

# The Kinetic Study of Malaysian Poultry Processing Dewatered Sludge (PPDS) Combustion Using Iso-Conversional Model Free Method

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**Abstract** – *The kinetic study of Malaysian Poultry Processing Dewatered Sludge (PPDS) from two different origins, namely PPDS 1 and PPDS 2, has been conducted by using thermogravimetric analysis (TGA). The temperature from 30°C to 1000°C was set in oxidizing atmosphere at four different heating rates. The TG and DTG profiles from the TGA result depicted that the combustion characteristic of both samples is different in every stage. Differences in fuel characteristic influenced the thermal behaviour of the samples. In this study, two models from the iso-conversional model free method, namely Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) models were adopted to calculate the kinetic parameters. The average activation energy of PPDS 1 is lower than PPDS 2, which describes that the reaction mechanism of PPDS 1 is easier and requires less time to complete compared to PPDS 2. The difference in extracting PPDS between two origins of waste at sludge water treatment process slightly affected the outcome of this analysis. Copyright © 2014 Penerbit Akademia Baru - All rights reserved.*

**Keywords:** Thermogravimetric Analysis, Biomass, Combustion, Kinetic, Activation Energy

## 1.0 INTRODUCTION

Biomass waste receives a major interest in ongoing renewable energy studies towards the efforts to meet the increasing energy needs of the modern society. In the practice of recovering energy from biomass waste material, an in-depth understanding of the thermal conversion process is essential, especially involving thermochemical reaction kinetics. Biomass can be effectively converted into the source of energy by applying thermochemical conversion process. In thermochemical conversion process of solid fuel, reaction kinetic is one of the important features, as well as its fuel characterization. Combustion reaction kinetics has been intensively investigated for the past few decades for a variety of conventional solid fuels and commonly found biomass waste materials. However, it is not well defined for currently proposed biomass waste such as poultry processing waste. A comprehensive understanding of how fast a reaction takes place and a well-defined minimum energy required during the combustion process of poultry processing waste will contribute to the new concept towards an efficient design and an effective operation of the thermal conversion process.

Poultry processing industry in Malaysia is currently growing to support the increasing demands of local consumption, as well as accommodate the needs of marketing and supplying chicken meat to Asian market. The slaughtering process of broiler industry generates a huge amount of

solid by-product that is not be intended for human consumption. The waste known as poultry processing dewatered sludge (PPDS) has been going through wastewater treatment, which contains internal organs, trimmings, feathers, blood and others [1]. According to Ibrahim *et al.* [2], this waste material obviously contributes towards environmental problems such as waste disposal due to scarcity of land, harmful to the surrounding environment as the waste undergoes a slow degradation process and produces an awful stench. PPDS fuel potential for biomass feedstock for the purpose of power generation has been investigated recently by many researchers [2][3][4]. Based on the conclusion, PPDS with high calorific value, high carbon content and low sulphur is comparable to coal, and therefore can be potentially used as a fuel for thermal conversion technologies in power generation plant.

The reaction kinetics of common solid fuels have been thoroughly investigated and published for coal, while some preliminary data is available for biomass waste materials such as wood [5], rice husk [6], date palm residues [7][8], oil palm waste [9] and sewage sludge [10]. However, the data pertaining reaction kinetics during combustion of PPDS in available literature is very limited. The purpose of this study is to determine the reaction kinetic parameter, namely activation energy of PPDS by using thermogravimetric analysis (TGA). In this study, the comparison of combustion behaviour and reaction kinetics of PPDS from two selected origins was conducted. Two different iso-conventional model free methods, namely Flynn-Wall-Ozawa method and Kissinger-Akahira-Sunose method were adopted to calculate the activation energy.

## **2.0 METHODOLOGY**

### **2.1 Material**

In this research work, PPDS samples collected from two different plants were analysed for their reaction kinetics in oxidizing atmospheres using non-isothermal thermogravimetric kinetic analysis. An iso-conventional method (model free) was used together with the data measured using a thermogravimetric analyzer (TGA) in obtaining the kinetic parameters.

The PPDS samples were taken from the plants located at the North region (Plant 1) and the South region (Plant 2) of Peninsular Malaysia. It is important to highlight that these two plants have similar production of waste but the processes in extracting the waste material are different. This biomass material derived by slaughtered poultry has high moisture content. Before proceeding with any analysis, the removal of moisture content of the sample was first performed by oven drying at the temperature of 105°C for 24 h.

### **2.2 Thermogravimetric Analysis (TGA)**

The samples were analyzed to determine the main properties that affect thermal conversion. These include proximate analysis, ultimate analysis and calorific value test. The data of proximate analysis including moisture content, volatile matter, fixed carbon and ash was assessed by using thermogravimetric analysis. Ultimate analysis was conducted to evaluate the content of carbon (C), hydrogen (H), nitrogen (H), and sulphur (S) of the sample. The analysis was done using the CHNS analyzer. Calorific value test was carried out to measure the higher heating value of PPDS sample, which was performed by using a bomb calorimeter.

Thermogravimetric analysis was carried out using thermogravimetric analyzer Labsys Evo Setaram. Approximately 10 mg sample was measured and filled in an alumina crucible. A non-

isothermal TGA under dynamic condition with the temperature from 30°C to 1000°C was ramped in oxidizing atmosphere. The experiment was repeated for heating rate,  $\beta$  equal to 5, 10, 15 and 20 K/min. The reason of varying these four heating rates is to allow for the calculation of kinetic parameters. On increasing the temperature, TG and DTG curves were continuously recorded by the TGA software.

### 2.3 Kinetic Theory

The model fitting and model free (iso-conversional) methods are the two models that are available to perform the calculation of kinetic analysis. However, compared to model fitting, iso-conversional method is often used by numerous researchers. Without prefixing the reaction order, the computation of kinetic parameters can be defined. The sufficient flexibility of model free to allows the change of mechanism during the direction of reaction, and minimizing the mass transfer limitation by using several heating rates is also the one of the reasons this model is applied by many researchers[11][12].

Devolatilization of biomass reaction mechanism is assumed to progress as a single reaction in a one-step global model [5] and can be expressed as:



where the rate constant of reaction,  $k$  can be explained by the Arrhenius equation.

$$k = A e^{-E/RT} \quad (2)$$

where  $E$  is the activation energy (kJ/mol),  $T$  is the absolute temperature (K),  $R$  is the gas constant ( $8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ) and  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ). The rate of conversion from solid state to volatile product (heterogeneous solid-state reaction) is described by the following equation:

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

where  $\alpha$  represents the degree of conversion,  $t$ ,  $k(T)$  and  $f(\alpha)$  represent the time, the rate constant and the reaction model, respectively. Equation (4) can be produced when converting equation (3) and obeys from the Arrhenius equation.

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

At a non-isothermal state with a constant heating rate,  $\beta = \frac{dT}{dt}$ , equation (4) can be transformed into the following equation (5).

$$\frac{d\alpha}{dt} = \frac{1}{\beta} A e^{-\frac{E}{RT}} f(\alpha) \quad (5)$$

By integrating both sides of equation (5),

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \quad (6)$$

The implementation of iso-conversional method involves a series of TGA experiment that can be done at various heating rates in the same condition [13]. In this study, two frequently used iso-conversional methods; the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were applied to determine the kinetic parameter. In order to complete the calculation for FWO method, the Doyle's approximation of  $p(\chi)$  was practised [14]. The corresponding temperature of fixed value conversion degrees was determined, which yield at every heating rate. The calculation using FWO method is expressed by the following equation (7). A plotted graph of  $\ln(\beta)$  versus  $1000/T$  yielded a straight line with slope  $-1.052E/R$  s. From this equation, the activation energy  $E$  can be obtained.

$$\ln(\beta) = \ln \left[ \frac{AE}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E}{RT} \quad (7)$$

For the calculation of activation energy using KAS method, the following equation (8) was used. The activation energy,  $E$  can be calculated from the slope,  $E/RT$  which was obtained by plotting the graph of  $\ln(\beta/T^2)$  versus  $1000/T$ .

$$\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{Eg\alpha} \right) - \frac{E}{RT} \quad (8)$$

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Fuel Analysis

Table 1 shows the fuel characteristics of both PPDS 1 and PPDS 2 for proximate analysis, ultimate analysis and calorific value test. The result shows that PPDS 1 has high content of moisture, fixed carbon and ash compared to PPDS 2. It is worth noticing that low moisture and ash content, and high volatile matter makes the material becomes an attractive fuel for thermochemical conversion process. High moisture content has a disadvantage that it will affect the combustion performance during the ignition stage [15]. In addition, high moisture content tends to reduce the calorific value. This can be proven by the findings in Table 1 where PPDS 2 with low moisture content has high calorific value than PPDS 1.

**Table 1:** Proximate, ultimate and calorific value analysis for PPDS 1 and PPDS 2

Analysis	PPDS 1	PPDS 2	± Percentage Difference (%)
<b><i>Proximate Analysis (wt. %)</i></b>			
Moisture Content	8.66	2.02	76.67
Volatile Matter	57.28	85.81	49.81
Fixed Carbon	22.46	8.51	62.11
Ash	11.6	3.66	68.45

***Ultimate Analysis (wt. %)***

Carbon	69.95	52.85	24.45
Hydrogen	10.66	8.87	16.79
Nitrogen	3.29	5.66	41.87
Sulphur	0.96	0.80	16.67
Calorific Value (MJ/kg)	22.9	23.43	2.26

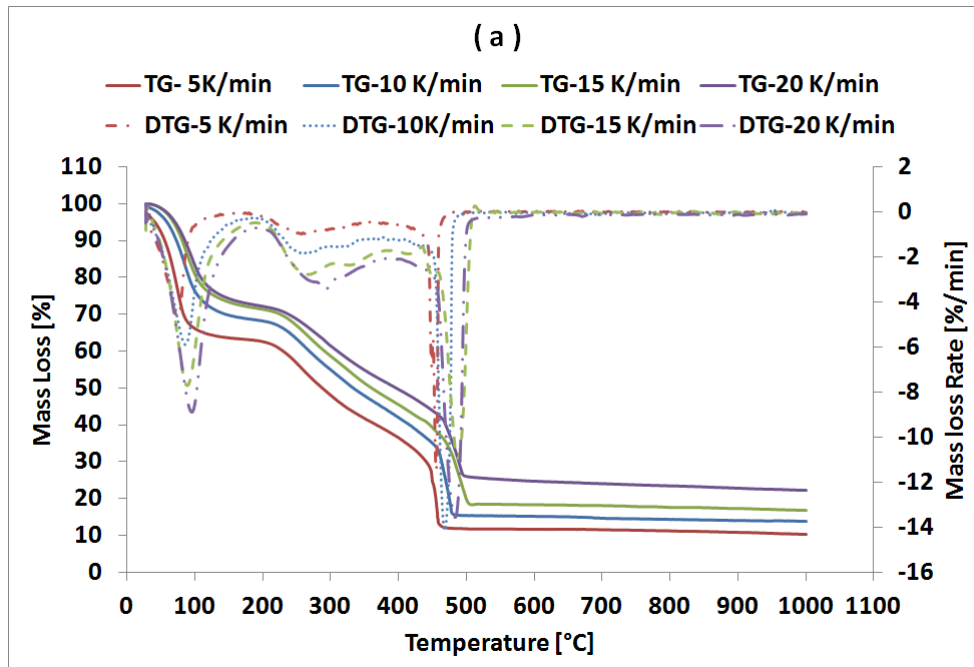
The calorific value of PPDS is significantly higher compared to other biomass and the value is close and comparable to coal [4]. Calorific value is an important characteristic that indicates the available energy per unit mass in the sample. High calorific value shows its viability for solid fuel resources. Ultimate analysis result shows that PPDS 1 has higher C, H and N content than PPDS 2. The next feature to be highlighted is nitrogen content. Compared to other biomass sample, nitrogen content for PPDS is considered high, which can cause problems related to emissions of nitrogen oxides in combustion process [16].

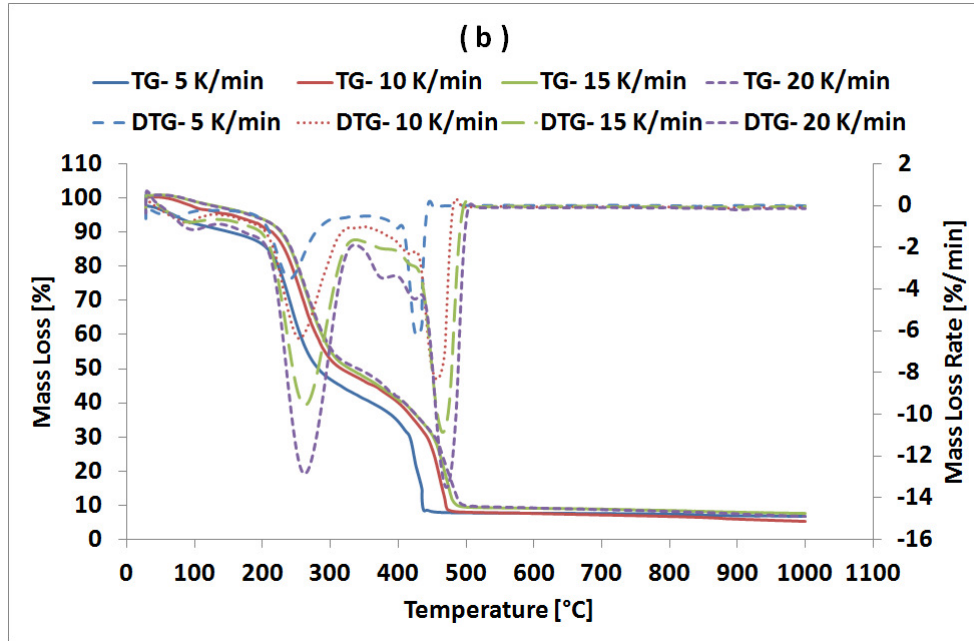
### 3.2 Thermal Behaviour

A non-isothermal thermogravimetric analysis (TGA) was conducted in this study with the temperature range between 30°C up to 1000°C in oxidizing atmosphere. Fig. 1(a) and Fig. 1(b) illustrate the TG and DTG curves captured by the software of TGA during the analysis at four different heating rates respectively. The mass of sample dwindled as the temperature increased. This can be described by the TG curves. The DTG curve reflects the percentage of mass loss per unit time against temperature. As can be seen from the graphs, the DTG curves show 3 different peaks, which can be described as (i) evaporation of moisture, (ii) devolatilization process and (iii) char combustion process.

The TG and DTG profiles at each stage are shown in Table 2. Tr refers to the temperature range, ML is the mass loss in percentage unit, DTGmax is the maximum mass loss rate and Tp refers to the peak temperature corresponding to the DTGmax. According to Table 2, for PPDS 1, evaporation of moisture in stage 1 happened at the temperature of 30°C-200°C, while devolatilization process and char of combustion took place at the temperature range of 200°C-400°C and 400°C-520°C respectively. Conversely, for PPDS 2, the temperature range for these 3 stage is between 30°C-160°C (evaporation of moisture), 160°C-340° (devolatilization process) and 340°-520°C (combustion of char). The DTG peak for PPDS 1 in the first stage is high for every heating rate. As can be observed from the table, DTGmax of PPDS 1 at this stage is greater than DTGmax of PPDS 2. The percentage of mass loss (ML) at this stage is also higher, which ranged from 28% to 37% for PPDS 1, while for PPDS 2, the ML is just around 4% to 13%. As for the temperature range during the first stage, PPDS 1 ends at T=200°C, whereas PPDS 2 stops earlier at T=160°C. To relate with the proximate analysis result in Table 1, PPDS 1 has higher moisture content than PPDS 2, thus it reacts actively and requires higher temperature to complete the process in the first stage, which can be attributed to evaporation of moisture.

At the second stage, the characteristics of both samples behave oppositely. The mass loss and DTGmax of PPDS 1 are less than PPDS 2 as listed in Table 2. This result influences the DTG curves, where its bend is shorter and wider for PPDS 1 while PPDS 2 has high value of peak height. PPDS 1 has low volatile matter, thus the reaction is slower compared to PPDS 2. On the contrary, high fixed carbon content in PPDS 1 caused higher peak height in DTG curve (DTGmax) in the third stage compared to PPDS 2. However, the mass loss percentage depicted not much difference for both samples in this stage. These results show good agreement with the study on combustion kinetic of biomass conducted by X. Fang et al. [17]. They stated that with high volatile matter than the fixed carbon content in biomass, the peak in DTG curves at the second stage during combustion is significantly higher than the third stage. This feature corresponds to the burning rate in combustion process.





**Figure 1:** TG and DTG curves at different heating rates for (a) PPDS 1 and (b) PPDS 2

**Table 2:** TG and DTG profiles of PPDS 1 and PPDS 2

Sample	Stage 1				Stage 2				Stage 3			
	Tr	ML	DTGmax	Tp	Tr	ML	DTGmax	Tp	Tr	ML	DTGmax	Tp
	(°C)	(%)	(%/min)	(°C)	(°C)	(%)	(%/min)	(°C)	(°C)	(%)	(%/min)	(°C)
PPDS1												
5	30- 200	37	-4.65	74.33	200- 400	27	-1	256.6	400- 465	24	-11.47	455.2
10	30- 200	32	-5.89	85.71	200- 400	26	-1.85	258.2	400- 500	26	-14.16	467.8
15	30- 200	29	-7.71	88.83	200- 400	25	-2.79	267.9	400- 518	28	-10.93	487.1
20	30- 200	28	-8.90	95.47	200- 400	22	-3.43	292.0	400- 520	24	-13.57	483.3
PPDS2												

5	30- 160	13	-0.25	74.33	160- 340	62	-3.53	239.7	340- 460	26	-6.28	428.0
10	30- 160	10	-0.81	89.04	160- 340	52	-6.37	254.3	340- 490	32	-8.33	457.2
15	30- 160	6	-0.8	93.09	160- 340	53	-9.58	262.2	340- 510	31	-10.88	465.6
20	30- 160	4	-1.3	106.3	160- 340	49	-20.3	272.0	340- 520	26	-13.48	465.9

### 3.3 Kinetic Analysis

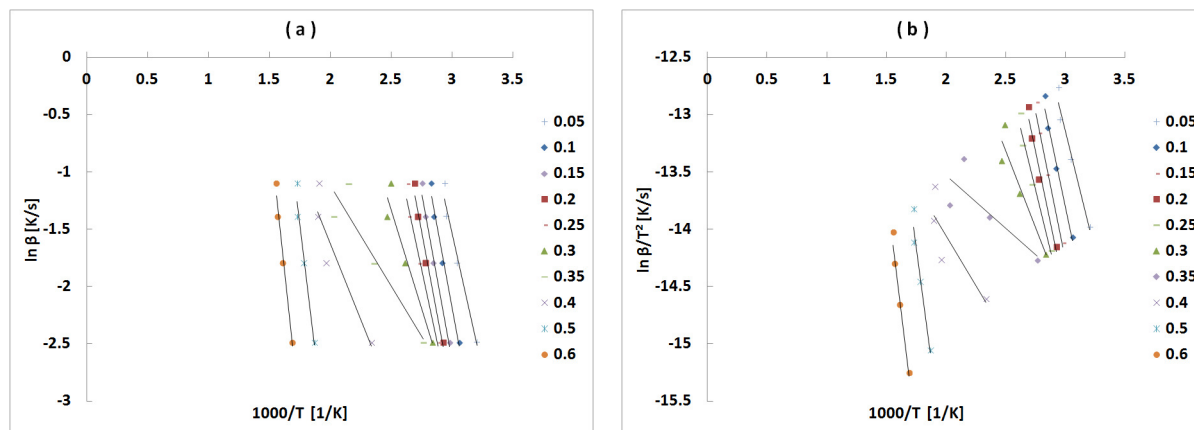
The data of TG curves in study have been used for the calculation of kinetic parameter. In this study, two different models from iso-conversional model free method, the FWO and KAS methods were applied. A few steps of rearrangement and modification of the mathematical equation for the kinetic parameters calculation as described in the kinetic theory section above will then derive an equation for both FWO and KAS method as stated in equation (7) and equation (8) respectively. The plotted FWO and KAS method regression lines for PPDS 1 and PPDS 2 are shown in Fig. 2 and Fig. 3 respectively. Ten conversions,  $\alpha$  ranged from 0.05 to 0.6 were employed to determine the variation of activation energy during the combustion process. As can be observed, each conversion gives a straight line where the slope,  $m$  is subsequently used to calculate the activation energy. The data in Table 3 demonstrate the calculated activation energy,  $E_a$  and correlation coefficient,  $R^2$  for both FWO and KAS methods. The apparent activation energy of PPDS 1 and PPDS 2 fluctuated at each conversion degrees.

In order to achieve better understanding of the relation between the apparent activation energy and conversion degrees, the curves in Fig. 4 have been plotted. As can be observed, the activation energies at each conversion degrees are different for both samples. The variation of activation energy at every conversion explained the needs of different energy value during the combustion process. It can be deduced that during the decomposition process, a complex multi-step mechanism occurs. Thus, differences in reaction mechanism at every conversion during the decomposition process explains the variation of activation energy [5].

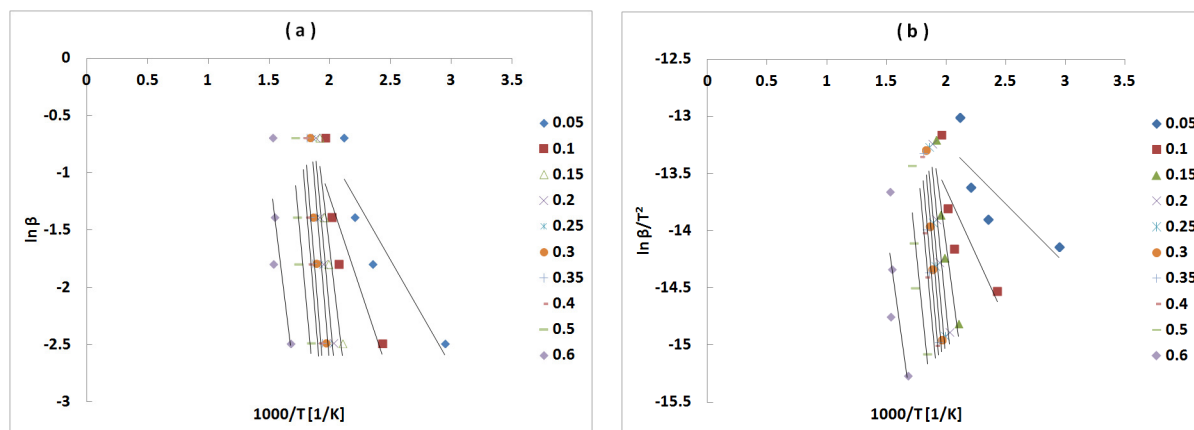
The activation energy for PPDS 1 dropped from conversion,  $\alpha=0.05$  until  $\alpha=0.35$ . The activation energy increased sharply until it reaches the highest value. In contrast, activation energy for PPDS 2 rose gradually, achieving stable value at conversion of 0.25 to 0.4 and reached a slight fall at the end. The distinction of apparent activation energy with respect to the conversion between PPDS 1 and PPDS 2 as shown in Fig. 5 reveals the fact that the thermal decomposition of both samples progresses in different ways. This may be due to the dissimilarity of fuel characteristic embedded in the samples as reported in Table 1. Regardless of the method used, the average activation energy for PPDS 2 is greater than PPDS 1. Since the activation energy defines the parameter of the minimum energy required to break down the chemical bond between atoms, reaction with high activation energy needs more energy and longer time to react [18]. Therefore, during the entire decomposition process, it can be concluded that the time reaction of PPDS 1 is lesser and proceeds easier than the reaction of



PPDS 2. In comparison between the models used, the value of activation energy obtained by the FWO method is higher than the KAS method. In this study, it can be suggested that FWO method is more appropriate and reliable to be applied for the activation energy calculation as most of the correlation coefficient,  $R^2$  values calculated are higher and close to 1. However, one should focus on discussing the differences of activation energy value at every conversion, which is related to the reaction mechanism in solid state rather than comparing the result between the two methods used.



**Figure 2:** Linear fitting plot of different conversion of PPDS 1 for (a) FWO method and (b) KAS method



**Figure 3:** Linear fitting plot of different conversion of PPDS 2 for (a) FWO method and (b) KAS method

**Table 3:** Kinetic parameters obtained from FWO and KAS methods for PPDS 1 and PPDS 2

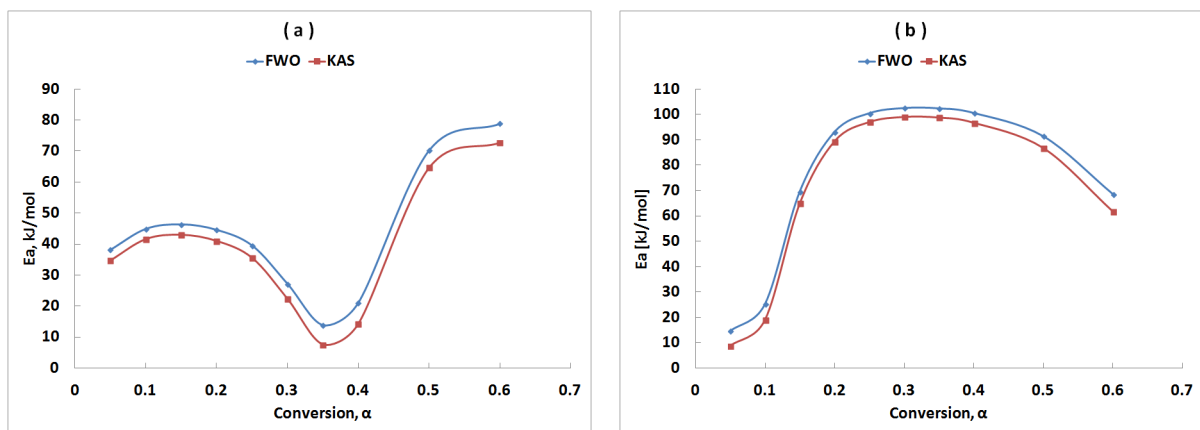
Conversion ( $\alpha$ )	Activation Energy, $E_a$ FWO method (kJ/mol)	$R^2$	Activation Energy, $E_a$ KAS method (kJ/mol)	$R^2$
<i>PPDS 1</i>				
0.05	38.22	0.967	34.79	0.957
0.1	44.98	0.976	41.67	0.970
0.15	46.42	0.979	43.05	0.973

0.2	44.64	0.976	41.05	0.967
0.25	39.56	0.967	35.58	0.957
0.3	27.18	0.929	22.32	0.889
0.35	13.86	0.883	7.63	0.664
0.4	21.13	0.862	14.37	0.727
0.5	70.34	0.958	64.75	0.946
0.6	78.90	0.977	72.76	0.971
Average	42.52		37.80	

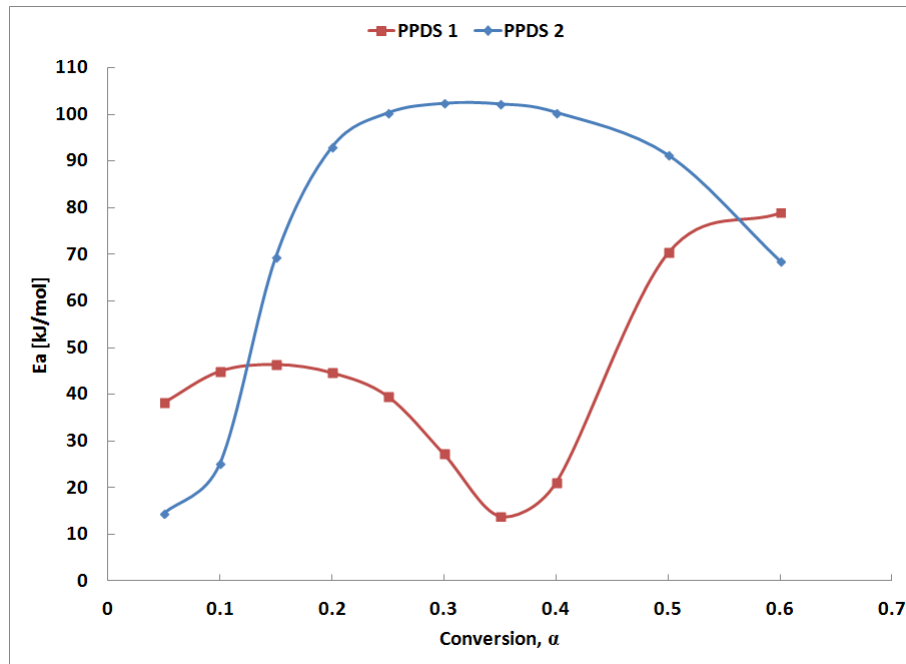
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**PPDS 2**

0.05	14.58	0.846	8.781	0.659
0.1	25.22	0.812	18.98	0.693
0.15	69.57	0.911	64.93	0.891
0.2	93.08	0.938	89.44	0.927
0.25	100.4	0.935	97.02	0.925
0.3	102.5	0.931	99.04	0.920
0.35	102.3	0.920	98.90	0.907
0.4	100.5	0.896	96.76	0.879
0.5	91.36	0.796	86.79	0.761
0.6	68.58	0.666	61.78	0.594
Average	76.81		72.23	



**Figure 4:** Plot of activation energy versus conversion for FWO and KAS method of (a) PPDS 1 and (b) PPDS 2



**Figure 5:** Plot of activation energy versus conversion of FWO method for PPDS 1 and PPDS 2

#### 4.0 CONCLUSION

Thermogravimetric kinetic analysis of PPDS sample from two different origins, namely PPDS 1 and PPDS 2 has been successfully carried out. Combustion characteristic in thermograms and kinetic parameters for both samples show different results. This study reveals that despite the same sample, PPDS from different origin does not reflect similar fuel characteristic and combustion behavior. This may be due to the process in extracting the sample at the water treatment stage. This point has to be considered as the condition in the next extended study to generalize the standard of the sample.

The outcome of this analysis is essential as it provides information on combustion kinetic behavior trends of PPDS biomass in Malaysia. The results obtained in this study are helpful to provide information about thermal characteristic that later may be beneficial to convert this kind of waste for solid fuel in thermochemical conversion applications. In conclusion, further investigations are still required to ensure the potential use of PPDS as a solid fuel.

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