

The influence of pyrolysis conditions on the products from the fixed-bed pyrolysis of the Jordanian oil shale

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Abstract

Two samples of oil shales from the Sultani and Jurf-Edarawish deposits in the south of Jordan were pyrolysed in a fixed bed reactor under nitrogen and nitrogen/steam atmosphere. A heating rate of 5, 10, 20 and 40 °C min⁻¹ to a final temperature of 950 °C was investigated in a fixed bed reactor and TGA. It was found that increasing heating rate shifted the reaction to a higher temperature and a decrease in the activation energy. The chemical composition and elemental analysis, of the oil shales were obtained. The condensed pyrolytic oils were fractionated into chemical classes using mini-column liquid chromatography. The molecular weight (MW) range of the derived oils was measured using size exclusion chromatography and the number average MW of the benzene, ethyl acetate and methanol fractions of the derived oil were obtained.

Keywords: Fixed bed reactor; TGA analysis; CHN analysis; Liquid chromatography fractionation; size exclusion chromatography; Jordan oil shale.

تأثير الظروف المحيطة في نواتج التحطيم الحراري للصخر الزيتي الأردني

ملخص

أخذت عينتان من الصخر الزيتي الأردني من منطقتي السلطانة وجرف الدراويش جنوب الأردن. وتم تحطيمهما حرارياً بوساطة مفاعل حراري ذي طبقة مثبة بوجود النيتروجين وبخار الماء وبمعدل تسخين حراري 2,10,20,40 درجة مئوية في الدقيقة ولغاية حرارة 950 درجة مئوية.

وجد بأن طاقة التنشيط لعملية التحطيم الحراري تقل مع زيادة معدل التسخين الحراري. أخذ الزيت المنتج وتم تحليله بوساطة عمود السائل الكروماتغرافي إلى مجموعاته الكيميائية بوساطة عدة مذيبات. تم حساب مدى ومتوسط عدد الوزن الجزئي للمجموعة الكيميائية للزيت المنتج.

Introduction

The global oil-equivalent of oil shale reserves is enormous. Jordan is one of the countries that contain proven reserves of 50 billion tons, which are wide-spread throughout the country. The Jordanian oil shale deposits occur in the sedimentary rocks of Camparian-Mastrichtian to Danian age. The main known deposits are found at El-lajjun (1.3 billion metric tones), Sultani, Attarat, Jurf-Edarawish and Wadi Maghar. Jordan has shown a special interest in the general properties of oil shale and has investigated direct combustion, retorting and shale oil processing [1]. Today, it is well known that the oil shale industry depends mainly on the cost of fuel products from oil shales, by using existing technologies, in comparison to the price of such products or fuels from crude oil. The cost of shale oil production and its fractions is influenced by production conditions.

Mainly, it has been shown that the pyrolysis temperature, the heating rate and the grain size affect the oil yield and the oil composition. Many workers such as Williams and Nazzal [2], Burnham [3] and Campbell et al. [4,5] have studied the influence of temperature in the range from 400 to 650 °C. The effect of heating rate, in the range of 2 to 40 °C min⁻¹ and of grain size, in the range of 0.2 to 5 mm diameter, have been studied by Nazzal [6], Shen et al. [7] and Williams and Nazzal [8]. These studies concluded that heating rate and grain size affect the entire oil shale pyrolysis mechanisms and that gas cracking mechanisms were governed by the critical pyrolysis temperature.

Further investigations of oil shale pyrolysis, by many workers [9-15], have examined the characteristics of kerogen degradation, by thermogravimetric analysis (TGA) of oil shale. TGA shows the record of the weight loss as the sample temperature is raised at a constant and uniform heating rate. Haddadin and Mizyed [9] and Dogan and Uysed

[14] have investigated the influence of pyrolysis temperature on the weight loss and they have shown that higher weight loss occurs at higher pyrolysis temperature. In this work, two oil shale samples from two different deposits in Jordan, were pyrolysed in a TGA up to a final temperature of 950 °C at a heating rate of 5, 10, 20 and 40 °C min⁻¹. The same samples were pyrolysed in a fixed-bed reactor and the influence of heating rate on the oil yield and composition was investigated. The derived oil was separated by liquid chromatography, while the molecular weight range of the oil and the number average MW of the oil fraction were investigated. The analysis of the evolved gases was also investigated by GC.

2. Experimental

2.1 Oil Shale Samples.

The investigated oil shale samples were obtained from the Sultani (SL) and Jurf-Edarawish (JED) deposits, located in the south of Jordan. Table (1) shows the elemental analysis for the general characteristics of both samples. The samples were sieved to pass a 240 US mesh screen, the sample weight was 70 mg.

2.2. Pyrolysis reactor

The fixed bed reactor consisted of a 200 cm³ stainless steel reactor, heated externally by an electric ring furnace to minimise secondary reactions such as thermal cracking, repolymerisation and recondensation, the sweeping gas of nitrogen and nitrogen/steam at a fixed flow rate is used to sweep the evolved gases quickly from the reaction zone. The maximum temperature and the heating procedure, including the heating rate, and isothermal time, were supplied by the furnace and controlled automatically by a programmable controller . The liquid condenser consisted of a glass liner contained within a series of cold traps, maintained at 0°C and connected to the reactor outlet. The

non-condensable outlet gases were sampled via a glass sampling tube, placed down stream of the condenser. Gas samples were obtained by using syringes via a rubber septum from the sampling tube. Figure (1) shows the schematic diagram of the fixed bed apparatus.

2.3. X-Ray Fluorescence (XRF) spectroscopy.

The major elemental compositions of the samples were analysed by X-ray fluorescence (XRF) spectroscopy. The samples were prepared as shown by the methodology of Brown and Brindley [16], by pressing approximately 1.0 g of fine grained shale into a pellet under pressure and then placing it in an aluminum holder. An ARL 9400 sequential spectrometer flitted with 93.0 KW end window Rh target X-ray tube was used. The analysis was based on a semi-quantitative basis.

2.4. Thermogravimetric Analysis (TGA).

Thermogravimetric analysis (TGA) of the shale samples were investigated using a Shimadzu-Model-50 series TG analyser, as shown and described by Williams and Ahmed [17]. Under a nitrogen atmosphere (nitrogen purge) the samples were heated at heating rate of 5, 10, 20 and 40 °C min⁻¹ to a final pyrolysis temperature of 950 °C. The TGA provides the continuous measurements of the sample weight as a function of time and / or temperature.

2.5. Oil separation.

The derived oils consisted of an aqueous phase and an oil phase. The oil was separated from the aqueous phase by centrifuging, decantation and removal of the aqueous phase by pipette. Asphaltenes were precipitated with n-pentane. The pentane soluble fraction was separated into chemical class fractions by liquid chromatography which consisted of 10 cm x 1.0 cm glass column packed with a silica, Bondesil sorbent, pretreated at 105 °C for two hours prior to use, as described by

Williams and Nazzal [2]. The formation of solid phase was prevented by mixing the oil with Chromosorb G/AW/DMCS 60-80 support and packed in the column above the analytical phase. The column was then sequentially eluted under vacuum with pentane, benzene, ethyl acetate and methanol to produce aliphatics, aromatics, ester and polar fractions, respectively. To investigate the overall composition of the oil, each fraction was analysed (in the next part of this work) by capillary column gas chromatography/mass spectrometry (GC/MS), for the presence of polycyclic aromatic compounds (PAC) in the aromatics fraction.

2.6. Size-Exclusion Chromatography (SEC).

The derived shale oils have been shown to be chemically complex, containing a large number of chemical compounds with a wide molecular weight range [2]. SEC is an analytical technique which gives rapid and broad classifications of the derived oils. This technique has been used successfully to analyse oils from a variety of sources, including oils derived from British oil shales [2,8], coal [18], heavy crude petroleum oils [19], tire waste [20] and oils derived from biomass pyrolysis [21]. However, there are few data on the application of SEC analysis of oils derived from oil shale pyrolysis. SEC allows molecules of different mass to be separated, according to their degree of penetration into the pores of a gel packed into a column as small spheres, during elution with a suitable solvent [18,19].

Size-exclusion chromatography is one of the principle analytical techniques in a number of industrial areas, because of its ability to provide molecular weight distributions. SEC was used to provide information on the total mass range of the shale oil sample. The mass range is set by the type of separating phase used. This technique is based on reversed elution order, with the largest molecular eluting first. For that, the larger molecules are excluded from the pores of the separating

phase and so pass through the voidage. Intermediate size molecules will permeate some of the pores and thus be retained longer. The separation of the sample is based on the size and configuration of the molecules and not their weight. However there is a good general correlation between the size and the weight of the molecules [22].

In this work, the separating phase was PLRP-5, (particle size is 5 μm pore size 100 \AA). Two columns of 15 cm in length and 4.6 mm ID were used in series. The columns temperature was held at 0 $^{\circ}\text{C}$. The solvent used was HPLC grade tetrahydrofuran (THF), which was degassed before use. A Merck Hitachi L-6000 HPLC pump was used at a flow rate of 0.257 ml min⁻¹. The effluent from the columns passed through two detectors. A Merck Hitachi L-4000 ultra-violet (UV) detector at 254 nm, which analysed the aromatic components of the effluent and a Varian RI-4 refractive index (RI) detector, which was a universal detector and analysed all the effluent from the columns. The signals from the two detectors were recorded on a chart recorder.

The SEC was calibrated with polystyrene of known molecular weight. Therefore, the type of standards used will only give an approximation of the actual molecular weight of the sample, due to the sample containing molecules, which may have differing configurations to polystyrene. Any difference in configuration between the calibration standards and the sample molecules means the sample molecules could be eluted slightly quicker or slower through the columns. Williams and Taylor [20] have shown more details of the method development and validation of the SEC equipment used in this work, as shown in Figure (2). About 10 μl of each sample was dissolved in 1 cm³ of THF and 5.0 μl of the diluted sample was then injected.

The data acquisition system was started, as the sample was injected. The run time for the data acquisition was 15 minutes and the mass

range, which was analysed in this time, was from 12000 amu to 40 amu.

The signal from the detectors was collected by the computer software and normalised to give the percent of sample in a molecular weight (MW) band, which were present in the computer software. The percent weight of oil in each MW band was plotted versus log of MW, to give a MW distribution plot of the sample.

3. Results and Discussion

3.1. Elemental analysis of the oil shales.

The major and minor elemental analysis (chemical composition) of the samples is shown in Table (2). JED sample shows higher concentrations of the major elements with an opposite trend of Na, K and P oxides. The SiO₂ plus Al₂O₃ (can be classed as acid constituents and the alkaline earth oxides) and CaO plus MgO (are basic constituents which forms the main influence on the fusibility of ash) are higher for JED sample. In addition to that, the ratios of K₂O/Na₂O and Al₂O₃/Na₂O of JED were higher than that in the Sultani sample, SL, were it could be considered as an indication of a lower content of organic carbon. The SiO₂/Al₂O₃ ratio, which has a positive correlation of oil yield, of JED is lower than that in Sultani deposit. The high concentration of P₂O₅ is reported that had a significant effect on the spent shale utilization in the cement industry. Minor element analysis showed a significant difference in both samples of Mo, Sr, Zn and V.

2.2. Thermogravimetric analysis.

Figures (3) and (4) show the differential weight loss curves (DTG) in relation to heating rate to a final pyrolysis temperature of 950 °C for both SL and JED oil shale samples, respectively. Increasing the temperature, a different pattern of thermal decomposition was obtained

for both samples. Burnham and Huss [23] reported that the lower temperature thermal decomposition of oil shale, up to 220 °C, produced weight loss, which was attributed to the loss of moisture, loss of inter-layer water from clay minerals and decomposition of the mineral nahcolite (NaHCO₃). Anabtawi and Nazzal [1] and Nazzal et al. [24] attributed this weight loss to the release of the adsorbed water. Haddadin and Mizyed [9] have also attributed this weight loss, up to about 220 °C, to a physical change in the kerogen prior to decomposition to pyrolytic bitumen, these changes being in the form of softening of the kerogen, molecular rearrangement accompanied by the release of gas [17]. These weight losses, at low temperature, were significant in both samples, with a higher percentage in JED sample. The temperature range can be divided into many ranges, for both samples, as shown in Table (3). It is clear from Figures (3) and (4) that the weight loss, as thermal decomposition, is the main one step for SL sample and two steps for JED sample in the temperature range from 200 to 700 °C. For both samples, these steps represent the loss of hydrocarbon materials and the evolution of gases and oil vapor. These suggestions agree with those of many workers. Anabtawi and Nazzal [1] suggested that the reaction of the first organic matter, reaction of the pyrolysis, dehydration of the complex matter and the reaction of the second complex matter, are the main reactions causing the weight loss. Williams [11], Dogan and Uysed [14] and Allred [25] studied the two-stage decomposition of oil shale. They observed that whether the decomposition is single-stage or two-stage depends on the type of the oil shale and the decomposition of kerogen to oil, gas and char products. Higher temperature decomposition between 700 and 950 °C was attributed to the decomposition of carbonate minerals (calcite, dolomite and ankerite).

Table 3 shows the analysis of DTG data, in relation to heating rate, in

terms of the onset of weight loss in the temperature range of 25 to 950 °C. The nomenclature used is shown in Figure (5). Tables (4) and (5) showed that with an increase in the heating rate there was a shift to higher temperature for MT1, MT2 and MT3 and a higher rate of weight loss for both oil shale samples. This shift can be concluded as a result of the difference between the intra-particle heat transfer and the heat transfer outside the particle or/and a result of a significant raise in the reactivity, which is the ratio of the rate of weight loss per unit time.

The thermogravimetric analysis results were used to determine the kinetic parameter, the pre-exponential factor (frequency factor) A and the activation energy E. The kinetic analysis of TGA, in this work, adopted a first order rate of reaction with respect to the undecomposed amount of oil shale. The rate of decomposition in this approach is given by :

$$\mathbf{dw/dt = -k (w-wf)} \quad \mathbf{(1)}$$

Where w is the weight of the undecomposed oil shale, wf is the weight of residue at the end of the reaction and k is the rate constant. The reaction rate constant k is also defined by the Arrhenius equation:

$$\mathbf{k = A e (-E/RT)} \quad \mathbf{(2)}$$

Where R and T are the universal gas constant and the absolute temperature, respectively. It can be denoted from equations (1) and (2) that :

$$\mathbf{\ln k = \ln A (-E/RT)} \quad \mathbf{(3)}$$

From a plot of ln k versus 1/T a straight line of (-E/RT) slope can be obtained. So the continuous recordings of the TGA of weight loss with time and temperature enable dw/dt and k to be determined and consequently the activation energy E and pre-exponential factor A to be calculated.

Tables (6) and (7) show the influence of heating rate on the calculated

kinetic parameters for the decomposition of both samples from SL and JED samples, respectively. Increasing the heating rate, in the same range of temperature, shows a decrease in both the pre-exponential factor and activation energy in the same range of temperature. At each heating rate, it was noted that A and E were increased at the higher temperature intervals, as shown in Tables (6) and (7) for both investigated samples, this could be attributed to greater rates of heat transfer occurring. In the other stages, reactions have much higher values for activation energy, this could be attributed to the loss of hydrocarbons and dehydration of the complex matter and the reaction of the second complex organic matter.

3

.3. Oil Fractions

3.3.1. Chemical class fractionation

Tables (8) and (9) show the chemical class fractionation of the derived oil in relation to the heating rate, under nitrogen pyrolysis atmosphere, for both samples, respectively.

It is clear that the decrease or increase of the aliphatics content in the oil, which was found to be less than 1.0 wt%, in this range the effect of heating rate on the aliphatics degradation or content was very small. The benzene fraction (high MW aromatics) increased by increasing the heating rate from 5 to 40 °C min⁻¹. The aromatic contents, as shown in Tables (8) and (9), were found to increase for the oil pyrolysed under nitrogen atmosphere.

The ethyl acetate fractions were found to increase from 33 to 35wt% for the oil pyrolysed under nitrogen atmosphere and were decreased from 38 to 34 wt% for the oil pyrolysed under nitrogen/steam atmosphere as shown in Tables (10) and (11).

The heating rate in the range of 5 to 40 °C min⁻¹ did not cause any significant change in the content of the methanol, for the oil derived

from the pyrolysis of both SL and JED samples.

In general, the influence of heating rate on the aliphatic and aromatics content was small. The formation of aromatic compounds via secondary reactions during pyrolysis has been attributed to either gas-phase cracking of aliphatics compounds [26] or via Diels-Alder type reactions [27-33] leading to the selective concentration of aromatic compounds.

Burnham [26] reported that oil degradation occurs by two overall processes, conversion of hydrogen-poor materials to coke, and cracking of aliphatic moieties to gas. He suggested that the low temperature oil shale retorting tends to cause aromatic molecules in the oil to coke before volatilization, leading to lower total oil yield and lower aromatic content in the oil. But at a higher retorting temperature, gas-phase cracking of aliphatics (free and attached to aromatics) dominates, increasing the aromatic content by selective concentration. The high heating rate could play the same effect on the Polycyclic Aromatic Compounds (PAC) concentration in the derived oil, by reducing the oil coking inside the particle, because of the high self-generating sweeping gas at the high heating rate.

3.3.2 Molecular Weight Range of the Oil and its Fractions

The obtained results showed a shift to a lower MW range by increasing the heating rate for both atmospheres. The molecular weight range of the oil pyrolysed under nitrogen is shown in Figures (6) and (7) for both samples SL and JED, respectively.

Figures (8) and (9) show the number and weight average MW of the oil and its fractions (benzene, ethyl acetate, and methanol), derived from the pyrolysis of SL and JED samples under nitrogen atmosphere. Examination of the number average MW of the oil and its fractions showed that the increasing order of the number average MW was the

following of ethyl acetate greater than that of benzene fraction, greater than that of oil, greater than that of methanol fraction, for the oil pyrolysed under nitrogen and nitrogen/steam atmosphere.

Increasing the heating rate under nitrogen pyrolysis atmosphere caused the weight average MW to increase in the following order, benzene fraction greater than that of ethyl acetate fraction, greater than that of the methanol fraction. But under nitrogen/steam pyrolysis atmosphere the weight average MW of ethyl acetate fraction was found greater than that of benzene fraction, greater than that of methanol fraction. In this range of heating rate (5 to 40 °C min⁻¹) these results of the weight average MW of the benzene fraction support the increase of the aromatics concentration in the oil with higher heating rate.

The MW range is higher for oils heated under nitrogen\steam than that heated under nitrogen alone. This may support the suggestion of Duvall et al. [34], that addition of steam produced a heavy polar material in the oil.

Williams and Nazzal [2] reported that where the final pyrolysis temperature increases, secondary reactions occur, resulting in higher concentrations of single-ring aromatic compounds which are formed in parallel with thermal degradation of alkanes, some of which will be of high MW. The increased production of single-ring aromatic compounds, and the decrease of higher MW aliphatic compounds will shift the measured MW to a lower range, for both nitrogen and nitrogen\steam atmosphere.

4. Conclusions

There was a marked influence of heating rate on oil shale pyrolysis. Increasing the heating rate in the range of 5 to 40 °C min⁻¹ using thermogravimetric analysis showed a marked decrease in the activation

energy and reduction in the pre-exponential factor for the thermal degradation of oil shale.

The effect of heating rate, in the studied range, on the aliphatic content in the derived oil was very small. Increasing the heating rate increased the aromatic content. The ester content, ethyl acetate fraction, in the derived oil increased by increasing the heating rate under nitrogen pyrolysis atmosphere, while the opposite trend was observed in the presence of steam. The heating rate, in the studied range, did not cause any significant change in the content of Polar material in the derived oil. Increasing the heating rate under both nitrogen and nitrogen\steam atmospheres caused a shift to a lower MW range, with higher values in the presence of steam. The number average MW of ethyl acetate fraction was higher than that of benzene fraction and methanol fraction.

5. References

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Table(1) General characteristics of Sultani and Jurf-Edarawish samples (wt%).

	Sultani	Jurf-Edarawish
Moisture	2.6	2.80
Organic carbon	12.5	9.6
Total Carbon	79.8	79.0
Hydrogen	11.1	10.0
Nitrogen	0.85	0.90
Oxygen	0.90	2.10
Sulfur	6.5	8.5
Calorific value (kJ kg ⁻¹)	6400	4650

Table (2) Elemental concentration of Sultani and Jurf-Edarawish oil shales.

Elements	Sultani	Jurf-Edarawish
<i>Major elements (wt%)</i>		
SiO ₂	28.2	29.5
TiO ₂	0.15	0.20
Al ₂ O ₃	3.0	3.80
Fe ₂ O ₃	1.15	1.60
MnO	0.01	0.01
MgO	1.0	0.20
CaO	25.2	39.0
Na ₂ O	0.25	0.10
K ₂ O	0.04	0.20
P ₂ O ₅	3.50	1.50
SO ₃	4.40	4.80
<i>Minor elements (ppm)</i>		
As	20	12
Cu	120	70
Mo	95	20
Ni	140	105
Pb	10	10
Rb	14	10
Sr	700	1200
Th	11	10
U	28	20
W	10	20
Y	27	35
Zn	660	200
Zr	50	50
Ba	50	40
Co	20	15
Cr	265	230
La	30	35
V	270	100
(K ₂ O/Na ₂ O) ratio	1.6	2.0
(Al ₂ O ₃ /Na ₂ O) ratio	12	38
(SiO ₂ /Al ₂ O ₃) ratio	9.4	7.8

Table (3) Weight loss in relation to pyrolysis temperature range for different heating rates for oil shale samples.

	Heating Rate (°C min ⁻¹)			
	5	10	20	40
<i>Sultani sample (SL)</i>				
<i>Temperature range °C</i>				
320-450	1.15	1.24	1.30	1.92
450-700	18.67	17.30	17.68	18.82
740-950	7.00	9.40	15.40	14.70
Total (25-950)	41.7	42.8	50.2	48.3
<i>Jurf-Edarawish sample (JED)</i>				
<i>Temperature range °C</i>				
100-150	0.11	0.56	-	-
330-550	7.54	5.20	4.49	2.53
590-870	6.92	6.57	8.27	4.61
870-950	20.8	23.5	21.2	18.4
Total (25-950)	48.6	47.8	44.9	42.8

Table (4) The maximum temperature (MT) ($^{\circ}\text{C}$) data of thermogravimetric analysis in relation to heating rate of oil shale samples.

	Heating Rate ($^{\circ}\text{C min}^{-1}$)			
	5	10	20	40
<i>Sultani sample (SL)</i>				
MT1	352	360	362	375
MT3	550	560	590	615
<i>Jurf-Edarawish sample (JED)</i>				
MT1	142	145	-	-
MT2	428	420	425	430
MT3	669	670	680	700

Table (5) The maximum rate of weight loss (MRWL) data of thermogravimetric analysis in relation to heating rate of oil shale samples.

Heating Rate °C min ⁻¹	Rate of Weight loss (wt% min ⁻¹)			
	5	10	20	40
<i>Sultani sample (SL)</i>				
MRWL 1	0.41	0.65	1.08	1.53
MRWL 2	1.37	1.60	4.18	5.55
<i>Jurf-Edarawish sample (JED)</i>				
MRWL 1	0.21	0.23	-	-
MRWL 2	0.79	0.86	1.91	205
MRWL 3	0.85	1.87	2.57	2.90

Table (6) The kinetic parameters for the decomposition of a Sultani (SL) oil shale in relation to heating rate.

<u>Heating Rate °C min⁻¹</u>	<u>Temperature range</u>	<u>E (kJmol⁻¹)</u>	<u>A(s⁻¹)</u>
5	320 - 450	188	1.1X10 ¹⁴
	450 - 700	225	7.5X10 ¹⁵
	740 - 800	210	2.0X10 ¹⁷
10	330 - 400	187	3.8X10 ¹³
	614 - 673	237	2.3X10 ¹³
	680 - 810	266	3.5X10 ¹³
20	370 - 440	135	3.5X10 ⁹
	650 - 710	270	4.5X10 ¹¹
	700 - 820	294	1.0X10 ¹²
40	390 - 410	100	2.3X10 ⁷
	430 - 670	150	5.2X10 ⁹
	660 - 870	180	2.0X10 ¹⁰

Table (7) The kinetic parameters for the decomposition of a Jurf-Edarawish (JED) oil shale in relation to heating rate.

<u>Heating Rate °C min⁻¹</u>	<u>Temperature range</u>	<u>E (kJmol⁻¹)</u>	<u>A(s⁻¹)</u>
5	100 - 150	176	2.2X10 ¹⁴
	330 - 550	190	3.7X10 ¹⁴
	590 - 800	207	6.2X10 ¹⁴
10	250 - 500	180	1.2X10 ¹⁴
	530 - 670	209	2.2X10 ¹⁴
	590 - 800	215	8.7X10 ¹³
20	220 - 460	120	8.2X10 ¹⁰
	500 - 650	140	4.5X10 ¹⁰
	630 - 810	195	206X10 ¹⁰
40	310 - 400	95	7.8X10 ⁸
	430 - 670	115	3.2X10 ⁸
	700 - 790	145	9.5X10 ⁷

Table (8) Chemical class fractionation of the derived shale oil from the pyrolysis of Sultani oil shale in relation to the heating rate under atmosphere of nitrogen (wt%)^a

Eluent	Fraction	Heating Rate (°C min ⁻¹)			
		5	10	20	40
Pentane-1	Aliphatics	7.0	7.1	7.1	7.2
Pentane-2	Low MW Aromatics	8.0	7.7	7.5	7.5
Benzene	High MW Aromatics	35	34	38	40
Ethyl acetate	Esters	32	33	33	34
Methanol	Polars	7.7	7.4	7.2	7.0

^a All results are the mean of three experiments.

Table (9) Chemical class fractionation of the derived shale oil from the pyrolysis of Jurf-Edarawish oil shale in relation to the heating rate under atmosphere of nitrogen (wt%)^a

Eluent	Fraction	Heating Rate (°C min ⁻¹)			
		5	10	20	40
Pentane-1	Aliphatics	6.6	6.8	7.0	7.0
Pentane-2	Low MW Aromatics	7.9	7.5	7.4	7.5
Benzene	High MW Aromatics	35	36	38	42
Ethyl acetate	Esters	30	34	35	35
Methanol	Polars	7.3	7.1	7.1	7.1

^a All results are the mean of three experiments.

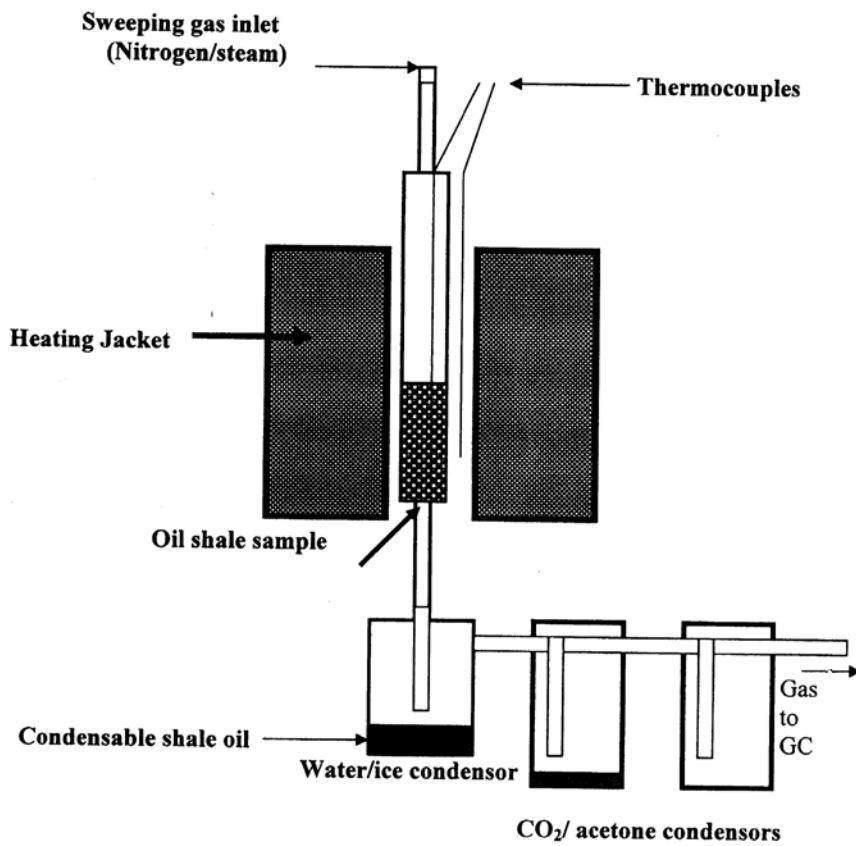


Figure (1) Schematic diagram of the fixed bed reactor

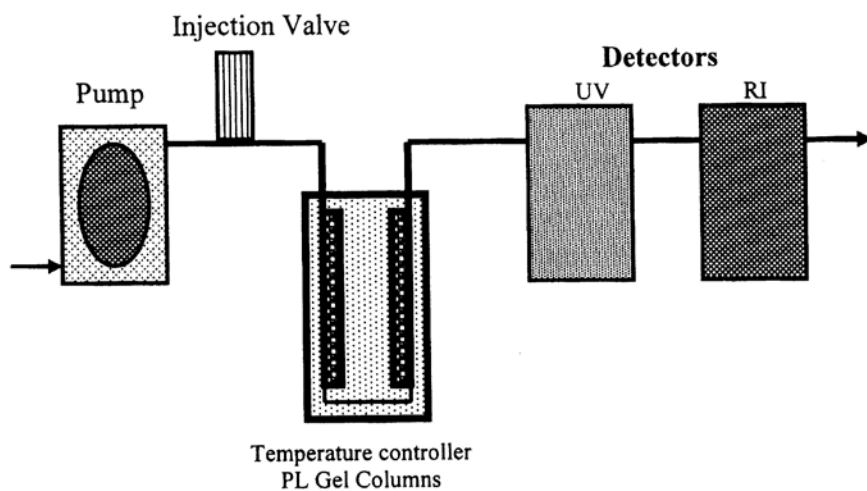


Figure (2) Schematic diagram of the size exclusion system

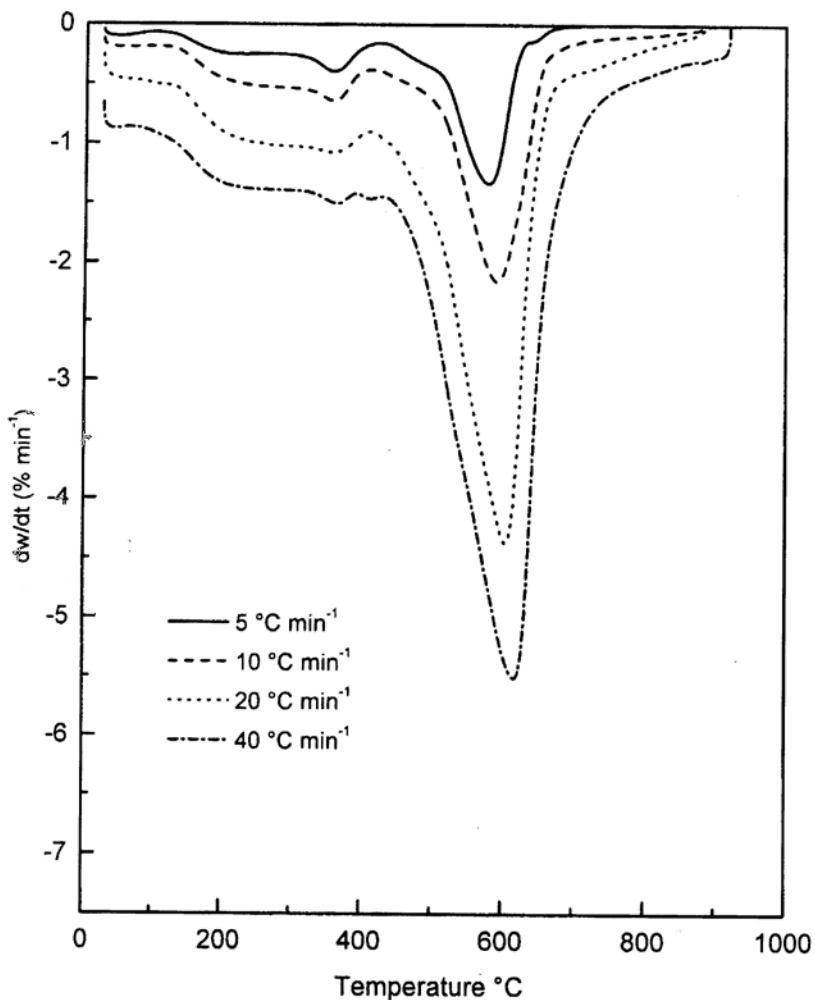


Figure (3) Rate of weight loss (DTG) of the Sultani oil shales in relation to heating rate.

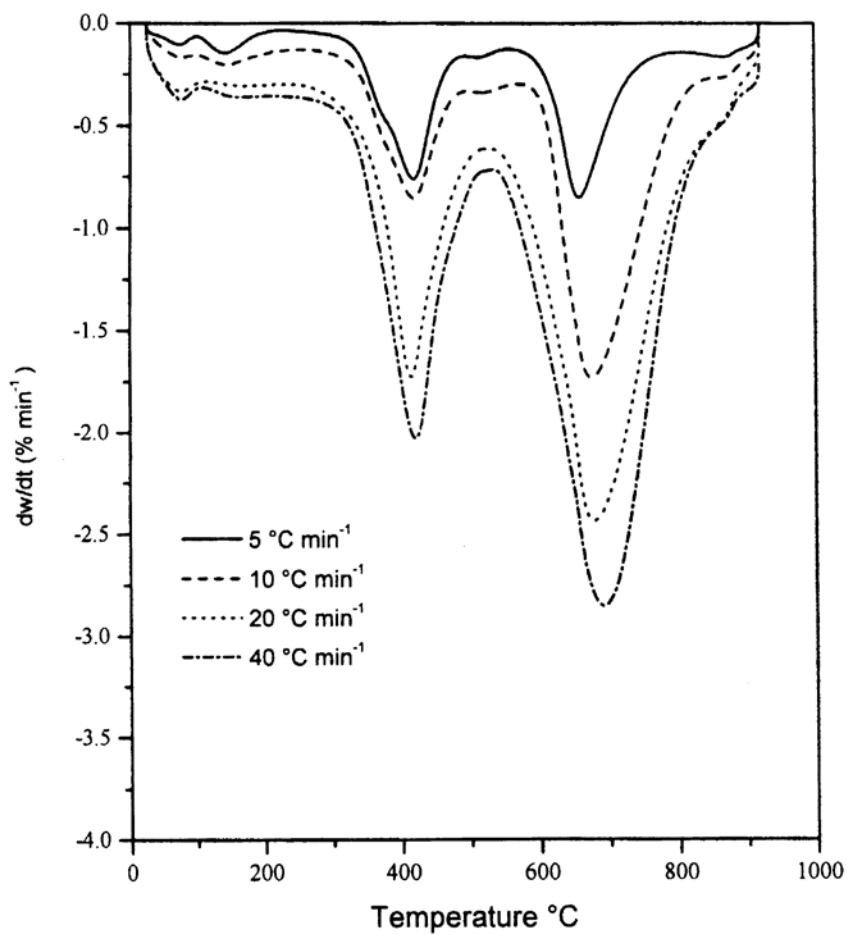


Figure (4) Rate of weight loss (DTG) of the Jurf-Edarawish oil shales in relation to heating rate.

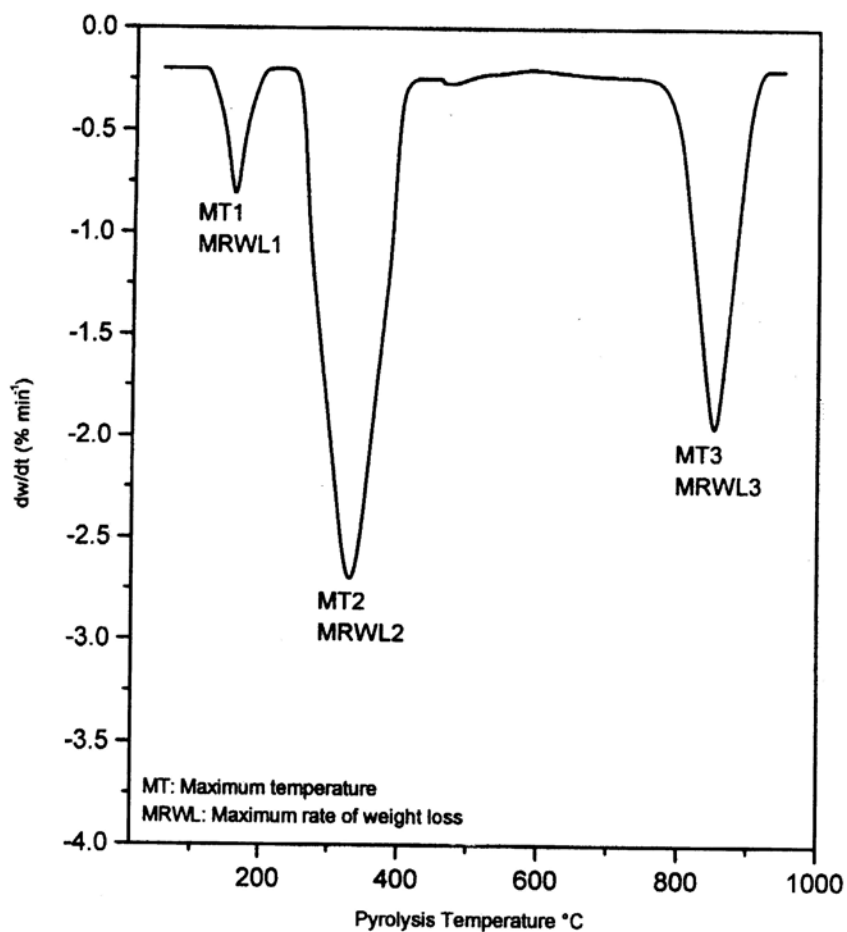


Figure (5) Nomenclature for the TGA analysis.

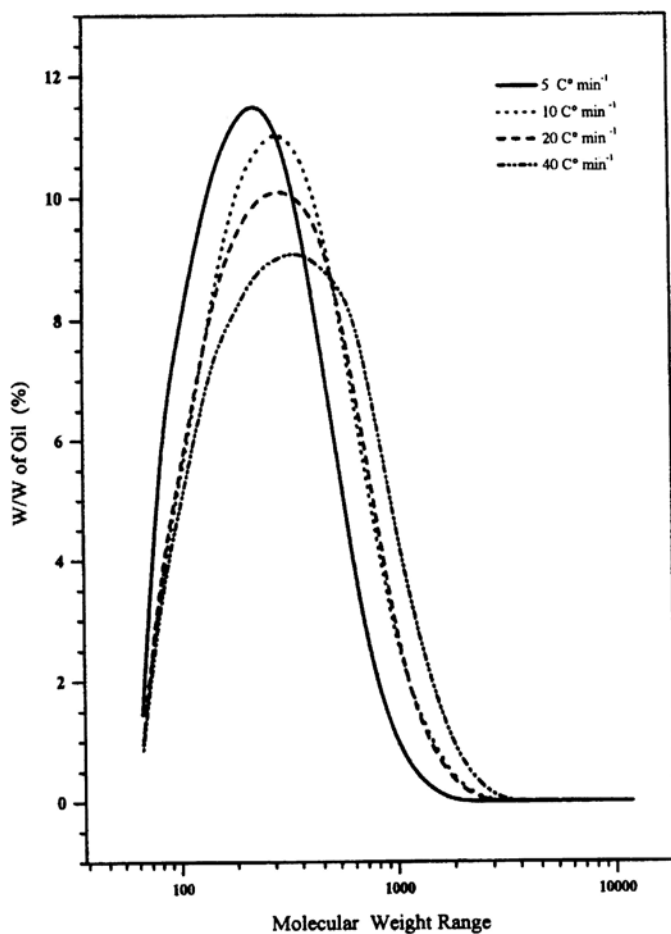


Figure (6) The molecular weight range of the oil derived from the pyrolysis of the Sultani oil shale.

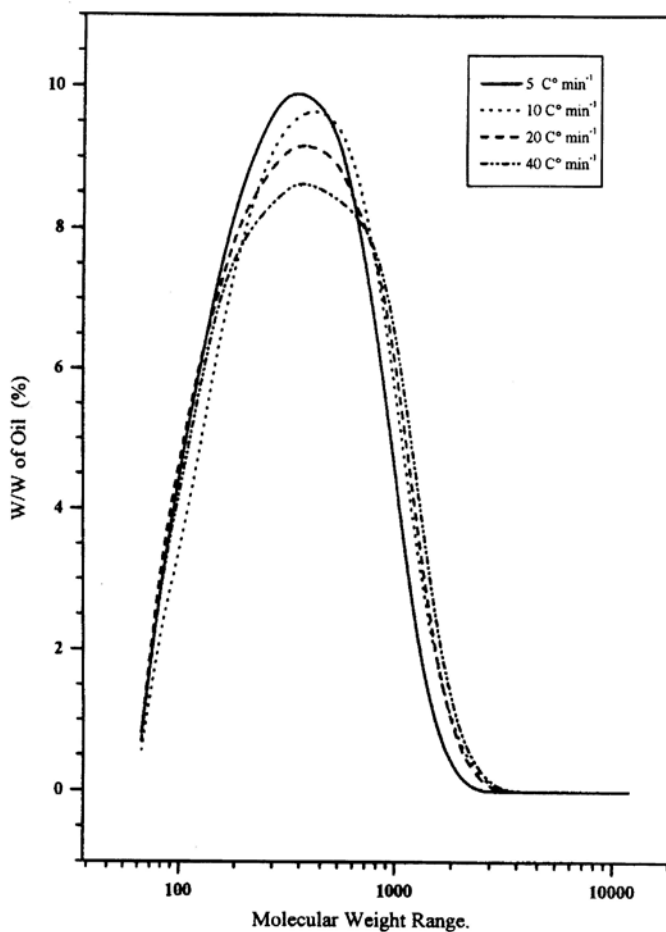


Figure (7) The molecular weight range of the oil derived from the pyrolysis of the Jurf-Edarawish oil shale.

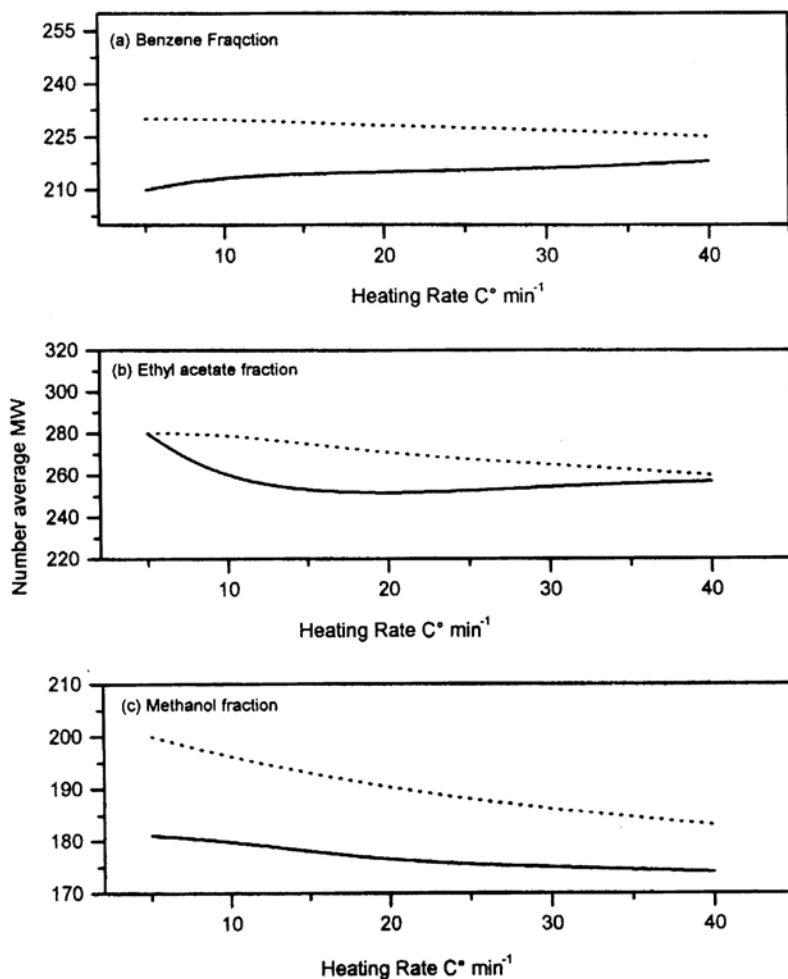


Fig. (8) The number average MW of the oil fractions from Sultani deposit, (a) benzene, (b) ethyl acetate and (c) methanol of the pyrolysed oil in relation with heating rate under nitrogen and nitrogen/steam pyrolysis atmosphere. — Nitrogen, and Nitrogen/steam atmosphere.

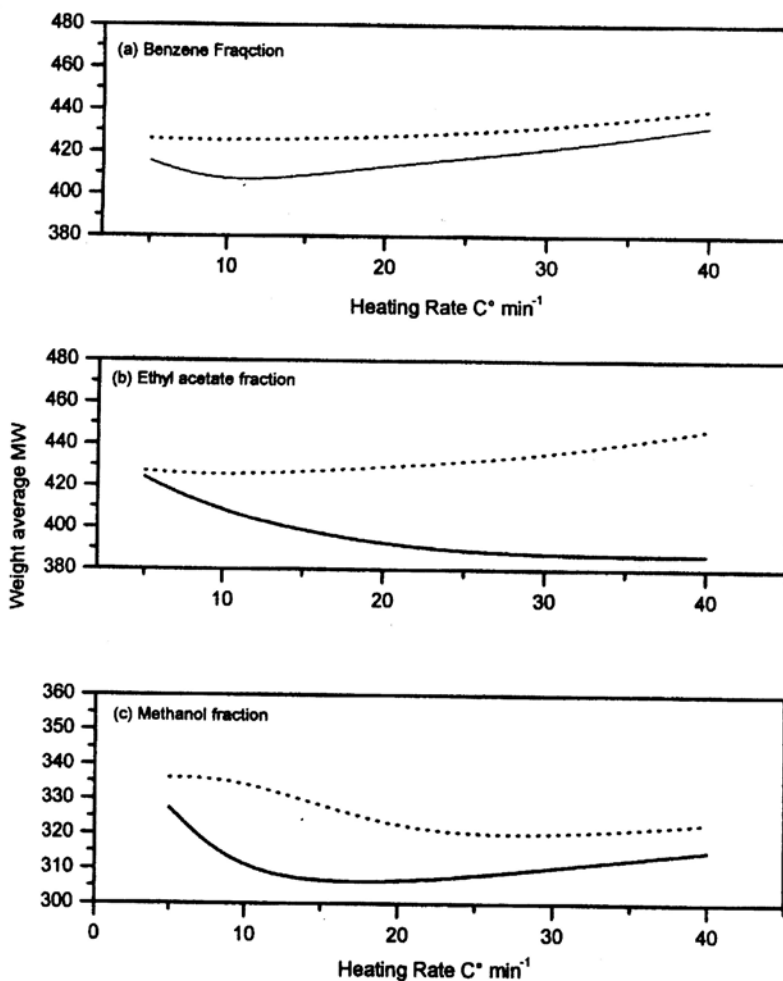


Fig. (9) The weight average MW of the oil fractions from Jurf-Edarawish deposit, (a) benzene, (b) ethyl acetate and (c) methanol of the pyrolysed oil in relation with heating rate under nitrogen and nitrogen/steam pyrolysis atmosphere. — Nitrogen, and Nitrogen/steam atmosphere.