Isoconversional Analysis of Corn Silk Thermal Decomposition Fitting Model by Pyrolysis Process

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INFORMASI ARTIKEL

ABSTRACT

The pyrolysis characteristics and kinetics of corn silk were studied through thermogravimetric analysis in the normal room temperature range of -900℃ under a nitrogen atmosphere at heating rates of 20, 30 and 40℃/minute. The results show that the pyrolysis process of corn silk is divided into three stages which can be associated with the process of dehydration or loss of water at a temperature of 65-150℃, followed by a second stage, namely the main devolatilization at a temperature range of 225-525℃ and the final stage, namely slow decomposition up to 900℃. The activation energy in the active pyrolysis stage was calculated using the Arrhenius fitting model and the isoconversional model using the Flynn-Wall Ozawa model and the Vyazovkin model. The resulting activation energies from the Arrhenius calculations are in the range of 195-215 kJ/mol and Ea using the Flynn-Wall Ozawa and Vyazovkin free model calculations of 195,355 and 215,522 kJ/mol, respectively.

Keywords: Thermal Decomposition, Activation Energy, Pyrolysis, Corn Silk.

A B S T R A K

Karakteristik pirolisis dan kinetika sutra jagung dipelajari melalui analisa termogravimetri dalam rentang suhu normal kamar-900 ℃ dibawah atmosfer nitrogen pada laju pemanasan 20,30 dan 40 ℃/menit. Hasilnya menunjukan bahwa proses pirolisis sutra jagung terbagi menjadi tiga tahap yang dapat dikaitkan dengan proses dehidrasi atau kehilangan air pada suhu 65-150 ℃, dilanjutkan dengan tahap kedua yaitu devolatilisasi utama pada rentang suhu 225-525 ℃ dan tahap akhir yaitu dekomposisi lambat hingga 900 ℃. Energi aktivasi pada tahap pirolisis aktif dihitung dengan menggunakan model fitting Arrhenius dan model isoconversional menggunakan model Flynn-Wall Ozawa dan model Vyazovkin. Energi aktivasi hasil dari perhitungan Arrhenius pada kisaran 195-215 kJ/mol dan Ea menggunakan perhitungan model bebas Flynn-Wall Ozawa dan Vyazovkin masing-masing sebesar 195.355 dan 215.522 kJ/mol.

Kata Kunci: Dekomposisi Termal, Energi Aktivasi, Pirolisis, Sutra Jagung

1. Introduction

Rising levels of carbon-dioxide in the atmosphere especially in densely populated countries are driving renewed interest in developing techniques to reduce global warming [1][2]. Fossil fuels are a non-renewable energy source and are still the world's main energy source [3]. Increased consumption and depleting reserves of fossil energy sources are important reasons for developing renewable energy which is expected to be a solution to replace or replace fossil fuels so as to reduce global warming. Of the various new and renewable energy sources, biomass fuel is one of the many energy sources that has the best potential as a substitute for fossil fuels and becomes an important contributor as an energy source in the next century. Biomass fuel has been considered as a nearly neutral fuel and provide substantial benefits because biomass absorbs CO_2 during growth and then releases CO_2 at the same amount during combustion so that it has the potential as a fuel that is safe for the environment [4][5][6].

In Indonesia, agricultural waste is one of the most abundant sources of biomass, especially corn. In 2017, the area of corn land is 5,375,378 hectares [7], corn silk produced is around 527 Kg per hectare [8] and an abundance of corn silk of about 2.85 million tonnes per year [3]. The abundance

of corn silk is an aspect that really needs attention in terms of its utilization. Several studies have been conducted regarding its use as low-fat meatballs [9], anti-obesity [10], antidiabetic effect of corn silk polysaccharides [11]. However, the potential of corn silk as a fuel raw material has not been investigated. Therefore, it is very important to conduct research to understand the potential of corn silk as a renewable fuel raw material which is expected to become a long-term energy reserve.

Common modes of thermal conversion of biomass are gasification, direct combustion, and pyrolysis. From several biomass conversion techniques, pyrolysis provides the advantage of converting biomass into biofuels where the main products are gas fuel, fuel oil and charcoal so they are easy to store [12]. Pyrolysis products are strongly influenced by the origin of the biomass and operating conditions such as reaction temperature, residence time and heating rate. Therefore, an in-depth understanding of their thermal behavior and kinetic parameters is essential to enable proper reactor design [13].

The aim of this research is to present the thermal characteristics and kinetic parameters of corn silk during the pyrolysis process through thermogravimetric (TG) analysis. Kinetic parameters were analyzed using the Arrhenius fitting model and Flynn-Wall Ozawa and Vyazovkin's free-isoconversional model.

2. Methodology of Research

2.1 Material

In this study samples of corn silk were obtained from Badas village, Kediri District, East Java, Indonesia. The sample drying process was carried out using an oven at 100 °C for 90 minutes. The dried samples were ground and sieved to achieve a mesh size of 60. The corn silk powder was then stored in tightly closed bottles. Prior to the TG test, the characterization in relation to its chemical and physical properties is shown in Table 1.

Table 1. Chemical and physical composition of Corn silk

Chemical elements (wt,%)		Physical properties (wt,%)		HHV (MJ/kg)
C	45.82 ± 4.01	Moisture	9.6 (ar)	
O	46.41 ± 3.58	Volatile matter	82.2 (db)	19.50
Mg	0.48 ± 0.30	Fixed carbon	32.4 (db)	
Al	0.45 ± 0.24	Ash	4.4 (db)	
Si	0.17 ± 0.15	Total sulfur	0.35 (db)	
P	1.27 ± 0.17			
Cl	0.97 ± 0.12			
K	3.56 ± 0.31			
Ca	0.34 ± 0.16			
S	0.62 ± 0.31			

ar: as received,   db: dry basis

2.2 Thermogravimetric Analysis

Thermogravimetric analysis (METTLER TOLEDO TGA / DSC1) used heating rates of 20, 30 and 40 °C/min. A low heating rate was chosen to favor homogeneous ignition and minimize mass transfer effects. The high heating rate causes a large temperature gradient across the sample, thus affecting the reaction kinetics [4]. Pyrolysis process from room temperature to 900 ℃, nitrogen continues to flow into the room at a constant rate of 50 ml/minute. The 10 mg sample was weighed and placed into the vessel to minimize the effect of the temperature gradient during thermal conversion. The computer works in synchronization with the furnace so that it records the mass loss of the sample during heating as a function of temperature and time. Subsequently, the TG curve was obtained, and a thermogravimetric (DTG) differential curve was generated from the first derivative of the TG. According to the two TG-DTG curves, the thermal behavior and characteristic parameters of corn silk pyrolysis were determined.

2.3 Kinetic Models

The reaction rate of solids in the heating process is modeled by the Arrhenius equation:

$$\frac{da}{dt} = k(T)f(a) = Ae^{\frac{-E}{RT}}f(a) \qquad (1)$$

where t is time (minute), $k(T)$ is the rate constant with respect to temperature, $f(\alpha)$ is a temperature-independent conversion function, A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ / mol), and T is the absolute reaction temperature (K).

Conversion (α), which shows the mass loss of the sample material which is expressed as the following equation:

$$a = 1 - \frac{mt - mf}{mi - mf} = \frac{mi - mt}{mi - mf} \qquad (2)$$

Where, mi is the mass of the initial sample, mt is the mass of the sample remaining at time (t), and mf is the final mass of the sample from the reaction process.

For non-isothermal reactions, the change in temperature with respect to time indicates the rate of heating, $\frac{dT}{dt} = \beta$. Substituting Equation (1) with $dt = \frac{dT}{\beta}$ and then by defining the nth order reaction model into the non-isothermal form as follows:

$$\frac{da}{(1-a)^n} = \frac{A}{\beta} e^{\frac{-E}{RT}} dT \qquad (3)$$

According to Equation (3), furthermore, the kinetic parameters of the solid thermochemical conversion can be evaluated.

For each conversion value (a), $ln\frac{\beta}{T^2}$ is plotted on $1/T$ a straight line with a slope is obtained $-E/R$. Thus, E obtained as a function of conversion.

3. Result and Discussion

The pyrolysis results of corn silk with varying heating rates of 20, 30 and 40°C/minute are shown in Figure 1 as follows:
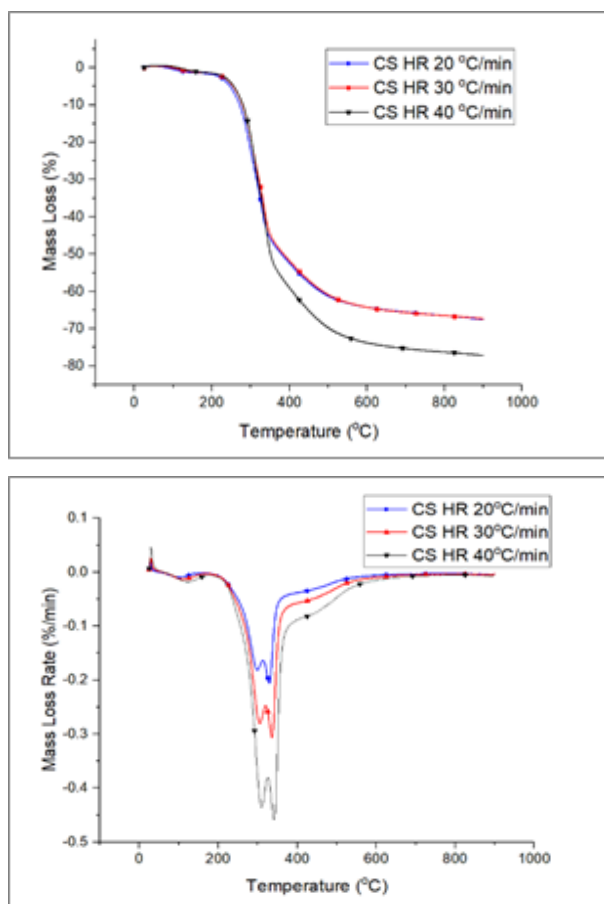
Figure 1. TG and DTG curves of pyrolysis of corn silk (CS) with heating rates of 20, 30 and 40°C/minute.

3.1 Effect of Heating Rate

In Figure 1 the shift in the peak decomposition temperature is shown in the DTG curve, where the peak temperature shifts to a higher temperature. This shows that an increase in the heating rate causes a slowdown in pyrolysis, which can be explained that an increase in the heating rate causes an increase in the initial decomposition temperature and will automatically increase the peak decomposition temperature to a higher temperature [14][15]. This can also be attributed to a decrease in heat transfer efficiency at higher heating rates. According to some literature, that at a lower heating rate, the heating of the biomass particles occurs more gradually and leads to better heat transfer in the biomass [16][17].

In general, pyrolysis is divided into three stages, namely the first stage (dehydration), the second stage (first devolatilization) or it can be called an active pyrolysis zone and the third (final devolatilization) or it can be called a passive pyrolysis zone. In the DTG and TG curves the first stage occurs in the temperature range of 65-150 °C where the rapid release of water content is indicated by the downward line of the TG curve due to a corresponding increase in water evaporation. The pyrolysis decomposition peak temperature values are shown in Table 2.

Table 2. The shift in the pyrolysis peak temperature of corn silk (CS) is based on variations in heating rate

The peak temperature of pyrolysis decomposition of corn silk (CS) was based on variations in heating rate	
Heating rate (C/minute)	T peak decomposition (°C)
20	329
30	335
40	339

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The active pyrolysis zone (second stage) is indicated by a line that decreases sharply in the temperature range of 225-373 °C on the TG curve. At this stage, degradation occurs through complex chemical reactions and gas that cannot be condensed is wasted. The passive pyrolysis zone (third stage) is characterized by a relatively flat TG curve in the temperature range of 525-900 °C. The third stage shows that the decomposition of solid residues occurs. This can be attributed to the decomposition of lignin at a slower rate compared to hemicellulose and cellulose, even covering a larger temperature range of 150-900 °C whereas the decomposition of hemicellulose and cellulose decomposition occurs over a temperature range of 200–350 °C and 200–500 °C [18][19].

3.2 Kinetic Parameter Analysis

Evaluation of kinetic parameters is implemented in the active pyrolysis zone (Second stage), where the thermal degradation of the material has occurred to a large extent. According to the TG-DTG curve, the characteristic parameters that determine the pyrolysis of corn silk can be determined as shown in Table 3.

Choose the nth order reaction model. The final rate equation for the Arrhenius method can be obtained by taking the logarithm of Equation (3) and making some rearrangements. Arrhenius equation to express the reaction rate into a linear equation as follows:

$$ln\left(\frac{d\alpha}{dT}\right) - n\,ln(1-\alpha) = ln\left(\frac{A}{\beta}\right) - \frac{E}{RT} \qquad (4)$$

Each n value is selected then the plot $ln(d\alpha/dT) - n\,ln(1-\alpha)$ versus ($1/T$) is drawn, resulting in a straight line with the associated correlation coefficient of (R^2) and then the curve of $R^2 - n$ can be plotted as shown in

Figure 2. The peak of the curve of $R^2 - n$ represents the highest value of R^2 and it is related to the most appropriate of R^2. This most appropriate value of n is then implemented to produce the final plot of $ln(d\alpha/dT) - n\,ln(1-\alpha)$ versus (1/T) which can be seen in Figure 3. The activation energy and pre-exponential factor were determined from the slope and intercept of the last plot [20].

Table 3. Characteristic parameters of corn silk pyrolysis with heating rate variations of 20, 30 and 40°C/minute

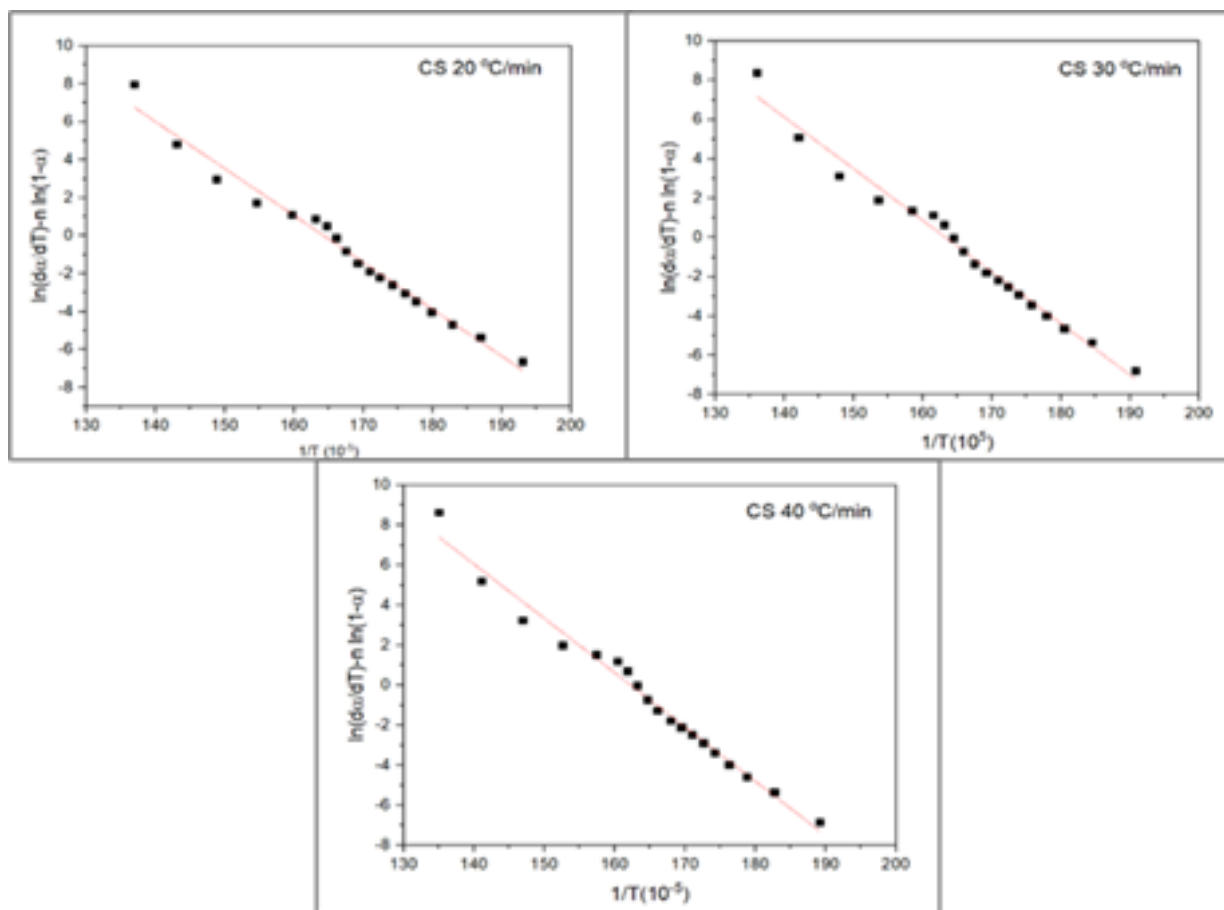| β	T_o (°C)	T_b (°C)	T_m (°C)	M_m (%/s)	Total mass loss (%)
20	194	500	328	0.17	61.206
30	193	503	335	0.28	61.068
40	193	509	338	0.42	70.347
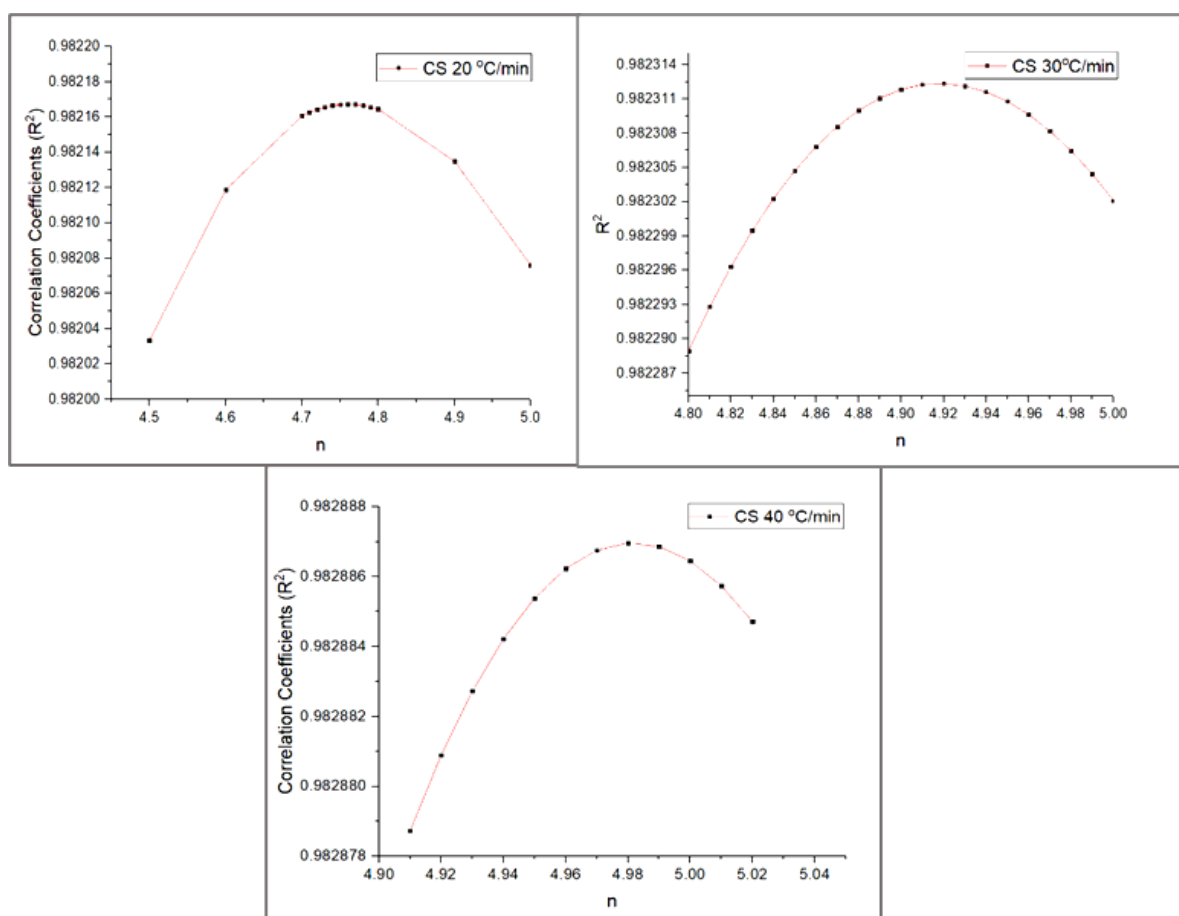
Figure 2. The Curve of $R^2 - n$ generated from the Arrhenius method.

In Figure 2 curve of $R^2 - n$ shown that the highest R^2 is 0.982 for corn silk at heating rates of 20 and 30°C/minute, 0.983 for corn silk with a heating rate of 40°C/minute with value n of 4.81, 4.92, dan 4.98 respectively. After obtaining the most appropriate value of n, the final plot of $ln(d\alpha/dT) - n\,ln(1-\alpha)$ versus (1/T) is shown in figure 3.

3.3 Analysis of The Activation Energies of The FWO and Vyazovkin Free Modes

Tables 4 and 5 show the kinetic parameter values of corn silk using the Arrhenius fitting calculation model and the Flynn-Wall Ozawa (FWO) and Vyazovkin isoconversional models. In the calculation of the Arrhenius model, it is known that the activation energy values at heating rates of 20, 30, and 40 °C/minute are 193.51, 205.82 and 212.72 KJ/mol which indicates that the activation energy Ea increases with increasing heating rate. This supports the understanding that the factors that affect the value of activation energy include heating rate, type of biomass, material/sample particle size, type of thermogravimetric analysis and the kinetic model used. [21].

Figure 3. Linear regression of the plot $ln(d\alpha/dT) - n\,ln(1-\alpha)$ versus ($1/T$)

Table 4. Kinetic parameters of the devolatilization zone of corn silk by the Arrhenius method.

β (ºC/min)	Trendline equation	R^2	Kinetics parameters		
			E (kJ/mol)	$log\,A$ (1/min)	n
20	$y = -23275.2 + 38.104$	0.982	195.55	17.85	4.81
30	$y = -24756.2 + 40.303$	0.982	205.82	18.98	4.92
40	$y = -25585.7 + 41.400$	0.983	212.72	19.58	4.98

3.4 Flynn-Wall Ozawa Model

For the calculation of activation energy using the Flynn-Wall Ozawa (FWO) method as follows:

$$ln\,\beta = ln\,\frac{0.0048AE}{R.g(a)} - 1.0516\,\frac{E}{R}\frac{1}{T} \qquad (5)$$

R is the gas constant, $g(a)$ shows the integral of the kinetic function/integral of the reaction model in the form of a mathematical definition and E denotes (activation energy).

3.5 Vyazovkin Kinetics Model

The Vyazovkin method is a non-isothermal method that has been used to study the kinetics of decomposition reactions for various types of biomass. In this method to calculate the activation energy shown in the following equation:

$$ln\,\frac{\beta}{T^2} = ln\left[\frac{RA}{Eg(a)}\right] - \frac{E}{R}\frac{1}{T} \qquad (6)$$

Table 5. Activation energy by calculating the Flyn and Wall Ozawa (FWO) and Vyazovkin models

Conversion/%	FWO			Vyazovskin		
	Slope	Ea (KJ/mol)	R^2	Slope	Ea (KJ/mol)	R^2
10	**-16.4762**	130.262	0.9999	-17.5582	145.978	0.9999
20	-19.3374	152.883	0.9966	-20.4605	170.108	0.9981
30	-20.0058	158.167	0.9982	-21.1526	175.862	0.9992
40	-23.7304	187.614	0.9914	-24.9003	207.021	0.9929
50	-22.4711	177.658	0.9984	-23.6638	196.741	0.9976
60	-24.005	189.785	0.9914	-25.2194	209.673	0.9921
70	-25.6325	202.651	0.9996	-26.8685	223.384	0.9949
80	-35.1885	278.201	0.9863	-36.4908	303.384	0.9657
90	-35.5812	281.307	0.9945	-36.9888	307.524	0.9892
Average		195.355			215.522	

In Table 5, the activation energy value using the FWO and Vyazovkin free isoconversional model calculations shows an increase in the activation energy value as the conversion value increases starting from a conversion value of 10 to 90 where the activation energy increases from 130 KJ/mol to around 282 KJ/mol where the average is 195,355 KJ/mol for FWO and 145 to 308 KJ/mold with an average activation energy value of 215,522 KJ/mol for Vyazovkin. This can be attributed to the degradation of lignin where lignin consists of three types of benzene-propane which makes it has high thermal stability [22][23], thus resulting in a slow reaction rate which also results in increased activation energy [24]. This is almost the same as the study by Guerrero et al, where a lower activation energy was found at a smaller conversion value [25].

4. Conclusion

The TG and DTG curves show that pyrolysis is divided into three different stages, the first is loss of water content (dehydration), the second is degradation through complex chemical reactions (active pyrolysis zone) and the third is the decomposition of solid residues that occurs (passive pyrolysis zone). The results of kinetic parameters using the calculation of the Arrhenius fitting model with activation energy values of 195.55, 205.82 and 212.72 KJ/mol at heating rates of 20, 30 and 40 °C/minute and calculations of the isoconvesional free model Flynn-Wall Ozawa and Vyazovkin average activation energy values of 195,355 KJ/mold and 215,522 KJ/mol.

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