Study of the Kinetics and Mechanisms of Thermal Decomposition of Ellajjun Oil Shale

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Abstract

Oil Shale kinetic parameters have been determined for Ellajjun oil shale samples. Estimation of activation energy and frequency factor was performed using different standard procedures. The employed standard methods are used to estimate the kinetic parameters using TGA/DGA data. Heating rates; 1, 3, 5, 10, 30, and 50 $^{o}Cmin^{-1}$ are used with a 100 $mlmin^{-1}$ nitrogen flow rate.

The kinetic parameters determined using Friedman, Kissinger-Akahira-Sunose (KAS) Method, Flynn-Wall-Ozawa (FWO) and other methods. The activation energy and pre-exponential factor estimated using Friedman, KAS, FWO did not produced the required matching results while Coats & Redfern procedure was the best to result in good estimates of the kinetic parameters that produced predicted curves in good match with experimental data.

Keywords: Pyrolysis, Oil Shale, TGA, Kinetics, Parameters.

Introduction

World reserves of conventional fossil fuels such as petroleum, natural gas, oil shale and coal are finite. The supply of energy has become a worldwide problem in recent years. Many countries have attempted to diversify their potential energy sources in order to alleviate the impact of oil price increases and their effect on the economy. Oil shale represents an enormous potential as a substitute but it needs technology development to improve the existing industry for dissemination.

Thermogravimetric analysis (TGA) of oil shale samples has been extensively used as a means of determining pyrolysis characteristics and also to determine kinetic parameters [1 -12]. Thermogravimetric analysis (TGA) is an analytical device used for accurately measuring weight change of a material subjected to a temperature history. The weight loss information can be used to construct kinetic models of the decomposition process.

Non-isothermal thermogravimetry (TG) has been applied in the study of the kinetics of thermal decomposition of Green River oil shale kerogen [10]. It was shown that the decomposition

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process involves two consecutive first order reactions. Kerogen decomposes to intermediate bitumen and the pyrolytic bitumen further decomposes into oil and gas.

Torrente and Galan [4] studied the kinetics of thermal decomposition of oil shale from Puertollano (Spain) by isothermal and non-isothermal thermogravimetry analyses. They reported that decomposition of the shale could be described by overall first-order kinetics. Kök [3] studied the thermal behavior of Seyitomer oil shale by thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC). It was reported that the decomposition took place in more than one reaction region where the apparent activation energies of the first region are higher. Higher heating rates resulted in higher reaction temperatures. It was shown that the decomposition process of the oil shale could be described by a pseudo first order reaction. Al-Ayed [13] investigated the kinetics of Ellajjun oil shale using a variable reaction order in which the calculated order varied between 1.85 and 2. Tiwari, P. and Deo, M. [8] indicated in their recent work that product evolution temperature is heating rate dependent, which negate iso-conversional procedure and augment the assumption of activation energy variation with heating rate.

Karabakan and Yurum [9] investigated the effect of mineral matrix of oil shales. They found out that pyrolysis reactions were catalyzed by alkaline earth metal and inhibited by silicates. The inhibition effect of the silicates seemed to be greater than the catalytic effect of the carbonates in the pyrolysis reactions of the original Göynük and Green River oil shales. Jaber and Probert [5] studied Jordanian oil shale samples using integral method in the analysis of TG data in order to determine the pyrolysis kinetics. It was observed that the magnitude of the total mass loss was mainly dependent on the final temperature, as well as, to a lesser extent, on the heating rate employed. Williams and Ahmad [6] studied oil shale samples in a thermogravimetric analyzer in relation to heating rate and temperature using non-isothermal and isothermal analysis respectively. The main region of mass loss corresponding to hydrocarbon oil and gas release was between 473–893 K.

The present research is an experimental study on Ellajjun oil shale samples using a TGA apparatus under non-isothermal conditions. The objective was to investigate the effects of heating rate and the nature of oil shale on the kinetic parameters. The obtained data are tested on different available kinetic models to determine activation energy and frequency factors of the decomposition kinetic equation. In order to achieve these objectives, kinetic models are proposed which allow a good correlation of the results obtained.

Theoretical approach

The application of dynamic TG methods holds great promise as a tool for unraveling the mechanisms of physical and chemical processes that occur during solids decomposition. In this investigation, known developed methods have been used to analyze the non-isothermal kinetics of Ellajjun oil shale. The pyrolysis process may be represented by the following reaction scheme:

$$\textbf{Oil shale}\ (\text{solid}) \rightarrow \textbf{Shale oil}\ (\text{liquid}) + \ \textbf{Hydrocrabons}\ (\text{gas}) \qquad (1)$$

The rate of transformation of material during pyrolysis is defined in-terms of conversion x; and is given as:

$$\frac{dx}{dt} = k(T)f(x) \qquad (2)$$

Where; $x = \left(\frac{w_{0-}w_t}{w_0}\right)$ (3)

where w_0 is total weight loss of sample recorded at 550^{o}C for each TG experiment at constant heating rate. The heating rate β is defined as:

$$\beta = \frac{dT}{dt} \qquad (4)$$

Equation (2) is expressed interms of heating rate as:

$$\frac{dx}{dt} = \beta\frac{dx}{dT} = k(T)f(x) \qquad (5)$$

Where $f(x)$ and $k(T)$ are functions of conversion and temperature, respectively. The function k (T), is the temperature dependency of the rate of mass loss, is often modeled successfully by the Arrhenius standard equation:

$$k(T) = k_o Exp(-E/RT) \qquad (6)$$

where E is the apparent activation energy, k_o the pre-exponential factor and R the universal gas constant.

Kissinger-Akahira-Sunose Method (KAS method)

Mathematical Development

This method (14, 15) is based on equation (2) in which upon re-writing to obtain the following:

$$dx/f(x) = \frac{k_o}{\beta}exp(-E/RT)dT \qquad (7)$$

If equation (7) is integrated with the initial conditions of $x = 0$ at $T = T_0$ to obtain the following expression:

$$g(x) = \int_o^x \frac{dx}{f(x)} = \frac{k_0}{\beta}\int_{T_o}^{T} exp\left(\frac{-E}{RT}\right)dT = \frac{k_oE}{\beta R}p\left(\frac{E}{RT}\right) \qquad (8)$$

Most of technique assumes that the pre-exponential factor k_o , the conversion function $f(x)$ and activation energy E are independent of temperature while frequency factor and activation energy are independent of conversion, x. The KAS method is based on the Coats and Redfern approximation (16)

$$ln(\beta/T^2) = ln(k_oR/Eg(x)) - E/RT \qquad (9)$$

Equation (9) when plotted will lead to activation energy and frequency factor estimation. Plotting LHS on y-axis for constant selected conversion values (iso-conversional points) against inverse of pyrolysis temperature on x-axis will culminate in kinetic parameters determination.

Equation (9) is plotted for kinetic parameters estimation and the obtained graphs are depicted in figure 1 below. In figure 1, plotting $ln(\beta/T^2)$ on y-axis for selected conversion points indicated as horizontal lines and different heating rates represented by inclined vertical lines. The activation energy values for each selected conversion point are indicated by the slope of the trend-line obtained. On the other hand, the frequency factor is calculated from the intercept value after substituting the appropriate quantities in the term, $(k_o R/Eg(x))$. The estimated values of activation energy and frequency factor are given in table I below:

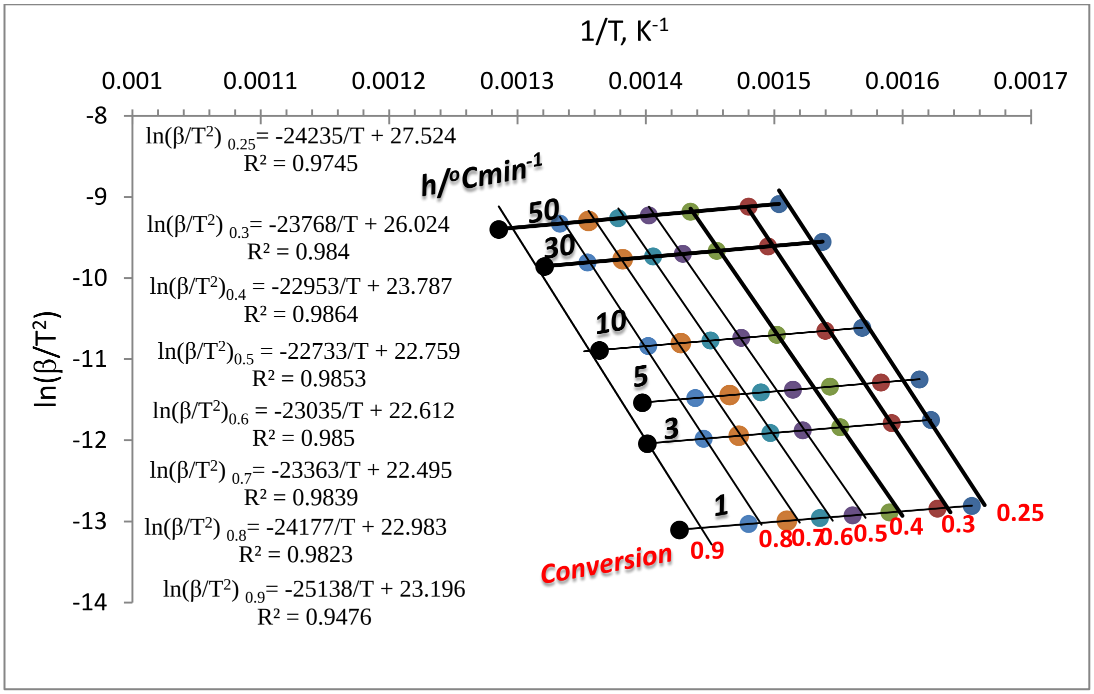

Figure 1. Estimated activation energy values with different iso-conversional points using KAS method.

The estimated values of activation energy and frequency factor values as tabulated in Table I are plotted as indicated in figure 2 The average values of activation energies at different iso-conversional points are calculated to be 197 kJ.mol^{-1} , the estimated values are plotted and compared with those calculated using Friedman method. From figure 2 it is quite clear that activation energy passes through a minimum value at 50%. Activation energy obtained through KAS method is varied within ± 8 kJ.mol^{-1} of the average value, while, the fluctuations in activation energy is much higher in those values obtained according to Friedman procedure.

Table I. Activation energy and frequency factor values obtained from figure 1

Activation Energy, Symbol	kJ/mol	Conversions	Frequency factor	Intercepts	R-value
$E_{0.25}$	201.5	0.25	7.3E+15	36.521	0.9745
$E_{0.3}$	197.6	0.3	2.0E+15		0.9841
$E_{0.4}$	190.8	0.4	3.3E+14	33.423	0.9864
$E_{0.5}$	189.0	0.5	1.7E+14	32.791	0.9853
$E_{0.6}$	191.5	0.6	2.3E+14	33.062	0.985
$E_{0.7}$	194.2	0.7	3.2E+14	33.401	0.9839
$E_{0.8}$	201.0	0.8	9.3E+14	34.462	0.9823
$E_{0.9}$	209.0	0.9	2.7E+15	35.525	0.9476

The activation energies calculated values are for the hydrocarbon evolution region. This fact is clear from the selected iso-conversional points at the beginning and at the end of each run. The initial weight loss of sample is attributed to the loss of moisture and structural water associated with clay. As a result, the initial conversion point selected for the determination of the kinetic parameters is 25% while the final point is taken at 90% which corresponds to 550 °C final pyrolysis temperature. The conversion is tailing with temperature at values higher than 90%.

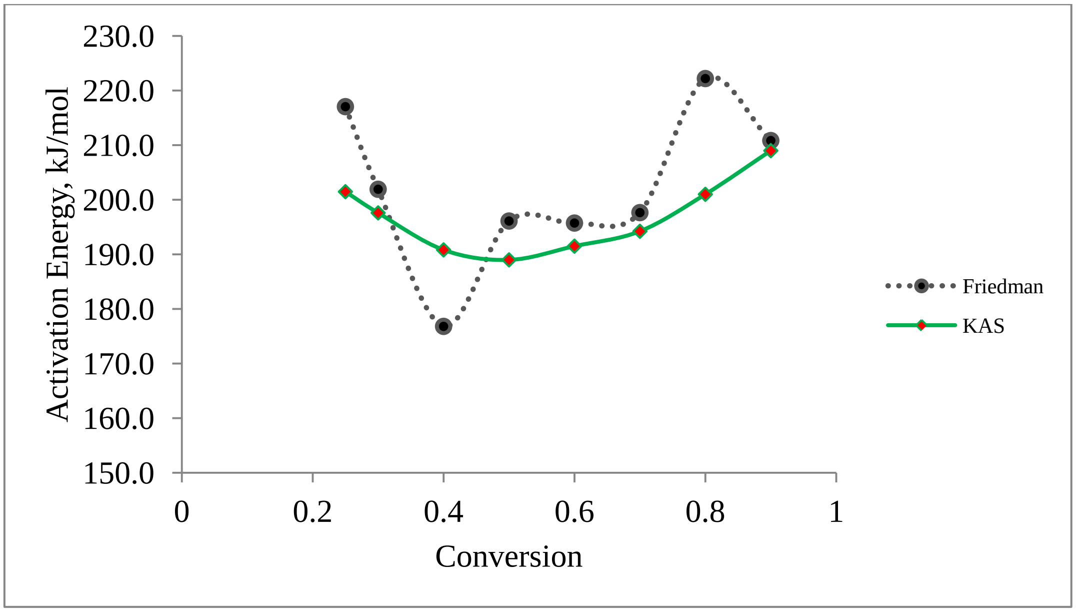

Figure 2 Estimated activation energy values with iso-conversion points using KAS method**.**

The activation energy (E) and frequency factor (k_o) estimated through KAS procedure are related to each other according to the following equations:

$$ln(k_o) = 0.292E - 22.44 \ , \quad 0.25 \le x \le 0.5, \qquad R^2 = 0.998 \qquad (10, a)$$
$$ln(k_o) = 0.142E - 5.714 \ , \quad 0.5 \le x \le 0.9, \qquad R^2 = 0.998 \qquad (10, b)$$

Equations (10) are obtained with $\mathbf{R^2}$ greater than 0.99. The two equations are probably due to the nature of the curve concavity where 50% conversion point is fitting both lines extremely well

Friedman method (17)

Mathematical Manipulations:

This method is a differential iso-conversional method and is directly related to equation (2). Friedman procedure is based on selected constant conversion points in the whole range of experiment irrespective of heating rate. In the present work, conversion points 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 have chosen.

In this method the conversion function $f(x)$ has been assumed to be of the standard form:

$$f(x) = (1 - x)^2 \qquad (11)$$

Equation (2) and introducing heating rate into the equation in its usual way of introduction, and if the logarithm is taken, the following form of equation is obtained:

$$\ln(\beta \frac{dx}{dT}) = -\frac{E}{RT} + \ln(k_o f(x)) \qquad (12)$$

Activation energies are estimated from equation (12), when plotting LHS at a selected constant conversion points that have been inferred from experimental data at different heating rates, (iso-conversional) against inverse of pyrolysis temperatures measured in Kelvin.

Figure 3 shows the determination of activation energies from the slopes of different conversion points. On the other hand, the pre-exponential factor is calculated from the trend-line equation of the plotted data. The obtained trend-line linear equation for the whole data is of the form:

$$y = mx + c \qquad (13)$$

Where: $\boldsymbol{y}$ represents the LHS of equation (12)
$\boldsymbol{m}$ slope that gives activation energy.
$\boldsymbol{x}$ inverse of pyrolysis temperature, K^{-1}.

c intercept; the quantity, $\ln\left(k_o f(x)\right)$, used to determined frequency factor at a given conversion function form and at selected iso-conversional experimental points.

Figure 3 is plotted to estimate activation energies at the studied heating rates and selected conversion points. It is clear from the graph and subsequently the calculated activation energy values as tabulated in Table I, that activation energies varies between 177 and 222 kJmol^{-1}.

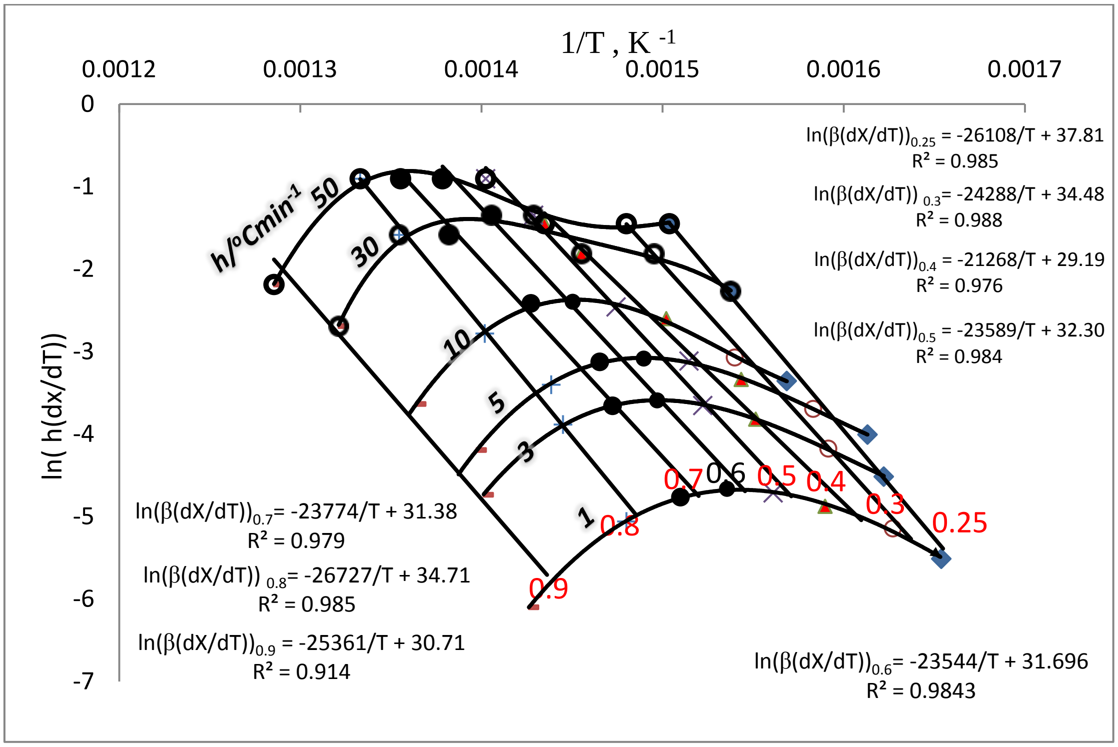

Figure 3 Friedman Method for activation energy and frequency factor estimation.

Meanwhile, the calculated values of frequency factor were 1.3*10^{13} and 2.9*10^{16} min^{-1} correspondingly. Since activation energy is reflect of the mechanism of chemical reactions, there is no direct relationship between conversion and the values of activation energy obtained.

The pre-exponential factor and activation energy are related to each other in the following form:

$$ln(k_o) = 0.178E - 1.267, \qquad R^2 = 0.951 \qquad (14)$$

Table II. Activation energy and frequency factor values obtained from figure 3

Activation Energy, Symbol,	kJ/mol	Conversions	Intercepts	Frequency factor	R-value
$E_{0.25}$	217.1	0.25	38.4	4.7E+16	0.985
$E_{0.3}$	201.9	0.3	35.2	1.9E+15	0.988
$E_{0.4}$	176.8	0.4	30.2	1.3E+13	0.976
$E_{0.5}$	196.1	0.5	33.7	4.3E+14	0.984
$E_{0.6}$	195.7	0.6	33.5	3.6E+14	0.984
$E_{0.7}$	197.7	0.7	33.8	4.7E+14	0.979
$E_{0.8}$	222.2	0.8	37.9	2.97E+16	0.985
$E_{0.9}$	210.8	0.9	35.3	2.2E+15	0.914

Figure 3 Shows that no definite relationship between activation energy calculated according to Friedman procedure and conversion. It is clear from the figure that activation energy decreases from: 217 to 177 kJ/mol from initial values of used conversions to about 40%. Low conversion is characterize by Pyrolysis reactions with low activation energies, the pyrolysis of oil shale resulted mainly from the rupture of weak chemical bond, probably the rupture of weak cross linked bonds, such as, C-O, C-S bonds (19,20) etc. Also, rupture of branched functional groups in kerogen long molecular structure. These weak bonds have low rupture energy which commensurate with pyrolysis gaseous products such as H_2O, CO_2, H_2S, H_2 and light hydrocarbons.

Campbell (21) studied the rate of evolution of CH_4, H_2, CO, CO_2, and C_2, C_3 hydrocarbons during pyrolysis of Colorado Oil Shale at linear heating rates varying from 0.5 to $4.0^{o}Cmin^{-1}$. More of hydrogen release was reported at lower heating rates. Methane formation and evolution initiated at temperature slightly lower than 350 ^{o}C and reaching a maximum value at 445 ^{o}C. Rate of methane release increased with a decrease in heating rate. Ethane and ethene (C_2) production increased to a maximum value at 450 ^{o}C and stopped at slightly higher than 550 ^{o}C. C_3 (propane and propene) production was found to occur at 450 ^{o}C and its formation was stopped at 525 ^{o}C. Oil release profile was corresponding closely to that observed for C_1 and C_2 profiles.

Flynn-Wall-Ozawa Method (FWO): (22, 23)

Mathematical Development

All the four methods examined in this research work assumed equation (2) is the main equation for oil shale pyrolysis. The Flynn-Wall-Ozawa method is derived from the integral iso-conversional method. Using Doyle's approximation for the integral that allows the quantity

$$ln\big(p(E/RT)\big) \cong\ -5.331 - 1.052\, E/RT \qquad (15)$$

$$dx/f(x) = \frac{k_o}{h} exp(-E/RT)dT \qquad (16)$$

If equation (16) is integrated with the initial conditions of $x = 0$ at $T = T_0$ to obtain the following expression

$$g(x) = \int_o^x \frac{dx}{f(x)} = \frac{k_0}{\beta} \int_{T_o}^{T} exp\left(\frac{-E}{RT}\right) dT = \frac{k_o E}{\beta R} p\left(\frac{E}{RT}\right) \qquad (17)$$

Combining equations (15) and equation (17) to obtain the final form used by FWO procedure as follows:

$$ln(\beta) = ln(k_o E/Rg(x))\ -5.331 - 1.052\, E/RT \qquad (18)$$

Hence, for iso-conversional points, the plot of LHS of equation (18) verses inverse of pyrolysis temperature obtained from experimental data recorded at different heating rates, would be a straight line whose slope can be used to evaluate the activation energy and the corresponding frequency factor. Figure 4 exhibit such a plot and the calculated kinetic parameters, namely, activation energy and pre-exponential factor have been tabulated in Table III.

Inspecting the values of activation energy as reported in table III, similar trend of those values obtained by KAS is observed. The activation energy passes through a minimum value at 0.5 conversions. On the other hand, the calculated frequency factors are much similar to those obtained by KAS procedure. The following equations are obtained for frequency factor and activation energy for FWO method of analysis.

$$ln(k_o) = 0.303E - 24.54, \quad 0.25 \le x \le 0.5, \qquad R^2 = 0.997$$
$$ln(k_o) = 0.138E - 6.637, \quad 0.5 \le x \le 0.9, \qquad R^2 = 0.998 \qquad (19)$$

Whilst KAS correlation obtained earlier for the kinetic parameters are as follows:

$$ln(k_o) = 0.292E - 22.44\ , \qquad 0.25 \le x \le 0.5, \quad R^2 = 0.997$$
$$ln(k_o) = 0.142E - 5.714\ , \qquad 0.5 \le x \le 0.9, \quad R^2 = 0.998 \qquad (20)$$

It is apparent from values as indicated by equations (19) and (20) that both methods are in agreement and predict same values for the kinetic parameters.

Table III Activation energy and frequency factor values obtained from FWO method.

Activation Energy,		Conversions	Intercepts	Frequency factor	R-value
Symbol,	kJ/mol				
$E_{0.25}$	201.6	0.25	36.7	7.59E+15	0.977
$E_{0.3}$	198.0	0.3	35.4	2.3E+15	0.986
$E_{0.4}$	191.9	0.4	33.7	4.16E+14	0.988
$E_{0.5}$	190.4	0.5	33.1	2.34E+14	0.987
$E_{0.6}$	192.9	0.6	33.4	3.09E+14	0.987
$E_{0.7}$	195.7	0.7	33.7	4.36E+14	0.986
$E_{0.8}$	202.3	0.8	34.7	1.22E+15	0.984
$E_{0.9}$	210.3	0.9	35.8	3.51E+15	0.953

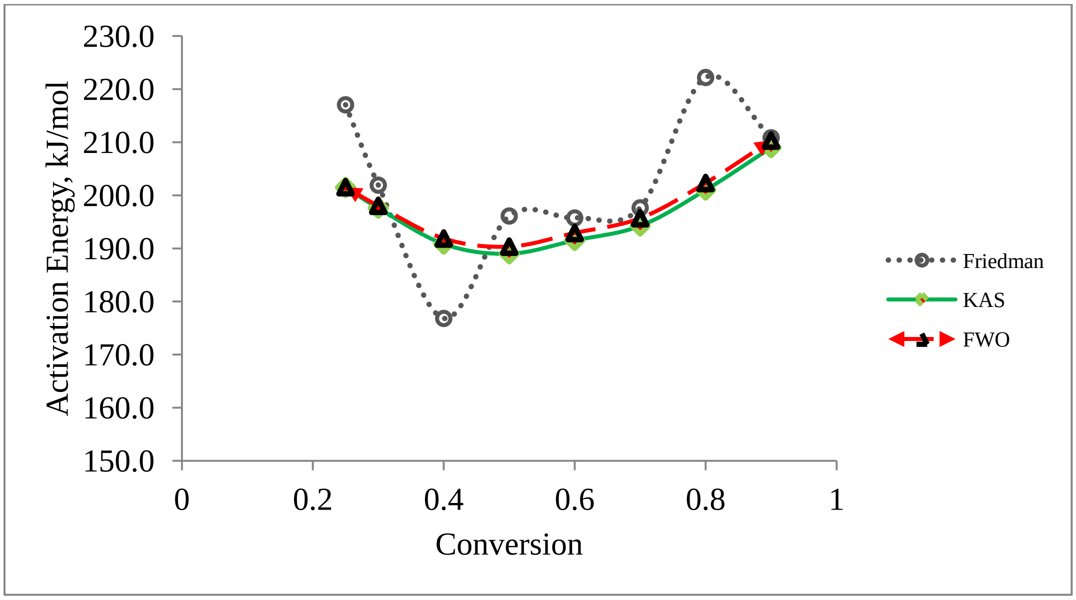

Figure 4 Activation energy as function of conversion calculated by different methods.

Conclusions

In the present research paper various developed methods for estimating kinetic parameters have been tested and checked their suitability to model Ellajjun Oil Shale pyrolysis kinetics.

Three models have been tested after brief mathematical manipulations to extract the final form of equation employed to estimate the activation energy and pre-exponential factor.

In summary, the examined procedures were found that some partial fitting to data was obtained. In conclusion, it cannot be said that any particular procedure fitted the experimental data completely.

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