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Shale Oil Solvent Extraction of Central Jordan El-Lajjun Oil Shale

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Abstract

The extraction of the organic matter (OM) from oil shale (OS) can be achieved by several processing techniques. Normally, these techniques can remove high proportion of the organic material contained in oil shale. In this work, organic solvents extraction experiments were implemented to investigate the effect of various parameters on Jordanian El-Lajjun oil shale extractability. Results indicate that the approximate organic matter content in studied El-Lajjun oil shale is 17.48%, and 75% of OS sample particles diameters are less than 270 µm. The grain size has minor effect on shale oil extraction via organic solvents. Among eleven solvents used, the highest yield is obtained via the tetrahedrofuran (THF), whereas, with the use of solvent mixtures, the highest bitumen yield is obtained through the mixture of THF and toluene. The solvation variability is related to mode of extraction and various physicochemical factors such as extraction temperature, pressure, solvent type and mixing time, which result in different OM yield. The results indicate that the solvent extraction could be potential for shale oil extraction from Jordanian El-Lajjun OS under certain conditions of temperature, pressure and solvent type used.

Keywords

Oil Shale, Organic Matter, Bitumen, Solvent Extraction, El-Lajjun, Jordan

1. Introduction

Oil shale (OS) deposits are widely distributed in the world. Oil shales are sedimentary rocks contain hydrogen rich organic matter (OM) that is known as kerogen and bitumen [1]. Kerogen is OM that has not gone through

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oil window of elevated temperature and pressure necessary to generate conventional light oil [2]-[4].

Jordanian oil shales belong to the upper cretaceous and lower tertiary formations [5], which are widespread throughout the country [6]. The oil shale is generally not exposed, and all the geological investigations so far conducted are based mainly upon shallow boreholes [6]. The OS in Jordan is basically kerogen rich, bituminous limestone that is deposited in shallow marine environment [7] [8]. The OM content of the Jordanian OS varies from locality to the other, but the general trend is that the central Jordan deposits are richer than those of the Yarmouk Basin [9]. Kerogen, the insoluble part of the OM, makes more than 80% of the total OM content. Bitumen content varies from few percent up to 20% of the total OM content [7].

The extraction of shale oil from its sources is usually undertaken above ground (ex-situ processing) and some recent technologies perform this *in-situ*. In both cases, the immature kerogen is converted to synthetic shale oil and OS gas. Most conversion technologies involve heating OS at temperature between 450˚C and 500˚C in the absence of oxygen [10]. Solvent extraction involves dissolving compounds from a solid into a solvent or from a solution into another solvent [11] [12]. Solvent extraction of an OM from OS consists of several steps, including solvation of the OM by extraction solvent, desorption from the matrix surface, and, finally, transportation of the OM into the bulk extraction liquid [13]. The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process [12]. One of the standard methods for shale oil extraction using solvent is the soxhlet extraction [13] [14]. Solvent extraction of shale oil can be carried out under super critical conditions in order to affect the extraction of kerogen from the raw OS material [15]-[17]. Stirrer tank reactors and accelerated solvent extractors can also be used. With the solvent extraction process, the effects of particle size, extraction time, extraction temperature, mixing rate, solvent-to-oil-shale ratio, and type of solvent are mostly important and should be considered [13] [18].

There is limited number of evaluation studies that are carried out in the field of processing of Jordanian OS. Those evaluation studies aimed to investigate the suitability of the well known OS processing methodologies to the use, processing, and extraction of shale oil from the Jordanian oil shales, e.g. [19]-[23]. The work on shale oil extraction from Jordanian oil shale is still open and limited research has been undertaken (e.g. [19] [24]-[26]). Still many aspects need to be investigated. This work presented here aims to investigate the extraction properties of El-Lajjun OS via organic solvents. Different methodologies have been implemented. Important factors controlled their extractability have been investigated.

2. Sampling and Methodology

Oil shale sample brought from open pit excavated in El-Lajjun in Central Jordan (**Figure 1**). The studied oil shale

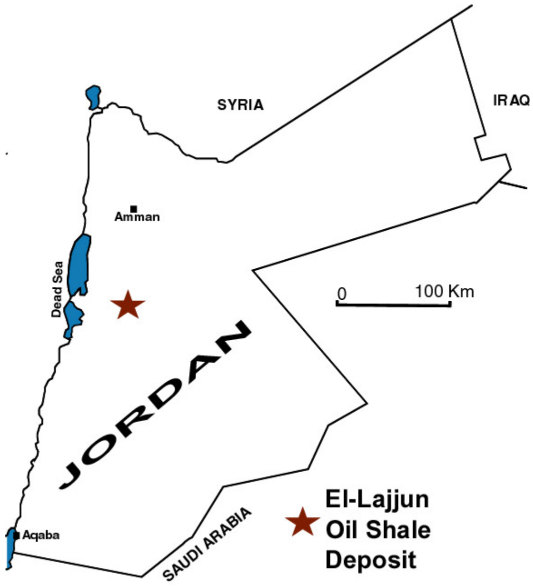

Figure 1. Location of El-Lajjun oil shale deposit.

Table 1. Solvent mixtures used and their percentage.

Mixture NO.	Solvent Type and Percentage (Vol. %)
Mix. 1	Benzene (50%); DCM (50%)
Mix. 2	Acetone (50%); Chloroform (50%)
Mix. 3	Chloroform (50%); Acetone (30%); Methanol (20%)
Mix. 4	Benzene (50%); DCM (50%)
Mix. 5	Benzene (30%); Methanol (70%)
Mix. 6	THF (70%); Toluene (30%)
Mix. 7	Toluene (30%); Methanol (70%)
Mix. 8	Acetone (50%); Ethanol (30%); Methanol (20%)
Mix. 9	THF (50%); Acetone (50%)

from El-Lajjun is very hard bituminous limestone. The outer OS surface is buff creamy due to weathering. Full sample preparation methodology is reported in previous papers [9] [27]. The methodology implemented covered OS petrography, mineralogy, organic carbon (TOC) determination and fisher assay. The OS sample has been analyzed for its TOC content via Carbon Determinator available at the Natural Resources Authority (NRA) in Amman. For size distribution test, a laboratory scale jaw crusher was used to reduce the sample size. Sample then fed to a ball mill for 10 mins. The ground portion was then sieved and the size distribution then be calculated.

Solvent extraction adopted in this study has been carried out in three different modes; namely soxhlet extraction, extraction via mixing and stirring, and lastly supercritical fluid extraction. Oil shale solvent extraction was carried out with eleven different solvents and nine solvent mixtures (**Table 1**).

In soxhlet extraction, about four grams of comminuted oil shale were transferred to a thimble which was then placed in the soxhlet chamber (100 ml). The soxhlet chamber was fitted to a distillation flask containing 200 ml of the solvent. Soxhlet extraction was carried out for 24 hrs. The extract then condensed by rotary evaporator and then dried under a stream of N_2 gas. The extractable organic matter (yield) was then determined.

To compare the performance of soxhlet extractor on shale oil yield with stirring performance, 200 ml of 1:1 mixture of THF-Acetone were used to extract the shale oil. Parameters investigated are temperature, time, and grain size effect. Under these conditions, OS sample was stirred on magnet hot plate at 1000 rpm. After the completion of each run, the sample was filtered and then the solvent was separated from liquor via rotary evaporator. Then the remaining part of the procedure was similar to that explained above for soxhlet extraction.

For elevated pressure and temperature conditions, a home-made reactor is designed by the authors and manufactured in the Royal Scientific Society, Jordan. **Figure 2** shows schematic diagram of the reactor. A sample with specific weight is charged with solvent and temperature and pressure are raised to set points where it remains constant during the extraction time.

3. Results and Discussion

Material characterization; mineralogy, composition, texture and quality is reported in Alnawafleh and Fraige [27]. El-Lajjun oil shale is considered to be of high quality [27]. It is primarily carbonate rich in organic matter. The approximate OM content is 17.48%. Minor amounts of quartz are also present. The allochems or bioclasts are mainly foraminifera.

3.1. Grain Size Distribution

Grain size distribution of the studied El-Lajjun OS is shown in **Figure 3**. The % cumulative fraction passing (undersize) is plotted against size. 52.8% of the sample is less than 150 µm. The d_{50} is incorporated in this rage (*i.e.* < 150 µm). The d_{75} = 270 µm, which means that 75% of the sample particles diameters are less than 270 µm and 25% are greater. This could advantage for any future mining and utilization of OS since 50% - 70% of the total energy used to recover ore is consumed in grinding [28].

3. 2. Effect of Solvent Type on Shale Oil Extractability

The effect of solvent type on the shale oil extractability is shown in **Figure 4** and **Figure 5**, respectively. Results

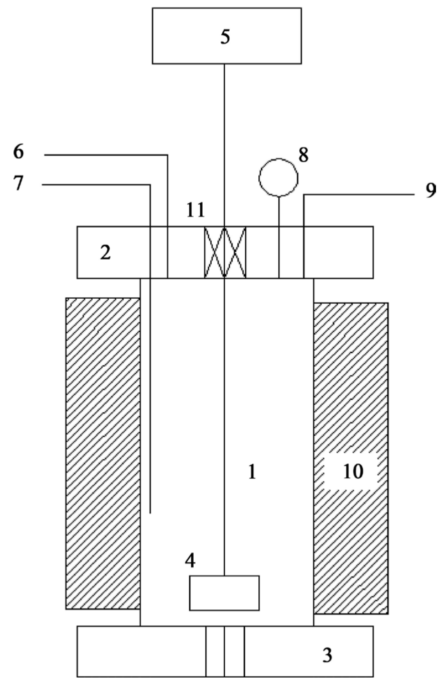

Figure 2. Schematic diagram of solvent extraction reactor. 1: main reactor body; 2: top cap; 3: bottom cap; 4: stirrer; 5: stirrer display and control; 6: liquid reactant line; 7: temperature measuring probe; 8: pressure measuring tap; 9: nitrogen gas line; 10: nlectric heater; 11: stirrer rod bearing and sealing.

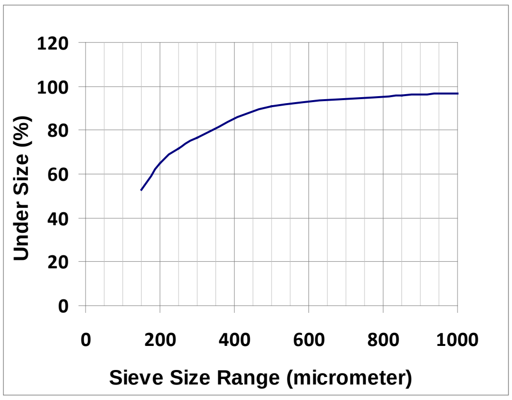

Figure 3. Grain size distribution curve for El-Lajjun OS.

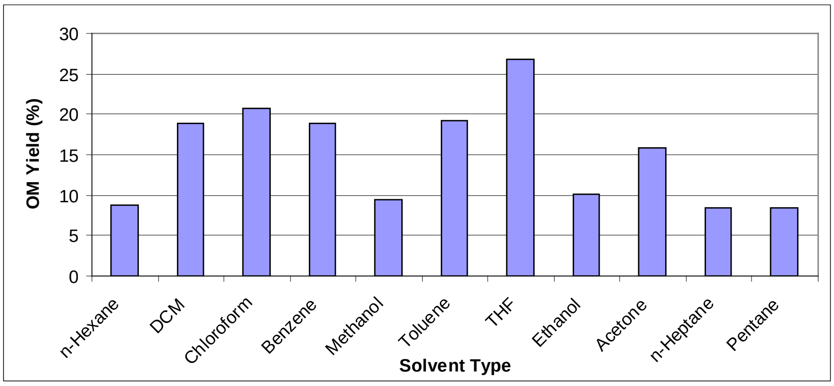

Figure 4. OM yield % of different solvent type via soxhlet extraction for 24 hrs; grain size < 150 µm.

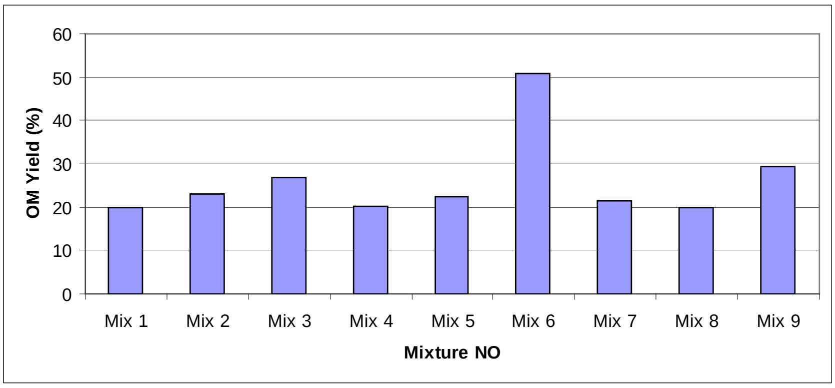

Figure 5. OM yield % of solvents mixtures via soxhlet extraction for 24 hrs; grain size < 150 µm.

show that different solvents have different OM yield and the polar organic solvents have better ability to dissolve the OM than non-polar solvents. This is due to several reasons include chemical composition of the solvent and the cohesion of atoms with each other which helps to attach OM and easily extract it. Another factor is that the polar solvents have low boiling points compared with non-polar ones which mean that the energy required to heat the non-polar is quite high compare with that of polar solvents [29]-[31]. As shown in **Figure 4**, the best polar solvent is THF (OM yield % = 27%) because of its complex chemical composition, cohesion between atoms, and strong structure that can dissolve the OM easily [31]. Due to the low boiling point of THF, more runs can be obtained via soxhlet extraction over 24 hrs. This might give more extraction yield. Quite similar results were obtained by Anabtawi and Uysal [32]. The THF also reported by Koel *et al*. [13] and Matouq *et al*. [33] gave the highest yield. A study by Shawaqfeh and Al-Harahsheh [26] and that by Bsieso [19] indicated that the yield was enhanced by the use of polar solvents. Among nine solvents mixtures used, mix 6 and mix 9 are considered to be the best yielding mixtures (**Table 1**, **Figure 5**).

3.3. Effect of Grain Size on Shale Oil Extractability

The effect of grain size on shale oil extractability via soxhlet extraction and mixing and stirring extraction is shown in **Figure 6** and **Figure 7** respectively. Via soxhlet extraction the highest yield is obtained generally for gain size > 250 µm. However, clear fluctuation in OM yield on different grain sizes is obtained. This fluctuation indicates that the grain size has minor effect on OM yield. Quite similar result has been reported by Anabtawi and Uysal [32].

In comparison with OM yield obtained with soxhlet extraction, the OM yield via mixing and stirring shows quite different trend especially for grain sizes > 300 µm. Beyond this size, the general trend in OM yield % is decreasing. This might be due to the mixing time of 10 mins that is not enough to dissolve much more quantities of OM. Compared with that of soxhlet extraction for 24 hrs, the yield via mixing and stirring is generally low. The extraction kinetics, dissolution thermodynamics, and the mode of mass transfer from the particles in different grain sizes can be differ resulted in different OM yield.

On fine grain sizes (*i.e.* < 250 µm) problems of agglomeration and coagulation could be raised which will impede agitation, hinder dissolution, and obstruct percolation processes. The solution drainage or settling velocity will be small due to high resistance to solvent flow inside the extractor under gravity settling condition [31].

3.4. Effect of Mixing Time on Shale Oil Extractability

The effect of mixing time on shale oil extraction is shown in **Figure 8**. Experiments carried out using THF-Acetone mixture (1:1) via stirring at 50˚C and 1000 rpm of the grain size fraction < 150 µm. Results show that the OM yield is increased with increasing mixing time. With increasing mixing time, the interaction between the OS particles and solvent molecules will increase, leading to better OM dissolution [31].

3.5. Effect of Extraction Temperature on Shale Oil Extractability

The effect of extraction temperature on shale oil extraction via mixing and stirring is shown in **Figure 9**. At nearly room temperature conditions, the OM yield is quite low compared with that at 50˚C in which the OM yield increased substantially. Preheating the OS to temperature below the boiling point of the solvent increases the OM solubility and extractability. Compared with these results from mixing and stirring experiments, significant OM release expressed as high OM yield is gained using supercritical fluid extraction (**Figure 10**). Higher extraction temperature especially in supercritical conditions resulted in higher oil yield [26] [34]. Increasing the temperature decreases the adhesiveness force, viscosity, and surface tension force of the oil contained in the shale and substantial extraction can be achieved in a relatively short time by heating the OS to a temperature of 50˚C [31]. The results presented previously show that the extraction behavior differs from one procedure to another under certain experimental conditions. Supercritical extraction is preferred to be followed.

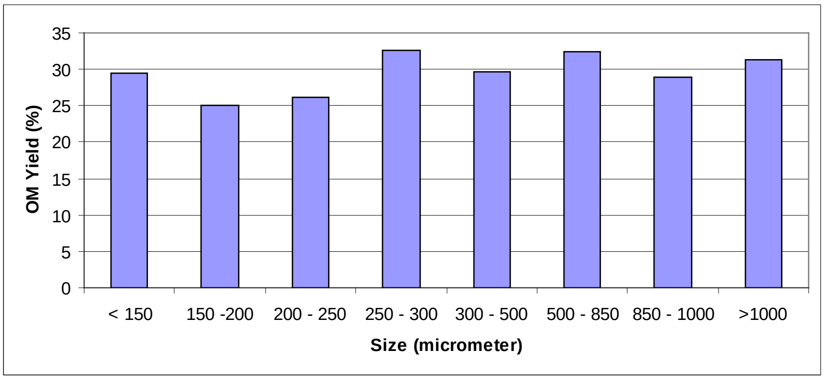

Figure 6. Effect of grain size on OM yield using THF-Acetone mixture (1:1) via soxhlet extraction for 24 hrs.

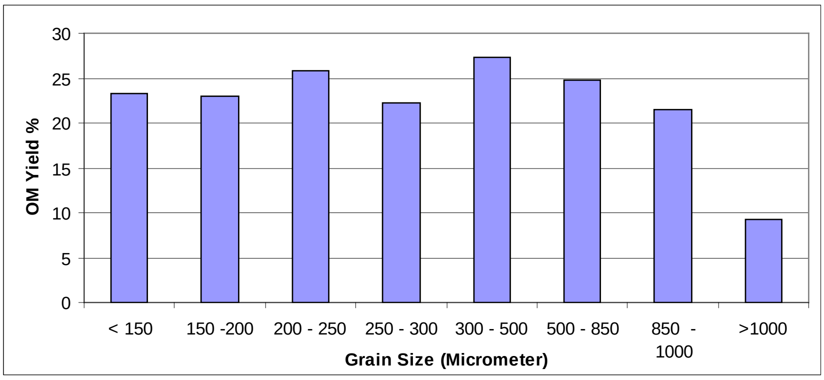

Figure 7. Effect of grain size on OM yield using THF-Acetone mixture (1:1) via stirring for 10 mins at 50˚C and 1000 rpm.

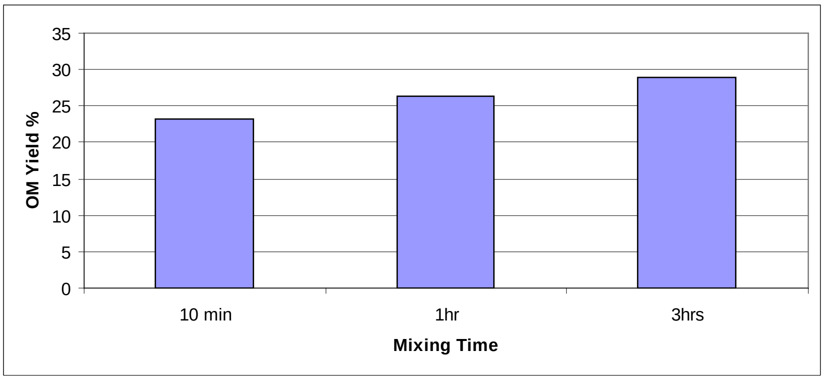

Figure 8. Effect of stirring time on OM yield using THF-Acetone mixture (1:1) via stirring at 50˚C and 1000 rpm, grain size <150 µm.

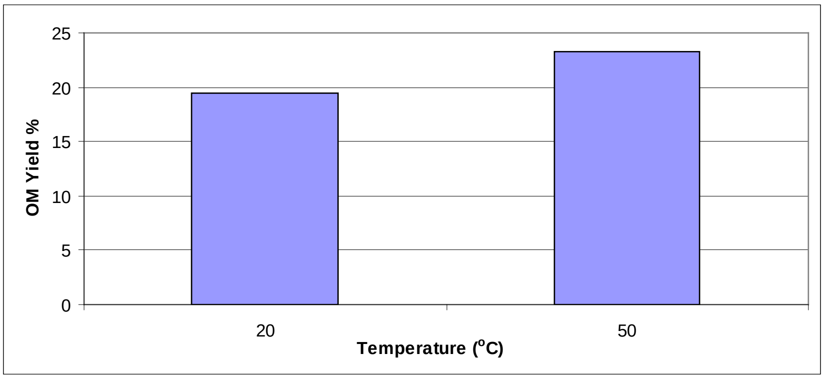

Figure 9. Heating temperature effect on OM yield using THF-Acetone mixture (1:1) via stirring at 1000 rpm for 10 mins, grain size < 150 μm.

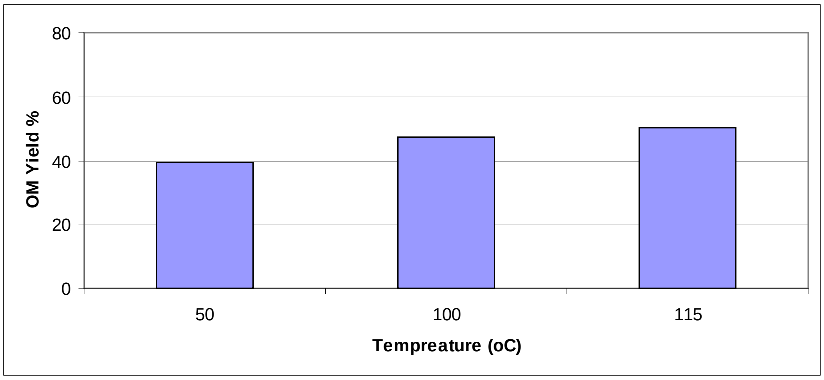

Figure 10. Yield increase via the designed reactor using THF-Acetone (1:1) at elevated temperature and increased mixing rate. Internal reactor pressure is 5 bars. Grain size < 150 μm. Extraction time 10 mins.

4. Conclusion

In this study the shale oil extraction from Jordanian OS via organic solvents has been investigated. 75% of El-Lajjun OS sample particles diameters are less than 270 μm. The grain size has minor effect of shale oil extraction via organic solvent and procedure implemented in this study. The THF is found to be the best solvent among eleven solvents (polar and non-polar) used in the extraction procedure via soxhlet extraction. The OM yield obtained by soxhlet extraction for 24 hrs is greater than that obtained via mixing and stirring. The OM yield is increased with increasing solvation/mixing time, pressure and temperature. Solvent extraction is better to be conducted under supercritical conditions. The solvent extraction could be potential for shale oil extraction under certain conditions of temperature and pressure and solvent used.

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