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Kinetic Study on Pyrolysis of Oil Palm Frond

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Abstract. The pyrolysis of oil palm frond is studied using thermogravimetric analysis (TGA) equipment. The present study investigates the thermal degradation behaviour and determination of the kinetic parameters such as the activation energy (E_a) and pre-exponential factor (A) values of oil palm frond under pyrolysis condition. The kinetic data is produced based on first order rate of reaction. In this study, the experiments are conducted at different heating rates of 10, 20, 30, 40 and 50 K/min in the temperature range of 323-1173 K under non-isothermal condition. Argon gas is used as an inert gas to remove any entrapment of gases in the TGA equipment.

1. Introduction

Biomass is an attractive feedstock for providing potential source of hydrocarbons with almost zero net carbon dioxide (CO₂) emission to the atmosphere environment. The efficient utilization of biomass as a source of clean energy and chemicals has attracted much research attention in recent years amid fossil fuel energy as well as clean energy drive. According to International Energy Agency (IEA), biomass contributed approximately about 10% of the world total primary energy supply in year 2009 [1]. It is reported that an approximate 140 billion metric tons of biomass waste generated from agriculture activities alone worldwide for year 2009 [2]. The high quantity of biomass wastes show that the demand of crops and agricultural activities in the world is currently growing in an accelerating rate and it is expected to increase continuously in the future. Therefore, the abundant supply of biomass waste will eventually be an issue to the environment if it is left unattended.

In order to solve the abundant supply of biomass waste generated globally, pyrolysis process is selected among the thermochemical conversion methods in this present study to reduce the dumping of biomass waste and also providing a solution to produce useful chemicals and clean renewable energy to meet the increasing demand of the ever increasing human population. Biomass pyrolysis is a process where the biomass waste undergoes a thermal decomposition using a heat source in the absence of oxygen to produce energy and conversion of useful oils and char [3]. The few advantages of using pyrolysis compared to other thermochemical processes such as combustion, gasification and incineration are that it does not required the burning of oxygen and does not involved the release of large amount of harmful compounds into the atmosphere [4].

For the present work, palm oil frond is selected as the biomass for the pyrolysis process. One of the main reasons because palm oil wastes are the main biomass resources in ASEAN countries [5]. The two largest palm oil producers in the world are Malaysia and Indonesia which produces an estimated amount of 30 and 8.2 million tons respectively in year 2000 and said to increase yearly [5]. Among the palm oil residues, oil palm frond is said to produce the most abundant and it is reported to produce an estimated amount of 10.88 tons per hectares per year [6-8].



In biomass pyrolysis, thermal degradation behavior can be observed by analysing at the degradation of the three main components in biomass which are cellulose, hemicellulose, and lignin. The breakdown of these individual components occurred at different temperature. In theory, hemicellulose is the first component to decompose under pyrolysis process in the biomass. As hemicellulose is a component that is found abundantly in branches and having a random and amorphous structure, it provides the component to be decomposed easily into more evolved volatiles and lesser tar at lower temperature [9]. After the decomposition of hemicellulose, cellulose decomposes as it is a natural polymer which contained a long chain of linked smaller glucose molecules [10]. It is due to this characteristics of cellulose that gives it a strong strength structure. Thereafter, it is followed by the decomposition of lignin. Lignin is a big group of aromatic polymers where it consists of several oxygen functional groups that results in requirement of higher heat to decompose lignin structures. Thus, the degree of temperature required to decompose biomass increases from hemicellulose, cellulose to lignin. However, thermal degradation behavior of these three components are different from each other and it is due to the component characteristics and structure of the component.

Few studies are reported in literature on the pyrolysis of biomass. Chin et al. [11] investigated on the pyrolysis of rubber seed shells using thermogravimetric analysis (TGA) equipment under non-isothermal condition in argon atmosphere to study the thermal degradation behavior and determination of kinetic parameters. Yang et al. [5] studied on the pyrolysis of palm oil wastes (palm shell, fiber, and empty fruit bunch) in a counter-current fixed bed to characterize the hydrogen rich gas products.

In the present study, TGA equipment is used to study the thermal degradation behaviour and kinetic analysis from the energy released from palm oil frond in pyrolysis process. The kinetic data is produced based on first order rate of reaction. In this study, the experiments are conducted at different heating rates of 10, 20, 30, 40 and 50 K/min in the temperature range of 323-1173 K under non-isothermal condition. Argon gas is used as an inert gas to remove any entrapment of gases in the TGA equipment.

2. Experimental

2.1. Material

Oil palm frond is obtained from a palm oil mill from West Malaysia. The characteristics of the oil palm frond is presented in Table 1.

Table 1. Characteristics of oil palm frond.

Proximate Analysis (weight%, dry basis)	
Moisture content	7.4
Volatile matter	72.5
Fixed carbon ^a	5.8
Ash	14.3
Ultimate Analysis (weight%, dry basis)	
Carbon	38.4
Hydrogen	5.5
Nitrogen	2.3
Sulphur	0.09
Oxygen	32.1
Other	21.6

Higher Heating Value (MJ/kg)	17.2
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*By difference

2.2. Experimental Technique

The analytical instrument used in the present work is the TGA equipment. TGA is a technique where the change in mass of the material as a function of temperature or time is measured under controlled atmosphere. A TGA equipment includes a sample pan where it is supported by a precision balance. The pan laid in a furnace is either heated or cooled in the TGA equipment. The change in mass is monitored during the experiment and a purge gas which can be either inert or reactive controls the sample condition that passes through the sample in the TGA equipment.

In the present work, an approximately 5.0 mg of sample is filled in a 70 μL alumina crucible of the TGA equipment under inert atmosphere of argon. The argon gas is set at the temperature of 323 K with a flow rate of 100 mL/min and fed to the system for 20 minutes. The argon gas supplied is to get rid of the entrapment of other gases present in the system and prevent any unwanted oxidation on the sample in the pyrolysis zone. Subsequently, all of the samples are heated from the temperature of 323 K to 1173 K at its respective heating rates. During this process, the temperatures are kept unchanged for 10 minutes. During the heating, the TGA equipment measured the mass of the sample and furnace temperature. The experiment is conducted where the thermogravimetric curves are plotted at different heating rates of 10, 20, 30, 40 and 50 K/min within a range of temperature of 323 to 1173 K. The reproducibility of the experiments is checked for accuracy of the data obtained.

2.3. Determination of Kinetic Parameters

For pyrolysis process, the first order rate equation is represented as in Equation (1) [6]:



where volatiles is the total amount of the gas and tar meanwhile k is the constant rate of pyrolysis where the temperature dependence is written in Arrhenius equation as shown in Equation (2):

$$k = Ae^{(-E_A / RT)} \quad (2)$$

where E_A is the activation energy (kJ/mol), T is the absolute temperature (K), R is the gas constant (8.314J/kmol) and A is the pre-exponential factor (1/min).

The rate of conversion from biomass to volatile product is presented by the following expression shown in Equation (3):

$$\frac{dx}{dt} = k(T)f(x) \quad (3)$$

where x represent the degree of conversion of the pyrolysis process, t is the time, $k(T)$ is the rate constant and $f(x)$ is the reaction model.

Conversion, x is described as the normalized form of the weight loss of decomposed sample and it is represent as in Equation (4):

$$x = \frac{m_i - m_a}{m_i - m_f} \quad (4)$$

where m_i is the initial mass of the sample, m_a is the actual mass of the sample used, and m_f is the mass after the pyrolysis process.

Equations (3) and (4) are combined to give a fundamental expression of analytical methods to calculate the kinetic parameters on the basis of TGA results as indicated in Equation (5):

$$\frac{dx}{dt} = A \cdot f(x) \cdot e^{-E_A / RT} \quad (5)$$

Since the linear heating rate, β is expressed as follow:

$$\beta = dT / dt \quad (6)$$

Thus, the combined expression can be written as shown in Equation (7):

$$\frac{dx}{dt} = \frac{1}{\beta} (A \cdot f(x) \cdot e^{-E_A / RT}) \quad (7)$$

Rearranging the expression gives:

$$\frac{dx}{f(x)} = \frac{1}{\beta} (A \cdot f(x) \cdot e^{-E_A / RT}) dT \quad (8)$$

By introducing $g(x) = \int_0^x \frac{dx}{f(x)}$, gives the following expression:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \int_{T_i}^{T_f} \frac{1}{\beta} (A \cdot e^{-E_A / RT}) dT \quad (9)$$

For first order reaction, $f(x) = 1-x$ meanwhile $g(x) = -\ln(1-x)$ provides:

$$-\ln(1-x) = \int_0^x \frac{dx}{1-x} = \int_{T_i}^{T_f} \frac{1}{\beta} (A \cdot e^{-E_A / RT}) dT \quad (10)$$

$$\ln[-\ln(1-x)] = \left(-\frac{E_A}{R}\right) \frac{1}{T} + \ln\left(\frac{ART^2}{\beta E_A}\right) \quad (11)$$

After plotting the linear graph of $\ln[-\ln(1-x)]$ versus $1/T$, the value of E_A can be found by calculating the slope of the graph where it represents the $-E_A/R$ whereas the $\ln(ART^2/\beta E_A)$ represents the intercept-c. Therefore, the pre-exponential factor, A can be obtained by using the temperature as $T_a = (T_i + T_f)/2$ where T_i is the initial temperature of the main mass loss in every stage and T_f is the temperature of the final mass loss in every stage.

3. Results and Discussion

3.1. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) Analysis for Oil Palm Frond

The illustration of thermogravimetry analysis (TG) in terms of weight percentage (wt%) versus temperature (K) is plotted to show the thermal degradation behaviour of oil palm frond. The TG curves of oil palm frond at different heating rates from 10 K/min to 50 K/min is shown in Figure 1. In Figure 1, the curve for TG curves show similar trend for each heating rate in the studied range. From the values displayed in Table 2, it is shown that the residual weight in terms of wt% of the sample increases with the increased of heating rates. In addition, the temperature for each stage increases with heating rates. A similar behaviour is also observed as found in the literature [11].

In Figure 1, the TG curves illustrate a slow increment of mass loss for all heating rates studied where the temperature starts from room temperature, 298 K to a temperature of 500 K. At this phase, the moisture of the oil palm frond is eliminated and it is classified as the evaporation process. After the removal of water present in the oil palm frond, the curves of mass loss show a significant decrease of 500 K to 650 K in all heating rates and it shows a major decrease in the mass of the biomass. This further explained that the oil palm frond is facing main devolatilization phase where it released volatile matters and carbon. The mass loss continues to increase but at a slower rate from temperature of 650 K to 1050 K and remained relatively constant from temperature of 1050 K to 1200 K. After the experiment is conducted, the solid remaining is in the range of 8.0 to 15.9 wt% in the range of heating rate studied.

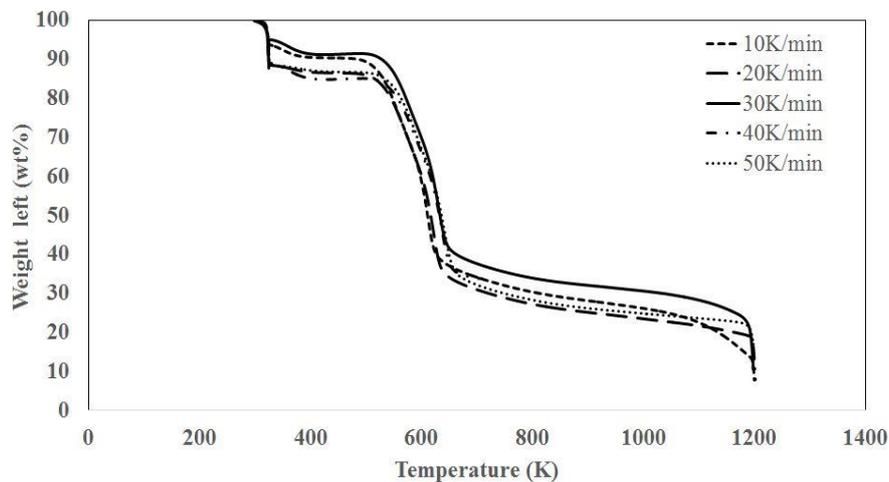


Figure 1. Thermogravimetric (TG) analysis for oil palm frond at different heating rates.

Table 2. Degradation temperature for oil palm frond.

Heating rate (K/min)	First stage ($T_1/T_{max,1}/T_2$)	Second stage ($T_1/T_{max,2}/T_2$)
10	468/559/571	571/614/641
20	471/573/585	585/622/663
30	480/581/598	598/631/687
40	488/591/600	600/639/695
50	495/594/604	604/642/704

Table 3. Amount of residue and maximum degradation rate values for oil palm frond.

Heating rate (K/min)	Residue (wt%)	Maximum degradation rate (wt%/min)
10	8.0	10.1
20	13.1	19.9
30	10.6	28.7
40	12.8	39.0
50	15.9	47.3

In Figure 2, the derivative thermogravimetry (DTG) analysis in terms of wt%/min versus temperature is presented. The kinetic scheme of DTG graph is illustrated with different heating rates. The DTG curve for pyrolysis of oil palm frond becomes more significant when heating rate increases from 10 to 50 K/min. This figure shows two peak exists which indicates two major decomposition stage occurring in the oil palm fronds as temperature increases from 323 to 1173 K. As the heating rate increased from 10 to 50 K/min, the DTG curves become more significant and distinct. A similar behaviour is seen in the results obtained from Rotliwala and Parikh [12]. The occurrence of this event is due to the slow decomposition of the lignin component in the oil palm frond sample. From this result, the occurrence of the two peaks in the DTG curve of the oil palm frond is heavily involved with the two groups of main reactions that includes the three main components found in biomass which are cellulose, hemicellulose and lignin. All the components present undergoes the process of decomposition at different temperature. The first peak from the DTG curve is associated with the decomposition of hemicellulose and some

lignin meanwhile the second peak from the DTG curve is associated with the decomposition of the cellulose component in the biomass.

From the analysis on the temperature range of the curve, the thermal degradation carried out on the hemicellulose, cellulose and lignin in the present study are found very close range from other biomass pyrolysis found in literature [11-12]. At a low heating rate such as 10 K/min, the overlapping of the two peaks shows a smoother sloping baseline compared to other heating rates in the DTG curve is due to the slow decomposition of lignin component in the slow heating rate under a wider temperature range. The pure components of hemicellulose, cellulose and lignin are normally found in woody biomass and therefore, there is a slight variation on the degradation temperature range of the components from both aforementioned studies and current studies as the temperature range of thermal degradation is depending on the type of biomass used for the studies. The chemical characteristics of oil palm frond and woody biomass is different. Hence, this will results in different degradation temperature, however, a similar degradation behaviour is observed in both of these biomass. As observed in the DTG curves, there is an increasing trend of lateral shift in the maximum temperature degradation of the first peak ($T_{max,1}$) and second peak($T_{max,2}$) when the heating rate increases from 10 to 50 K/min in the oil palm frond. This occurrence is caused by the thermal lag which is defined as the difference in temperature of the sample environment controlled by the TGA equipment and the temperature of the sample [13]. Normally, thermal lag occurs in the decomposition of heat transfer at different heating rates, kinetics of the decomposition and heat conductivity property of the oil palm frond particle. The maximum degradation rate is recorded from the range of 10.1 to 47.3 wt%/min.

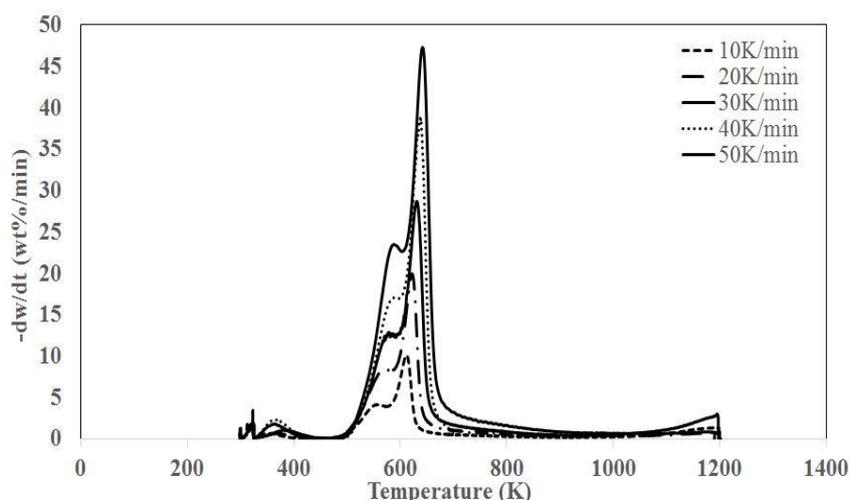


Figure 2. Derivative thermogravimetric (DTG) analysis for oil palm frond at different heating rates.

3.2. Kinetic Analysis for Oil Palm Frond

The values for the kinetic parameters such as activation energy (E_A) and pre-exponential factor (A) are assumed to be in first order of reaction and are determined using an integral method are presented in Tables 4 and 5. Figure 3 displayed one of the exemplary plot of $\ln(-\ln(1-x))$ vs. $1/T$ using heating rate of 10 K/min. Similar trends are exhibit in different heating rates. The predicted E_A values ranged from 29.05 to 64.60 kJ/mol meanwhile the A values ranged from 45 to 176927 min^{-1} in the studied heating rates.

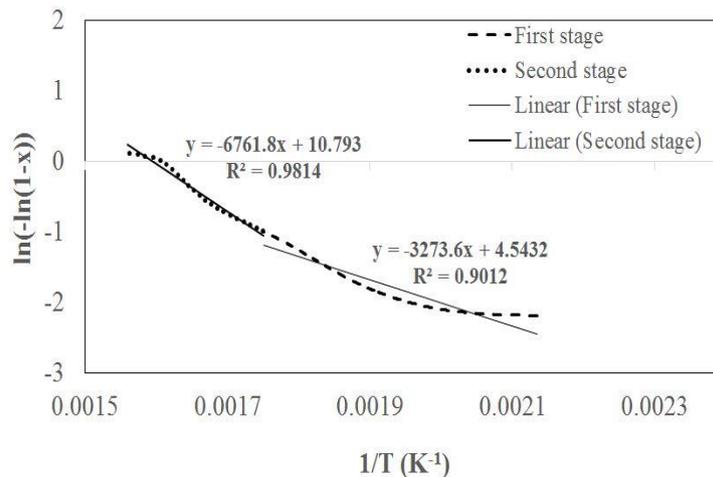


Figure 3. Arrhenius ($\ln(-\ln(1-x))$) versus $1/T$ plot at 10 K/min for oil palm frond in pyrolysis process.

Table 4. Kinetic evaluation for pyrolysis of palm oil frond for first stage decomposition

Heating rate (K/min)	First stage		
	E_A (kJ/mol)	A (1/min)	R^2
10	33.77	55	0.9539
20	29.56	45	0.9506
30	38.11	316	0.9537
40	29.05	60	0.9543
50	32.92	196	0.9535

Table 5. Kinetic evaluation for pyrolysis of palm oil frond for second stage decomposition

Heating rate (K/min)	Second stage		
	E_A (kJ/mol)	A (1/min)	R^2
10	56.22	8828	0.9814
20	52.93	9200	0.9598
30	60.89	46826	0.9775
40	57.74	31578	0.9873
50	64.60	176927	0.9891

4. Conclusions

In this research study, oil palm frond is used as the biomass sample for pyrolysis process using the thermogravimetric analysis (TGA) equipment to study the thermal degradation behaviour and determine the kinetic parameters such as activation energy and pre-exponential factor values. The heating rate studied are from 10 to 50 K/min in the temperature range of 323-1173 K under non-isothermal condition. The temperature range for the first and second stage of degradation in the pyrolysis of oil palm fronds are 468-604 K and 571-704 K respectively. It is estimated that the activation energy and pre-exponential

factor values is in the range of heating rate studied are 29.05 - 64.60 kJ/mol and 45-176928 min⁻¹ respectively.

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