

PYROLYSIS KINETICS OF OIL-PALM SOLID WASTE

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ABSTRACT

Pyrolysis of oil-palm shells, a cheap and abundantly available solid waste from palm oil producing process, was carried out using thermogravimetric analysis. The effect of heating rates (10, 15, 20 and 25°C/min) on the kinetic parameters (activation energy, frequency factor and reaction order) was investigated. The oil-palm shells were pyrolyzed in an inert atmosphere using nitrogen as a medium gas. It is observed that the kinetic behavior of the samples can be divided into three zones. The first zone was in the temperature around 300-380°C, the second zone was 380-450°C while the third zone was from 450-850°C. The analysis have shown that the reaction orders for the regions I, II and III were second, first and zero orders, respectively. While the activation energy for the zones I, II and III were found to be in the range of 54-65, 34-41 and 5-8 kJ/mol, respectively. Results also showed that the activation energy was relatively constant at different heating rate.

Keywords: Pyrolysis, Reaction order, Activation energy, Oil-palm shells, TGA

I. INTRODUCTION

Biomass includes a wide range of fuels such as wood, agricultural crops, forest and agricultural residues. Biomasses such as cherry stone [1], pinewood [2], olive pulp [3], coconut shell [4], almond shell, nutshell, apricot shell, and grape seed [5] were used to produce activated carbon. In Malaysia, which is the largest palm oil producer in the world, about 2 million tonnes (dry weight) of oil-palm shells and 1 million tonnes of extracted fibers are estimated to be produced annually [6]. Oil-palm shells could be a source for fuels, energy generation and activated carbon production.

Amongst thermochemical transformation, pyrolysis has received much attention, since the process conditions can be optimized to produce liquids, which may be upgraded to fuels, and solid. Char may be useful as a fuel, either directly (briquettes) or as char-oil and char-water slurries and also in activated carbon production [7].

Development of proper thermochemical conversion processes for oil-palm shells and design and operation of related equipment require the determination of kinetic parameters (i.e., activation energy, frequency factor and reaction order) of the pyrolytic process and detailed understanding of the pyrolytic mechanism. Thermogravimetric analysis (TGA) is one of the most common techniques used to investigate thermal events and kinetics during pyrolysis of biomass [8, 9, 10, 11]. It provides a measurement of weight loss of the sample as a function of time and temperature. 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 [9, 10]. Nassar (1999) [10] identified two thermal events during the pyrolysis of both bagasse and rice straw by assuming a pseudo first-order reaction. Mansaray and Ghaly (1999) [9] investigated the behavior of rice husks in a similar manner and two thermal events were identified in the firing process. Reina et al (1998) [11] carried out a thermogravimetric study of the pyrolysis of three different types of waste wood (forest wood, oil furniture and used pallets) in a TGA equipment using dynamic and isothermal techniques. They reported that the own chemical composition of each type of wood play a fundamental role in the kinetic behavior of their decomposition. The interesting fact that emerges out of past studies conducted in thermogravimetric analysis (TGA) to date is that the understanding of kinetics of the thermal decomposition of fuels is crucial to the designing and operation of conversion systems.

This work aims to identify the thermal events taking place during pyrolysis of oil-palm shells using thermogravimeter analysis (TGA). The kinetic parameters (activation energy, reaction order, and frequency factor) for the thermal decomposition of oil-palm shells were determined.

II. EXPERIMENTAL PROCEDURE

The oil-palm shells were collected from Seberang Perai Selatan, Malaysia. The starting material were washed and soaked for a day to remove the oil-residue and dirt. Then, it was dried in an oven at 105 °C for 24 hours. The samples were then ground and sieved to several specific particle size ranging; 0.5-1.0 mm, 1.0-2.0 mm, and 2.0-3.0 mm. The samples sized 1.0-2.0 mm was used in the experiments.

Pyrolysis was carried out using Thermal Gravimetric Analyzer (TGA-7) supplied by Perkin-Elmer, USA. The TGA unit was equipped with the analyzer that was coupled with a TG controller (TAC 7/DX). Highly purified nitrogen (99.9995% purity) was used to create inert atmosphere inside the furnace. Different heating rates varied from 10, 15, 20 and 25°C/min were applied on the samples. The samples were heated up to temperature of 850°C and hold until the remaining weight is unchanged.

The thermogravimetric analysis was done in order to find out the proximate analysis of the samples that was expressed in term of moisture, volatile matter, fixed carbon and ash contents (Table 1). The sample was heated from room temperature up to 110°C in an inert atmosphere for a complete dehydration and followed by decomposition at 850°C for 7 minutes to determine the quantity of volatile matters. The atmosphere then changed to be oxidizing. The sample was then cooled to 800°C and maintained at this temperature until its weight remained unchanged. The data acquisitions and processing were performed by the Pyris software version 3.72.

Table 1: Proximate Analysis of the Oil-Palm Shell (wt%)

Moisture	Volatile matter	Carbon	Ash
9.5	74.6	15.8	<1

III. THEORY

Reaction kinetic parameter; activation energy, reaction order, and frequency factor can be determined by thermogravimetric analysis. In this pyrolysis solid-state reaction, Arrhenius equation is being applied. The decomposition reaction can be expressed as [13]:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} (1-\alpha)^n \quad (1)$$

where A is frequency factor of the pyrolytic process, E_a is the activation energy of the pyrolytic process, R is the universal gas constant, T is absolute temperature, n is the order of reaction, t is the time and α is defined in terms of the change in mass of the sample and is given as:

$$\alpha = \frac{w_0 - w}{w_0 - w_f} \quad (2)$$

where w_0 , w and w_f are initial, actual and final weight of the sample, respectively. In order to determine the values of the kinetic parameters, integration is used to solve equation (1). For a constant heating rate q ($q=dT/dt$), the reaction rate equation (1) is expressed by the following equation:

$$\frac{d\alpha}{dT} = \frac{A}{q} e^{-E/RT} (1-\alpha)^n \quad (3)$$

Separating variables, re-arranging and integrating equation (3), and equation (4) can be obtained:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{A}{q} \int_0^T e^{-E/RT} dT \quad (4)$$

Since the limited integral $\int e^{-E/RT} dT$ has no exact integral, and the function $e^{-E/RT}$ can be expressed as an asymptotic series and integrated, with the higher-order terms ignored [13]. The following can be obtained:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{qE} \left[1 - \frac{2RT}{E} \right] e^{-E/RT} \quad (5)$$

Rearranging and expressing equation (5) in a logarithmic form:

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{qE} \left[1 - \frac{2RT}{E} \right] \right] - \frac{E}{RT} \quad \text{for } (n \neq 1) \quad (6)$$

The term $2RT/E$ is $\ll 1$ at the operating conditions studied, equation (6) becomes

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \ln \left[\frac{AR}{qE} \right] - \frac{E}{RT} \quad \text{for } (n \neq 1) \quad (7)$$

If $n = 1$, the following equation is to be applied

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{qE} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad \text{for } n = 1 \quad (8)$$

Thus, a plot of K,

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] \quad \text{vs.} \quad \frac{1}{T} \quad \text{if } n \neq 1$$

or

$$\ln \left[-\frac{\ln(1-\alpha)}{T^2} \right] \quad \text{vs.} \quad \frac{1}{T} \quad \text{if } n = 1,$$

should result in a straight line of slope $-E/R$ for the proper value of n . The criterion used for acceptable values of E and A is that the final value of n should yield values of E whose linear correlation coefficients are the best.

IV. RESULTS AND DISCUSSION

Figure 1 shows the residual weight fractions of oil-palm shells undergoing pyrolysis at various heating rates, 10, 15, 20 and 25 °C/min. The TG curves showed an initial decrease in the weight of samples between 50 and 130 °C due to the release of moisture in the samples. This was not taken into account for the determination of thermal events.

It is evident from the three step nature of the TGA curves and three peak characteristics of the derivative thermogravimetry (DTG) curves (Figure 2) that oil-palm shells exhibit three distinct reaction zones during thermal decomposition. Each zone has its own characteristics. The first zone was found in the temperature around of 300-380 °C, the second zone was in the range 380-450 °C while the third zone was from 450-850 °C. At temperatures in

the range of 30-130 °C, small endotherms, corresponding to the evolution of water present in the samples and external water bounded by surface tension, were observed. However at temperatures 300-380 °C, very rapid degradation rates of oil-palm shells were observed in the first reaction zone whereas lower thermal degradation rates were observed in the second reaction zone between 380-450 °C. A very low degradation was observed in the third reaction zone in temperature between 450-830 °C. At temperature above 830°C, the thermal degradation of oil-palm shells ceased, leaving 10-20% residue. It could be also seen from Figure 2 that there is no obvious lateral shift in the thermograms for different heating rates.

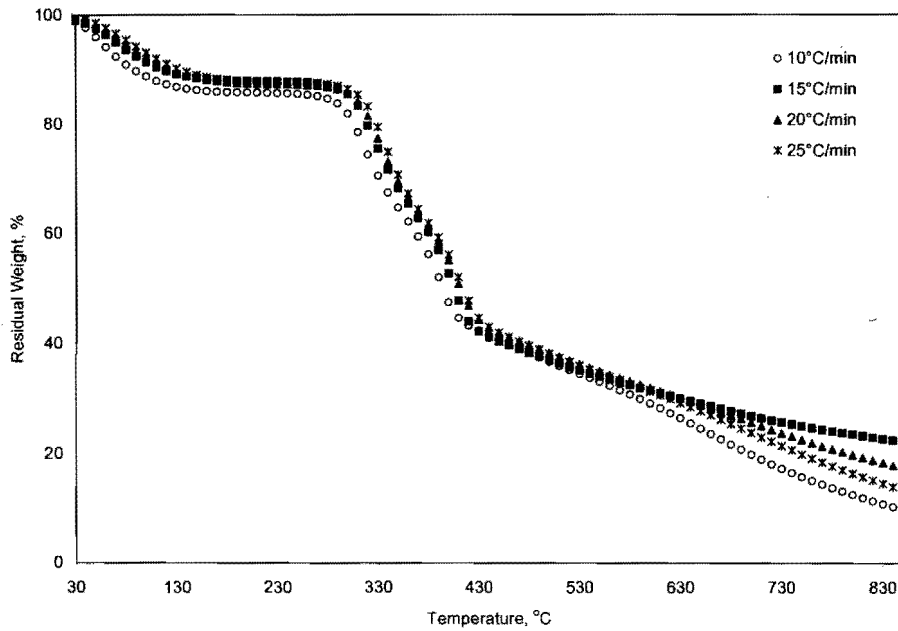


Figure 1: Residual Weight Fractions for Pyrolysis of Oil-Palm Shells at Various Heating Rates

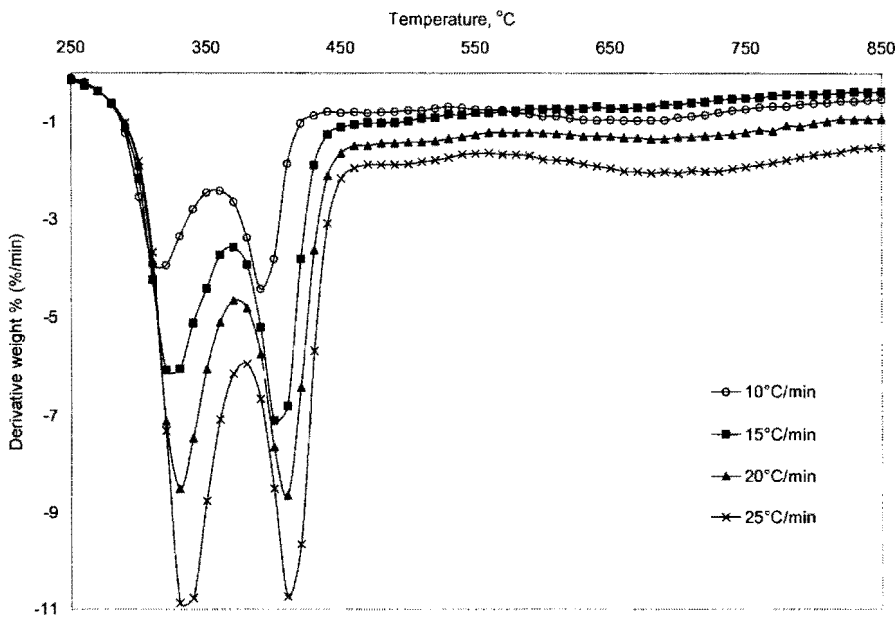


Figure 2: Derivative Thermograms (DTG) for Pyrolysis of Oil-Palm Shells

The rapid trend degradation rates of oil-palm shells observed in the first and second reaction zones is due to the high volatile content and low fixed content (Table 1) in biomass samples. The polymers of cellulose, hemicellulose and lignin, which constitute the macromolecular structure of the biomass and other woody materials, are linked together with weak ether bonds (R-O-R). These bonds are less resistant to heat at low temperatures (400-500 °C) [14].

Because of the three-step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic parameters to describe the thermal degradation over the entire temperature range with higher accuracy. Therefore, the kinetic parameters (activation energy, pre-exponential factor and order of reaction) of each of samples were determined with high correlation coefficients (all above 0.98) for the first, second and third reaction zones separately by applying the multiple linear regression analysis method to the thermogravimetric data. The kinetic parameters obtained for the three reaction zones are presented in Tables 2-4. It can be seen from Table 2 that for all heating rates shown in first reaction zone, the orders of reaction were around 2, indicating a second-order reaction mechanism for the pyrolysis of oil-palm shells. Similarly, it can be noted that for the second and third reaction zones (Tables 3 and 4) for all heating rates shown, the orders of reaction were first and zero, indicating a first and zero-order reaction mechanisms, respectively for the pyrolysis of oil-palm shells.

Table 2: Kinetic Parameters for the Zone I

Heating rates (°C/min)	Activation energy, E (kJ/mol)	Reaction order, n	Frequency factor, A (s ⁻¹) x 10 ⁻⁴	R ²
10	54.0	1.9	1.53	0.99
15	61.7	1.9	5.62	0.99
20	63.1	2.0	8.36	0.99
25	65.3	2.0	12.60	0.99

Table 3: Kinetic Parameters for the Zone II

Heating rates (°C/min)	Activation energy, E (kJ/mol)	Reaction order, n	Frequency factor, A (s ⁻¹)	R ²
10	33.9	0.7	25.3	0.99
15	39.4	0.7	60.4	0.99
20	40.7	1.0	877.0	0.99
25	40.9	1.0	877.0	0.99

Table 4: Kinetic Parameters for Zone III

Heating rates (°C/min)	Activation energy, E (kJ/mol)	Reaction order, n	Frequency factor, A (s ⁻¹)	R ²
10	7.9	0	2.13	0.99
15	5.7	0.35	0.76	0.99
20	6.1	0	1.59	0.99
25	7.1	0	1.84	0.99

It can also be seen that as the heating rate was increased from 15 to 25 °C/min, the activation energy for first, second and third reaction zones remained almost constant, in the range 61.7-65.3, 39.4-40.9 and 5.8-7.1 kJ/mol, respectively. However, for heating rate of 10°C/min, slightly lower activation energies were observed for first and second reaction zones.

It can also be seen from Tables 2-3 that the frequency factor was dependent on heating rate, increasing progressively from 1.53x10⁴ to 12.60x10⁴ and 25.33-8.77x10² for first and second reaction zones, respectively. The results show that the activation energy was remained constant when higher heating rate applied while frequency factor, A was steadily increased. This suggested that the pyrolytic reaction would be easier and faster when higher

heating rate is applied. However for the third reaction zone, the frequency factors were independent on heating rate (Table 4).

The lower kinetic parameters obtained in the third zone compared to those obtained in the first and second reaction zones, may be due to the fact that lignin, which has lower decomposition rates than cellulose and hemicellulose components of oil-palm shells, was condensed to char [15]. Similar results have been reported by Mansaray and Ghaly (1999) [9] in their study of pyrolysis of rice husk.

Hornof et al [16] studied the effect of lignin content on the thermal degradation of wood pulp and found that the reactions above 330 °C are mostly dominated by the decomposition of lignin, which is the case in the second and third reaction zones. They also observed significant decreases in the degradation rate and activation energy with increasing lignin content above 330 °C.

Figures 3-5 show the linearization of $\ln K$ against $1/T$ at different heating rates for their respective regions. The regression correlation value, R^2 of those linear straight lines is acceptable where the value is almost 1. The slope of each line was found to be nearly identical and this produce identical value of activation energy required for the reaction to occur in the pyrolytic process for each heating rates.

Figure 6 shows that activation energy for each reaction zone is uniform along the pyrolytic process. Energy required to activate the first reaction zone is the highest compared to others. In this period, almost all the organic compounds inside the sample have been released to the atmosphere. Weight of the sample loss very tremendously and this is proved by the weight loss characteristic in Figure 1 and 2. It is estimated that 40% of the sample weight is loss during the reaction in zone I.

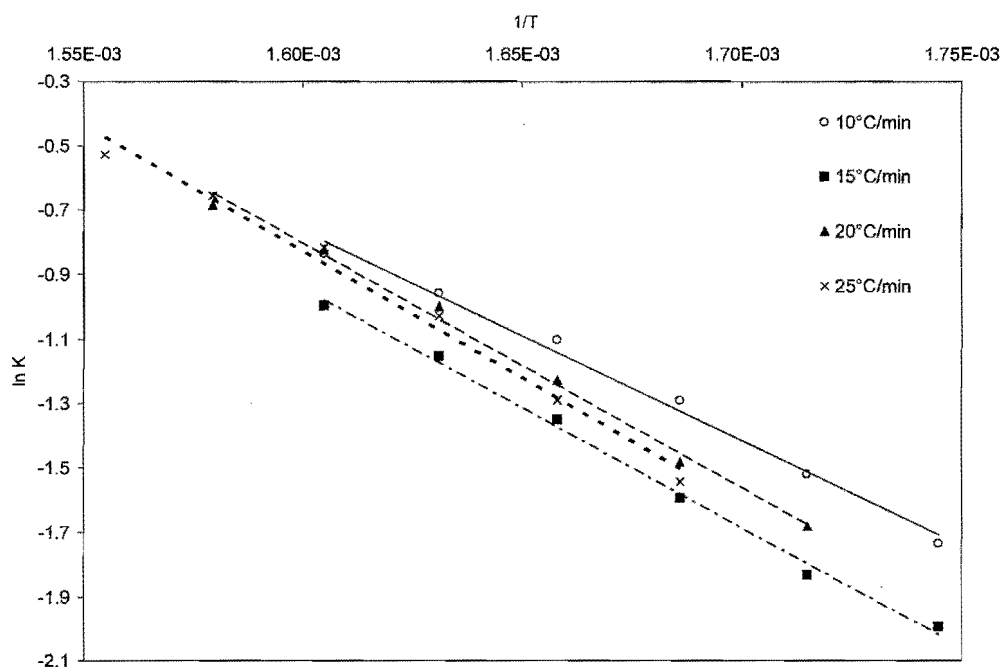


Figure 3: Arrhenius-Plots of the Degradation through the First-Reaction Zone at Various Heating Rates

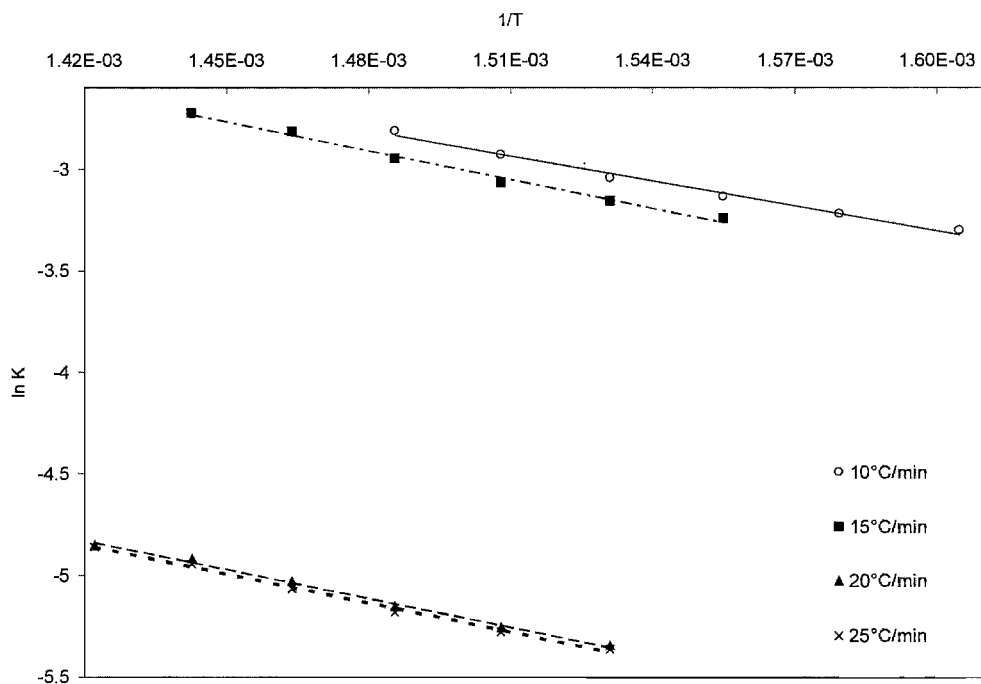


Figure 4: Arrhenius-Plots of the Degradation through the Second-Reaction Zone at Various Heating Rates

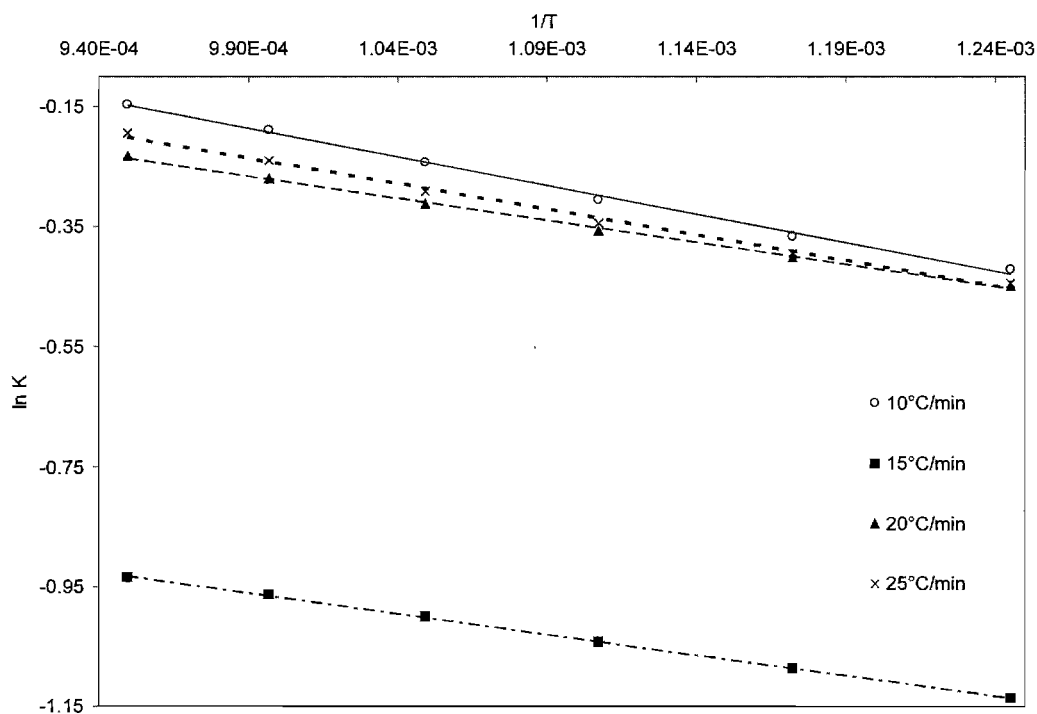


Figure 5: Arrhenius-Plots of the Degradation through the Third-Reaction Zone at Various Heating Rates

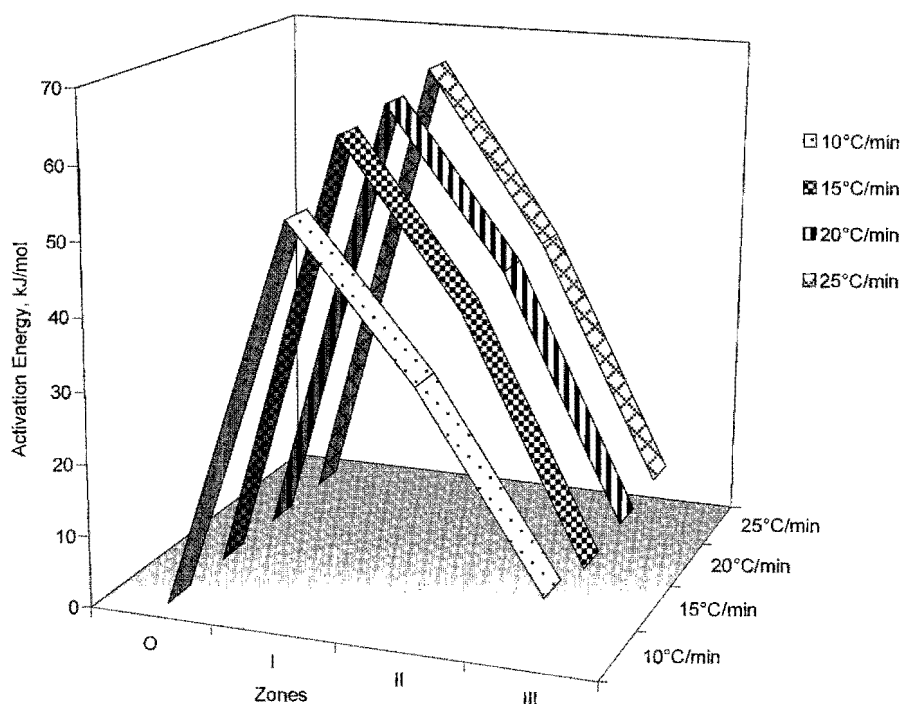


Figure 6: Plots of Activation Energy versus Reaction Zones at Different Heating Rates

Based on the thermogravimeter analysis, heating rate was found to have no significant influences on the pyrolysis of oil-palm shell, a cheap and abundantly available solid waste. Kinetic parameters (activation energy, frequency factor and reaction order) were obtained by curve-fitting the experimental data. Pyrolytic reaction for oil-palm shell was found to be divided into three different zones. Each zone has its own characteristics. The first zone was found in the temperature around of 300-380 °C; the second zone was in the range 380-450 °C while the third zone was from 450-850 °C. The analysis shown that the reaction orders for the zone I, II and III were second, first and zero, respectively. The activation energies for zones I, II and III were found to be in the range 54-65, 34-41 and 5-8 kJ/mol; respectively. Results show that as heating rate was increased, the activation energy remained relatively constant, but the frequency factor was shown to depend on heating rate.

Nomenclature

A	frequency or pre-exponential factor of the pyrolytic process (s^{-1})
E	activation energy of pyrolytic process (J/mol)
K	reaction rate constant (s^{-1})
n	order of reaction
q	Constant heating rate, (K/min)
R	universal gas constant, 8.3145 (J/mol K)
T	absolute temperature (K)
T_0	initial or ambient temperature (K)
t	time (s)
W	weight fraction of raw material
w	actual weight of the sample (mg)
w_0	initial weight of sample (mg)
w_f	final weight of sample (mg)

α fraction of starting material consumed ($\alpha = \frac{w_0 - w}{w_0 - w_f}$)

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