

# Utilizing the Decomposition of Onelga Oil Shale to Fix Kinetics Parameter and Heat Energy for Pyrolyser-Reactor

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**Abstract** – Oil shale in Nigeria is an emerging resource and the heat energy required to refine the kerogen content is a stiff challenge. The aim of this work is to develop the kinetics of the decomposition of the newly found oil shale in order to provide a viable process when it is explored. A dataset of thermo gravimetric analysis (TGA) of the Onelga oil shale is provided and two distinct kinetic models have been employed. The experimental techniques involve the decomposition reaction process prior to thermogravimetry/differential thermogravimetric analysis (TGA/DTGA) for non-isothermal heating conditions. The minerals in oil shale have been removed by treating the sample with hydrochloric acid. On the other hand, the pyrolysis experiments have been performed by increasing the heating temperature up to 900 °C at heating rate of 10 °C/min in an inert atmosphere of nitrogen gas. The plot of the concentration with respect to time has provided the decomposition of oil shale and yield of oil and gas. For the TGA, the second stage is significant because the organic matter decomposes and this the hydrocarbon matter decomposes within the range of 220-580 °C. At high temperatures of 750-900 °C, the loss due to decomposition of mineral matter has occurred and the bitumen has charred completely. Direct Arrhenius and integral methods have been suitable to determine the activation energies of the pyrolysis reaction. The activation energies for the organic matter of Onelga raw and acid treated Onelga oilshale samples have been 203.00–291.92 and 156.94–238.95 kJ/mol respectively. Thus, the removal of mineral matter alters the kinetic parameter of the process of oil volatility from the organic matter. The deviations in kinetic parameter between the model and the preliminary experimental data have been negligible and this validates the models obtained. **Copyright** © 2021 Praise Worthy Prize S.r.l. - All rights reserved.

**Keywords:** Thermo-Gravimetric Analysis, Oil Shale, Activation Energy, Pyrolysis, Kinetic Model

## Nomenclature

$A$	Arrhenius factor	$R_{water}$	Latent heat of vaporization for water
$b$	Constant given by E/R	$R$	Universal gas constant.
$C$	Concentration of shale reactant	$T$	Absolute temperature [K]
$C_{gas}$	Specific heat capacity of gas	$T_{sh}$	Temperature of shale at evaporation
$C_{p,sh}$	Specific heat capacity of shale	TGA	Thermo-Gravimetric Analysis
$C_{oil}$	Specific heat capacity of oil	DTGA	Differential Thermo-Gravimetric Analysis
$C_{p,water}$	Specific heat capacity of water	GC-MS	Gas Chromatography-Mass Spectrometer
$D$	Constant at intercept	FTIR	Fourier Transform Infrared
$E$	Activation energy		
$m_{oil}$	Mass of gas condensed to oil		
$m_{moisture}$	Mass of moisture		
$m_{sh}$	Mass of shale sample		
$n$	Order of the reaction		
$Q_{py}$	Heat needed to start pyrolysis		
$Q_{sh}$	Heat due to shale		
$Q_{re}$	Heat due to retort		
$Q_{gas}$	Heat carried by the gas		
$Q_{oil}$	Heat carried by oil		
$Q_{bitumen}$	Heat carried by non-evaporated shale		
$Q_{moisture}$	Heat due to initial moisture		
$Q_{py,unit}$	Unit retorting heat		
$R_{oil}$	Latent heat of vaporization for oil		

## I. Introduction

Pyrolysis occurs in retort from which fuels can be produced; the feedstock could be planted such as sugarcane waste, which can be pyrolyzed in a fixed bed pyrolyzer [1]. The forest fuel (birch leaf) has been reported by [2]. However, oil shale is a common feedstock in pyrolysis. The organic matter in oil shale is known as kerogen, which is the insoluble fraction or the organic matter possessing similar properties to crude oil and natural gas. A minute amount of this organic is bitumen, which is soluble in petroleum solvent. Oil shale has mineral components, which may affect product yield, kinetics, and the mineral content varies from one

geological region to another; some of them comprise carbonate minerals, which include dolomite, siderite, calcite, and aluminosilicate minerals [24]. Other ones are quartz, feldspar, and clay, which are silicate minerals.

Some regions contain a minute quantity of sulfide minerals, including marcasite and pyrite [3]. These minerals and metals can be obtained as a by-product after processing of oil shale, these by-products include alum ( $KAl(SO_4)_2 \cdot 12H_2O$ ), Nahcolite, sulphur, zinc, copper and other radioactive elements (uranium) [4]. In order to analyse the organic content, the common methods of calculating the kinetics are direct Arrhenius method, Coats-Redfern methods, Kissinger-Akahira-Sunose KAS, Friedman methods [5], Criado method, Flynn-Wall-Ozawa method [6] and many more [7]-[9]. Besides the fact that the mineral content influences the kinetic parameter, in all these methods reasonable assumptions are required. The use of different methods may result in different values, because the parameters may be determined under isothermal or non-isothermal system [10]. [11] has investigated the pyrolysis processing of oil shale samples using both isothermal and non-isothermal thermogravimetric analysis. Both Arrhenius and Coats Redfern have been used to estimate the kinetic parameters and it has been concluded that there is no significant difference between isothermal and non-isothermal TGA [12]. Although the estimated kinetics parameter for some samples under non-isothermal means, using Direct Arrhenius and integral method has not given the same value as the reported value from [5].

The kinetic model that describes the processing of the oil shale to yield oil and gas that are suitable and adoptable in refinery involves complicated reaction processes. Numerous research on the pyrolysis of oil shale using retorting have been reported without an indication of a general constant assigned to kinetic parameter [3]-[12], [13]. The absence of this fixed value is probably due to the constituent mineral and the hydrocarbon composition, which are defined by geological differences. Therefore, the knowledge gap in these kinetic analyses is that the peculiar hydrocarbon content decomposing is the defining factor that specifies the value of the kinetic parameter. The values for the kinetic parameter will vary with respect to the organic chemicals that constitute the feedstock of any pyrolysis.

For newly found oil shale, the kinetic model is not easily obtained because the resulting analytical tool may yield a trend that are irregular and will not fit a random kinetic model. This can be attributed to the limited available analytical techniques that can measure general kerogen decomposition. The major difficulty in this is that some pyrolysis leads to complicated kinetic parameter, which is probably not the right definition of the kinetics of the decomposition. Therefore, it is thought that the oil shale can be decomposed prior to subsection to analytical test in order to identify the indicator kinetic model that will adequately define the kinetic parameter of a pyrolysis reaction, which is the focus of this study. Obtaining the kinetic parameter for all the oil shale in

different geographical location is still a stiff challenge because there are no standard values that satisfy all the samples at various geographical locations. Here, preliminary decomposition is done to provide the indicator of the kinetic model that enables the estimation of this parameter, because the change in kinetic parameters in reference to minerals present in the oil shale by using non-isothermal TGA is tried. This research presents the investigated parameter peculiar to Onelga oil shale and the associated mineral including a complete TGA dataset for the pyrolysis of Onelga oil shale in order to confirm which kinetic models can match the TGA data and subsequently provide heat energy requirement for reactor design capable to carryout pyrolysis. This has been done by perturbation and decomposition rather than computing the relative computation which are complex. When kinetic parameter is coupled with heat balances, decomposition is better understood. While thermodynamics gives steady state data of the decomposition process, chemical kinetics portrays the transient conditions of the process during the decomposition. The temperature data obtained in the process is significant and it is identified with the rate at which species are degraded and formed, and the rate at which the reaction heat is evolved. Under heat, substance degradation response is exceptionally delicate to temperature and a lot of heat is delivered during the process. The heat discharged gives the positive criticism that supports decomposing the substance: heat transfer raises the reactant temperature with the goal that this process continues at a high rate, which is critical to plant design and fabrication, as it is needed to guarantee adequate time for chemical reactions when designing a reactor.

Section I deals with the significance and the previous finding on kinetic model applied to the decomposition of oil shale. Section II deals with the methodology adopted for utilizing the entire range of temperature required for the decomposition of Onelga oil shale under pyrolysis; the predetermination of suitable kinetics to prescribe the reaction kinetics is provided in section II. To this end the Arrhenius model and the Coats- Redfern method have been employed to prescribe further the decomposition of Onelga oil shale since they provide standard means to obtain kinetic data. Thus, in Section II, the temperature range that has been predetermined in the first stage of the experiment has been the temperature range adopted in the TGA technique. The theory of the kinetic studies is also presented in Section II. In Section III, the characteristic functional group peculiar to the oil shale sample has been well presented. The temperature data and the concentration change in kerogen have been used to provide and define the adequate kinetics of the decomposition reaction of the material. The discussion focuses on the kinetic model, which is discussed over the classical method because it agrees with the initial pyrolysis carried out. The results are discussed in Section III, where the experimental procedure is a mean by which possible experimental errors have been eliminated. The

thermal induction technique allows for the calculations of energy requirement. Thus, the research work has utilized the decomposition of materials to fix the kinetics parameter and the heat energy necessary to design a reactor or pyrolyser. In Section IV, the basic findings have been expressed as conclusions. In this section, the temperature data in the decomposition of oil shale has been stated to be utilized in the determination of the heat energy requirement for the retorting.

## II. Methodology: Collections of Oil Shale Samples and Experimental Technique

The oil shale samples have been collected from Onelga, Rivers state in Niger Delta basin, Nigeria. The effect of mass and heat transfer has been controlled in order to minimize the error in the determination of kinetic parameter of the oil shale [14]. The samples have been dried in the oven at 40 °C for 2 hours. The ratio of the concentrated hydrochloric acid to oil shale is 1:10 by weight of the 80 μm size. The raw oil shale sample has been first characterized using FTIR (Fourier Transform Infrared) and Gas Chromatography-Mass Spectrometry (GC-MS). A PerkinElmer TGA 4000 thermogravimetric analyzer (TGA) has been used for pyrolysis. The TGA 4000 has a balance capacity of 1500 mg, a balance precision of 0.01% and a temperature range ambient to 1000 °C. It is different from other analyzers due to its top-loading sample pan that is above the balance with a stem support rod. Nitrogen has been used as the purge gas. 1000 mg of each sample have been analyzed non-isothermally at a heating rate of 10 °C/min and have been heated to 800 °C.

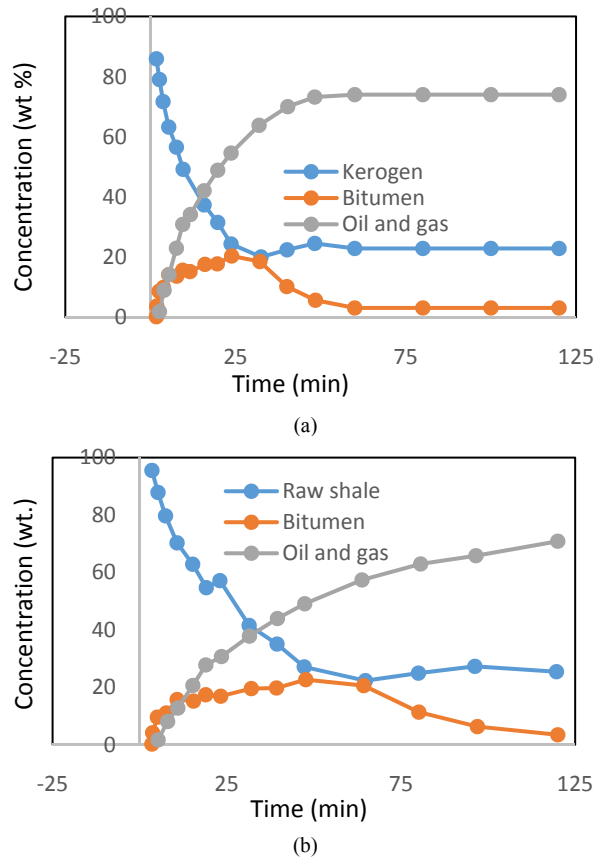
### II.1. Technique for the Identification of the Kinetic Model of the Decomposition of Onelga Oil Shale

The concentration of oil shale/kerogen, bitumen, and evolved vapour constituting gas and oil has been determined as C defined by the ratio of final quantity of kerogen (wt) to its initial (wo). Using the same feed weight of 1000 mg, the residual bitumen and the evolved gas and oil content have been recorded. The plot of the corresponding formation of bitumen and oil + gas in terms of concentration change with time is provided in Figures 1.

The oil and gas content in the treated sample is about 80% whereas the raw sample contains 60% of oil and gas content. Clearly, the sample contains other materials, which are about 20% of the total weight of feed sample with the remaining constituting the evolving gas and oil content. The interrupting materials are minute mineral content. This preliminary check on Onelga oil shale includes the application of Equation (1):

$$\ln k = A + b/T \quad (1)$$

where  $T$  is the absolute temperature (in K) and  $A$  and  $b$  have been sought for as constants via 52 observations.



Figs. 1. Average decomposition curves of acid treated oil shale (kerogen) (a) and decomposition curve of raw oil shale (b)

Here the constant  $b$  has been given by  $E/R$  with  $R$  as the universal gas constant. In this process, it has been possible to obtain an experimental value assigned to the constant  $A$  (which ranges between 19.05 and 370/s for both raw and acid treated samples).  $E$  has values between 203.00 and 291.92 kJ/mol for raw oil shale whereas a range of 156.95–238.95 kJ/mol has been yielded for acid treated oil shale. In these 52 observations,  $E$  is the activation energy for the equation and  $A$  is the frequency factor that suggests that a probable kinetic model for the newly found Onelga oil shale would be applied to the Arrhenius model and a close model which integrates the kinetic equation (1). For the specific rate constants for Onelga oil shale under thermal decomposition at increasing  $T$  value up to 478 °C, each specific rate constant  $k$  which had the units of a frequency ( $\text{time}^{-1}$ ) has been the specific rate constant for the first-order reaction.

However, for any second order reaction, the units for  $k$  have included a concentration term, which is gram per mole per minute ( $\text{g mole}^{-1} \text{min}^{-1}$ ). Since it is theoretically acceptable to determine concentration as a percentage of total insoluble organic matter referenced to initial organic composition, the order term in the units for  $k$  is one.

Thus, the Arrhenius model and the Coats- Redfen method are employed to prescribe further the decomposition of Onelga oil shale. When “wt” is the weight loss of sample at a time (initial weight – weight at time $t$ ), “wo” is the total weight loss (initial weight -

final weight) [15]. Applying the kinetics theory, the evaluation of the decomposition data is expressed and Equations (2) and (3) hold:

$$\frac{dC}{dt} = K(1 - C)^n \quad (2)$$

$$K = Ae^{-E/RT} \quad (3)$$

Therefore combining Equations (2) and (3), Equation (4) holds:

$$\frac{dC}{dt} = Ae^{-E/RT}(1 - C)^n \quad (4)$$

where  $A$  is the frequency or Arrhenius factor,  $E$  is the activation energy,  $T$  is the temperature,  $k$  is the rate constant,  $R$  is the gas constant and  $n$  is the order of the reaction. Assuming the first order kinetics for oil shale pyrolysis [11], that is  $n$  equals to unity, the decomposition process of figure 1 has provided a clue that the two kinetic methods that can estimate the kinetic parameter of Onelga oil shale are the direct Arrhenius and the Integral (Coats and Redfen) methods. The natural logarithm of the Arrhenius method is given by Equation (5):

$$\ln\left(\frac{1}{1 - C} \frac{dC}{dT}\right) = \ln \frac{A}{D} - \frac{E}{RT} \quad (5)$$

Plotting  $\ln\left(\frac{1}{1 - C} \frac{dC}{dT}\right)$  against  $1/T$  gives a straight line of slope  $-\frac{E}{R}$  and the intercept of the line has been used to determine the frequency factor of the oil shale [13]. For the integral method, the activation energy and the frequency factor have been also determined using the integration method, which has been developed by Coats and Red fern by integrating Equation (6):

$$\ln\left\{-\ln\frac{(1 - C)(E + 2RT)}{T^2}\right\} = \ln\frac{AR}{DE} - \frac{E}{RT} \quad (6)$$

A plot of  $\ln\left\{-\ln\frac{(1 - C)(E + 2RT)}{T^2}\right\}$  against  $\frac{1}{T}$  will give a slope equals to  $-\frac{E}{R}$  and the intercept is  $\ln\frac{A}{D}$  [16].

### III. Results and Discussion

The oil shale has been characterized and then subjected to kinetic studies in the subsequent section.

#### III.1. Characterization of Onelga Oil Shale Using FTIR and GC MS

The major functional groups found in Onelga oil shale include aliphatic hydrocarbons (which mainly include: methyls (CH<sub>3</sub>), methylenes (CH<sub>2</sub>), and methenes (CH), Carbonyl groups (C=O), and Hydroxyl (OH) groups (carboxylic acids). Alongside these groups, there silicate

compounds such as quartz, dolomite, and few more minerals peculiar to the sample areas Figure 2 and Table I presents the entire group. A similar description is reported by [16]. The oil shale sample has been analyzed using GC-MS in Table II. All the compounds in the sample are presented in Table II at the peak area with the corresponding reaction time.

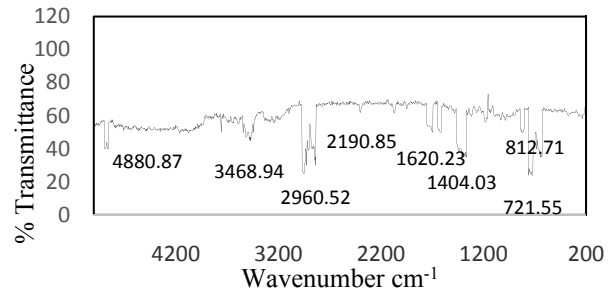


Fig. 2. Spectra for Onelga oil shale sample

TABLE I  
RESULTS FOR FTIR ANALYSIS OF ONELGA OILSHALE

Frequency, cm <sup>-1</sup>	Bond or group type	Compounds
721.55	C-C chains	Paraffin chains
812.71	C-H deformation	Alkyl substituted aromatic rings, conjugated and fused rings
700 – 1000	Silicate impurities	dolomite, kaolinite, ankerite, siderite, aragonite, calcite, quartz and clay minerals
very wide band	CH <sub>3</sub> and CH <sub>2</sub> groups	alkanes, alkenes, cycloalkanes, cycloalkenes, isoalkanes, cycloparaffins
1404.03	In acyclic and cyclic structures	Structures containing phenolic, alcoholic and carboxyl groups
3468.94	OH groups	Aldehydes, Ketones, Esters, Carboxylic acids, Amides and Anhydrides

TABLE II  
ANALYSIS RESULTS OF THE OIL SHALE SAMPLE USING GC-MS

Reaction Time	Peak area (%)	Compound
6.050	1.60	Butanoic acid, 4 – (2,4,5 – trichlorophenoxy) – methyl ester Succinic acid, 2-methoxyethyl nonyl ester
6.594	6.27	Succinic acid, 2-methoxyethyl undecyl ester Ethylbenzene, o-xylene, Ethylbenzene
7.032	3.38	2- (Benzoyloxy) ethyl methyl carbonate Benzeneethanol, alpha., beta.-dimethyl – Ethylbenzene
8.652	1.22	Benzimidazole, 2 – (4-pyridyl) – 5- (4-pyridylmethylenamino)- Cyclopropanecarboxamide, 1,2,2-tricyano-N-(4-Bromophenyl) -2-(4-chlorophenoxy) acetamide
18.861	1.28	Dimethylmalonic acid, heptyl 2-methylpent-3-yl ester Dimethylmalonic acid, decylisohexyl ester Dimethylmalonic acid, heptyltridecyl ester
23.296	15.45	Cyclohexasiloxane, dodecamethylcyclohexasiloxane
24.191	1.41	1 – (p-Fluorophenyl)-4-piperidone Borinic acid, diethyl – 3,3,5 – trimethyl – 1- cyclohexen-1-yl ester Quinolin-2 (1H)-one, 3-butyl-6-fluoro-4-hydroxy-
24.691	37.31	Cycloheptasiloxane, tetradecamethyl- Cycloheptasiloxane, tetradecamethyl-N-Benzyl-N-ethyl-p-isopropylbenzamide
25.880	21.74	Cyclooctasiloxane, hexadecamethyl – Cyclooctasiloxane, hexadecamethyl-Silane
26.993	10.33	Cyclononasiloxane, octadecamethyl – cyclononasiloxane

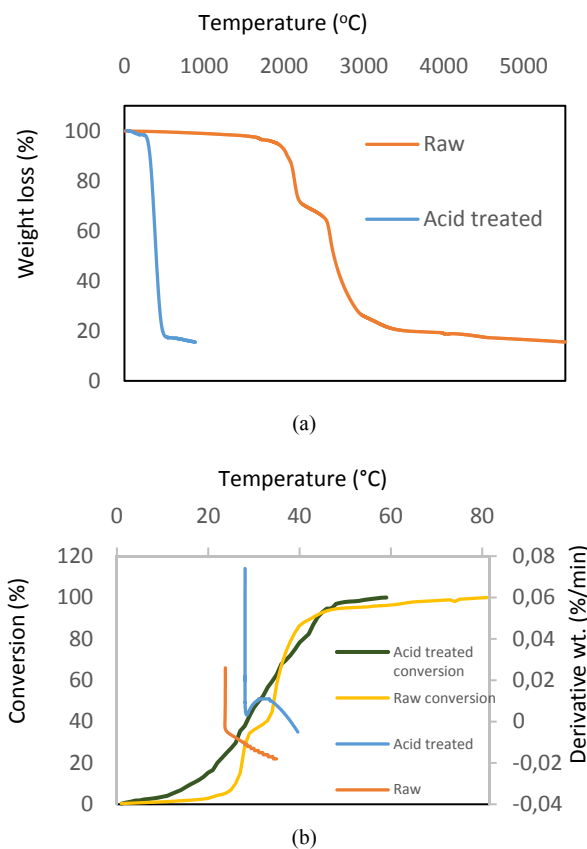
### III.2. Thermogravimetric Analysis of Onelga Oil Shale

The TGA results for both raw and acid treated samples presented in Figures 3 indicate that for the raw oil shale, the weight loss decreases from 100% at 23.48 °C to 15.69% at 886.8 °C while the one of acid treated sample decreases to 15.465% at 889.15 °C from 28.06 °C

It can be seen from the TGA and DTGA curve in Figure 3(a) that the decomposition of both raw and acid treated Onelga oil shale are in three stages which conform with the decomposition trend of [6] and [11].

The weight loss at approximately 220 °C and 280 °C for both raw and acid treated oil shale is attributed to evaporated water or interlayer water in the shale (clay) matter or moisture in the sample. Physical changes in the kerogen structure have been significant prior to decomposition of pyrolytic bitumen. These changes are in the form of molecular rearrangement. At 220 °C-580 °C for the raw sample and 280 °C-530 °C for the acid treated sample, a drastic decrease in the weight loss of the oil shale samples has occurred. According to [8], the significant weight loss at this stage is due to the decomposition of hydrocarbons (kerogen and bitumen).

The volatility of the feed hydrocarbons in the oil shale samples has been observed. At this stage, the weight loss rapidly decreases from 98.477% to 19.767% within the short temperature range 220 °C-580 °C and 97.213% to 17.458% in the temperature range of 280 °C-530 °C for both raw and acid treated sample respectively.



Figs. 3. (a) TGA result of raw and acid treated oil shale samples, (b) DTGA result of raw and acid treated oil shale samples

One type of oil shale can be distinguished at this stage from another type [6]. Onelga sample contain Cyclootasiloxane, hexadecamethyl-Silane and other compounds stated in Table II. It is also of the type with aliphatic chains and other probable functional group in Table I. Usually, kerogen exhibits a two-stage decomposition process to yield oil, gas and char [17].

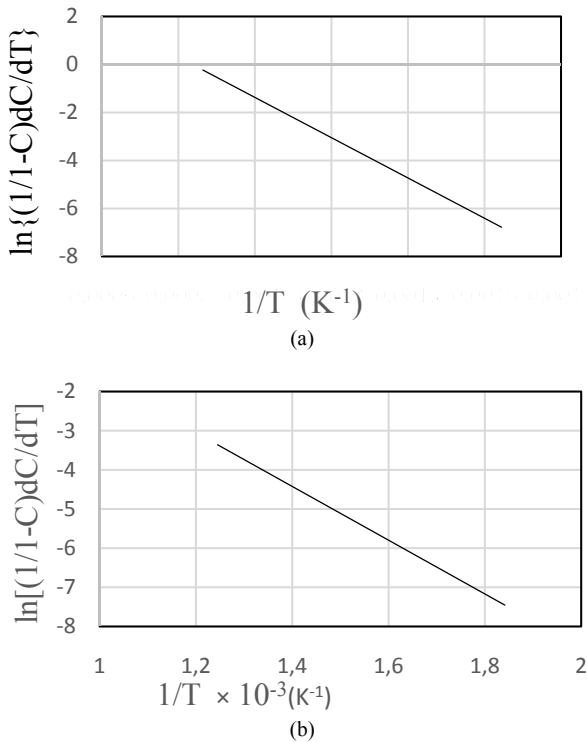
This pyrolysis decomposes the kerogen content of the Onelga oil shale to pyrolytic bitumen and then bitumen to shale oil and shale gas, which are the final products.

The TGA/DTGA curve has indicated one-step decomposition, which is a complex reaction that involves series of parallel reactions similar to [11]. At 600-880 °C, the decomposition of the aragonite, calcite, siderite, chalk and other silicate minerals (quartz, kaolinite etc.) is proposed. Comparing the raw and the acid treated sample as shown in for Figure 3(a), the raw sample takes more time and energy before decomposition reaches completion. Figure 3(b) presents the pyrolysis reaction; the maximum decomposition temperature ( $T_{max}$ ) of the samples has been found out to be 433.61 °C and 389.37 °C and the maximum conversion rate at the maximum decomposition temperature has been found out to be -4.53 and -5.444 %/min for the raw and acid treated samples respectively. In Figure 5(a), the conversion of kerogen, which rapidly proceeds from 3.6 at 285 °C to 95.4 at 615 °C for the raw sample and 3.1% at 280 °C to 97.8% at 540 °C for the acid treated sample, is plotted.

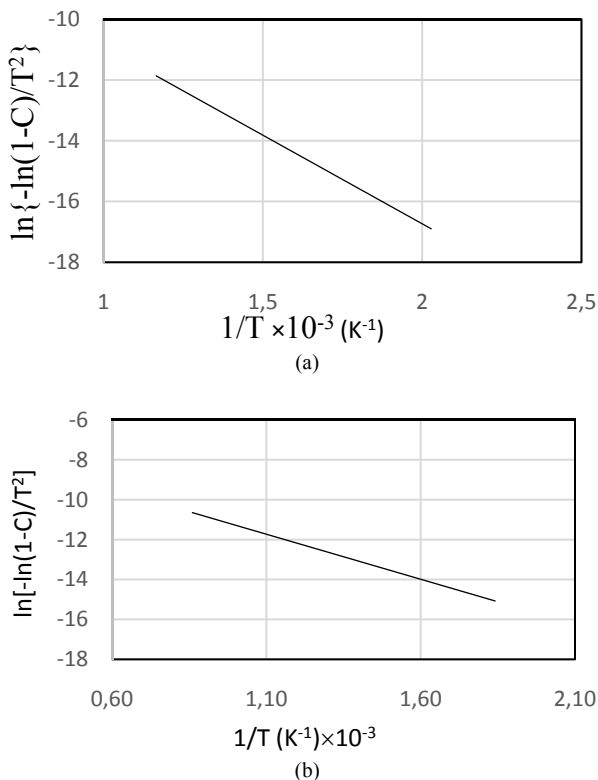
The conversion of acid treated sample is faster and occurs at lower temperature. Thus, for irreversible reactions, the kinetic parameter of oil shale will vary.

### III.3. Direct Arrhenius Method for Onelga Oil Shale

Figures 4 present the direct Arrhenius kinetic model for the raw and acid treated oil shale. The respective pre-exponential factor of  $1.1 \times 10^4 \text{ s}^{-1}$  and  $0.18 \times 10^4 \text{ s}^{-1}$  has been obtained. The activation energies for the raw and the treated sample are 279.37 kJ/mol and 238.95 kJ/mol respectively; the coefficients of correlation ( $R^2$ ) are 0.9299 and 0.9693. The integral method for the oil shale has yielded the model in Figures 5. Figures 5 present the integral kinetic model for the raw and acid treated oil shale. The pre-exponential factors for raw and acid treated oil shale are  $369.8 \text{ s}^{-1}$  and  $52.05 \text{ s}^{-1}$  respectively. 'E' has corresponding activation energy for raw and treated sample as 203.00 kJ/mol and 156.95 kJ/mol respectively, and the coefficients of correlation are 0.9458 and 0.9429. Hence, the removal of the mineral matter in oil shale by acid treatment has affected the kinetic parameters by reducing the activation energy of pyrolysis reactions of the oil shale sample. Probably, the diffusion of the organic matter present in the oil shale all through the mineral matrix has needed an elevated temperature and energy relatively more for pyrolysis reaction to reach completion. The activation energies calculated for the pyrolysis reaction involving acid treated oil shale have been lower than the value obtained for the raw oil shale samples.



Figs. 4. Direct Arrhenius plot for raw (a) and acid treated (b) Onelga oil shale



Figs. 5. Integral method for raw sample (a) acid treated (b) shale sample

However, the activation energies obtained using integral method for both samples have been found out to be lower than the one obtained using direct Arrhenius method. With this, the values calculated here are

comparable to the ones found in literature for Moroccan oil shale in [6]. The effect of minerals on the evaluated kinetic parameters for source rock using rock-eval pyrolysis has been considered [18]. The effect has showed that by pyrolysis of mixtures of sedimentary minerals with various concentration of isolated kerogen, the kinetic parameters reflect the added mineral matters in the presence of quartz, calcite, and dolomite shifted and the activation energy to higher values when compared to the ones observed for the kerogen (acid treated oil shale) which are mineral free [18]. Kinetic parameters as calculated by different literatures are unique for their respective oil shale, [11], [10], [19], [20] and [14]. The differences between the results determined in this study and the ones reported for oil shale from other countries are probably due to the fact that the kerogen type are not the same (the constituent oil and fractions in the kerogen are different). Kerogen type has been found out to vary with activation energies [6]. The kinetic method of the TGA data may also influence the calculated activation energy because the amount and type of mineral matter present in the sample are valid factors that may cause this different value. It is inferred that kinetic parameters are unique for their respective kinetics determination methods, which means that the activation energy is independent of the kinetic methods used to calculate it and different oil shale decomposes at different rate. For the Onelga oil shale, where the maturity of the oil shale is yet to be identified, the parameter value may be dependent on this fact even when the characteristic functional grouping are typical of oil shale generally.

#### III.4. Thermodynamic for the Decomposition of Onelga Oil Shale

The same temperature data recorded for pyrolysis fractions during determination of activation energy have been obtained for the laboratory reactor. The heat calculated for decomposing Onelga oil shale has been based on thermometer reading of the pyrolysis reaction. During this retort process, the basic calculations turn out to benefit engineer as an estimate of the heat required for similar process can be made. Thus, an economic analysis of the process is feasible. It is also useful for upscale where large project retorting plants are to be built. Here the heat balance for the reactor is expressed in equation (7). The heat due to oil shale is  $Q_{sh}$  and the heat due to retort is  $Q_{re}$ . The summation of these two heat components is equal to the sum of the heat prior to degradation during the pyrolysis, the heat conveyed by pyrolysis products and the moisture that are foremost removed from the feed sample. The balanced equation is in agreement with [21]. The constants are also quoted by [22]:

$$(Q_{sh}) + (Q_{re}) = Q_{py} + \sum (Q_{gas} + Q_{oil} + Q_{bitumen} + Q_{moisture}) \quad (7)$$



where  $Q_{gas}$ ,  $Q_{oil}$  and  $Q_{bitumen}$  are the heat carried by the gas, oil and non-evaporated shale sample (referred to as bitumen), the heat due to the initial moisture that has been evaporated prior to decomposition denoted as  $Q_{moisture}$  should be included.

The heat due to oil shale is  $1.520 \times 10^{-3}$  kW calculated in Equation (8):

$$Q_{sh} = (m_{sh} C_{p,sh} T_{sh}) \quad (8)$$

where  $m_{sh}$ ,  $C_{p,sh}$ ,  $T_{sh}$  are the mass of shale sample fed into the reactor, specific heat capacity of shale (1.05 kJ/(kg °C) and the temperature measured when no product has been evolving. During this stage, a unit retorting heat ( $Q_{py,unit}$ ) has been evaluated until a constant value has been obtained for  $m_{sh} - m_{moisture}$ .

This mass has been multiplied by  $Q_{py,unit}$  in order to obtain the initial pyrolysis-heat  $Q_{py}$  necessary for the decomposition to proceed. The initial heat reached to start retort is  $Q_{py}$  or  $6.575 \times 10^{-3}$  kW calculated as:

$$Q_{py} = (m_{sh} - m_{moisture}) Q_{py,unit} \quad (9)$$

where  $m_{sh} - m_{moisture}$ , is the mass of shale after the evaporation of moisture content and  $Q_{py,unit}$  is the unit retorting heat at pyrolysis. The heat of the gas fraction is  $7.633 \times 10^{-3}$  kW calculated in Equation (10):

$$Q_{gas} = (m_{gas} C_{p,gas} T_{re}) \quad (10)$$

where  $m_{gas}$ ,  $C_{p,gas}$  and  $T_{re}$  are the mass of evolved gas that are non-condensable, the specific heat capacity of the gas is 6.17 kJ/(kg K) and  $T_{re}$  is the temperature measured during the evolving of non-condensable gases.

The heat of the oil fraction is  $3.075 \times 10^{-3}$  kW calculated in Equation (11):

$$Q_{oil} = m_{gas} (C_{p,oil} T_{re} + R_{oil}) \quad (11)$$

where  $m_{oil}$ ,  $C_{p,oil}$  and  $R_{oil}$  are the mass of evolved gas that are condensed into oil, the specific heat capacity of the oil which is 2.26 kJ/(kg °C) and the latent heat of vaporization of the condensed oil 368.46 kJ/(kg) and  $T_{re}$  is the temperature measured during the vaporization of the condensed gases. The heat carried by the non-evaporated shale sample (bitumen) is  $22.083 \times 10^{-3}$  kW calculated in Equation (12):

$$Q_{bitumen} = (m_{bitumen} C_{p,bitumen} T_{re}) \quad (12)$$

where  $m_{bitumen}$ ,  $C_{p,bitumen}$ ,  $T_{re}$  are the mass of the non-evaporated shale, (bitumen) the specific heat capacity of the bitumen which is 1.8 kJ/(kg °C) and the temperature measured during the evolving of non-condensable gases.

The heat of the initially evaporated moisture content of shale sample is  $3.710 \times 10^{-3}$  kW calculated in Equation (13):

$$Q_{moisture} = m_{moisture} C_{p,water(l)} (100 - 50) + R_{water} + C_{p,moisture(g)} (360 - 100) \quad (13)$$

where  $m_{moisture}$  is the mass of moisture,  $C_{p,water(l)}$  (or 4.19 kJ/kg °C) is the specific heat capacity of moisture evaporated and condensed as water  $R_{water}$  (or 2261 kJ/kg) is the latent heat of vaporization for water  $C_{p,moisture(g)}$  (or 1.99 kJ/kg °C) is the specific heat capacity of moisture evaporated and remain as gas in the process. By evaluation of equation (7), then  $Q_{re}$  is  $41.555 \times 10^{-3}$  kW. On each side of equation (7) the total heat contained by the material under decomposition is  $43.075 \times 10^{-3}$  kW which is the heat energy balancing the heat output specifically for the material. It should be noted that the external power used for direct heating of equipment is different from the heat contained by materials. This heat contained is necessary to obtain the activation energy necessary for the decomposition of materials and is useful for internal design of pyrolysis equipment in form of heat energy. Aspen hysys are emerging means of simulating equipment when experiments are expensive: an example is the current research on design of separator by [23].

#### IV. Conclusion

The preliminary technique required for the conversion of kerogen by small increase in temperature occurs as a reaction process that follows closely the Arrhenius law.

Thus, it enables the estimation of the product yield and the kinetic model that eliminates the probable requirement for the trial of several methods before a kinetic model is defined. Therefore, a set of reactions where all the participating processes or rate constant obey the kinetic relationship that yield the kinetic model should be the first step taken to obtain models. However, the presence of the mineral matters in oil shale requires higher temperature for the material decomposition at the stage where there is significant weight loss. These mineral associated with oil shale affect the hydrocarbon materials present in the shale samples, which invariably affect the yield of gas and oil. Therefore, the removal of the mineral matters affects the kinetics and the pyrolysis mechanism of oil shale by altering the activation value this implies that the activation energy is dependent on the kinetic method used in evaluating it. The heat energy carried by individual fraction of the decomposition process is useful for thermodynamic analysis that enhances reactor design. For Onelga sample, the heat energy carried by the gas fraction is large enough to be recommended for recycle, which can reduce the cost of total heat energy requirement. The temperature data in the decomposition of oil shale has been used in the determination of the heat energy requirement for the pyrolyzer, which can be used in an equipment of similar processes especially in the emerging Aspen hysys simulation of pyrolyzer-reactor. Fluidized catalytic cracking is finding application in the production of oil from oilshale. This fluidization can be done and the heat

requirement for the process may be compared with the energy values in this research.

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