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Sulfur distribution in the oil fractions obtained by thermal cracking of Jordanian El-Lajjun oil Shale

Adnan Al-Harashseh, Awni Y. Al-Otoom*, Reyad A. Shawabkeh

Chemical Engineering Department, Mutah University, P.O. Box 7, Mutah Karak 61710, Jordan

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Abstract

The extracted shale oil by the thermal cracking process of the El-Lujjan oil shale showed that the yield of oil was around 12 wt%. The amount of sulfur in this shale oil was found to increase (from 7 to 9.5 wt%) with the increase of the boiling point for different distillate fractions. Sulfur in Jordanian oil shale was found to be mainly organic sulfur with negligible amounts of inorganic sulfur. Sulfur was found to be in the aromatic form in these fractions. Different forms of thiophenes were found in all fractions of the shale oil extracts without a distinct change in the concentration of any specific compounds with these extracts. Alkylthiophenes were the dominant phases in these fractions.

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1. Introduction

Oil shale is considered one of the largest energy resources in the world. The oil equivalent of oil shale around the world is estimated to be around 30 times the reserve of the crude oil [1]. It is estimated that in-place oil shale in the world is around 411 billion tons which is equivalent to 2.9 trillion US barrel of shale oil [2]. A conservative estimate of oil shale reserves in Jordan is around 50 billion tons which makes around 12% of the world reserve [3]. The shallow near surface deposits of oil shale in Jordan that can be utilized by the open cut mining method is estimated to be around 50 billion tons of oil shale [4].

Oil shale reserve in Jordan distributed over seven deposits; El-Lajjun, Sultani, Jurf Eddarawish, Wadi Mgher, and Khan Ez Zabib. Table 1 presents the main properties of oil shale from major deposits.

* Corresponding author. Tel.: +962 3 2372380; fax: +962 3 2375861.

E-mail address: alotoom@mutah.edu.jo (A.Y. Al-Otoom).

Table 1
A typical analysis of the largest oil shale deposits in Jordan

	Ash content	Density (g/cm ³)	Calorific value (kJ/kg)
El-Lujjan	54.5	1.81	6906
Sultani	55.5	1.96	6380
Jurf Ed-darawish	58.4	2.1	4603

Table 2
Proximate analysis (ad) for the El-Lujjan oil shale deposit used in this study

Property	Proportions (wt%)
Moisture	1.1
Volatile matter	44.0
Ash	54.5
Fixed carbon	0.4

The shale oil yield for the Jordanian oil shale ranges between 10 and 13%, depending on the particle sizes [5]. Shale oil from Jordanian oil shales is mainly aliphatic with small amounts of oelfinic and aromatic compounds. It contains *n*-alkanes with predominant quantities of *n*-C25 [6].

Although oil shale has been utilized as a source of liquid fuel in many places, its future is still uncertain. This is mainly due to its low economical and environmental feasibility.

Sulfur exists in all fossil fuels, which results in many problems. One major problem is the production of the toxic Sulfur Dioxide during the combustion of these fuels. A major part of the organic sulfur in

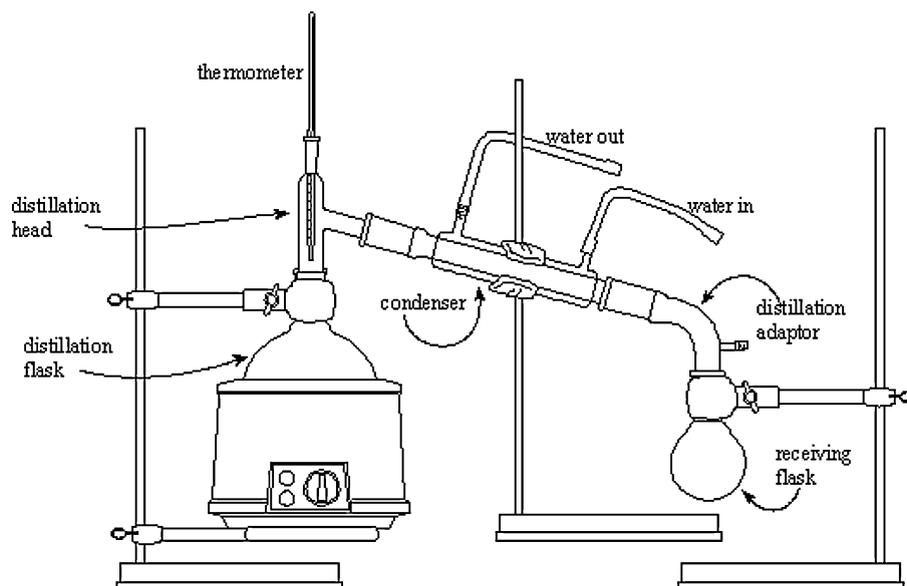


Fig. 1. Apparatus used for fractionation of the shale oil extract.

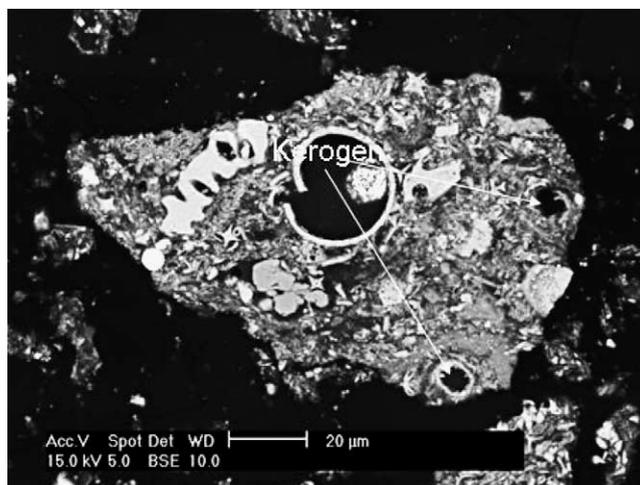


Fig. 2. Scanning electron microscope image for a cross-section of a sample of oil shale used in this study.

these fuels is present as thiophenic compounds. In oil shale, alkyl Thiophenes is one of the most common sulfur containing pyrolysis products [7,8]. They are mainly a C1–C4 alkylated thiophenes with predominantly linear carbon skeleton. It has been also shown that most of the sulfur compounds in oil shale are contained as aromatic compounds in the aromatic fractions of the shale oil [9,10].

The sulfur content of the Jordanian oil shale is relatively high; the sulfur content of the major oil shale deposits is between 2.4 and 3.1% [4]. In 1998, Damsteâ et al. [11] have indicated that Jordanian oil shale obtained from Jurf Ed Darawish deposits contains low molecular weight linear carbon skeleton

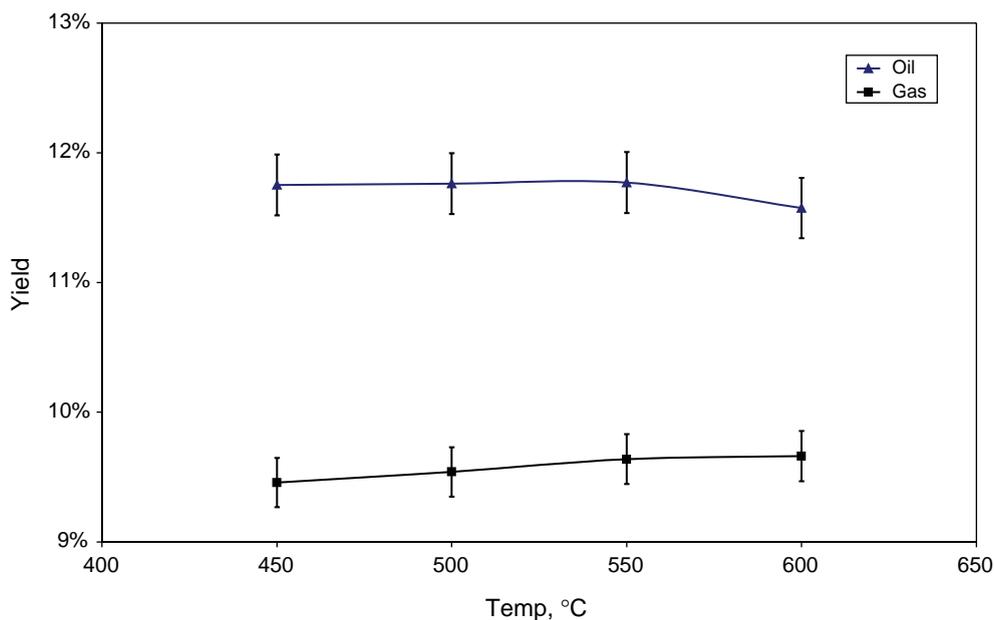


Fig. 3. The yield of the oil and gas during thermal cracking of El-Lujjan oil shale.

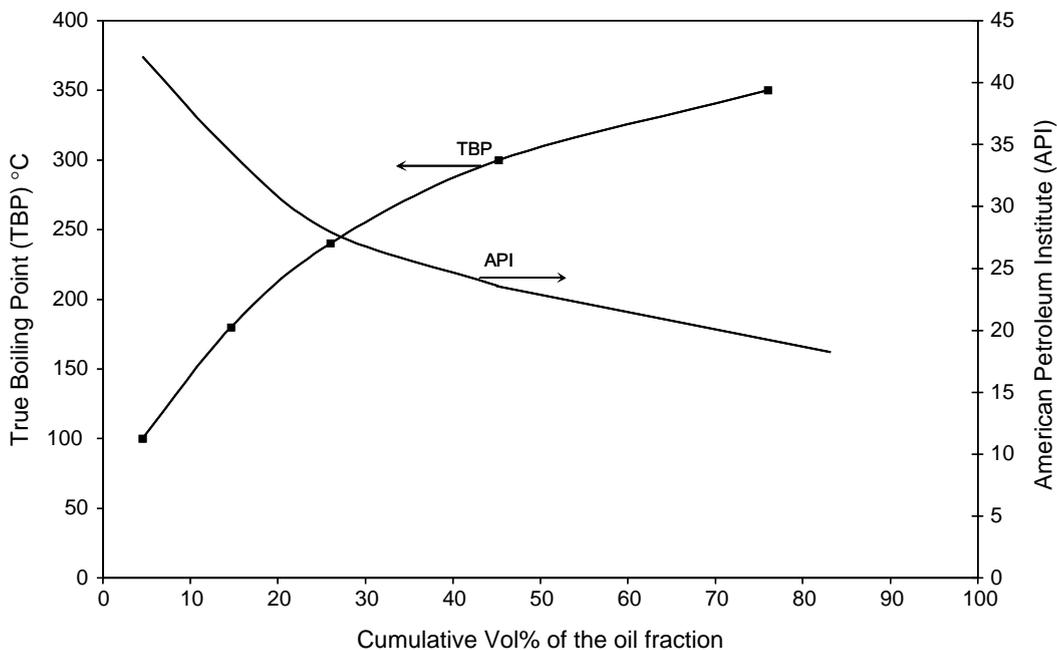


Fig. 4. The American Petroleum Institute (API) index and the True Boiling Points (TBP) for the fractions of the distillation from the oil extract.

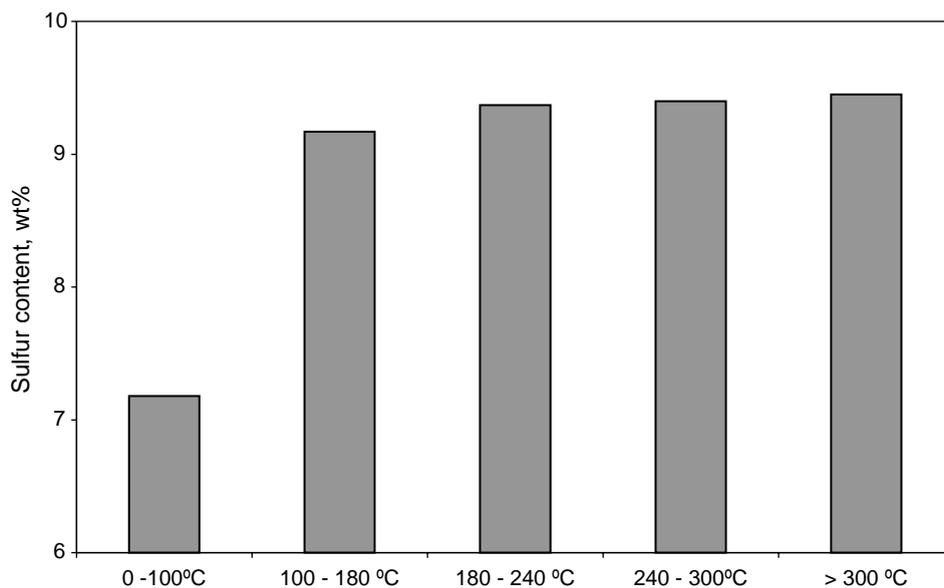


Fig. 5. The distribution of the sulfur in the fractions of the distillation of the oil extract.

alkylthiophenes. These alkylthiophenes were obtained from a pyrolysis even at low temperatures (150 °C). Authors suggested that they are formed by thermal degradation of multiple (poly)sulfide-bound linear C5–C7 skeletons. However, linear carbon skeleton alkylthiophenes were unstable at higher pyrolysis temperatures (> 330 °C) because of their thermal degradation at higher temperatures.

This work is part of an ongoing project to characterize the extraction of oil shale resulted from thermal cracking process with a special emphasis on the sulfur distribution. As mentioned earlier, sulfur can play a major role in the decision of utilizing oil shale. Therefore, this particular work focuses on finding the nature of sulfur distribution in different shale oil distillate fractions of oil shale from El-Lujjan deposits. This will help researchers in finding possible separation processes to remove sulfur compounds from shale oil.

2. Experimental

2.1. Materials

A standard sample of oil shale was brought from the El-Lujjan deposit by the Jordanian Natural Resources Authority. Samples were crushed and sieved to less than 200 μm . Table 2 represents the proximate analysis of El-Lujjan deposits.

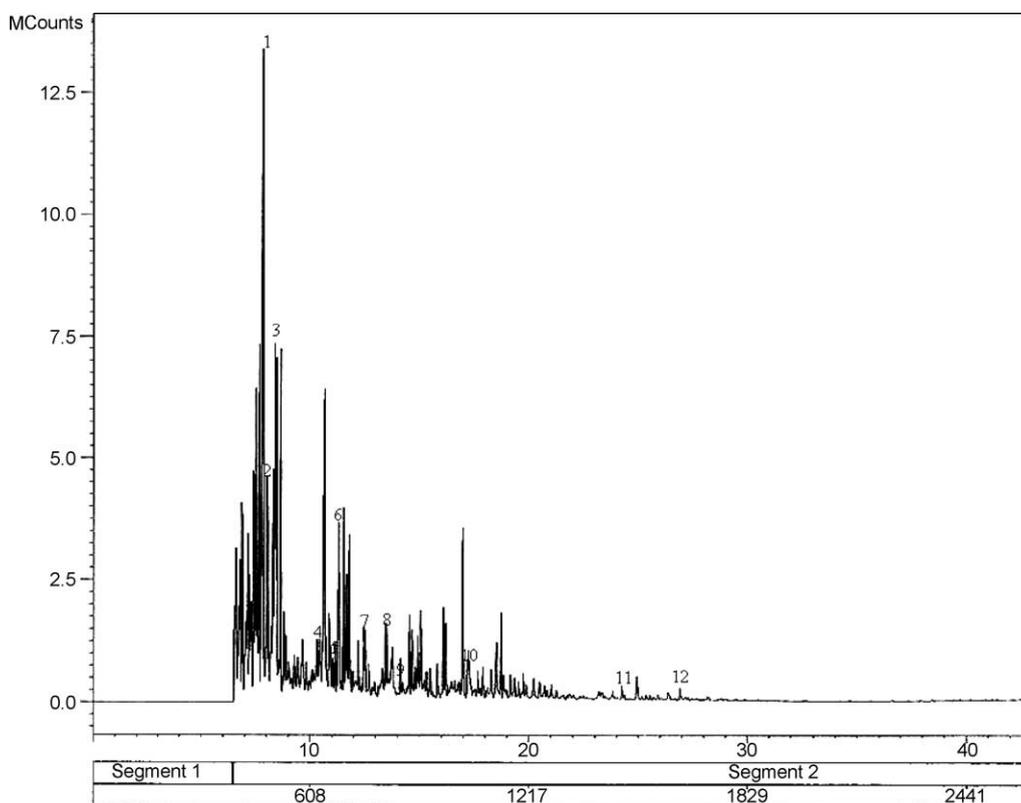


Fig. 6. Gas chromatography for the fraction < 100 °C.

2.1.1. Determination of the yield of shale oil by thermal cracking; Fisher Assay

This method was employed to extract shale oil from oil shale by thermal cracking according to the standard ISO 647 at a temperature of 500 °C. In 2003, Kraisha et al. [6] showed that the composition of shale oil extracted from Jordanian oil shale does not depend on the pyrolysis temperature. The apparatus used to perform this task mainly consists of a furnace made up of two cylindrical layers of steel, which forms the heating elements. A sample of 50 g of oil shale sample is placed inside a retort heated in the furnace at a heating rate of 5 °C/min–500 °C. The weight of the shale oil, retorted shale, and the gases are determined by simple material balance calculations. Several experiments were carried out to determine accurately the shale oil yield and to obtain enough shale oil samples for fractionation process.

2.1.2. Fractionation of the shale oil extract

A simple distillation apparatus was used to determine the weight percent of the shale oil fractions which was obtained by thermal cracking process described previously. Fig. 1 presents a schematic diagram for the apparatus used for the fractionation process. The distillates were obtained according to the following temperatures ranges: less than 100, 100–180, 180–240, 240–300 and greater than 300 °C. The densities of these fractions were also determined.

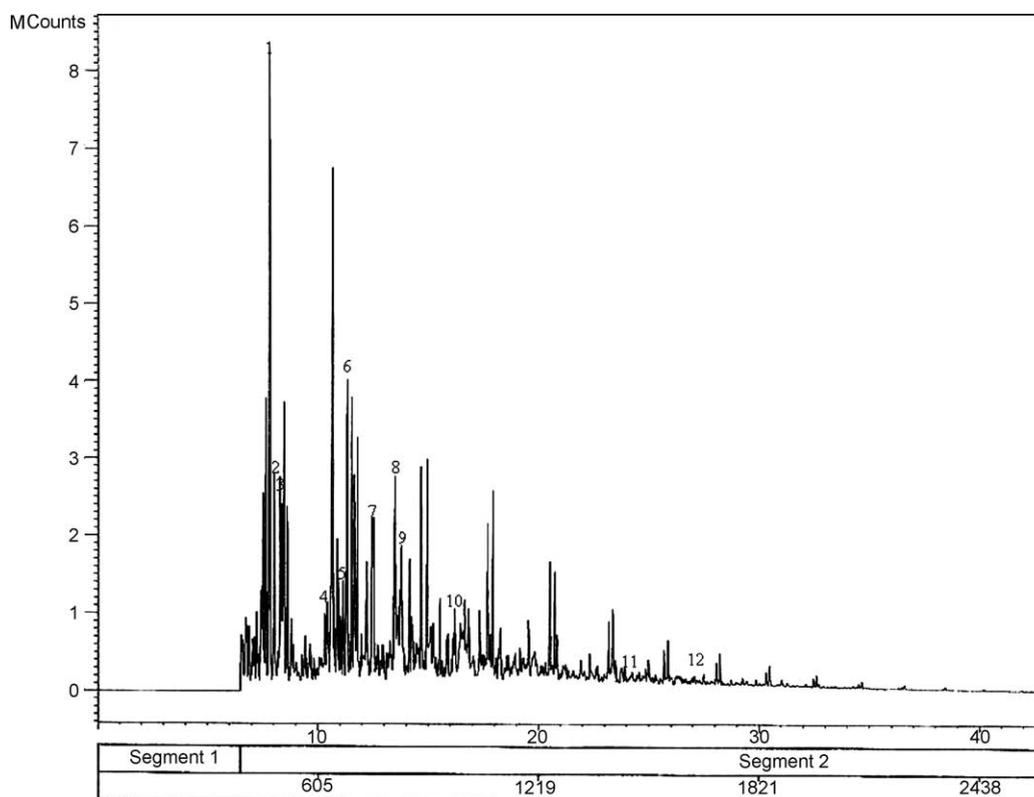


Fig. 7. Gas chromatography for the fraction 100–180 °C.

2.1.3. Total sulfur analysis

Sulfur was determined by converting all the sulfur present in the shale oil extracts to sulfur dioxide (SO_2) at around 1400 °C. SO_2 is detected using an infrared detector.

2.1.4. Gas chromatography/mass spectrometer

A Varian CP-3800/Saturn 200MS was used to analyze the samples of the shale oil fractions. It is equipped with both flame ionization and flame photometric detectors. A capillary column of 30 m \times 0.32 mm coated with 5% phenol and 95% dimethylpolysiloxane coating. Helium was the carrier gas; the temperature was raised up to 300 °C at a rate of 4 °C/min. Samples were taken from the shale oil extract, then diluted in toluene and filtered before injecting them into the Gas Chromatography (GC).

3. Results and discussion

Results from scanning electron microscope showed that kerogen present in oil shale is mainly contained in a spherical shell of minerals. Fig. 2 presents an image of a cross-section for a sample of oil shale used in this study. Using Energy Dispersive Spectrum (EDS) analysis, the kerogen was composed

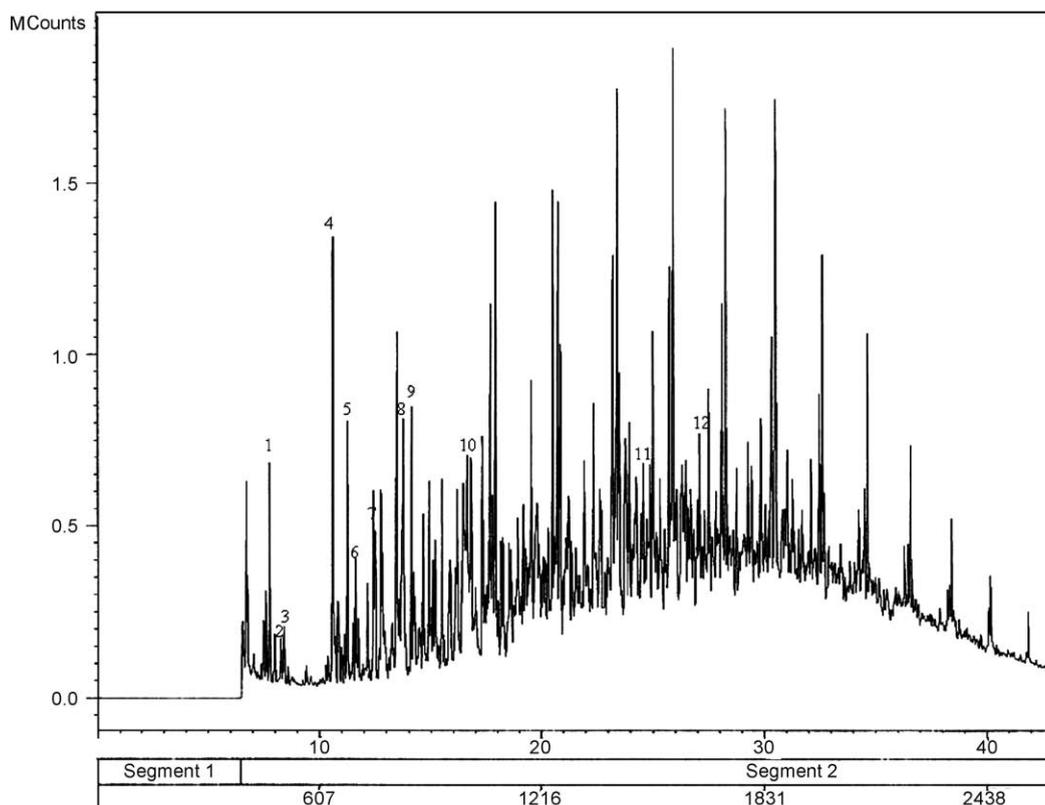


Fig. 8. Gas chromatography for the fraction 180–240 °C.

of mainly Carbon, Hydrogen, and Sulfur. It was also clear that sulfur exist as organic sulfur. Very few amounts of inorganic sulfur were encountered.

The shale oil yield and the gas yield for the oil shale from the thermal cracking experiments were determined in order to verify earlier findings mentioned previously. The extracted shale oil by the thermal cracking process of the El-Lujjan oil shale showed that the yield of shale oil was around 12 wt%. Fig. 3 shows that the shale oil yield as well as the gas yields. It is clear that the oil yield does not change significantly with temperature.

The results presented in Fig. 4 provide an indication for the true boiling curve (TBP) and the American Petroleum Institute Index (API) based on simple laboratory experiments. It is clear that more than half of the fractions have a boiling point greater than 300 °C. The average of API index is around 25.

The sulfur contents of the distillation fractions were also obtained. Results shown in Fig. 5 indicate an increase of the sulfur content with increasing the temperature. As expected, the sulfur content increases with increasing the molecular weight.

Figs. 5–10 show the chromatography of the distillate fractions with peaks number to identify the sulfur compounds. The identification of these peaks are summarised in Table 3. It was clear from these results that sulfur exists in the form of thiophenes in these fractions. Decylthiophene, dimethylthiophene,

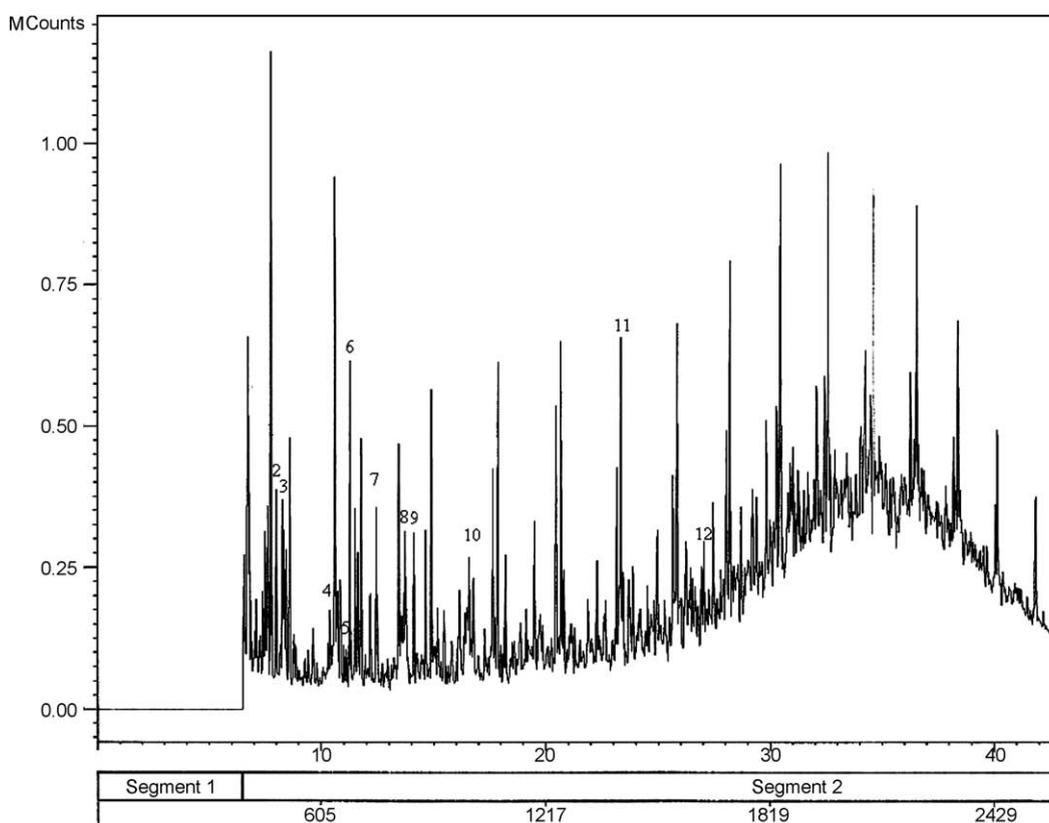


Fig. 9. Gas chromatography for the fraction 240–300 °C.

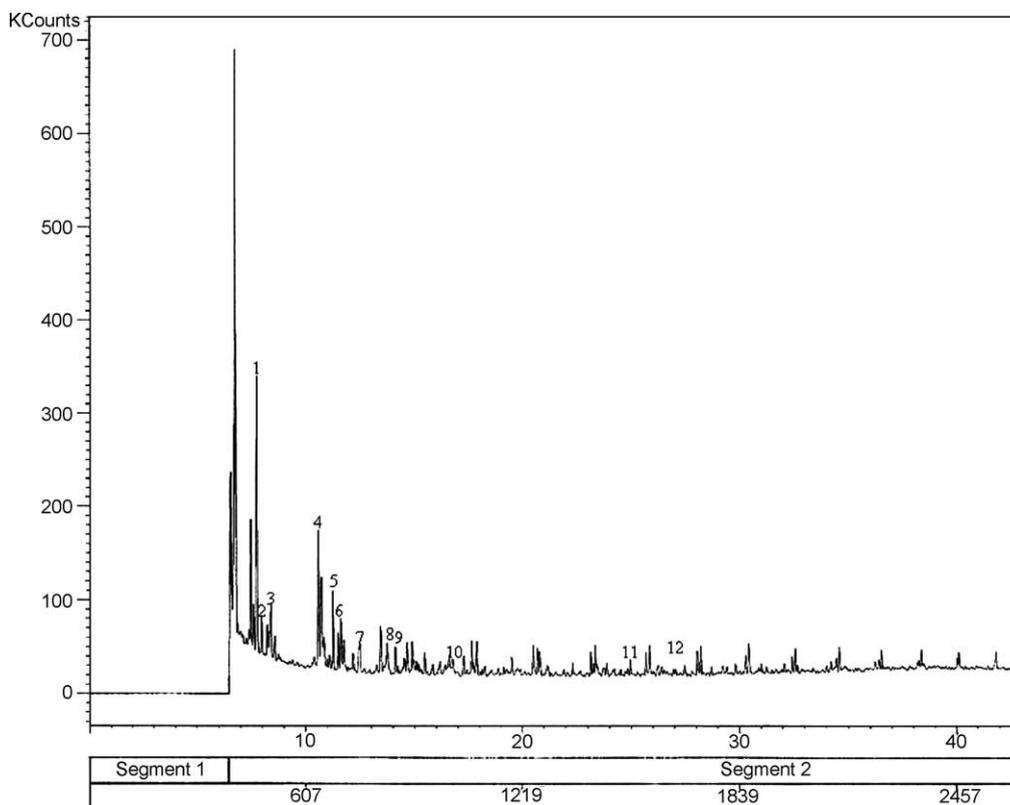


Fig. 10. Gas chromatography for the fraction > 300 °C.

ethylthiophene, proylthiophene, and octylthiophene constitute most of the sulfur present in shale oil distillates. Different forms of thiophenes were found in all fractions of the shale oil extract. There was no distinct change in thiophenes along these extracts. Fig. 11 illustrates the distribution of sulfur compounds in these distillates.

Table 3
Sulfur compounds identified by the GC-MS

Peak number	Compound
1	Thiophene, 2-decyl-
2	Thiophene, 2,3-dimethyl-
3	Thiophene, 2-ethyl-
4	Thiophene, 2-propyl-
5	Thiophene, 2-(1-methylethyl)-
6	Thiophene, 2,3,4-trimethyl-
7	Thiophene, 2-(2-methylpropyl)-
8	Thiophene, 2-butyl-
9	<i>meta</i> -Methoxybenzenethiol
10	Thiophene, 2-(1-methylethyl)-
11	Thiophene, 2-octyl-
12	Thiophen, 2-nonyl

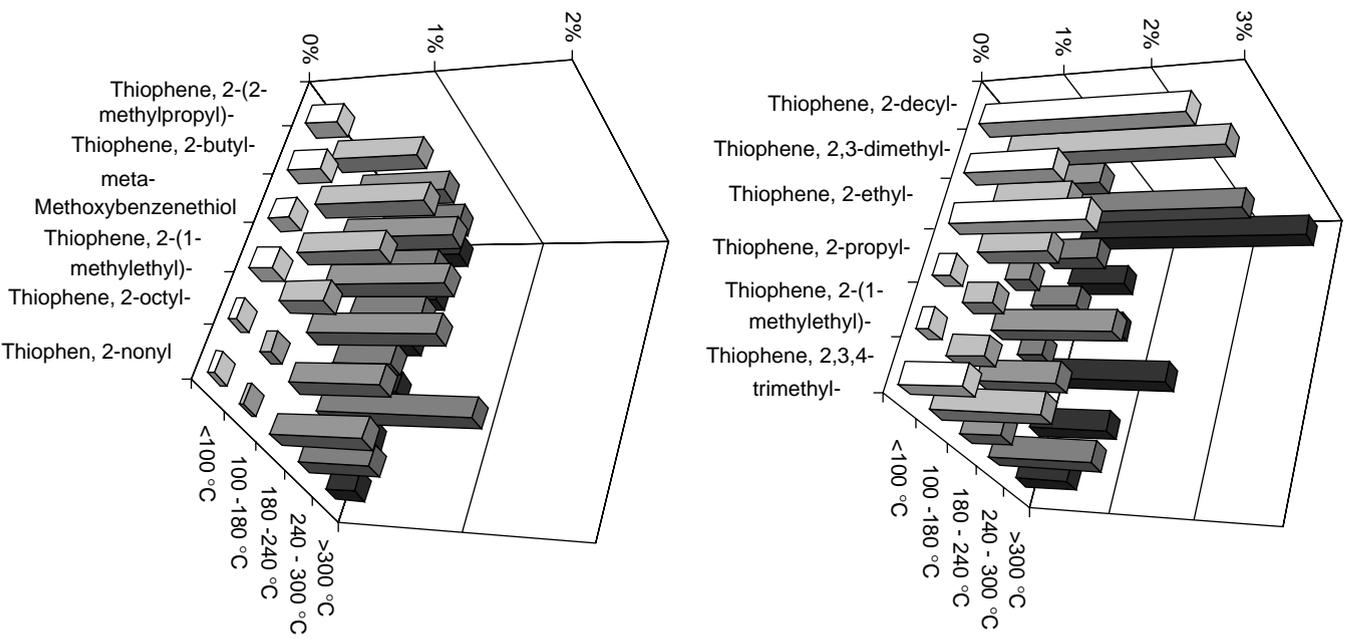


Fig. 11. The distribution of the sulfur compounds in the distillate fractions.

Thiophenes are considered to be an extraordinary reactive substance, which can be converted into various valuable chemicals. Some of these thiophenes cannot be obtained by synthetic methods. Therefore, the presence of these compounds in Jordanian oil shale can be very beneficial to local economy. Methods for utilizing thiophenes from oil shale are presented in a recent study by Blokhin and Zaretsky [12]. Thiophenes can be utilized for the synthesis of well-known chemicals like herbicides, antioxidants and psychological active compounds. Another important use of thiophenes is the production of organosilicate liquids which have unique properties such as high operational range with constant viscosity when used as a lubricant oil for machineries [13].

A new direction for utilizing Jordanian oil shale other than as a source of energy can be established. The new direction should focus of the feasibility of separation of valuable thiophenes from the extracted shale oil. Technical feasibility should also focus on the effect of using thiophenes in medical, agricultural and industrial applications.

4. Conclusions

The average shale oil yield obtained at different pyrolysis temperatures was relatively constant at 12 wt%. Sulfur in the Jordanian oil shale was found to be mainly of an organic type. The amount of sulfur in shale oil obtained by thermal cracking of El-Lujjan oil shale was found to increase (from 7 to 9.5 wt%) with the increase of the boiling point for different distillate fractions. It was found to be in the form of aromatics in the shale oil obtained by the thermal cracking process at low temperature. Alkylthiophenes were the major constituents of these sulfur compounds. It is believed that the low temperature of thermal cracking leads to breaking the bridges between the sulfur containing compounds (thiophenes) in the kerogen without affecting the structure of these thiophene. Different forms of thiophenes were found in almost all fractions of the distillates without any significant trend to any particular compound of these thiophenes with the distillation temperature. However, the total sulfur was found to increase with increasing the boiling point of these fractions.

Future work should focus on the separation of thiophenes from Jordanian shale oil which can be used for many industries including pharmaceuticals, herbicides and many others.

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