphology of *Ulin* wood residue and char products of pyrolysis were then analyzed by SEM (Scanning Electron Microscopic) analysis, as shown in Fig. 1-4. The *Ulin* wood residue had no visible pores. Meanwhile, the sample of chars had visible pores. It was observed that the pore size of the char decreased with the increasing pyrolysis temperature. From low to high-temperature pyrolysis, the pore sizes of the char were 0.0167, 0.011, and 0.0071 mm, respectively [22].

2) *Kinetic Study*: It was assumed that the reaction was represented by a one-step global reaction, in which the process of the devolatilization was occurred as a single reaction.



The volatiles was defined as the total of gas and tar. The notation of k denoted reaction rate constant of the Arrhenius equation, as written in Equation (2).

$$k = A \exp\left(\frac{-E_A}{RT}\right) \quad (2)$$

A denoted pre-exponential factor (min⁻¹), E_A denoted activation energy (kJ/mol), R denoted gas constant (8.314 J/K/mol).

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS OF ULIN WOOD, PINEWOOD, AND SUB BITTUMINUS COAL [22]

Materials	Proximate analysis, %			Ultimate analysis, %			
	Fixed Carbon	Volatiles	Ash	C	H	N	O
<i>Ulin</i> wood residue	22.83	74.32	2.85	49.28	5.64	0.30	44.78
Pine wood	15.49	81.27	3.24	46.69	5.89	0.00	47.42
Sub bituminous coal	49.00	48.40	2.60	58.37	5.12	0.85	35.66

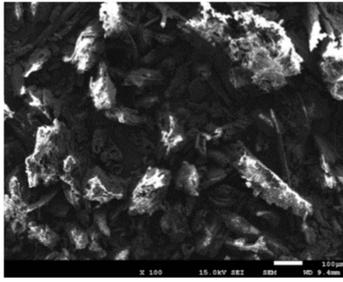


Fig. 1 Ulin wood residues morphology [22]

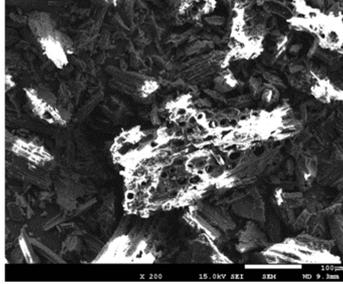


Fig. 2 Char morphology at temperature pyrolysis 573 K [22]

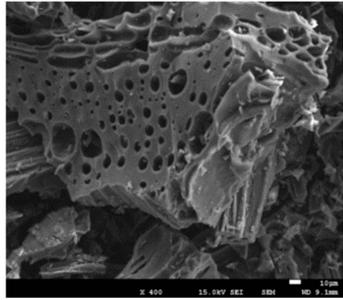


Fig. 3 Char morphology at temperature pyrolysis 773 K [22]

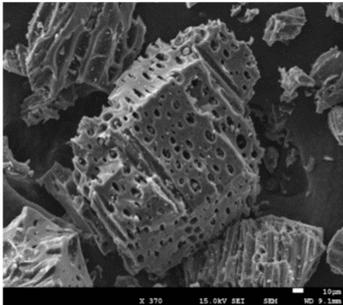


Fig. 4 Char morphology at temperature pyrolysis 973 K [22]

The following equation represented the decomposition rate:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

The notation α represented conversion, which was followed by equation:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (4)$$

where m_0 was initial mass, m_t was mass at a specific time, while m_f was mass at the final reaction. Whereas $f(\alpha)$ was the function of conversion that depends on the reaction model. For this case, $f(\alpha)$ was defined by the following equation:

$$f(\alpha) = (1 - \alpha)^n \quad (5)$$

where n was reaction order. The heating rate (β) for non-isothermal TGA was defined as:

$$\beta = \frac{dT}{dt} \quad (6)$$

Equations (2), (5), and (6) were substituted into Equation (3), then became:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} (1 - \alpha)^n \exp\left(\frac{-E_A}{RT}\right) \quad (7)$$

Equation (7) was derived into a linear equation, so the kinetic parameters were then evaluated from the plot of y-axis versus x-axis. Iso-conversional methods proposed in the kinetic study were *Kissinger-Akahira-Sunose* (KAS) and *Flynn-Wall-Ozawa* (FWO). Moreover, Kissinger [23] had developed the derivative of Equation (7) without consideration of conversion effect.

a) *Kissinger-Akahira-Sunose (KAS) method*

Kissinger-Akahira-Sunose (KAS) method was one of iso-conversional method which was derived from Equation (7) into the following equation [24]:

$$\ln\left(\frac{\beta_i}{T_{oi}^2}\right) = \ln\left(\frac{A_{\alpha}R}{E_{A\alpha}g_{\alpha}}\right) - \frac{E_{A\alpha}}{RT_{oi}} \quad (8)$$

where β_i was heating rate, T_{oi} was the temperature for each predefined conversion at a different heating rate, $E_{A\alpha}$ was the activation energy for each conversion, A_{α} was the pre-exponential factor for each conversion, g_{α} as the integral of $f(\alpha)$. The slope of the graph ($-E_{A\alpha}/R$) was used to calculate activation energy. Meanwhile, the intercept of the plot of $\ln(\beta_i/T_{oi}^2)$ versus $1000/T_{oi}$ denoted pre-exponential factor.

b) *Flynn-Wall-Ozawa (FWO) method*

Flynn-Wall-Ozawa (FWO) method was another iso-conversional method that was used the Doyle approximation into the Equation (7). The linear equation was based on the following equation [24,25]:

$$\ln(\beta_i) = \ln\left(\frac{A_{\alpha}E_{A\alpha}}{Rg_{\alpha}}\right) - 5.331 - 1.052 \frac{E_{A\alpha}}{RT_{oi}} \quad (9)$$

The activation energy and pre-exponential factor were determined by calculating the slope ($-1.052E_{A\alpha}/R$) and the intercept of the plot of $\ln(\beta_i)$ versus $1000/T_{oi}$.

c) *Kissinger method*

The Kissinger method was based on the maximum rate of decomposition. For first order reaction, the Equation (7) was derived into this following equation [23]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (10)$$

where T_m denotes the temperature at the maximum decomposition rate (DTG curve). To evaluate the kinetic parameters, it was plotted in the graph of $\ln(\beta/T_m^2)$ versus $1000/T_m$. The slope ($-E/R$) was determined from the graph to calculate activation energy. Meanwhile, the intercept of the graph was used to calculate the pre-exponential factor. The result of kinetic parameters was assumed to be constant along with the reaction mechanism.

III. RESULTS AND DISCUSSION

A. Thermogravimetric Analysis

The characterization of mass decomposition of *Ulin* wood residue could be determined by thermogravimetric analysis that shows TG and DTG curve. The samples were heated from 298 until 1473 K by varying the heating rate, 5, 10, 20, and 50 K/min, which flowed by 100 mL/min of nitrogen (N_2). The mass fraction profile (TG) of *Ulin* wood residue is shown in Fig. 5, and the DTG curve is shown in Fig. 6. From Fig. 5 we can see that *Ulin* wood residue has started to decompose at around 500 K. The higher the heating rate, the decomposing of mass started at a higher temperature. From temperature 500 K, the process of mass decomposition ran rapidly until temperature around 700 K. Then, above temperature around 700 K, the process ran slowly.

There are three main regions of mass decomposition that is shown in Fig. 5. The first region lies on the temperature range about 430-500 K. The decomposed mass was too small, so the change of the mass is not visible. In this region, the water content and light volatiles component were evaporated. The second region lies on the temperature range around 500-700 K. This region can be defined as an active pyrolysis area where most cellulose and hemicellulose were decomposed, and it is the main decomposition. The third region lies on the temperature above 700 K. This region is called a passive pyrolysis area where lignin was decomposed. Lignin characteristic is quite stable against heat so that the decomposed mass is quite small.

The rate of decomposition of *Ulin* wood, as shown in Fig. 6, two peaks represent of hemicellulose and cellulose decomposition. According to literature, the slight slope at low temperature is hemicellulose decomposition, and at a higher temperature with the maximum peak is cellulose decomposition. The tail of the curve is lignin decomposition that decomposes lightly at high temperatures.

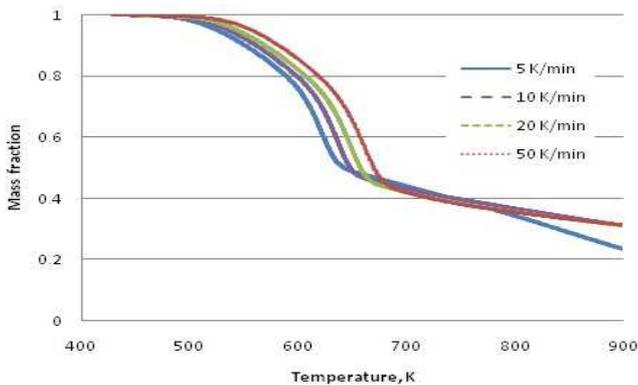


Fig. 5 Mass fraction (TG) of *Ulin* wood residue by TGA record

The TG and DTG curves with a variation of heating rate tend to be shifted toward higher temperatures. The starting point and final point of the active pyrolysis region lies at a higher temperature for the higher heating rate. The range of decomposition rate of active pyrolysis is extensive for higher heating rates. The higher of heating rate, the maximum decomposition rate lay in higher temperatures and had a higher value. These phenomena indicate that there is a limitation of heat transfer. An immediate amount of energy is needed to the system and needs a longer reaction time to

reach a temperature that equivalent to furnace temperature when the heating rate is low. Whereas at a higher heating rate, the reaction time is shorter so that the sample need a higher temperature to decompose.

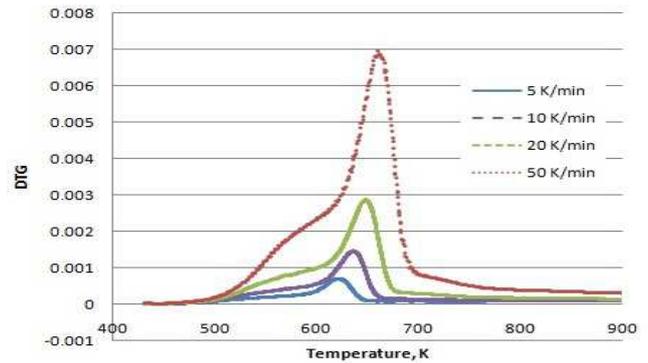


Fig. 6 DTG curve of *Ulin* wood residue

B. Kinetic Study

The kinetic parameters were observed by investigating the effect of the heating rate of thermogravimetric analysis with iso-conversional method. In this case, we used *Kissinger-Akahira-Sunose* (KAS) and *Flynn-Wall-Ozawa* (FWO) method to evaluate kinetics. Then, the results were compared with Kissinger method, as non iso-conversional method. The KAS method was calculated by Equation (8), whereas the FWO method was calculated by Equation (9). For kinetic parameters of Kissinger method, it was calculated by Equation (10). Conversion as temperature function was calculated by using Equation (4), then the curve of conversion at different heating rates versus temperature is shown in Fig. 7. The conversion range of 0.05-0.65 was predefined, which lay on the range of the primary decomposition for all heating rate curve. For each conversion at a different heating rate, the temperature was found and was substituted into Equations (8) and (9). Fig. 8 shows the plot of KAS method for each conversion at the different heating rates and Fig. 9 shows the plot of FWO method. The plot of the y-axis and x-axis at the different heating rate for each conversion resulted iso-conversional lines. The slope of iso-conversional lines was calculated to obtain the activation energy (E_A), meanwhile, the intercept was calculated to obtain the pre-exponential factor (A). The Kissinger method plot is shown in Fig. 10. The maximum temperature is taken to be a point of constant conversion, then taken for each different heating rate [26] and were observed from Fig. 6. This method did not need to calculate the activation energy for each conversion. The activation energy was assumed to be the same for each conversion. From plotting the Equation (10), it was obtained the activation energy, pre-exponential factor, and the square of correlation factor.

Table II shows the calculation of activation energy (E_A) and pre-exponential factor (A) from KAS, FWO, and Kissinger method plot for each conversion. The value of activation energies (E_A) was at the range of 167.2777-321.0035 kJ/mol for KAS method and 167.4655-250.6480 kJ/mol for FWO method. The average values for both methods are near similar, 253.5514 and 245.2512 kJ/mol, respectively. The average values of R^2 were 0.9849 and

0.9858, respectively. It was observed that the kinetic parameters for both KAS and FWO methods were not the same for each conversion. The values of activation energy and pre-exponential factor were proved as a function of conversion. They tended to rise from low to high conversion for both methods. The reaction model did not regard the KAS and FWO method. However, it indicated that the reaction was a multi-step mechanism at solid-state, and the values of kinetic parameters depend on conversion. Solid-state decomposition was quite complex, so the using iso-conversional method was quite simple to describe the kinetic phenomena.

Meanwhile, the values of activation energy, pre-exponential factor, and the square of correlation factor are 237.4478 kJ/mol, $4.09 \times 10^{19} \text{ min}^{-1}$, and 0.8520, respectively. Compared with the average value of the KAS and FWO method, the activation energy of the Kissinger method was similar, but the R^2 was less than both iso-conversional method. The Kissinger method was only to observe the mechanism reaction at the maximum rate of decomposition so that the complexity of the reaction could not be detected [27].

Some researchers have investigated about kinetics pyrolysis of another wood and its derivative by using TGA with many kinds of conversional method. Poletto [28] studied the kinetics of pyrolysis of *Pinus elliottii* and *Pinus taeda* using Flynn-Wall-Ozawa (FWO) method. The TGA carried out at four different heating rates, 5, 10, 20, and 40°C/min. The activation energy of *Pinus taeda* and *Pinus elliottii* varied between 150-171 and 164-197 kJ/mol, respectively. Ge et al. [29] studied the kinetic pyrolysis of some wooden board, density board, core-board, particleboard, plywood, and pine board. The kinetics parameter calculated by Kissinger and Coats-Redfern method. The TGA performed at a heating rate 10, 15, 20, 25, and 30 K/min. The activation energy for each wooden board was 196.85, 212.88, 201.49, 153.25, 167.35 kJ/mol, respectively.

Khan et al. [30] studied the impact of ionic liquids (ILs) namely 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) and 1-butyl-3-methylimidazolium acetate ([BMIM][OAc]) on to rubber wood pyrolysis. They compared the kinetics parameters of the untreated rubber wood (RW), the ([BMIM][Cl]) treated rubber wood (RW-Cl), and the ([BMIM][OAc]) treated rubber wood (RW-OAc). The kinetics parameters were calculated using KAS, FWO, and Starink method. The TGA performed at a heating rate: 5, 7.5, and 10 °C/min. The average activation energy of RW, RW-Cl, and RW-OAc using FWO method are 120.15, 87.32, and 85.64 kJ/mol, respectively. The average activation energy of RW, RW-Cl, and RW-OAc using FWO method was 117.10, 77.73, and 76.63 kJ/mol, respectively. At the same time, the average activation energy of RW, RW-Cl, and RW-OAc using Starink method are 117.61, 81.16, and 80.47 kJ/mol, respectively.

If we analyzed from the results of some researchers about the kinetics parameters of pyrolysis of various wood, the value of activation energy was around 70-280 kJ/mol, calculated by iso-conversional method. The composition and chemical properties of the wood, for example, hemicellulose, cellulose, lignin was varying for each type of wood,

affecting the value of kinetic parameters. Moreover, the pre-treatment of the wood sample was also affecting the value of the kinetic parameters.

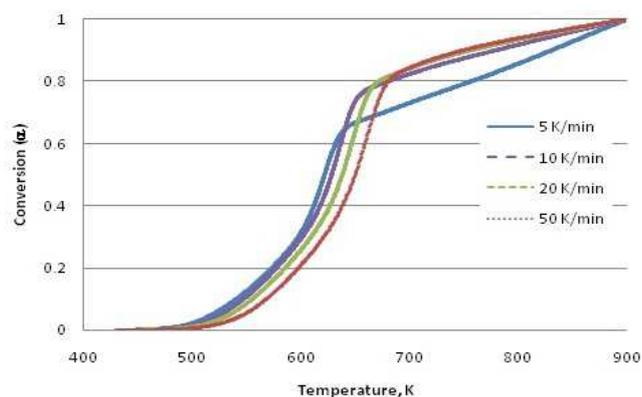


Fig. 7 Conversion vs. temperature at a different heating rate

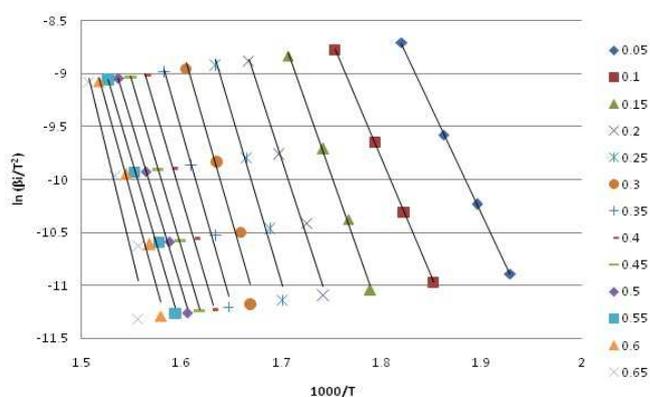


Fig. 8 KAS method plot

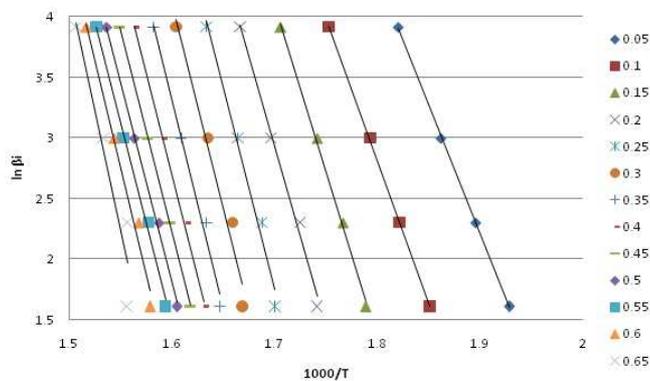


Fig. 9 FWO method plot

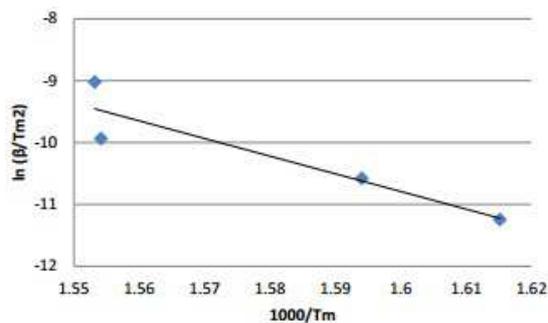


Fig. 10 Kissinger method plot

TABLE II
THE COMPARISON OF KINETIC PARAMETERS OF *ULIN* WOOD PYROLYSIS BY USING KAS AND FWO METHOD

α	E_A (kJ/mol)			A (min^{-1})			R^2		
	KAS	FWO	Kissinger	KAS	FWO	Kissinger	KAS	FWO	Kissinger
0.05	167.2777	167.4655	237.4478	1.36×10^{12}	1.46×10^{18}	4.09×10^{19}	0.9990	0.9990	0.8520
0.10	185.9010	185.4844		3.90×10^{13}	3.69×10^{19}		0.9990	0.9990	
0.15	221.9838	220.0997		4.00×10^{16}	2.83×10^{22}		0.9970	0.9970	
0.20	238.6949	236.2219		5.54×10^{17}	3.57×10^{23}		0.9910	0.9910	
0.25	266.7963	263.0923		7.64×10^{19}	4.16×10^{25}		0.9830	0.9840	
0.30	270.6207	272.1017		7.71×10^{19}	6.39×10^{25}		0.9710	0.9730	
0.35	275.9417	264.4358		1.19×10^{20}	8.82×10^{24}		0.9890	0.9890	
0.40	267.7939	262.1439		1.52×10^{19}	4.07×10^{24}		0.9980	0.9980	
0.45	265.2997	260.7214		6.69×10^{18}	2.40×10^{24}		0.9990	0.9990	
0.50	263.7201	264.7519		3.87×10^{18}	4.23×10^{24}		0.9970	0.9970	
0.55	267.7939	279.5306		6.89×10^{18}	5.83×10^{25}		0.9940	0.9950	
0.60	283.3411	315.4104		1.05×10^{20}	3.98×10^{28}		0.9830	0.9840	
0.65	321.0035	250.6480		8.98×10^{20}	3.07×10^{27}		0.9040	0.9100	
Average	253.5514	245.2512	237.4478	6.94×10^{21}	1.88×10^{25}	4.09×10^{19}	0.9849	0.9858	0.8520

IV. CONCLUSION

Thermogravimetric analysis is widely used to estimate the decomposition at solid-state and could be determined the kinetic parameters. In this work, *Ulin* wood residues were heated at a temperature range of 298-1473 K and heating rates: 5, 10, 20, and 50 K/min under nitrogen (N_2) gas flow of 100 mL/min. Moreover, it also different. It was observed the decomposition of mass and decomposition rate (TG and DTG) as the influence of heating rate. The higher heating rate, the curve of TG and DTG were tended to shift to the higher temperature. Iso-conversional method was used to analyze the kinetic parameters. In this case, this study used *Kissinger-Akahira-Sunose* (KAS) and *Flynn-Wall-Ozawa* (FWO) method for evaluating kinetic parameters. The results showed that activation energy depended on conversion. It indicated the multi-step mechanism without regarding the model reaction. The average value of activation energy for KAS and FWO method were 253.5514 and 245.2512 kJ/mol, respectively. The average value of R^2 were 0.9849 and 0.9858, respectively. Meanwhile, the value of activation energy and R^2 of Kissinger method were 237.4478 kJ/mol and 0.8520, respectively.

NOMENCLATURE

A	pre-exponential factor	min^{-1}
E_A	activation energy	kJ/mol
R	gas constant	J/K/mol
T	temperature	K
R^2	coefficient of determination	-
Greek letters		
α	conversion	-
β	heating rate	K/min

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