Oxidation and Heating Kinetics of Refinery Sludge

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Abstract: Refinery sludge is one of the major industrial wastes that needs to be handled and treated . Therefore, this study aim to investigate the Kinetics of devolatilization and oxidation of the refinery sludge collected from a typical petroleum refinery plant located in Malaysia . Thermo Gravimetric Analyzer (TGA) was used in this study for modeling of the devolatilization and oxidation processes in presence of nitrogen inert gas and oxygen. Two reaction models are proposed here to describe the devolatilization while the oxidation reactions can be adequately described by a three-parallel-reaction models. The results show that the significant devolatilization reactions occur in the range of 192.76 - 500 ^{o}C. After a temperature of 500 ^{o}C the oxidation reactions are predominant. The activation energy, reaction order and pre-exponential factor were determined using three heating rate 10, 20 and 30 ^{o}C min^{-1} and appropriate temperature are monitored to optimize the de-volatilization and oxidation reactions of the refinery sludge. The results show that, the heating rate has no significant effect of activation energy value. But Increasing the heating rate appeared to increase the start and end temperatures of each stage and shift DTG peaks to a higher temperature,. For all heating rates the third reaction of the three parallel oxidation reaction model has the highest activation energy ranged from 126.830- 472.277 kJ mol^{-1} with the lowest H/C ratio. The proposed reaction models could give useful information for treatment of refinery mixed sludge and design a proper system for oxidation and heating processes.

Keywords: TGA, Kinetics, oxidation, devolatilization, refinery sludge.

INTRODUCTION

Petroleum refineries generate relatively large amounts of sludge waste from, tank bottoms, waste water, and so on. The accumulation of crude storage tank is a comparatively serious problem experienced by most refineries worldwide. The settling out of crude oil heavy fractions rust and sand can ultimately cause refinery problems when sludge is introduced into the plant. It can cause fouling of heat exchangers as explained in [1].

The Oil sludge contains mainly heavy organic compounds and a large amount of combustible matters with high heating values, so break down large molecules into smaller ones by pyrolysis has been proven to be an alternative to dispose it . The benefit of using such a process not only minimizes or disposes the volume of solid waste but also yields valuable products, by converting this stored energy into a usable energy source, [2].

The pyrolysis of oil sludge was investigated by thermogravimetry/mass spectroscopy (TG/MS) and in a horizontal quartz reactor with an electrical laboratory furnace under different pyrolysis conditions such as the influence of heating rate from 5 to 20 ^{o}C min^{-1}, final pyrolysis temperature from 400 to 700 ^{o}C, various interval holding stage, and three additives including a fluid catalytic cracking catalyst, NaOH and Cu(NO$_3$)$_2$.3H$_2$O were employed as the catalyst for promoting oil sludge pyrolysis in terms of less solid residue production [3].

The kinetics of pyrolysis of API separator sludge obtained from an oil company in Thailand were studied [4]. Results showed that typical derivative curves of the sludge consist of two major peaks. The first peak was found between 230 and 270 ^{o}C while the other was found between 415 and 400 ^{o}C.

An alternative approach for modelling the sludge as a continuous mixture by using an Arrhenius type- kinetics expression was proposed in [5]. They employed a two-step technique to construct the distribution of model parameters such as activation energy, pre-exponential factor and the reaction order. Their skeleton model could be utilized for thermal contractor design, without taking into account the detailed structure of the chemical scheme involved.

The pyrolysis of waste sludge was investigated using thermogravimetry/mass spectrometry (TG/MS) and a fixed-bed reactor. Two types of sludge were used, namely mixed sludge and oil sludge. In TGA/MS measurements, two degradation steps were observed. Degradation of organic structures, in sludge took place in the first step, while inorganic materials in sludge were mainly decomposed in a second step (above 500 ^{o}C). The total weight losses of pyrolysis process was found to be 66 and 62 wt% for mix Sludge and oil sludge, respectively, [6].

The degradation kinetic of oil sludge in the presence of carbon dioxide, have reported one reaction model with activation energy E of 71.8 kJ mol^{-1} ,frequency factor A of $3.26 * 10^5$ and reaction order n of 2.66. And two reaction models with kinetics parameter of E of 69.3, and 126 kJ mol^{-1}, A of $4.83 * 10^5$ and $1.2 * 10^9$, and n of 2.92 and 1.48 for the first and seconded reaction respectively. Also three reaction models with E of 66.2, 84.3 and 126 kJ mol^{-1}, A of $4.44 * 10^5$ and $1.99 * 10^6$, and $1.2 * 10^9$, and n of 2.96 , 2.19 and 1.48 for the first, seconded and third reaction respectively, [7].

The five-parallel-reaction kinetic models have been proposed to predict the experimental results at various constant heating rates (5.2, 12.8, and 21.8 K min^{-1}) and different concentrations of oxygen atmosphere (4.83, 8.62, 12.35, and 20.95 Vol % O$_2$) in the temperature range of 380-1123 K . The significant reactions were found to be occurred in the range 415- 931 K. Below a temperature of 613 K, pyrolysis reactions are predominant. Including the pyrolysis reactions, the overall oxidative thermal decomposition of oil sludge described by a five-parallel-reaction model [8].

The kinetics of the pyrolysis process was investigated by one-reaction and two-reaction global kinetic model by three methods for (KAS method, Flynn and Wall method and Friedman method). It was found that, The arithmetic means of the activation energy calculated by KAS, Flynn–Wall and Friedman method are 112, 117, 113 kJ mol^{-1}, respectively, which are almost same. Advantages that can be attributed to KAS method are that it can locate the peak maximum temperature besides the unnecessary knowledge of the reaction mechanism to calculate E. Nevertheless its dependence in the accuracy of the peak position may be the main disadvantage of the method. Considering the difficulty in locating the values of maximum peak temperature and other parameters associated with the peak temperature by using KAS method, Flynn and Wall method could give a better result. But since it is based on mathematical approximation, therefore Friedman method can be considered to be the best among the three methods.KAS method, and Flynn and Wall method give better result[9].

A simple method without any omission was used for computing the thermal degradation kinetics model of the sewage sludge based on the TG curves. All the TG curves are divided into three parts which are beginning decomposition temperature range, main decomposition temperature range, and final decomposition temperature range. The second one is employed to determine the parameters for more than 70% of the total mass loss occurs in this range. The kinetics parameters obtained at different heating rates of 10, 15, 20, and 50 ^{o}C min^{-1} such as the reaction order, reaction energy and pre-exponential factor are obtained, which are in the range of 3.9 - 4.1, 82.3–109.2 kJ mol^{-1} and $7.7 * 10^6$ - $2.8 * 10^9$ min^{-1}, respectively. According to their developed method, indicate that this method is appropriate for simulating pyrolysis kinetics of sewage sludge, [10].

Many papers have been published about the pyrolysis, biodegradation and combustion characteristics of sewage and oily sludge. However, not much has been reported on the kinetics of devolatilization and oxidation of refinery sludge. Refinery sludge is a mix sludge of a typical petroleum refinery plant located in Malaysia. This sludge is made up of biological (effluent treatment), petroleum base (crude tank farm) and mixed sludge (from pond/lift station desludging). Of the three mentioned above, the biological sludge makes up the major portion of refinery sludge. This biological sludge usually contains heavy metals (copper, lead, cadmium, arsenic, zinc etc.), polyaromatic hydrocarbon and other heavy bottoms hydrocarbon which can have an adverse effect on human and the environment. This sludge is categorized under schedule waste 3. The aim of this work was to investigate the kinetics of devolatilization and oxidation of selected local refinery sludge by means of thermo gravimetric analysis (TGA). The basic behavior of thermal conversion and thermal reaction kinetics of the sludge were investigated from room temperature to 800 ^{O}C under an inert atmosphere.TGA analysis was carried out in pure N$_2$ to investigate the devolatilization kinetics reaction and in oxygen to study the kinetics of oxidation. The current TGA method used here to consider only the weight loss by heating the sludge at high temperatures at various heating rate. The kinetics parameters such as activation energy, reaction order and pre-exponential factor were determined by the modified shrinking core-model (Friedman model) then the influence of heating rate was also incorporated to modify the Friedman model.

MATERIAL AND METHOD

The refinery sludge sample used in this work was treated sludge where the sludge undergoes a dewatering, compression by the addition of a polymer followed by air drying process. The "as-received" sample appears to be black, viscous and in the form of semi-solid cake at ambient temperature. the characteristic properties of this sample (proximate and ultimate analysis based on ASTM methods D 5142 and D 5373 respectively and calorific value of the sample was measured by employing a bomb calorimeter in accordance with ASTM D 5865 are shown in table 1.

TABLE (1) Analysis of refinery sludge properties

Ultimate analysis (wt %)					Proximate analysis (wt %)				Heating Value kJ g^{-1}
C	H	N	S	O	moisture	volatile	Fixed carbon	ash	
56.4	7.8	5.32	2.03	28.44	6.05	58.14	23.71	12.1	26.783

The semi-solid sludge collected from the local petroleum refinery was dried for 24 hours at 378 K. Approximately 4 mg of the dried sample was placed in the pan of the Perkin Elmer Pyris 1 TGA unit. The sludge sample was thermally heated from room temperature to 800 ^{O}C at various heating rates of 10, 20 and 30 °C min^{-1}. Under pure N_2 gas atmosphere with a flow rate of 20 ml min^{-1} to investigate the kinetics of devolatilization. In order to investigate the kinetics of oxidation of refinery sludge, the test was repeated using similar above conditions, but the N_2 replaced with oxygen gas.

RESULTS AND DISCUSSION

Thermo gravimetric analysis provides a prior knowledge of initial and final temperatures for thermal degradation of sludge, [6]. From TG and DTG curves the devolatilization and oxidation process of the refinery sludge can be divided into two and three main stages over the temperature range for various heating rates(β =10, 20 and 30 ^{o}C min^{-1}). The weight loss with time at a fixed flow rate and different heating rates was recorded to evaluate the kinetics of devolatilization and oxidation of dry refinery sludge. in order to describe the difference between the pyrolysis behaviour (under nitrogen) and oxidation reaction (under oxygen) of the sludge at the same condition and heating rate of (β = 20 ^{o}C min^{-1}) the weight fraction % and derivative weight %. min^{-1} were plotted versus the reaction temperature as it shown in figure 1,a and figure 1,b respectively.The results of TG and DTG of (figure 1,a&b) show a comparison between the devolatilization (under N_2) and oxidation (under O_2) processes of two runs at same conditions (heating rate of 20 ^{o}C min^{-1} and final temperature of 800 ^{o}C). from the figure1,a the TG shows curves of the devolatilization and oxidation processes have a similar trend till 500 ^{o}C then the degradation of the former was due to release of inorganic components . but the later one shows a sharp degradation from 500-800 ^{o}C. this is could be due to fixed carbon released as CO_2.

The devolatilization and oxidation of the sludge took place in four degradation stages. A first period of mass reduction before 200 ^{o}C is about 4.78 wt. % and 7.83 wt.% was due to released of moisture content for the former and the later process respectively. At the second degradation stage, the mass decrease is observed between 200 and 390 ^{o}C involves weight loss around 41.788 wt.% and 33.25 wt.% of the original weight this loss mainly related to volatilization and decomposition of organic matters in the sludge.The third period of mass observed between (390-500 ^{o}C) and involves weight loss around 21.822 and 21.249 wt.% and this is caused by decomposition of more complex organic structures corresponding to a larger fraction , [6]. After temperature of 500 ^{o}C the devolatilization weight loss slightly reduced to around 7.321wt.% and this mass loss could be due to degradation of inorganic compounds as indicated by [2, 3 and 6]. Whereas for the oxidation process the weight loss of about 24.143 wt, this was due to combustion of carbon and degradation of inorganic materials occurred together at this stage for oxidation process only. After 500 ^{o}C the volatile material released from the sludge sample and only fixed carbon remained which is oxidized under oxygen at temperatures ranged from 500 ^{o}C to 800 ^{o}C.The oxidation of fixed carbon is shown in figure 1, b by the third DTG peak located between 500 -640 ^{o}C.

From fgure1,b it can be seen that the devolatilization process shows two peek located between 200-500 ^{o}C while the oxidation shows three peaks located between 500-640 ^{o}C. The residue of devolatilization and oxidation process are found to be 26.296 and 13.476 %. the later process residue is considered as ash content for the proximate analysis.
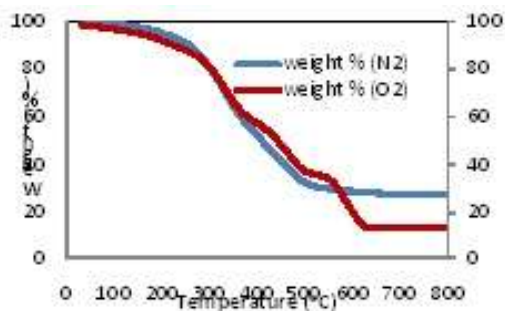
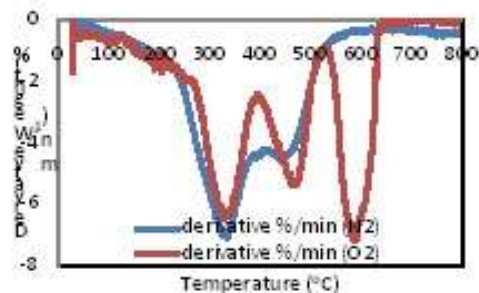**FIGURE 1,a . A plot of weight % vs. temperature at heating rate β = 20 °C min⁻¹**

Figure 1,b. A plot of derivative weight in min⁻¹ temperature at heating rate β = 20 °C min⁻¹

Effect of Heating Rate on Devolatilization and Oxidation Process

The influence of using various heating rates, 10, 20 and 30 °C min⁻¹ on Refinery sludge devolatilization and oxidation processes are shown by DTG and TG curves at figure 2, a-d. As it can be seen from figure 2,a (under nitrogen) and figure 2,b (under oxygen), that the DTG curve has two and three peaks respectively for all heating rates with slightly different position. Here in this part the influence of heating rate on peak positions and weight loss % at different stages will be investigated in details.The heating rate has slight effect on the temperature ranges for devolatilization and oxidation processes (figure 2,a-d). However, shifting the start and end temperatures of each stage to a bit higher value is shown by increasing the heating rate, and this is could be due to the heat transfer limitations. This in agreement with [2,9] At low heating longer time could be required for the purge gas to reach equilibrium with the furnace temperature which provide a larger thermal energy to the system and the temperature needed for the sample to decompose is also low. While at the same time the opposite occurs at high heating rate (a shorter reaction time with higher temperature needed to decompose the sample). This causes shifting of DTG (maximum reaction rate curve) to the right, [11]. Because of the a consequence of heat and mass transfer limitations (surface particle temperature higher than core of a particle temperature), it is recommended to have a small particle, homogenous sample and heat transfer surface between the sample and the crucible as large as possible, [12]. It has been approved that the large sample mass loading and a higher heating rate tend to deflect the measured temperature from the actual sample temperature [13].

Table 2 shows weight loss percentages at various temperature ranges for devolatilization and oxidation processes. From table 2 it can be seen the higher heating rate did not affect the total weight loss at any stage. It can be seen that the weight loss % form room temperature up to 200 °C for devolatilization process was observed to be in a range of 2.312 - 4.780 % while for oxidation process the range is 4.732 - 7.839 % , which is higher for the later process. this could be due to oxidation of hydrogen presence in the sample at low temperature to form more molecules of H_2O which then released at temperature ≤ 200 °C.

From the same table it can be seen that the weight loss in the inert nitrogen at temperature range of 200-390 °C (vm1) was in range of 39.318 - 43.537 while the weight loss in oxygen for the same temperature ranges was in range of 33.25 -37.733. The lower weight loss for the later could be due to oxidation of some volatiles matter with formation of a liquid complex oxidized compounds which are very difficult to release at temperature ≤ 390 °C. These oxidized compounds are found to be released at higher temperature above 500 °C. This is could be explained by counting the total weight loss % after 500 °C for both processes. As it can be seen that the total weight loss after 500 °C for the oxidation process were 3.007 %, 4.002 %, and 5.43824 % higher than the total weight loss % for devolatilization process, for the heating rate 10, 20, and 30 °C min⁻¹ respectively.

FIGURE 2,a DTG curves of the refinery sludge devolatilization at heating rates 10, 20 and 30 °C min^{-1}

FIGURE 2,b DTG curves of the refinery sludge oxidation at heating rates 10, 20 and 30 °C min^{-1}
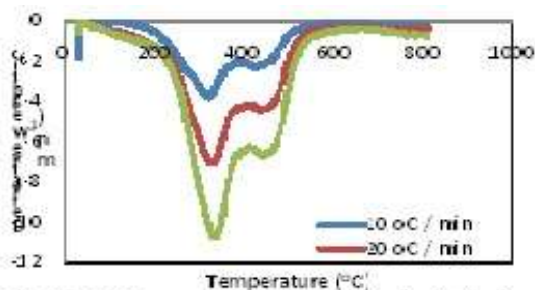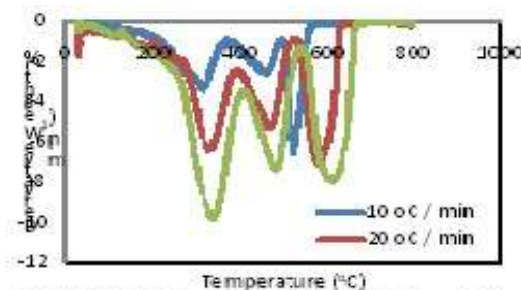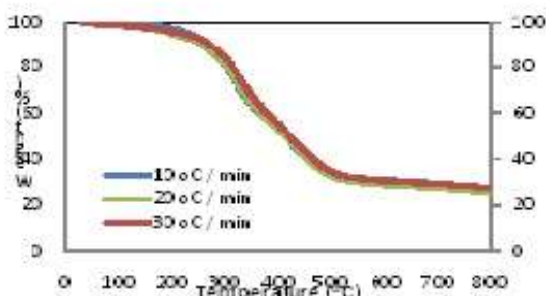
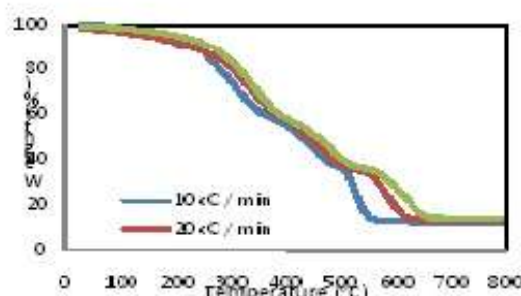FIGURE 2,c TG curves of the refinery sludge devolatilization at heating rates 10, 20 and 30 °C min^{-1}

FIGURE 2,d TG curves of the refinery sludge oxidation at heating rates 10, 20 and 30 °C min^{-1}

TABLE (2) devolatilization and oxidation wt.% at different heating rate and temperatures ranges.

Temp range (^{o}C)	Devolatilization wt. %	Heating rate (^{o}C min^{-1})		
		10	20	30
Room temp-200	Moisture	2.312	4.78	3.912
200-390	Vm1	43.537	41.788	39.318
390-500	Vm2	21.33	21.822	22.194
500-800	inorganic	7.012	7.321	7.323
At 800	residue	25.794	26.296	27.159
Temp range(^{o}C)	Oxidation wt. %	Heating rate (^{o}C min^{-1})		
		10	20	30
Room temp-200	Moisture	6.043	7.839	4.732
200-390	Vm1	37.733	33.25	35.671
390-500	Vm2	20.411	21.249	19.56
500-800	Fixed carbon+ inorganic	23.713	24.143	25.859
At 800	ash	12.1	13.476	14.06124

A third stage of mass decrease is observed between 500-800 ^{o}C is a relatively small weight loss (around 7.012-7.323) wt.% of the original weight). The weight loss of oil sludge in this temperature range might be mainly attributed to the decomposition of inorganic materials calcium (such as $MgCO_3, CaCO_3$, etc.) as recommended in [2]. based on the above analysis It was observed that the final devolatilization residue is approximately 25.794 - 27.159 wt.% of the original weight, which is consistent with the sum of fixed carbon and ash . Also a higher heating rate leads to a higher fraction of final solid residue, which in agreement with [14]. The oxidation process shows an ash content ranged from 12.1-14.06 wt.% of the original weight.

Kinetics Models

Friedman model is an improvement of shrinking core model which assumes that, the reaction happen only on the surface of spherical particle and non-reacted core would shrink gradually in reaction process. when reaction is the control step the shrinking core model can be written as:

$$\frac{dx}{dt} = 3\tau[1-x]^{2/3} \tag{1}$$

Where t is particle consuming time
adapted From [15].

By using integrated model (Friedman model), however the global kinetics of refinery sludge devolatilization and oxidation can be described in [16] as

$$\frac{dx}{dt} = k(1-x)^n \tag{2}$$

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{3}$$

The conversion (x) can be defined as:

$$x = \frac{w_o - w_t}{w_o - w_e} \tag{4}$$

By rearranging equations (2) and (3) into the following form as per equation (5):

$$\ln\left(\frac{dx}{dt}\right) = \ln\left[k_0(1-x)^n\right] + \left(\frac{-E^F}{R}\right)\left(\frac{1}{T}\right) \tag{5}$$

The slope of the natural logarithm of conversion rate [(dx/dt) vs. 1/T] gives the value of Friedman activation energy' E^F 'Rearranging equation (5) gives rise to the equation (6):

$$\ln\left(\frac{\frac{dx}{dt}}{\exp\left\langle -\frac{E}{RT}\right\rangle}\right) = \ln k_0 + n\ln(1-x) \tag{6}$$

The Friedman activation energy was determined by equation (5), and the values for $(1-x)$ and (dx/dt) was derived from the experimental data. The pre- exponential factor k_0 and reaction order n could be easily constructed by finding the slopes and intercept of equation (6) at various conversion rates of (x). Equation (7) can be further refined value to obtain the value for 'E^R' by rearranging Equation (6) to give:

$$\ln\left(\frac{dx/dt}{(1-x)^n}\right) = \ln K = \ln k_0 + \left(\frac{-E^R}{R}\right)\left(\frac{1}{T}\right) \tag{7}$$

By incorporating the heating rate in Friedman model Thus, the activation energy could be also obtained as :

$$dx/dT = k_0/\beta \exp\left(-E/RT\right)(1-x)^n \tag{8}$$

$$\beta = dT/dt \tag{9}$$

$$\ln\left(\frac{dx/dT}{(1-x_i)^n}\right) = \ln\left(\frac{k_0}{\beta}\right) - \frac{E^\beta}{R}\frac{1}{T_i} \tag{10}$$

The n-value is determined by equation (6) optimized based on high linear correlation coefficient of the straight line

using part of the data at each stage. after the reaction order (n) is selected carefully, a plot of $\ln\left(\dfrac{dx}{dT(1-x)^n}\right)$ versus 1/T

will yield a straight line with slope of (E/R) and intercept of $\ln(k_0/\beta)$ at a given temperature range. The kinetics results are shown tables 3,4 and 5 for three different heating rates 10, 20 and 30 ^oC min^{-1} respectively.

TABLE (3) Kinetic parameters of devolatilization and oxidation of refinery sludge at heating rate of 10 ^{o}C min^{-1}

devolatilization stages (Temp range ^{o}C)	E^F KJ mol^{-1}(R^2)	E^R KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	E^β KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	n (R^2)
Stage 1 (200-390)	35.060 (0.962)	39.625 (0.938) [327.013]	39.957(0.954) [351.280]	2.5 (0.803)
Stage 2 (390-500)	44.297(0.982)	91.213 (0.983) [14.836 × 10^5]	90.257 (0.984) [12.675 × 10^5]	2.701 (0.803)
Oxidation stages (Temp range ^{o}C)				
Stage 1 (200-390)	35.625 (0.991)	40.073 (0.993) [295.302]	39.383 (0.993) [255.848]	1.786 (0.868)
Stage 2 (300-500)	43.199 (0.981)	94.422 (0.989) [29.285 × 10^5]	93.466 (0.992) [25.019 × 10^5]	2.847 (0.804)
Stage 3 (500-800)	258.374 (0.913)	472.277 (0.996) [24.348 × 10^{30}]	485.937 (0.969) [37.924 × 10^{31}]	1.96 (0.923)

TABLE (4) Kinetic parameters of devolatilization and oxidation of refinery sludge at heating rate of 20 ^{o}C min^{-1}.

devolatilization stages (Temp range ^{o}C)	E^F KJ mol^{-1}(R^2)	E^R KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	E^β KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	n (R^2)
Stage 1 (200-390)	31.036 (0.85)	52.262 (0.868) [95.091 × 10^2]	54.274 (0.936) [22.375× 10^3]	3.643 (0.822)
Stage 2 (390-500)	48.479 (0.898)	100.117 (0.917) [66.319 × 10^6]	103.609 (0.960) [15.144 × 10^7]	2.963 (0.707)
Oxidation stages (Temp range ^{o}C)				
Stage 1 (200-390)	50.325 (0.963)	55.919 (0.971) [13.467 × 10^3]	54.107 (0.962) [88.904 × 10^2]	2.681 (0.824)
Stage 2 (390-500)	44.122 (0.966)	99.078 (0.99) [92.488 × 10^3]	97.473 (0.99) [70.302 × 10^5]	2.712 (0.813)
Stage 3 (500-800)	210.777 (0.929)	279.916 (0.991) [16.587 × 10^{16}]	280.265 (0.992) [1.736 × 10^{10}]	1.352 (0.892)

From the table 3, 4 and 5, it can be observed that the devolatilization process was described by two stages or bi-component reaction model, while the oxidation process was described by three stages or tri-component reaction model. The tables show three value of activation energies (Friedman activation energy(E^F) , Refined activation energy (E^R) , and the activation energy at heating rate β (E^β) all given in [kJ mol^{-1}]. The reaction order (n) with its correlation coefficient (R^2),

and pre-exponential factor (k_0) in min^{-1} are also shown. From table 3 at low heating rate 10 ^{o}C min^{-1} it can be seen that an easy desorbs of low molecular weight compound with activation energy of 39.625 kJ mol^{-1} and 40.073 kJ mol^{-1}, followed by releasing of a higher molecular weight compounds at higher temperature with a higher E value of 91.213 kJ mol^{-1} and 94,422 kJ mol^{-1} for stage 1 and 2 for devolatilization and oxidation processes respectively. As it can be seen the activation energy values for the later process is a little bit higher indicates the weight loss for the former is much easier. And for all heating rate the first reaction has a lower activation energy values than the second reaction indicate that the former corresponding to the weight loss at the low temperatures takes place much easier than the later. This in agreement with literature [8, 4, and 14].

In oxidation process of refinery sludge it can be also observed that for all heating rates the higher thermal desorption energy observed in Stage-3 as compared to Stage-1 and stage-2 indicates higher molecular weights hydrocarbons in the former. the explanation of this is that after releasing of volatile matter with high H/C ratio, the remain residue has very low H/C ratio and poor combustion reactivity which leads to a high activation energy. As documented in [17] that a high H/C ratio has high combustion reactivity and low activation energy value. Generally the activation energies values depend on the different types of species or hydrocarbons molecular weight attached to sludge surface or solid residue.

As the heating rate increased from 10 ^{o}C min^{-1} to 30 ^{o}C min^{-1} (Table 3 and 5), the refined activation energy values slightly increased from 39.625 kJ mol^{-1} to 52.619 kJ mol^{-1} and from 91.213 kJ mol^{-1} to 101.015 kJ mol^{-1} for stage 1 and 2 for devolatilization process and from 40.073 kJ mol^{-1} to 56.477 kJ mol^{-1} and from 94.422 kJ mol^{-1} to 102.836 kJ mol^{-1} for stage 1 and 2 for oxidation process. But the activation energies values decreased from 472.277 kJ mol^{-1} to 126.83 kJ mol^{-1} as the heating rate increased from 10 ^{o}C min^{-1} to 30 ^{o}C min^{-1} (the third stage of oxidation process), this indicates that at higher heating rate the release of compounds occurred rapidly with short residence time and no condensation of tar could occur form the first and second stage leaving less tar content for the third stage which required a lower activation energy to be releases from the sample.

From the same table (3 4 and 5) it can also be seen that k_0, pre-exponential factor which indicates the collision frequencies is also increasing from Stages -1 to stage -3. The lower activation energy in Stage -1 may indicate that species may be present at the outer surface and the other two much deeper in the intra or inter spaces of the ash . The reaction orders for all heating rate Stages- 3exhibits an order of 3.821 to 0.77and it selected carefully by maximizing the correlation coefficient.

TABLE (5) Kinetic parameters of devolatilization and oxidation of refinery sludge at heating rate of 30 ^{o}C min^{-1}.

devolatilization stages (Temp range ^{o}C)	E^F KJ mol^{-1}(R^2)	E^R KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	E $^\beta$ KJ mol^{-1}(R^2) [k_0 min $^{-1}$]	n (R^2)
Stage 1 (200-390)	44.347 (0.945)	52.619 (0.913) [16.123×10^3]	53.168 (0.899) [24.323×10^3]	3.821 (0.834)
Stage 2 (390-500)	64.957 (0.841)	101.015 (0.90) [63.085×10^3]	102.262 (0.965) [10.624×10^7]	2.622 (0.854)
Oxidation stages (Temp range ^{o}C)				
Stage 1 (200-390)	44.006 (0.963)	56.477 (0.976) [20.785×10^3]	56.362 (0.985) [20.419×10^3]	2.73 (0.919)
Stage 2 (390-500)	44.172 (0.968)	102.836 (0.985) [26.429×10^6]	100.433 (0.985) [17.386×10^6]	3.069 (0.807)
Stage 3 (500-800)	140.041 (0.911)	126.830 (0.912) [12.360×10^6]	127.262 (0.91) [12.130×10^6]	0.77(0.976)

Rearranging the equation (10) gives calculated conversion (x_i^{cal}). The plotting of x_i^{cal} against x_i^{exp} is used to evaluate the correlation between calculated data and experimental data and the correlation coefficient of the plots with straight line (y = x) are presented

$$\ln\left[\frac{x_{i+1}^{cal} - x_i^{cal}}{(T_{i+1} - T_i) \times (1 - x_i^{cal})^n}\right] = \ln\left(\frac{k_0}{\beta}\right) - \frac{E}{RT_i} \tag{11}$$

$$MRE = \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{x_i^{exp} - x_i^{cal}}{x_i^{exp}}\right]^2}{n}} \tag{12}$$

where n is the number of data, [9].

In this study, the contrast between experimental and calculated conversion is conducted to validate the kinetics parameters. All the plots of x_i^{exp} against x_i^{cal} and the correlation coefficient of the plots with straight line (y = x) are presented in figure 3
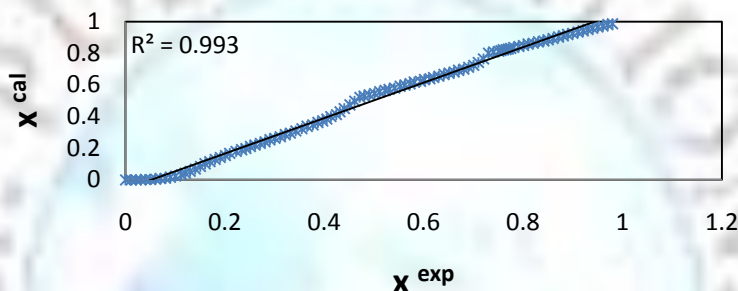

FIGURE 3: Calculated versus experimental values of conversion at heating rates of 20 ^{o}C min^{-1} for oxidation process.

As it can be seen from Fig. 3 that the calculated data fit the experimental data very well except for a few points deviation with the high correlation coefficient of 0.993. Furthermore in order to validate the latest model and to verify the applicability of the kinetic parameters the coefficient of determination (R^2) and The mean relative error MRE are represented in table 6 . From table 6 the correlation coefficient ranged from 0.978 to 0.997 with mean relative error ranged from 0.00039 to 0.0058 indicate the bi- stages and tri-stages reaction models respectively fit the experimental data very well to describe the kinetics of devolatilization and oxidation process of refinery sludge.

TABLE (6) correlation coefficient and mean relative error for simulated and experimental pyrolysis and oxidation results obtained for three different heating rates.

Model	Heating rate ^{o}C min^{-1}	R^2	MRE
pyrolysis	10	0.978	0.00301461
	20	0.996	0.005775227
	30	0.994	0.003967828
oxidation	10	0.997	0.001395096
	20	0.993	0.000392219
	30	0.995	0.001785328

CONCLUSION

Since, there is no available data on TGA studies on the kinetics of devolatilization and oxidation of dry refinery sludge from the local Malaysia petroleum refinery. Therefore this study proposed new models at different heating rates and the results obtained from our studies could be very useful for the proper design of a devolatilization and oxidation system and to add value for refinery waste sludge disposal. This study proposed a bi-stage model for devolatilization process as well as tri-stage model for oxidation process. These models are tabulated as:

β (°C min⁻¹)	Devolatilization model	Oxidation model
10	$$\frac{dx_{VM1}}{dt} = 327.013 \exp\left(\frac{-39.625}{RT}\right)(1-x)^{2.5}$$ $$\frac{dx_{VM2}}{dt} = 14.836 \times 10^5 \exp\left(\frac{-91.213}{RT}\right)(1-x)^{2.701}$$	$$\frac{dx_1}{dt} = 295.302 \exp\left(\frac{-40.073}{RT}\right)(1-x)^{1.786}$$ $$\frac{dx_2}{dt} = 29.285 \times 10^5 \exp\left(\frac{-94.422}{RT}\right)(1-x)^{2.847}$$ $$\frac{dx_3}{dt} = 24.348 \times 10^{30} \exp\left(\frac{-472.277}{RT}\right)(1-x)^{1.96}$$
20	$$\frac{dx_{VM1}}{dt} = 95.091 \times 10^2 \exp\left(\frac{-52.262}{RT}\right)(1-x)^{3.643}$$ $$\frac{dx_{VM2}}{dt} = 66.319 \times 10^6 \exp\left(\frac{-100.117}{RT}\right)(1-x)^{2.963}$$	$$\frac{dx_1}{dt} = 13.467 \times 10^3 \exp\left(\frac{-55.919}{RT}\right)(1-x)^{2.681}$$ $$\frac{dx_2}{dt} = 92.488 \times 10^3 \exp\left(\frac{-99.078}{RT}\right)(1-x)^{2.712}$$ $$\frac{dx_3}{dt} = 16.587 \times 10^{16} \exp\left(\frac{-279.916}{RT}\right)(1-x)^{1.352}$$
30	$$\frac{dx_{VM1}}{dt} = 16.123 \times 10^3 \exp\left(\frac{-52.619}{RT}\right)(1-x)^{3.821}$$ $$\frac{dx_{VM2}}{dt} = 63.085 \times 10^3 \exp\left(\frac{-101.015}{RT}\right)(1-x)^{2.622}$$	$$\frac{dx_1}{dt} = 20.785 \times 10^3 \exp\left(\frac{-56.477}{RT}\right)(1-x)^{2.73}$$ $$\frac{dx_2}{dt} = 26.429 \times 10^6 \exp\left(\frac{-102.836}{RT}\right)(1-x)^{3.069}$$ $$\frac{dx_3}{dt} = 12.360 \times 10^6 \exp\left(\frac{-126.830}{RT}\right)(1-x)^{0.77}$$

NOMENCLATURE

TGA	Thermogravimetry analysis	k_0	Pre-exponential factor (min⁻¹)
DTG	Differential thermogravimetry	f (x):	function of conversion x
E^F:	Friedman activation energy [kJ mol⁻¹]	x_i^{cal}	predicted conversion
E^R	Refined activation energy [kJ mol⁻¹]	x_i^{exp}	measured conversion
E^β:	activation energy at heating rate β [kJ mol⁻¹]	dx/dt	: conversion rate
β	heating rate °C min⁻¹	w_0:	initial mass (mg)
k	reaction rate constant (min⁻¹)	w_t:	mass of sample at time (t) (mg)
n	reaction order	w_e	mass at the end of the test (mg)
R^2	correlation coefficient	MRE	mean relative error
T	Temperature [K]	R	Gas constant J Mol⁻¹ K⁻¹

ACKNOWLEDGMENT

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