Kinetics of Oil Shale Pyrolysis and Oil Composition

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Abstract

The oil shale industry is going through a revolution of sorts. After the oil crisis in the 1970s, a great deal of effort was spent on research and development and on pilot technologies. The oil price collapse in the early and mid eighties led to the total discontinuation of the oil shale research and development programs. Extensive research was conducted both in on-surface and in-situ production methods. Even though some large pilot underground retorting operations were performed, the on-surface (mining and processing) methods were closest to full-scale (~10,000 barrels/day) commercial implementation. The in-situ production technologies have seen a significant revival since some recent advances. The slow thermal pyrolysis of the organic matter in shale leads to a light oil product that would not require additional thermal upgrading. In this paper we present isothermal and non-isothermal kinetics of the pyrolysis of the Greenriver shale using thermo gravimetric analyses.

Introduction

Oil shale can be a viable alternative source for fast depleting natural sources of petroleum. The organic part in the oil shale undergoes chemical decomposition on thermal heating, known as pyrolysis and a liquid substance (shale oil) is produced. The yield and quality of the pyrolysis products depend on source material (geological availability, quality, size of the rock and its constituents), temperature, pressure, and time of the reaction. The main constituent of this organic part of the shale is Kerogen (which can be represented approximately as $C_{200}H_{300}SN_5O_{11}$, ~10 wt/wt % of rock shale), and small percent of bitumen is present. The extent of kerogen decomposition, yield of the products and kinetics of the reaction also depend on the environment of thermal heating, like in the presence nitrogen (pyrolysis) or air (combustion).

In this study, the kinetics of the Mahogany oil shale are obtained using thermal gravimetric analysis (TGA, Q-500). The present study covers isothermal (300-600°C) and

non-isothermal (0.5 to 50°C/min) decompositions of crushed Mahogany Oil Shale (single particle size, 100 mesh) with TGA in N$_2$ (Pyrolysis) and air (Combustion) environments. Data obtained from TGA are analyzed in detail. Different mathematical approaches for both the cases are applied to determine the kinetic parameters (activation energy, Ea and pre-exponential factor, A) with the assumption of first order reaction. Comparisons between pyrolysis and combustion kinetic data, and with the data in the literature, are included in this work. For isothermal experiments, the data were fit using the integral method and the activation energy and pre-exponential factor, for the N$_2$ environment were 135 kJ/mol (100 kJ/mol for air) and 1.2E+09 (5.1E+07 for air) respectively. Non-isothermal kinetic data were derived using four different methods, namely, direct Arrhenius plot, integral method, Friedman approach and the maximum rate method. The goodness of the fit and values of kinetic parameters are different, and depend on the mathematical method used for the same sample. Data and detailed analyses are provided in this extended abstract. The tradeoff between activation energy and pre-exponential factor is also considered in obtaining a good fit.

Experimental Section- TGA

The mahogany oil shale samples were crushed to 100 mesh size and then dried for four hours to remove moisture, if any was present (there was no weight loss found during drying in the TGA experiments). The TGA experiments were performed with 20-30 mg of oil shale and other operating conditions such as purging time (10 min) and flow rate of purge gas (60ml/min) were kept fixed for all experiments. For the isothermal experiments, the thermal induction time was kept as low as possible (100°C/min, the maximum ramp rate of TGA Q-500 and 5 hour reaction time). The non-isothermal experiments were performed to 1000°C (the highest temperature possible in TGA Q-500). All of the experiments were repeated and found to be reproducible.

Kinetic Expression- Mathematical models

Different mathematical approaches were used to determine the kinetic parameters (activation energy, Ea and pre-exponential factor, A) with the assumption of first order reaction. The kinetics of the pyrolysis of Mahogany oil shale were studied for different, constant heating rates and constant temperature profile. Tables 1-4 show the experimental

conditions used for both the cases. Some of the non-isothermal and isothermal experiments were done with N_2 and Air environments.

The kinetic parameters were determined using the following simple mechanism.

Kerogen $\longrightarrow$ Products
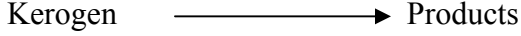
The decomposition profile of kerogen in the air environment gives two peaks for both isothermal and non-isothermal cases. Thus two successive first-order (series) reactions were used to model and analyze the data. The reaction is assumed in the form,

Kerogen $\longrightarrow$ Bitumen $\longrightarrow$ Products
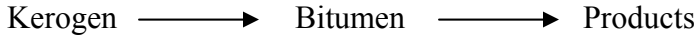
Where, bitumen is the intermediate product.

As some pre-test experiments with TGA (up to 1000°C) indicate, 10-12 wt % of the total shale is organic (assumed to be kerogen here). Thus all the data were normalized on the basis of 10 wt/wt % of the kerogen. The conversion of kerogen to product is defined as,

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_\infty)} \quad \text{or} \quad \alpha = \frac{(W_0 - W_t)}{(W_0 * X)} \tag{1}$$

Where, $W_0 =$ Initial Weight of the sample, (mg), W_t = Weight of the sample at time t, (mg), $W_\infty =$ Weight of the sample at the end of the experiment, (mg), X = Percent of the organic part, decomposing during experiment time (max 10%).

With first-order reaction, the rate law is expressed as follows.

$$\frac{d\alpha}{dt} = A.\exp(\frac{-Ea}{R.T}).(1-\alpha) \tag{2}$$

Where, A = Frequency (Pre-exponential) factor, (S^{-1}), Ea = Activation energy, (KJ.mol^{-1}), R =Gas constant, (8.314 KJ. mol^{-1} K^{-1}), T =Temperature, (K).

The value of X is not fixed in this work but, used as the actual value. In the isothermal experiments, the thermal induction period is not included in the analysis of data, thus the decomposition of the organic continues during this period. The conversion data were normalized from the isothermal condition to the end point of the analysis. Non-isothermal TGA data were analyzed in the range of organic weight loss. Conversion profiles for each non-isothermal experiment were normalized from zero to one. The temperature at which the weight derivative begins to rise is chosen as the zero conversion point and the temperature at which weight derivative returns to the base line is the end point (complete conversion of the organic part) of the analysis.

Different methods were employed to study the kinetics of the Mahogany oil shale. For the isothermal data, the integral method was employed, and for non-isothermal analysis, four methods (differential, integral, Friedman, and maximum rate method) were used.

Isothermal: Integral method

The integral form of the equation (2) can be written as

$$\ln(1-\alpha) = -k.(t-to) \tag{3}$$

Where, t_o is the time at the start of the constant- temperature period (when isothermal condition is reached). In this study, the thermal induction part is eliminated from the kinetic analysis and correspondingly the W_∞ is corrected.

Non-isothermal: Differential (Direct Arrhenius plot) method

The kinetic rate expression for non-isothermal experiments with Arrhenius dependency can be derived by introducing heating rate (β) in equation (2)

$$\frac{d\alpha}{dT} = \frac{A}{\beta}.\exp(\frac{-Ea}{R.T}).(1-\alpha) \tag{4}$$

Where, $\beta = \frac{dT}{dt}$

$$\ln\left[\frac{1}{(1-\alpha)}\right]\frac{d\alpha}{dT} = \ln(\frac{A}{\beta}) - (\frac{-Ea}{R.T}) \tag{4}$$

The plot of $\ln\left[\frac{1}{(1-\alpha)}\right]\frac{d\alpha}{dT}$ against 1/T will give the starlight line, and values of *Ea* and A can be obtained by this line.

Non-isothermal: Integral method

Overall conversion vs. temperature curves

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)} = \frac{A}{\beta}\int_{T^\circ}^T \exp(\frac{-Ea}{R.T})dT$$

Finally equation can be rearranged as,

$$\ln\left[\frac{-\beta.\ln(1-\alpha)}{RT^2}\right] - \ln(1-\frac{2RT}{Ea}) = \ln(\frac{A}{Ea}) - (\frac{-Ea}{RT}) \tag{6}$$

The value of Ea and A can be obtained by a least square fit of the equation (e) to the experimental data. This can be done either iteratively or directly. The simplified form of the integral method used is,

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln(\frac{A.R}{Ea.\beta}) - (\frac{Ea}{RT})$$

Non-isothermal: Friedman method

Friedman procedure assumes successive first order reaction

$$\ln(\frac{d\alpha}{dt}) = \ln\left[A(1-\alpha)\right] - (\frac{Ea}{R.T}) \qquad (7)$$

Non-isothermal data can be analysed for specific conversion point (α) for all different heating rate, and the plot for $\ln(\frac{d\alpha}{dt})$ verses 1/T will gives a straight line. The slope and intercept will give the activation energy and pre exponential factor respectively.

Non-isothermal: Maximum rate method

Maximum rate method is a mathematical tool, which explains the maximum rate at a point when following condition is satisfied,

$$\frac{d\alpha^2}{dT^2} = 0$$

Thus, for first order reaction (n=1), equation (4) gives:

$$\ln(\frac{\beta}{T_m^2}) = \ln(\frac{A.R}{E} - (\frac{Ea}{R.T_m}) \qquad (8)$$

Where T_m, is the temperature at the maximum reaction rate and α_m will be the conversion at that condition.

T_m can be calculated from weight loss curves with different heating rates for the same sample. Apparent activation energy Ea and apparent frequency factor A can be determined by linear slope and intercept, respectively, equation (8).

Results and Discussion

TGA Curve

The total extractable kerogen content in Mahogany Oil Shale is about 10 % of the total weight. There was no significant weight loss during pre heating observed which

confirmed the absence of moisture in the sample. This was confirmed in TGA experiments, where no peak detection and weight loss was seen below 150°C, Figure 1. The reproducibly of the data was observed in all experiments, for example, Figure 1. There are two derivative peaks in all non-isothermal experiments, corresponding to organic and carbonate decompositions. The carbonate decomposition commenced at 525°C or above depending upon the heating rate and gave a weight loss of about 25-30%. There was a shift in maximum rate toward higher temperature with the increase in heating rate from 0.5 to 50°C/min. This difference is due to shorter exposure time to particular temperature at faster heating rates Figures 2 and 3.

In the nitrogen environment, only one peak is present in the range of the 300-550°C indicating that only one reaction or process occurs in this temperature range. While in air environment there are two peaks in the same temperature range, which indicate there are two reactions occurring simultaneously.

Two possible mechanisms were tested

1. A single step mechanism involving, kerogen → Products (N_2)
2. A two step mechanism represented as kerogen → Bitumen → Products (Air)

Isothermal

For isothermal experiments, the data were fit using the integral method. The activation energy and pre-exponential factors, for N_2 environment were 135 kJ/mole and 1.2E+09 respectively, while in air environment these were 100 kJ/mole and 5.1E+07 respectively.

Non Isothermal

Non-isothermal kinetic data were derived with four different methods, namely, direct Arrhenius plot, integral method, Friedman approach and Maximum rate method. The goodness of the fit, and the values of kinetic parameters are different, and depend on the mathematical method used for the same sample.

Conclusion

The kinetic mechanism of organic decomposition is different in different environments (N_2 and air). Fast heating provides a shift in decomposition rate curve towards higher temperature. Activation energy is more in N_2 than in air environment for the isothermal case. For non-isothermal experiments, different method gives different values for kinetic

parameters. The best fit tradeoff relationship between activation energy and pre exponential factor for N_2 is found with Friedman procedure while for air with maximum rate method.

References

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2. " Kinetics of Pyrolysis of Moroccan oil Shale by Thermogravimetry", Deepak S. Thakur and H Eric Nuttall, Ind. Eng. Chem. Res. 26, 1987, 1351-135

3. Study of different kinetic models for oil shale Pyrolysis, Shuyuan Li, Changtao Yue, Fuel Processing technology 85, 2003, 51-61

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5. "Study of Pyrolysis of Oil Shale", Shuyuan Li, Changtao Yue, Fuel, 82, 2003, 337-342.

Table: 1

ISOTHERMAL					N_2_normalized data	INTEGRAL APPRAOCH			
T	Total time	Initial weight	Start_ Isothermal temp		Normalization factor	N2		Slope	
^oC	min	mg	Time	Weight Loss	X	1/T	R^2	K	lnK
300	720	26.758	3.33	99.17	0.0917	0.00174	0.5163	0.0008	-7.1309
350	240	26.69	3.82	98.75	0.0875	0.0016	0.8893	0.0045	-5.40368
400	240	22.643	4.36	98.21	0.0821	0.00148	0.9644	0.0311	-3.47055
450	240	24.688	4.96	96.01	0.0601	0.00138	0.8157	0.2973	-1.21301
500	240	25.001	5.59	**89.29**					
550	180	23.953	6.3	**88.38**		These data can not be analyzed as before reaching Isothermal condition they lost more than 10% weight ,which corresponding to organic part in shale			
600	30	24.101	6.96	**87.89**					

Table: 2

ISOTHERMAL			Air_ normalized data			INTEGRAL APPRAOCH			
T	Total time	Initial weight	Start_ Isothermal temp		Normalization factor X	Air		Slope	
oC	min	mg	Time	Weight Loss		$1/T$, K	R^2	K	lnK
300	240	23.643	2.7	99.27	0.0927	0.00174	0.873	0.0365	-3.31044
350	240	23.391	3.82	98.14	0.0814	0.0016	0.8752	0.1909	-1.65601
400	240	23.241	4.31	96.85	0.0685	0.00148	0.8455	0.8725	-0.13639
450	180	32.162	4.88	94.32	0.0432	0.00138	0.864	2.8006	1.02983

Table: 3

NONISOTHERMAL		Start		End		max			R^2	slope	Intercept	Activation energy	A
Heating rate	Initial weight												
Beta	mg	T	wt %	T	wt%	Tmax	wt%	%/min					
0.5	22.645	255.66	98.68	421.6	91.98	392.76	93.52	0.039	0.961	9351	10.8	77.744214	24510
1	28.642	269.6	98.84	437.6	92.52	398.33	94.21	0.062	0.959	9002	10.07	74.842628	23624
2	26.94	280.06	98.67	456.4	91.57	414.15	93.48	0.181	0.962	10379	11.8	86.291006	266505
5	25.972	348.93	97.83	474	90.59	432.29	92.83	0.074	0.977	14873	17.93	123.65412	3E+08
10	38.452	349.79	98.26	490	90.33	445.62	92.74	1.348	0.972	14905	17.54	123.92017	4E+08
20	29.493	371.61	98.42	504	89.32	460.18	92.08	3.549	0.979	17757	21	147.6317	3E+10
50	22.374	377.32	98.57	530.6	88.87	477.03	92.11	9.099	0.967	17218	19.56	143.15045	2E+10

Table: 4

NONISOTHERMAL		First Peak							Second Peak					
Ramp rate	Initial weight	Start		End		max			End		max			weight loss
Beta	mg	T	wt %	T	wt%	Tmax	wt%	%/min	T	wt%	Tmax	wt%	%/min	%
0.5	18.688	179	99.33	311.3	91.84	279.9	94.8	0.11	396.4	87.09	340.2	89.2	0.108	12.91
1	20.261	199.1	99.41	323.8	92.05	294.1	94.71	0.1103	400.39	86.98	354.42	89.26	0.107	13.02
2	19.981	201.9	99.51	339.1	92.44	305.9	95.2	0.097	421.5	87.71	367.1	90.07	0.094	12.29
5	30.562	211.4	99.56	358.5	92.54	323.8	95.32	0.4545	459.65	87.28	392.22	89.87	0.437	12.72
10	34.986	216.5	99.98	374.9	92.31	337.1	95.18	0.9074	499.49	86.87	409.59	89.82	0.747	13.13
20	21.695	215.5	99.62	389.2	92.42	341.1	95.9	1.697	504.6	86.93	425.93	89.87	1.445	13.07
50	30.223	227.7	99.58	395.3	93.19	351.4	95.97	3.466	522.99	86.97	450.45	89.8	3.902	13.03

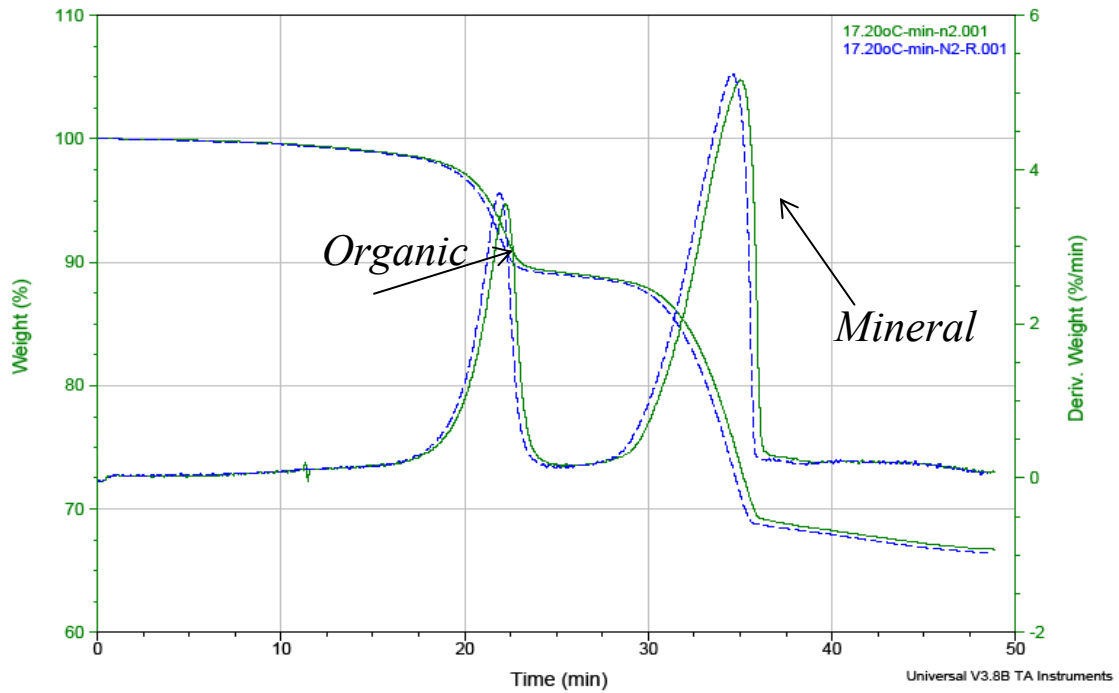Figure: 1 TGA Curve -Reproducibility of Data (Two Peaks)

Figure: 2 Non- isothermal data in N_2 environment (Single step mechanism for organic part)
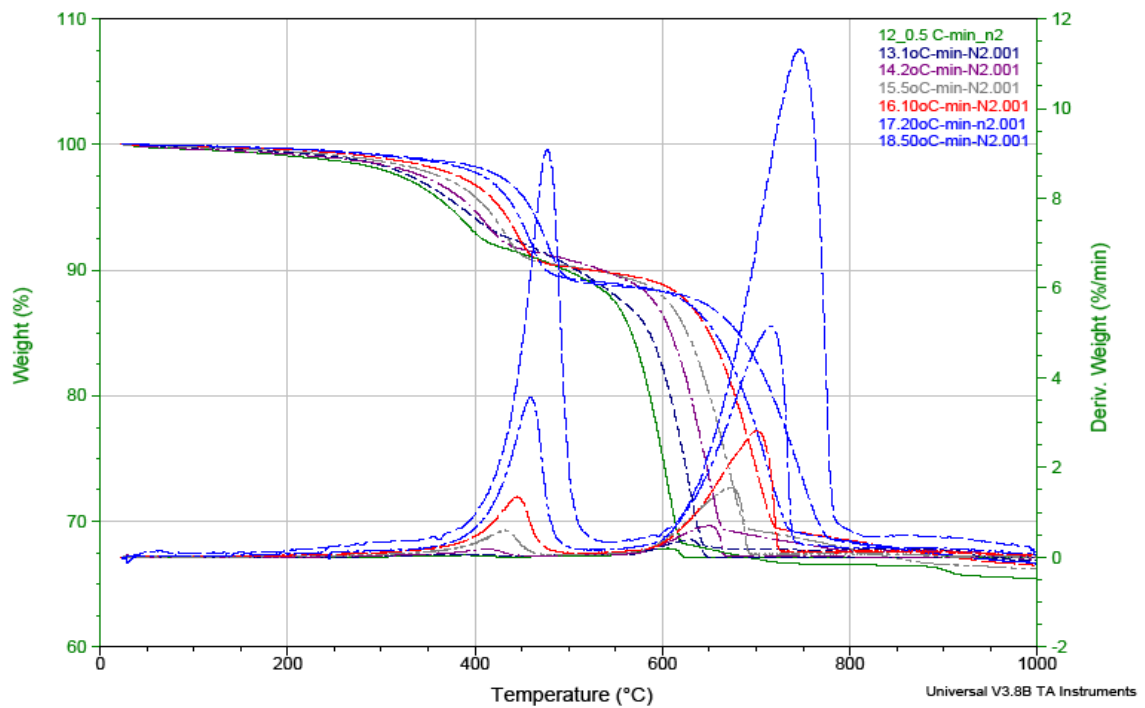
Figure: 3 Non- isothermal data in Air environment (two step mechanism for organic part)

Legend:
OS_O.5C_Air
OS_01C_air.001
OS_02C_Air.001
OS_05C_air.001
OS_10C_air.001
OS_20C_air.001
OS_50C_air.001

Universal V4.3A TA Instruments