

## MICROWAVE-ASSISTED SOLVENT EXTRACTION OF SHALE OIL FROM JORDANIAN OIL SHALE

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**Abstract.** Oil shale as an alternative to oil is considered a major possible source of energy in Jordan which has an estimated 50 billion tons of geological proven reserves that are widely distributed all over the country. Many methods have been used for extracting shale oil from oil shale. This investigation suggests the application of a novel technique, namely microwave-assisted extraction. Several solvents were tested for extractive capacity at different temperatures (50 to 140 °C) by the microwave irradiation of the investigated oil shale. The extraction results showed that all the solvents except hexane followed a sigmoid behaviour. Methanol exhibited the highest extractive capacity of about 23% of shale oil. Several particle sizes in the range of 94–910 µm were examined and the results indicated that shale oil extraction is not diffusion controlled. The dynamic effect of extraction was also considered and found to have a very little effect after 10 minutes of irradiation.

**Keywords:** extraction, microwave, oil shale, shale oil, solvent.

### 1. Introduction

It is well established that the world today is mostly dependent on fossil fuel as the major source of energy. It is also well realized that the world needs alternative sources for energy. Such sources include wind, solar, biofuels, geothermal and nuclear, to name some.

One energy source that might be promising is oil shale as an alternative to oil. Oil shale (OS) is a layered sedimentary rock that contains abundant quantities of kerogen. The shale is mainly composed of calcium compounds

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(calcium carbonate content is about 40 to 70%), in addition to sulfur compounds (ca 3%), total organic matter (ca 20%), and silica compounds (5 to 25%).

The organic fraction of oil shale is made up of two parts, namely kerogen and bitumen. The kerogen part is composed of high molecular weight insoluble materials that need high energy in order to be broken down and therefore liquefied. On the other hand, bitumen, which constitutes around 10–20% of the original organic matter of OS, is usually soluble and therefore is considered extractable.

When oil shale is heated to temperatures above around 450 °C, the kerogen in the shale decomposes, releasing shale oil (SO), gas and spent shale. The average oil content of Jordanian OS is generally in the range of 5 to 15% [1].

Jordan's supply of energy depends heavily on imported oil and natural gas. OS is considered a major possible alternative source of energy in Jordan which has an estimated 50 billion tons of geological proven reserves of OS that are widely distributed all over the country [1].

One way of making use of OS is by direct feeding the as received OS from mining sites to power plants in the same way as coal. This is being done, for example, in Estonia which has one of the world's highest grade deposits with an average heating value of about 8.3 MJ/kg [2, 3].

Another way of benefitting from OS is the extraction of SO from it by heating. Several technologies are used to extract SO and gas from OS deposits. For example, in the USA, a number of Research, Development & Demonstration (RD&D) projects have employed different extraction processes, namely [4]:

- underground mining and surface retorting (used by Oil Shale Exploration Co. – OSEC)
- in situ/heated gas injection (used by Chevron)
- in situ/steam injection (used by EGL Resources, Inc. – EGL)
- in situ conversion process (ICP) using self-contained heaters (used by Shell)
- two-step ICP using hot water injection (used by Shell)
- electric ICP using bare wire heaters (used by Shell).

One common item among the above techniques is the use of heat for the recovery of SO. The difference between the last five techniques mentioned above is the source of heat. In addition to the above projects, there have been several studies on the effect of heating on the extraction of SO [5–10].

Another technique that has long been investigated is the use of solvent extraction of SO. Several researches have been reported on this topic where investigators used different solvents under different conditions [11–16]. Some scientists have even used biosurfactants to extract SO from OS [17].

One approach for heating OS is to use microwaves. Several investigators applied this source of energy for retorting OS [18–21]. Heat transfer in traditional heating equipment transfers energy both slowly and locally. In addition, heat gradients within the system may develop. These effects may

result in localizing overheating leading to heterogeneity and/or degradation of the system. On the other hand, microwave irradiation, usually used in organic synthesis, is a powerful and efficient technique for extraction, where heat is uniformly distributed across the sample. It is also claimed that microwaves participate in the interactions that might build between solvent and matter to be extracted by the generation of “hot spots”. Microwaves rotate molecules having certain polarities and may generate hot spots that maximize the interaction between solvent and analyte, kerogen in our investigation [22, 23]. Halogenated solvents such as carbon tetrachloride, as well as supercritical fluid solvents like carbon dioxide have also been applied to OS extraction under microwave irradiation [24, 25].

In this work, the application of microwaves to Jordanian OS was investigated as an enhancement to solvent extraction of SO. Several solvents were tested for extractive capacity at different temperatures by the microwave irradiation of the investigated OS. The effects of time and particle size were also studied.

## 2. Experimental

### 2.1. Materials and instrumentation

All solvents used in this work (ethanol, methanol, acetone, dimethylformamide (DMF), and hexane) were of analytical grade. The microwave instrument was from Biotage, Germany (model Initiator 2.0).

### 2.2. Oil shale sample preparation

Oil shale was obtained from Al-Lajjun deposit site, Jordan. The properties of the deposit were as follows [1, 26]: average oil content 12 wt%, total organic matter 22.1 wt%, calorific value 1590 kcal/kg, calcium carbonate 54.3 wt%, sulfur 3.1 wt%, density 1.81 g/cm<sup>3</sup>, and moisture 2.43 wt%. Table 1 presents the results of Fischer Assay analysis of the investigated OS, showing its oil content to be 12.07%.

**Table 1. Fischer Assay analysis of oil shale**

Component	wt%
Total water	2.0
Total oil	12.07
Spent shale	81.30
Gas loss	4.63

Thermal gravimetric analysis (TGA) of the investigated OS, presented in Figure 1, shows that there are four stages of the weight loss profile. The first stage occurs below the temperature of 200 °C, which corresponds to the loss of interlayer water and volatile compounds. The second stage occurs between 200 and 500 °C where the real decomposition of the organic matter

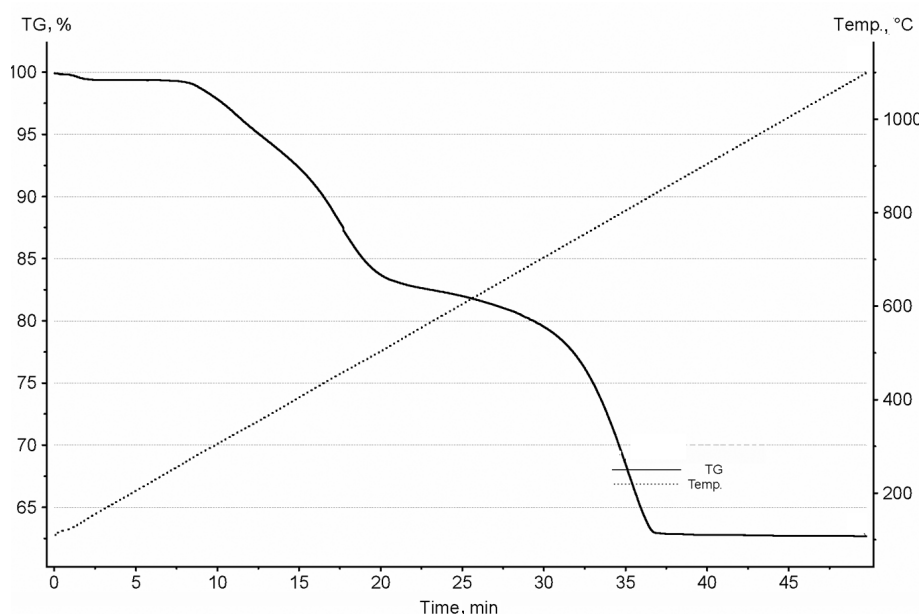


Fig. 1. Thermal gravimetric analysis (TGA) of oil shale.

and devolatilization take place. The third stage, which was observed at a temperature between 500 °C and 660 °C, corresponds to the cracking of heavy hydrocarbons. The final stage (above 660 °C) is related to the dissociation of clay materials and the carbonate minerals components of the OS specimen, which is a highly endothermic reaction. It is also clear that calcination is taking place at around 750 °C.

The oil shale was crushed, milled and then sieved to the average particle sizes of 910, 610, 428, 268, 153 and 94  $\mu\text{m}$ . The sieved shale was then washed with deionized water to remove salts and water soluble matter. The washed shale particles were then dried in an oven at 103 °C. The dried shale particles were thereafter kept in an oven at 50 °C for further use.

### 2.3. Extraction capacity as a function of temperature

To determine the effect of temperature on the extractive capacity of investigated solvents the following procedure was followed for all samples. Five grams of 428  $\mu\text{m}$  OS particles was placed in a 20 ml vial to which 15 ml of the investigated solvent was then added and the vial was thereafter sealed with a cap. The investigated solvents at this stage were acetone, DMF, hexane, methanol and ethanol. Magnetic stirring bars were used to keep homogeneity inside the vial. The above shale/solvent mixture was then placed in the microwave reactor. The temperature was controlled at 50, 80, 100, 120 or 150 °C. The sample mixture was kept at one of the above specified temperatures for 10 minutes. The pressure was the autogenous pressure of the system which varied depending on the solvent used;

however, it never reached 18 bars (the tripping pressure of the system). After irradiation, the sample was allowed to cool down to room temperature and then was centrifuged for 7 minutes at 5000 rpm (inside the same vial).

The centrifuged sample was thereafter decanted. The decanted liquid was mostly composed of the solvent added at the beginning of the experiment, in addition to any kerogen that had been extracted by the solvent used. The solid leftover (the remaining shale) was then composed of the non-soluble matter of OS, remaining kerogen not extracted by the solvent, and some solvent sticking to the shale. The next step was to remove the remaining solvent in the shale. To achieve this, the shale residue was washed twice with 15 ml of the corresponding solvent followed by centrifugation and decantation under ambient conditions. The matrix was then washed with methanol and dried in an oven at 50 °C for 24 hr. The dried shale was weighed (inside the same vial that contained the solid shale during the entire procedure) and the obtained weight compared to the initial 5 grams of OS used. The weight difference would be attributed to the extracted SO.

#### **2.4. Extraction capacity as a function of time**

To determine the effect of time on the extractive capacity of investigated solvents the following procedure was followed for all samples. Three grams of 268  $\mu\text{m}$  OS particles was placed in a 20 ml vial to which 15 ml of the investigated solvent was added and the vial was sealed with a cap. The investigated solvents at this stage were acetone, DMF, hexane, methanol and ethanol. Magnetic stirring bars were used to keep homogeneity inside the vial. The above shale/solvent mixture was then placed in the microwave reactor. The temperature was controlled at 130 °C. The samples were irradiated for 10, 13, 16, 20, 30, 40 and 50 minutes each. After the above irradiation, the sample (still inside the same vial) was centrifuged for 7 minutes at 5000 rpm. The centrifuged sample was then treated using the same procedure described above.

#### **2.5. Extraction capacity as a function of particle size**

To determine the effect of particle size on the extractive capacity, a single solvent, methanol, was tested. Six different OS particle sizes were used, namely 910, 610, 428, 268, 153 and 94  $\mu\text{m}$ . Fifteen ml of methanol was added to three grams of OS of selected particle size and irradiated for 10 minutes at 130 °C. The samples were then treated using the same procedure as above.

### **3. Results and discussion**

Figure 2 shows the effect of time on the extractive capacity of investigated solvents interacted with OS particles (268  $\mu\text{m}$ ) that were simultaneously irradiated with microwaves, raising the temperature to 130 °C, then keeping

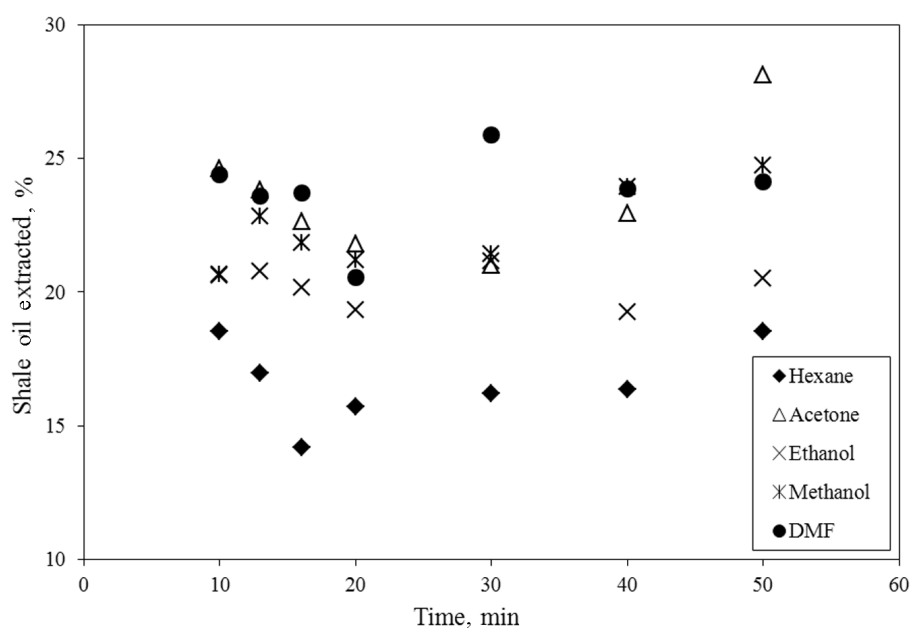


Fig. 2. Percentage of shale oil extracted by different solvents interacted with oil shale that was simultaneously irradiated with microwaves, raising the temperature to 130 °C, as a function of time.

the temperature constant for the specified times. The percentage of SO extracted was calculated using the following equation:

$$(\text{wt}\% \text{ SO})_{\text{extracted}} = \frac{(\text{wt of OS})_{\text{original}} - (\text{wt of OS})_{\text{after extraction}}}{(0.12)(\text{wt of OS})_{\text{original}}} \times 100\% , \quad (1)$$

where 0.12 represents the average SO fraction in the original OS sample. It is observed that the percentage of SO extraction (SOE) fluctuated within about  $\pm 2$  points for most solvents. However, in general it can be concluded that a 10-minute irradiation period can be chosen as an optimum time to further investigate the other parameters.

Figure 3 shows the effect of temperature on the extractive capacity of investigated solvents interacted with OS particles (428  $\mu\text{m}$ ) that were simultaneously irradiated with microwaves, raising the temperature to the specified values, then keeping the temperature constant for 10 minutes. It is clear that the percentage of SOE generally increases with increasing temperature. However, the SOE for hexane demonstrates a limited dependence on temperature. It is also noticed that for acetone, DMF and methanol the SOE trends follow a sigmoid shape.

For comparison purposes, a classical Soxhlet extractor was used to determine extractables present in OS at both low and high temperatures.

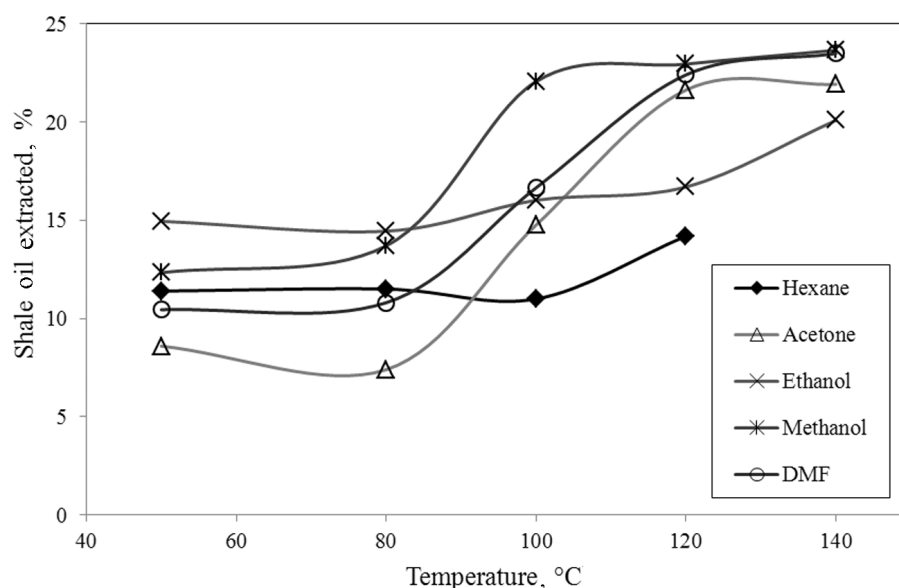


Fig. 3. Percentage of shale oil extracted by different solvents interacted with oil shale that was simultaneously irradiated with microwaves, raising the temperature to the indicated values for 10 minutes.

Two solvents were used for this purpose, namely methanol and DMF, having boiling points of 65 and 152 °C, respectively. The extraction yields were found to be 2.0 wt% of total OS for methanol, and 0.75 wt% for DMF (these are equivalent to 16.6 and 6.2 wt% of oil content of OS, respectively). When these values are compared to the results shown in Figure 3, it can be noticed that microwave-solvent extraction enhanced the yield of both the above solvents by 38% and 271%, respectively.

It is also seen from Figure 3 that in the case of methanol-extraction at 65 °C the yield is around 13%, which is lower than the yield of the Soxhlet solvent extraction; however, microwaves are not expected to be effective at such low temperatures due to the limited number of microwave pulses needed. Moreover, in Soxhlet experiments the pure solvent is circulated many times during the extraction process, whereas in the microwave-assisted solvent extraction the solvent is used only once.

Further analysis of the results of Figure 3 in light of Hansen solubility parameters, shown in Table 2 [27], indicate that at low temperatures (below 90 °C) hydrogen bonding (HB) forces might be dominating the intermolecular interaction between solvent and SO. Solvents having higher HB values produced higher SOE. Hexane, with an HB value of 0, produced an intermediate SOE which may solely be attributed to dispersion forces. On the other hand, at higher temperatures (above 90 °C) polar forces might lead to the interactions where solvents with high Hansen polar solubility parameters produced higher SOE.

**Table 2. Hansen solubility parameters for different solvents [27]**

Solvent	Hansen solubility parameters, MPa <sup>1/2</sup>		
	Dispersion	Polar	Hydrogen bonding
Acetone	15.5	10.4	7
Dimethylformamide	17.4	13.7	11.3
Ethanol	15.8	8.8	19.4
Hexane	14.7	0	0
Methanol	15.1	12.3	22.3

Furthermore, assuming that the shale/solvent system approached equilibrium, one may define a solution/extraction equilibrium constant,  $K$ , as [28]:

$$K = \frac{\text{wt of SO extracted}}{\text{wt of SO not extracted (remaining in shale)}} \quad (2)$$

Using this definition, the effect of temperature can be represented by the famous van't Hoff equation [29]:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (3)$$

where  $\Delta H^\circ$  is the overall enthalpy change for the solution process,  $T$  is the absolute temperature, and  $R$  is the universal gas constant. Assuming constant  $\Delta H^\circ$  over the relatively narrow investigated temperature range, the above equation can be integrated and written as:

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4)$$

This equation shows that  $\ln K$  is linear with respect to  $1/T$ . Therefore, a plot of  $\ln K$  vs.  $1/T$  could in principle be used to determine the enthalpy of the SO dissolution process. The above equation could also be written as [30]:

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

where  $\Delta S^\circ$  is the entropy of the system. A plot of experimentally determined values of  $\ln K$  vs.  $1/T$  was made, and the data were fitted using a linear fit. The values of the slopes of the linear fits and the corresponding intercepts (shown in Table 3) were used to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  as follows:

$$\Delta H^\circ = -(\text{slope}) \times R \quad (6)$$

$$\Delta S^\circ = (\text{intercept}) \times R \quad (7)$$

The calculated values of the enthalpies and entropies are also shown in Table 3.



**Table 3. Thermodynamic results for investigated oil shale/solvent pairs**

	Hexane	Acetone	Ethanol	Methanol	DMF
Intercept, Kelvin	-1.0522	3.532	-0.3024	2.154	2.8031
Slope	-338.16	-1978.6	-489.79	-1341.8	-1643.2
$\Delta H^\circ$ , kJ/mol	2.81	16.45	4.07	11.16	13.66
$\Delta S^\circ$ , J/mol K	-8.75	29.37	-2.51	17.91	23.31

A quick conclusion from the calculated  $\Delta H^\circ$  values would be that all investigated SO/solvent/OS dissolution processes are endothermic manifested by the positive  $\Delta H^\circ$  values, which may explain the increase in SO extraction with increasing temperature. In addition, the calculated values of  $\Delta H^\circ$  are relatively low. Actually, they are in the range of energy required to disrupt secondary valence bridges (ca 2 to 20 kJ/mol), and a little bit approaching the lower values of the energy of hydrogen bonds (ca 20 to 40 kJ/mol) [28], with the exception of hexane and ethanol. This suggests a moderate temperature dependence of the dissolution process.

Figure 4 shows the effect of OS particle size on the extractive capacity of methanol in SOE. It is observed from this figure that there is a slight decrease in SOE as OS particle sizes were increased. Although the superficial external surface area increased by about one order of magnitude,

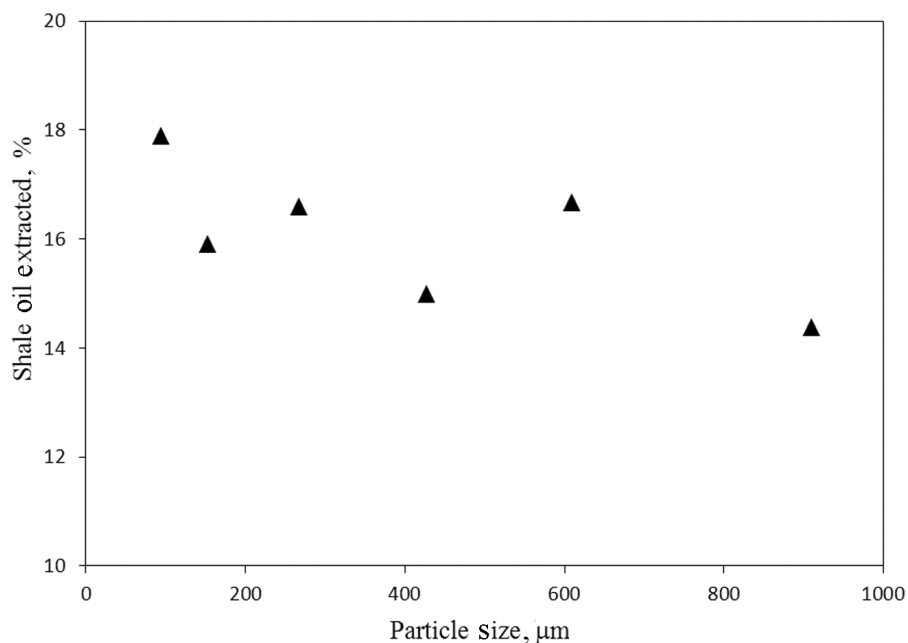


Fig. 4. Percentage of shale oil extracted by methanol as a function of oil shale particle size (system temperature 130 °C, time of extraction 10 minutes).

the SOE values increased by less than 20%, indicating that extraction is not diffusion controlled.

#### 4. Conclusions

It is concluded from this investigation that the application of microwave-assisted extraction of shale oil from Jordanian oil shale can be considered a promising technique depending, however, on the solvent used. Methanol was capable of extracting about 23% of shale oil from oil shale at a temperature as low as about 100 °C, in as fast as about 10 minutes of irradiation. The extraction is concluded to be not diffusion controlled. The temperature dependence of the extraction process seemed to follow a sigmoid behavior for acetone, methanol and DMF.

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