

A Comprehensive Kinetic Study of Bida Oil Shale Kerogen Pyrolysis Through Isoconversional and Distributed Activation Energy Modeling

Victor E. Peters¹. *Nura Makwashi², Adeola G. Olugbenga³, Muhammad A. Abba⁴, Abubakar A. Ibrahim⁵, Muhammad U. Garba⁶

¹Chemical Engineering Department, Federal University of Technology, Minna.

^{2,4,5}Chemical and Petroleum Engineering Department Bayero University Kano, P.M.B. 3011, Nigeria.

³Chemical Engineering Department, University of Abuja, Nigeria.

⁶Petroleum and Gas Engineering Department, Federal University of Technology, Minna.

petersvictor52@gmail.com | nmakwashi.cpe@buk.edu.ng | adeolagolu@futminna.edu.ng | muhammadauwalabba259@gmail.com | aaibrahim.cpe@buk.edu.ng | umar.garba@futminna.edu.ng

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ORIGINAL RESEARCH

Abstract— Oil shale kerogen pyrolysis is typically crucial for optimizing production efficiency. This research investigates the thermal degradation behavior of Bida oil shale kerogen using thermogravimetric analysis (TGA) at varying heating rates (10, 20, 30, and 40 °C/min). This study employs kinetic analysis methods including Kissinger (K), Flynn–wall–Ozawa (FWO), Kissinger-Akahira-Sunose, (KAS) and Distributed Activation Energy Model (DAEM) to elucidate the complex decomposition behavior. The research provides novel insights into the temperature-dependent variations in oil shale pyrolysis, revealing significant impacts of heating rates on decomposition temperatures and kinetics. Notably, increasing heating rates led to a shift in decomposition temperatures, attributed to differences in heat transfer efficiencies within the sample. Distinct stages of decomposition were observed, with devolatilization initiating around 260°C and progressing rapidly until approximately 526 °C, followed by a gradual decline in decomposition rate. Kinetic analysis using KAS, and FWO provided valuable insights into activation energies (E_a) and pre-exponential factors (A). E_a ranged from 64.945 to 86.94 kJ/mol, indicating a complex decomposition mechanism influenced by varying conversion levels. The DAEM further elucidated the kinetics of oil shale decomposition, highlighting the heterogeneity of pyrolytic processes under different heating rates. The average E_a and frequency factor calculated using the DAEM method were 64.95 kJ mol⁻¹ and 1.87 × 10⁵ min⁻¹. It was observed that the results obtained from the methods differed from each other due to the complex mechanism of reaction occurring during the pyrolysis process and the effect of different heating rates. The findings contribute to refining kinetic models for oil shale pyrolysis, shedding light on critical factors shaping thermal degradation behavior.

Keywords—Bida Oil Shale, Kerogen Pyrolysis, Kinetic Analysis, Thermogravimetric Analysis, Distributed Activation Energy Model.

1 INTRODUCTION

Fossil fuels continue to be the predominant source of primary energy worldwide, fulfilling around 81% of global energy requirements (Abas et al., 2015). In the United States, fossil fuels accounted for 80% of primary energy consumption in 2019. The escalating costs associated with conventional fossil fuels have spurred a global quest for alternative energy sources. Recently, there have been significant discoveries of promising low-carbon alternatives such as biofuels and natural gas, indicating a shift in the composition of liquid fuels as the energy landscape evolves (Holechek et al., 2022; Alruqi et al., 2023, Li et al., 2024). The International Energy Agency's 2011 World Energy Outlook predicts significant transformation in the energy sector by 2035. It foresees the emergence of a new oil sources to replace nearly half of the declining global conventional oil production. Among these unconventional resources are 'unconventional natural gas, which includes shale gas, tight gas, and coalbed - often referred to as tar sands or natural bitumen. Oil shale consists of sedimentary rock containing organic compounds known as kerogen (Dyini, 2003).

Unlike conventional oil, this organic matter has not undergone the requisite geological pressure, heat, and time for transformation. One of the key attributes of oil shale is its potential as an energy source, particularly in its capacity to meet the transportation needs of a growing population without necessitating significant alterations to existing infrastructure (Colorado School of Mines, 2020). The organic matter found in oil shale can be converted into products similar to conventional liquid hydrocarbon fuels, including gasoline, diesel fuel, and other valuable derivatives (Strizhakova and Usova, 2008; Dyni, 2003).

Commercial oil shale production typically involves pyrolysis retorts. Optimizing these retort conditions for cost-effective and high-yield oil productivity necessitates a deep understanding of the specific characteristics of the exploited oil shale, including its kinetics, rates of pyrolysis reactions and mechanisms of kerogen. Key specifications like g oil content, mineral composition, and crystalline structure provides valuable insights into these complex reaction mechanisms (Foltin, 2017).

Conversely, the rates and reaction mechanisms primarily depend on the kerogen concentration within the shale, which varies throughout the decomposition process. Oil loss from the shale occurs through either evaporation or chemical reactions (Pan et al., 2015; Michael, 1988). Consequently, numerous studies on oil shale pyrolysis kinetics have employed experimental techniques such as, thermogravimetric analysis (TG), differential thermal

*Corresponding Author: nmakwashi.cpe@buk.edu.ng

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analysis (DT), rock-eval pyrolysis and triple quadrupole mass spectrometry (TQMS) to measure the conversion or concentration of oil within the shale as a function of temperature and time. Various kinetic models, including isoconversional differential, isothermal, non-isothermal and integral methods, have been applied to this experimental data. These models are typically rooted in the kinetic rate equation, which is a function of conversion and order of reaction. Solving this equation enables the determination of kinetic parameters such as activation energy and frequency factor, which govern the reaction rate.

Recent kinetic modeling of oil shale has adopted diverse approaches. Some studies use a single activation energy value to estimate all the kinetic parameters, while others employ a distribution of activation energy values across the entire pyrolysis process (Al-Ayed et al., 2017). Distributed activation energies characterize the various reactions during oil shale pyrolysis, spanning from primary to secondary thermal cracking. Low activation energy values are associated with the release of gases such as carbon monoxide, hydrogen and light hydrocarbons at lower pyrolysis temperatures. Intermediate activation energies correspond to the decomposition of large kerogen molecules over a wider temperature range, while higher activation energy values at elevated temperatures reflect the breakage of stronger chemical bonds. The activation energy values, influenced by heat, thermal conductivity, and the physical properties of raw oil shale. Furthermore, studies have highlighted the impact of heating rates on the pyrolysis reactions of oil shale. The type and quantity of evolved hydrocarbons change with varying heating rates, which are indicative of the heat flux applied to the material (Campbell et al., 1980).

Therefore, the aim of this paper is to provide a comprehensive analysis of the kinetic parameters associated with Bida oil shale pyrolysis. This research marks the first detailed reporting of these crucial parameters for Bida oil shale located in the Northern part of Nigeria, shedding new insights into its pyrolysis behavior and contributing to the broader understanding of oil shale pyrolysis kinetics.

2. MATERIALS AND METHODS

In this study, the methodology applied in the preparation of Bida oil shale samples from Northern Nigeria for experimentation involved two key steps. In the initial step, the oil shale was subjected to crushing, followed by sieving for a duration of 2 minutes. This sieving process aimed to achieve a particle size ranging between 0.25 and 0.5 mm.

2.1 THERMOGRAVIMETRIC ANALYZER (TGA)

The pyrolysis data for the kinetic study were acquired using a thermogravimetric analyzer (TGA). Thermal gravimetric analysis (TGA) is a well-known technique for monitoring chemical processes by tracking changes in weight. This particular TGA is rated for operating

temperatures up to 1000°C and has a total gas flow capacity of 100 ml/min for sweep/reacting and balance gases (Clayton, 2002). The central component of the TGA is its electrically heated furnace, which enables precise temperature control throughout the experiments. It offers a wide range of heating rates, with a maximum rate of 100°C/min and a minimum of 0.1°C/min. The electric heating elements within the furnace vessel facilitate the uniform heating of the sample. Reproducibility in the data is ensured through accurate control of mass flow rates and the ability to adjust heating rates. Temperature measurements just above the sample basket are monitored and controlled by a thermocouple with four ports, further enhancing the precision of the experimental setup.

2.2 CHEMISTRY AND REACTION PATHWAY (MECHANISMS)

Kinetic study provides the structure for describing chemical reaction rate and enables scientist to relate the rate to reaction mechanism which describes how the molecules metamorphose through intermediates to the final products (Li et al., 2024; Chorkendorff, and Niemantsverdriet, 2003; Clayton, 2002). The Kinetic models used for the pyrolysis of the oil shale were based on the concept of Arrhenius equation which describes how the temperature depend on the reaction rate. Before any reaction occur, the reactant species must become excited and there exists a state of equilibrium amid normal and excited molecules. The organic part of the oil shale is a solid material which is not soluble in water and it is called kerogen. The thermal degradation of kerogen yields volatile matters in gaseous form, liquid oil and solid char.

2.4 KINETIC EXPRESSION - MATHEMATICAL MODEL EQUATIONS AND ASSUMPTIONS

Several mathematical approaches have been used to estimate the kinetic parameters (pre-exponential factor (A) and activation energy (Ea) with the assumption of 1st order reaction. The activation energy (Ea) is a crucial parameter that offers insights into the energy barrier a reaction must overcome to take place. It quantifies the amount of energy required for a reaction to initiate and progress, thereby providing valuable information about the reaction's feasibility and speed. On the other hand, the pre-exponential factor (A) signifies the rate at which reactant molecules collide with each other's in a way that leads to successful reactions. Together, these kinetic parameters provide a comprehensive understanding of the reaction kinetics, shedding light on the underlying mechanisms governing the thermal decomposition of oil shale (Al-Harashsheh et al., 2011).

The analysis of the kinetics of the pyrolysis of the oil shale samples was conducted with N₂ at different heating rates (10, 20, 30 and 40 °C min⁻¹). Following the breakdown of kerogen, the event involves during the transformation of oil shale from solid state (kerogen) to volatile product can be represented by the following equation; this experiment involves a one-step global model which assumes that the devolatilization scenario proceeds as a single reaction

producing a chemically changed solid called bitumen and gas.

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{1}$$

Where α is denoted by the extent of conversion, t is the time, K is the specific reaction rate constant and $f(\alpha)$ represent the model of reaction. The extent of conversion can be represented as follows;

$$\alpha = \frac{m_{ini} - m_{tim}}{m_{ini} - m_{fin}} \tag{2}$$

m_{ini} and m_{tim} are the Bida Basin oil shale initial weight and weight of the at time t , whereas, m_{fin} represent the final weight of the Bida Basin oil shale. Noting that the rate constant of the Bida Basin oil shale decomposition is given by Arrhenius equation;

$$K = A_{fre} \cdot \exp\left(\frac{-E_{act}}{RT}\right) \tag{3}$$

Where, A_{fre} , E_{act} and R are the frequency factor, (1/S), Activation energy, (KJ/mol), and R gas constant, (8.314 KJ/Mol.K) respectively. While T is absolute Temperature, (K), and the order of reaction (n) is assumed unity.

Combination equation (1) and equation (3) gives the fundamental equation (4) commonly use to calculate kinetic parameters, using TGA results as basis.

$$\frac{d\alpha}{dt} = A_{fre} \times f(\alpha) \times \exp\left(\frac{-E_{act}}{RT}\right) \tag{4}$$

Where $\frac{d\alpha}{dt}$ is the conversion rate of oil shale. The expression for conversion, $f(\alpha)$ and its derivative are commonly use for the description of solid-state 1st order reaction, hence $f(\alpha)$ can be written as;

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where n represent reaction order. Therefore the expression of reaction rate (6) is obtained by substituting equation $f(\alpha)$ into equation (4);

$$\frac{d\alpha}{dt} = A_{fre} \times (1 - \alpha)^n \times \exp\left(\frac{-E_{act}}{RT}\right) \tag{6}$$

A linear relation between temperature and time is given as

$$T = T_0 - \beta t \tag{7}$$

Where β , T_0 and T represent constant heating rate, starting temperature, and pyrolysis temperature at time t . there for equation (7) becomes;

$$\beta = \frac{dT}{dt} \text{ consequently } dt = \frac{dT}{\beta} \tag{8}$$

substituting equation (8) into (6) and rearranging equation (6) gives;

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot (1 - \alpha)^n \cdot \exp\left(\frac{-E_{act}}{RT}\right) \tag{9}$$

The above equation expresses the part of mass loss in the time and is used to evaluate E_a and A at constant heating rate using non-isothermal TG data. Noting that the model-free non-isothermal methods is used to calculate the kinetic parameters, which uses an experimental data set at varied heating rates (Garba et al., 2018).

Model-free methods: Model free methods which are isoconversional in nature allows for evaluating the kinetic parameters of oil shale without modelist assumptions or knowing the exact reaction mechanism (Slopiecka et al., 2012).

Kissinger method: Kissinger method assumes a constant value of activation energy, that is, it does not calculate activation energy when value of conversion increases progressively (Slopiecka et al., 2012; Strizhakova and Usova, 2008). This method involves plotting the terms $\ln(\beta/T_{2max})$ against $1000/T_{max}$ from equation (10) below, where T_{max} is the peak temperature extracted from DTG curve.

$$\ln\left\{\frac{\beta}{T_{2max}^2}\right\} = \ln\left\{\frac{A_{preR}}{E_{act}}\right\} - \frac{E_{act}}{RT_{max}} \tag{10}$$

Activation energy which can be extracted from the slope $-E/R$ and A_{fre} from the intercept $\ln(AR/E)$ of the linear graph.

Kissinger-Akahira-Sunose: The KAS method involves plotting $\ln(\beta/T_2\alpha)$ against $1000/T\alpha$ (Kissinger, 1956) and is based on equation (11) below;

$$\ln\left\{\frac{\beta}{T_{ai}^2}\right\} = \ln\left\{\frac{A_{\alpha}R}{E_{\alpha}g(\alpha)}\right\} - \frac{E_{\alpha}}{RT_{ai}} \tag{11}$$

where E_{α} is apparent activation energy that can be extracted from the slope $(-E_{\alpha}/R)$ and A_{α} is frequency factors calculated from a linear graphs and intercept correspond to $\ln\{A_{\alpha}R/E_{\alpha}g(\alpha)\}$. The Integral model of the reaction, $(g(\alpha))$ is represent a constant if the value of conversion is known.

Flynn-Wall-Ozawa method: The FWO method is used to calculate apparent activation energy (E_{α}) by plotting $\ln(\beta)$ against $1000/T_{\alpha}$ from equation (12) (Foltin et al., 2019; Ahmed et al., 2019)

$$\ln\beta = \ln\left\{\frac{A_{\alpha}E_{\alpha}}{Rg(\alpha)}\right\} - 5.331 - 1.052 \frac{E_{\alpha}}{RT_{\alpha}} \tag{12}$$

Where E_{α} can be obtained from the slope of $(-E_{\alpha}/R)$ and A_{α} is frequency factors which is evaluated from the intercept $(\ln\{A_{\alpha}E_{\alpha}/Rg(\alpha)\} - 5.331)$ of the linear graphs.

Distributed Activation Energy Model (DAEM): DAEM method is based on the assumptions that in a decomposition reaction, a number of first order irreversible reaction equal distant reactions that are occurring with a distribution of activation energy. For each reaction, a distinct activation energy value is obtained, therefore, E_a of the whole reaction system is presented in the form of a specific continuous distribution function. Oil shale decomposition kinetics is approximated using the Miura integral method as follows;

$$1 - \frac{v}{v_{\infty}} = \int_0^{\infty} \Phi(E, T) \times f(E) dE \tag{13}$$

$$\Phi(E, T) = \exp\left\{-\frac{k_0}{\beta} \int_0^T \exp(-E/RT) dT\right\} \tag{14}$$

Where;

$$T = T_0 + \beta t \tag{15}$$

β is the heating rate given by

$$\beta = dT/dt \tag{16}$$

The activation energy distribution function, $f(E)$ can satisfy the equation (17):

$$\int_0^{\infty} f(E) dE = 1 \tag{17}$$

Meanwhile, the function $\Phi(E, T)$ is calculated and summarized as follows:

$$\Phi(E, T) = \exp\left\{-\frac{k_0 RT^2}{\beta E} \exp(-E/RT)\right\} \tag{18}$$

According to the Miura integration method, Equation (13) is simplified upon deformation as follows:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) - \ln\left\{-\ln\left(1 - V/V_\infty\right)\right\} - \frac{E}{RT} \quad (19)$$

Where V , V_∞ and $\Phi(E, T)$ are the total volatilization at time, t , volatilization content and temperature-dependent activation energy of decomposition of Oil Shale Eact. Whereas, $f(E)$ is normalized activation energy, E distribution curve for the 1st order reactions and K_0 is the frequency factor, R is the ideal gas constant, V/V_∞ is the conversion rate of pyrolysis products at point t . From Equation (18), $\Phi(E, T) = 0.58$, allowing for a further simplification of Equation (19) into the following Arrhenius equation (20):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT} \quad (20)$$

Therefore, DAEM method involves plotting $\ln(\beta/T^2)$ against $1/T$ and is based on equation (20) above; where E is apparent activation energies obtained from the slope $-E/RT$ and the intercept is $(\ln AR/E) + 0.6075$ of the linear graphs (Miura and Maki, 1998).

3 RESULTS AND DISCUSSION

3.1 THERMOGRAVIMETRIC CHARACTERISTIC

The weight loss curves in Figure 1 depict the thermal degradation of oil shale, showcasing the weight reduction at various heating rates. These curves exhibit characteristic of Z-shaped downward slope commonly observed during the thermal decomposition of materials. This analysis reveals distinct stages in the process. The devolatilization process initiates at approximately 260°C, rapidly progressing as the temperature increases until reaching around 526°C. Beyond this point, the rate of weight loss gradually diminishes towards the final temperature.

A noteworthy observation is the substantial impact of increased heating rates on the thermal analysis, as shown in Figure 1. The augmentation of heating rates induces a noticeable shift in the TG curves towards higher temperatures, influencing the maximum decomposition rate. This phenomenon can be ascribed to heat transfer drawback that arise because of differing thermal efficiencies particularly as the heating rates become high. Essentially, during the analyses conducted at lower heating rates, the system receives a larger and more efficient heat transfer, necessitating more time for the purge gas and sample furnace to equilibrate at the same temperature.

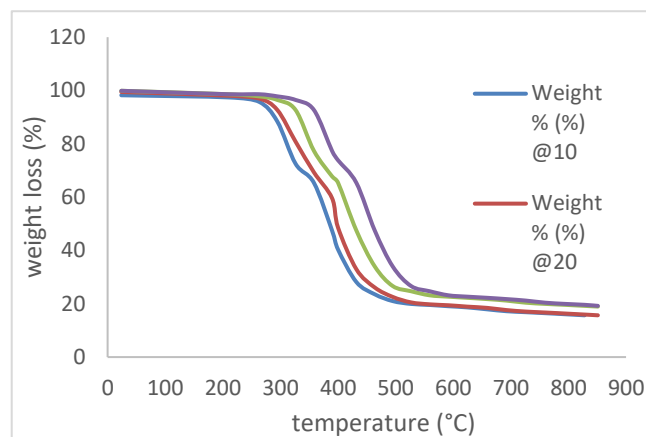


Figure 1: TG weight loss (%) curve for oil shale at 10, 20, 30 and 40 °C min⁻¹

On the other hand, at higher heating rates, the sample requires less time to decompose, resulting in a higher temperature and shifting the TG curves to elevated temperatures. It's important to note that these findings align with existing literature on oil shale under similar conditions.

Figure 2 displays the DTG curves, offering a more detailed representation of the oil shale devolatilization process (Abu et al., 2020). Increasing heating rates are observed to expand the DTG envelop and temperature profile of oil shale without altering the thermal profile. The results reveal a three-stage thermal decomposition process for oil shale: The first stage, occurring from room temperature to ~190°C, involves low-temperature weight loss specifically because of the moisture evaporation, such as interlayer and internal water from clay minerals, influenced by their crystal structure. Concurrently, there is the cracking of certain minerals, such as sodium bicarbonate. The second stage, within the temperature range of ~250-600°C, entails the decomposition of organic matter, predominantly hydrocarbon decomposition, followed by the release of oil vapor and gas. This phase represents the core of oil shale pyrolysis (active pyrolysis). Additionally, it encompasses the melting and intermolecular reorganization of organic matter, occurring in the range of 200 to 350°C, depending on the heating rate, marking the physical changes preceding kerogen cracking into tar. As shown in the Figure, the removal of highest amount of volatiles occurs mainly around of 340-650°C. At this stage the macromolecular organic and inorganic minerals undergo polycondensation, decomposition and chain cleavage reactions. On the other hand, the decomposition of carbonates, such as calcite, dolomite, and iron-rich dolomite occurs at a stage in which the temperature ranges between ~600-850°C (Garba et al., 2018).

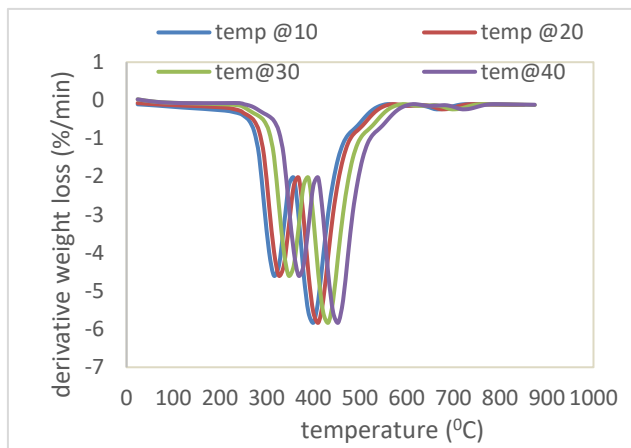


Figure 2: DTG curves at different heating rates for oil shale

As the heating rate increases, several notable trends become evident in the pyrolysis of oil shale. Firstly, the onset temperature, the peak and the final temperature of Bida Basin oil shale pyrolysis all indicates higher temperature value. This phenomenon results in an expanded devolatilization temperature range and an increase in the peak value of oil shale weight loss. The rationale behind these observations lies in the intensified heat supply at higher heating rates. Consequently, the degree of oil shale decomposition at specific temperature points rises, leading to an elevation in the peak weight loss value, see Table 1.

Hence, the shift in temperatures primarily occurs because at higher heating rates, there is insufficient time for effective heat flow penetration into the interior of oil shale particles. This temperature differential between the surface and interior of the particles becomes more pronounced, delaying the onset of internal pyrolysis reactions and influencing what can be referred to as 'thermal hysteresis.' Therefore the higher the heating rate, the more the pyrolysis temperature gradient, promoting the movement of pyrolysis reactions of organic matter towards the high-temperature envelop. These observations are similar with findings reported by Abu et al. (2020).

Furthermore, it is observed that the DTG peaks of the second phase are considerably more than the peaks of the 1st and 3rd phases, suggesting the greater intensity of the second-phase reaction when compared to the other phases (Cai and Bi, 2008).

Table 1: Influence of different heating rate on Bida oil shale decomposition

Varied Heating Rate of Oil Shale, β (°C/min)	Oil Shale Peak Decomposition Temp, (Tp)	Oil Shale Mass Loss Rate, (%/min) at Tp
10	400.1	5.831
20	410.59	5.831
30	431.86	5.831
40	453.05	5.831

3.2 KINETIC ANALYSIS

3.2.1 Isoconversional Methods

The primary objective of this kinetic study is to ascertain the activation energy, which serves as the quantify of ease of occurrence of chemical reaction. Reactions characterized by lower activation energies proceed more readily compared to those with higher activation energies (Popescu and Segal, 1998). To achieve this goal, the data derived from thermogravimetric analysis were subjected to model-free methods for the computation of essential kinetic parameters (e.g. Ea, A and correlation coefficient, Rk).

Therefore, the parameters (Ea, A and Rk) were estimated using three distinct methods: Kissinger, Kissinger-Akahira-Sunose (KAS), and Flynn-Wall-Ozawa (FWO). In the Kissinger method, the Ea and A were calculated from different heating rates (10°C/min, 20°C/min, 30°C/min, and 40 °C/min) using Equation (10), where Tm represents the peak decomposition temperatures corresponding to each of the heating rates.

The Kissinger plot, illustrating $\ln(\beta/T_m)$ against $1000/T$ (K⁻¹) for the decomposition of oil shale, is presented in Figure 3. The regression equations and the coefficient of determination (R²) are also provided. The activation energy (Ea) and pre-exponential factor (A) were calculated from the slope and intercept, respectively. The results obtained using the Kissinger method yielded an Ea of 86.94 kJ/mol and A of $1.59 \times 10^6 \text{ min}^{-1}$.

The kinetic parameters for KAS and FWO methods were computed using Equations (11) and (12), respectively, with respect to a specified conversion value, α . Figure 4 illustrates the variation in conversion with the corresponding temperature of oil shale at different heating rates. To determine the kinetic parameters for both KAS and FWO, a consistent conversion value (α) ranging from 0.1 to 0.9 was selected, each paired with its corresponding temperature at different heating rates. The KAS plots, portraying $\ln(\beta/T_2\alpha)$ against $1000/T\alpha$ for various conversion values, are presented in Figure 5(a). Similarly, Figure 5(b) displays the FWO plots of $\ln(\alpha)$ against $1000/T$ for different conversion values. For all the methods, the activation energies and intercepts were calculated from the slopes and intercepts of their respective graphs. The resulting correlation coefficients (R²) were notably high in most cases, ranging from approximately 0.8108 to 0.9838.

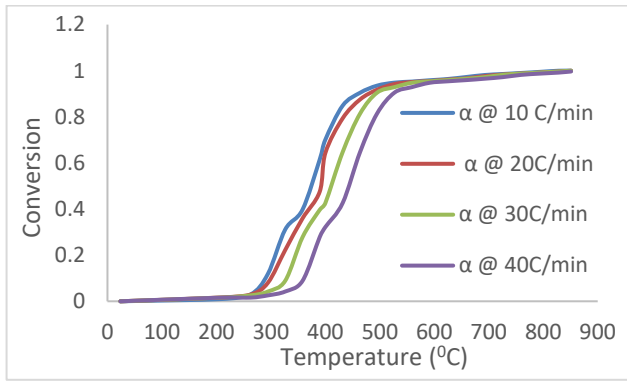


Figure 4: Effect of temperature on conversion of oil shale at different heating rates.

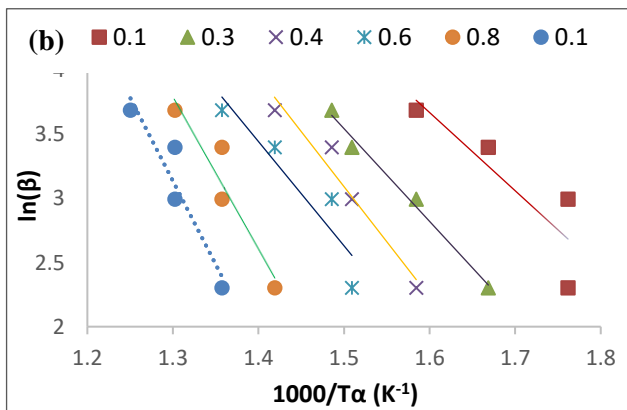
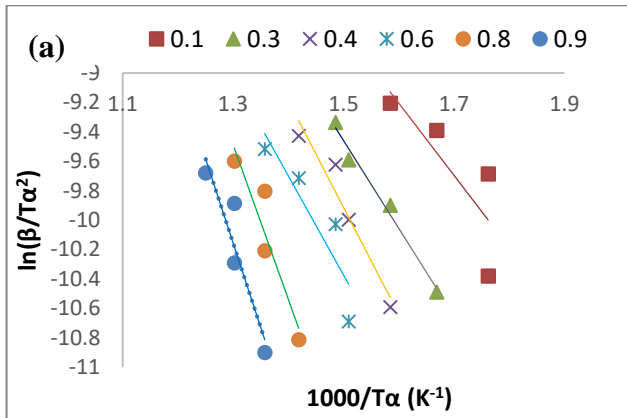


Figure 5: Analysis of kinetic parameters of oil shale using (a) KAS and (b) FWO method

From the analysis of Figure 6, it become apparent that the value of activation energy for KAS and FWO is 64.945 kJ mol⁻¹ and 76.305 kJ mol⁻¹ which can be seen to be different for the selected values of conversion which reflects the presence of a complex mechanism that occurs in the solid structure and also that activation energy depends upon conversion. It's worth noting that model-free isoconversional techniques are employed to calculate Ea as a function of conversion without making assumptions about the reaction model. This stands in contrast to the Kissinger method, which provides a single activation energy value for the entire process.

Hence, the activation energy obtained from the Kissinger method (~86.94 kJ/mol) exceeds that derived from the KAS method (64.945 kJ/mol) and the FWO method

(76.305 kJ/mol). This divergence arises because the Kissinger method accounts solely for the peak temperature (T_{peak}) of the sample, while the KAS and FWO methods encompass a broader temperature range based on varying degrees of conversion (isoconversional). A similar observation is also noted in the pre-exponential factor values.

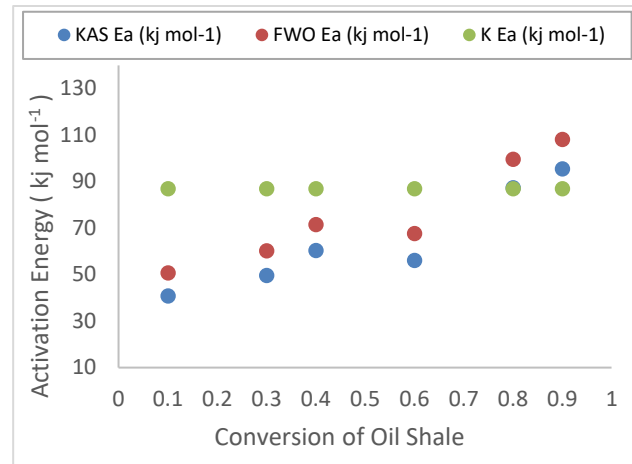


Figure 6: Effect of Ea as a function of conversion β of the oil shale.

3.2.2 Distributed Activation Energy Model (DAEM)

Results obtained from the thermogravimetric analysis of the sample were further analyzed using the Distributed Activation Energy Model (DAEM) to obtain the key kinetic parameters, including Ea and A. The DAEM model provides insight into the distribution of activation energies governing pyrolytic mass conversions under varied heating rates. Therefore, Figure 7 illustrates the behaviour of the kinetic parameters as functions of oil shale conversion (α), ranging from 0.1 to 0.90. Hence, linear and parallel trends observed for different values of V/V_{∞} (0.1– 0.9) at various heating rates suggest that the decomposition of the sample can be effectively described by 1st-order reactions that is taking place simultaneously.

The activation energy (E) and frequency factor (A) varies from 40.82 to 95.44 kJ/mol-1 and 6.93×10^2 to 7.37×10^5 min⁻¹ respectively. On average, the values for E, A, and the coefficient of determination (R^2) are approximately 64.945 kJ/mol-1, 1.87×10^5 min⁻¹, and 0.8549 respectively. These variable values of activation energy and frequency factor stress the complexity nature of the pyrolytic decomposition observed during thermal analysis. Thermogravimetric analysis (TGA) stands as a widely utilized technique for evaluating the thermal decomposition of oil shale.

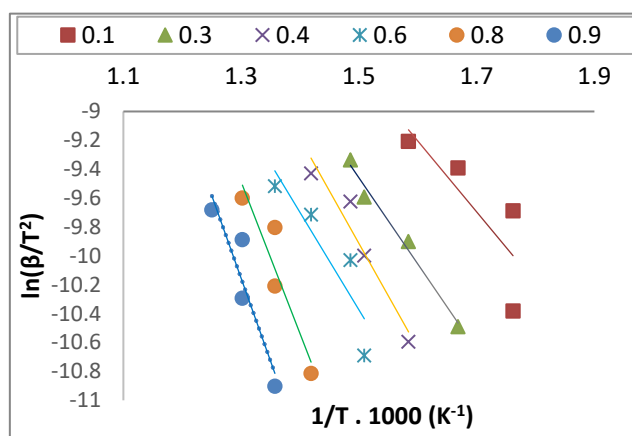


Figure 7: Analysis of kinetic parameters of oil shale

Various methods, including isoconversional techniques like Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO), as well as others such as Kissinger, Coats and Redfern, and Distributed Activation Energy Model (DAEM), are commonly employed for calculating kinetic parameters. A comparison of the mean activation energy values obtained from each of these methods with data from literature reveals that the kinetic parameters are specific to each individual case of oil shale.

For instance, a study by Miura and Maki (1998) shows a non-isothermal TGA on Nigerian Lokpanta oil shales, observed activation energy values that ranges from 73.2 to 75 kJ/mol, which closely aligns with the values calculated in this study (76.305 kJ/mol, 64.945 kJ/mol, 86.94 kJ/mol) using the FWO, KAS, and Kissinger methods, respectively. Conversely, Zhang et al. (2021) calculated the value of E as 167 kJ/mol for non-isothermal TGA of Spanish Puertollano oil shale. Additionally, results obtained for Turkish's oil-shale indicated activation energies for the lower-temperature degradation and the primary decomposition stage of around 26 kJmol⁻¹ and 43 kJmol⁻¹ respectively. These variations in results can be attributed to the effect of process parameters, such as particle size and heating rate.

Furthermore, it is important to recognize that oil shale, particularly its kerogen component, possesses a complex heterogeneous nature. Consequently, obtaining identical experimental results for nominally the same sample can be challenging. Therefore, it is essential to maintain consistency in experimental techniques, including sample preparation procedures, analysis methods, and the chosen kinetic model, to facilitate meaningful comparisons.

4 CONCLUSION

This research investigates the thermal degradation behavior of Bida oil shale kerogen using thermogravimetric analysis (TGA) at varying heating rates (10, 20, 30, and 40 °C/min). Employing kinetic analysis methods such as Kissinger (K), Flynn-Wall-

Ozawa (FWO), Kissinger-Akahira-Sunose (KAS), and the Distributed Activation Energy Model (DAEM), the study provides novel insights into the temperature-dependent variations in oil shale pyrolysis. The results reveal significant impacts of heating rates on decomposition temperatures and kinetics, with higher heating rates shifting decomposition temperatures due to differences in heat transfer efficiencies within the sample.

Distinct stages of decomposition were identified, with devolatilization starting around 260°C and progressing rapidly until approximately 526°C, followed by a gradual decline in decomposition rate. The kinetic analysis using isoconversional methods provided valuable insights into activation energies (E_a) and pre-exponential factors (A), indicating a complex decomposition mechanism influenced by varying conversion levels. Activation energies ranged from 64.945 to 86.94 kJ/mol. The DAEM further elucidated the kinetics of oil shale decomposition, highlighting the heterogeneity of pyrolytic processes under different heating rates. The average activation energies and frequency factor calculated using the DAEM method were 64.95 kJ/mol and $1.87 \times 10^5 \text{ min}^{-1}$. The differences in results obtained from various methods underscore the complex reaction mechanisms occurring during the pyrolysis process and the effects of different heating rates.

Overall, the findings contribute to refining kinetic models for oil shale pyrolysis, enhancing the understanding of critical factors shaping thermal degradation behaviors. This study has significant implications for optimizing oil shale processing strategies and advancing the fundamental understanding of pyrolysis mechanisms.

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