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Fractional Yield, Extract Composition and Variability from Jordanian Oil Shales

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Abstract

Surface and subsurface oil shale (OS) rocks in Jordan have potential economic value for the country and still unutilized. This research paper focuses on central and southern OS deposits in Jordan. Brief characterization of four OS deposits is presented. Size distribution test and elemental analysis were performed. Shale oil was extracted via three solvation methods: Soxhlet extraction, extraction via mixing and stirring, and lastly super-critical fluid extraction. Major shale oil fractions were obtained from extract fractionation on chromatographic column. The nuclear magnetic resonance spectroscopy technique was used to study qualitatively the fractional composition of OS extract. Results show that all studied OS deposits have quite similar trend in their particle size distribution and their elemental composition. These OS deposits are found to be varying in their solvation behavior, fractional yield, and shale oil composition. Highest yield is obtained from polar solvents. The OS extraction via solvation processes is promising under certain extraction conditions such as super-critical conditions. The solvation variability of Jordanian OS indicates that different extraction techniques suit different OS deposits. Such variability should be considered in any future extraction options.

Keywords

Jordan, Oil Shale, Solvent Extraction, Variability, Fractional Yield

1. Introduction

Jordan has few conventional resources of oil and natural gas, and its energy is largely depends on imported resources from neighboring countries. Therefore, Jordan could save much of its imported energy by utilizing its oil shale reserves. The most important oil shale deposits in Jordan are of Late Cretaceous to early Tertiary age [1] [2]. Jordanian OS is kerogen-rich bituminous limestone [3]. The Jordanian oil shale properties vary from one deposit to another indicating that different extraction techniques suit different OS deposits [3] [4].

The most important OS deposits in Jordan are located in central Jordan such as El-Lajjun, Sultani, Attarat Umm Ghudran and Wadi Maghar [5]. The future of OS in Jordan is still uncertain and most of the studies conducted so far on Jordanian oil shale have focused on El-Lajjun OS deposit. The organic content of El-Lajjun OS deposit varies laterally and vertically [3] [4]. The central Jordan OS has the highest average oil content. However, relatively high sulphur content is reported [6]. Based on Jaber *et al.* [7] and Jaber and Probert [8], the sulphur content is 7% to 9% of the organic matter (OM) content and the oil yield from Jordanian OS is up to 10%.

There are wide utilization options for OS resources. Among these options are pyrolysis, combustion, and extraction techniques. Solvent extraction techniques have attracted many researchers over the last three decades. Several solvent extraction methods have been developed for the extraction of shale oil with organic solvents. Among these methods are Soxhlet extraction, ultrasonic extraction, and super-critical extraction (e.g. [9]-[18]). Pyrolysis is reported to be the most effective known method used to extract the oil contained in shales [19]. Different controlling parameters are found to influence the shale oil extractability. Among these factors are particle size, temperature, solvent-feed ratio and the mixing intensity [20]. The quantity of solvent used is also considered as a critical factor [15] [21].

A study by Alnawafleh and Fraige [18] shows that solvent extraction is preferable to be conducted under super-critical conditions, and the solvent extraction technique when applied on Jordanian oil shale could be potential under certain extraction parameters. This research paper covers OS deposits from central and southern Jordan, and aims to study their solvation variability. The focus will be on certain parameter controlling their solvation behavior. Fractional yield and shale oil composition are also considered.

2. Material and Methodology

2.1. Sample Preparation and Characterization Procedures

Oil shale samples were provided from four major oil shale locations in central and southern Jordan (**Figure 1**). Full sample preparation methodology and characterization experiments were presented in Alnawafleh and Fraige [22] [23]. Analyses performed covered OS petrography, mineralogy, organic carbon content, and Fisher assay. Size distribution test was carried out at Al-Hussein Bin Talal University. A laboratory scale jaw crusher was used to reduce the size of oil shale samples. The crushed OS then fed to a ball mill for 10 mins. After sieving the ground OS, retained OS masses were recorded and the size distribution curves for each sample then constructed.

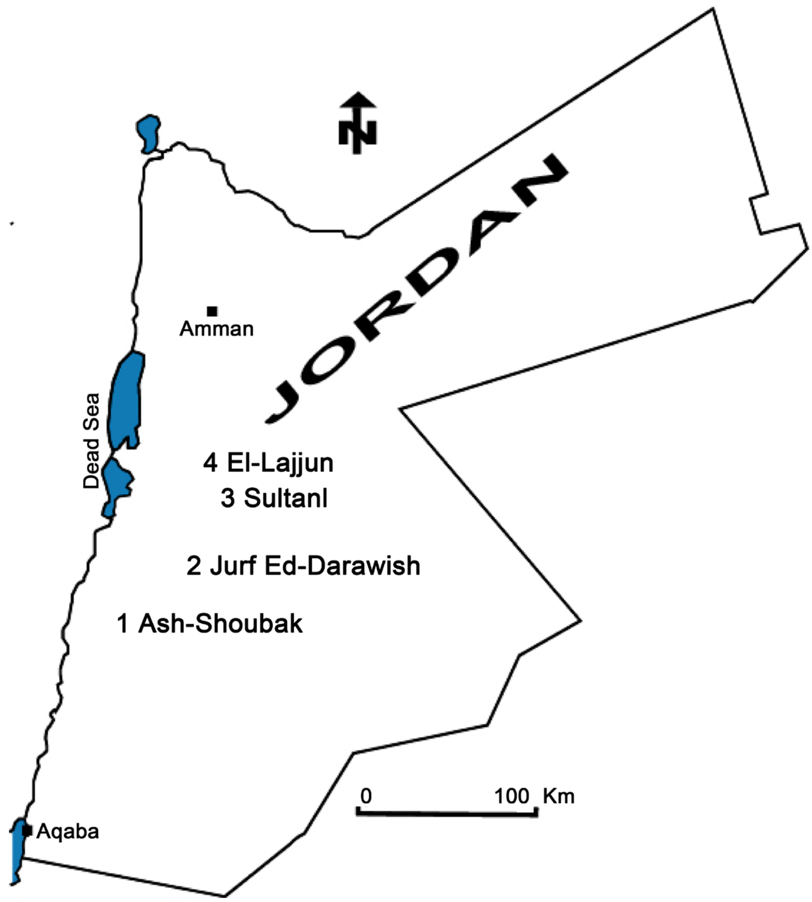

Figure 1. Location of the studied oil shale deposits in central and southern Jordan.

The average elemental composition % of the total solid samples was analyzed using EuroVector elemental analyzer model: EA 3000 A available at AL al-Bayt University, Jordan.

2.2. Shale Oil Extraction Procedures

Shale oil solvent extraction was carried out in three solvation protocols: Soxhlet extraction, extraction via mixing and stirring, and lastly super-critical fluid extraction via extraction reactor designed locally for this purpose (see Alnawafleh and Fraige, 2015a). The purpose is to compare the performance of extraction between them. Eleven different solvents and two solvent mixtures were used in the extraction experiments. Solvent mixture one (Mix. 1) is THF (50%); Acetone (50%), whereas, solvent mixture two (Mix. 2) is Chloroform (50%); Acetone (30%); Methanol (20%).

In the Soxhlet extraction, four grams of finely 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 extraction solvent. Each extraction run was carried out for 24 hrs. Extraction via mixing and stirring involves stirring the OS sample on magnet hot plate at 1000 rpm using 200 ml of solvent. The stirred sample then filtered. Supercritical extraction involves shale oil extraction via the designed reactor and relatively high pressure and temperature conditions. Within the reactor, OS sample and solvent used are charged and the pressure and temperature are raised to the desired values. In all protocols, the extraction solvent was separated form liquor via rotary evaporator and the extract was then dried under a stream of N2 gas. The organic matter (OM) yield was then determined.

2.3. Extract Fractionation

Chromatographic column of silica gel and alumina (1.3 cm i.d., 70 cm height) was used to fractionate the obtained extract from Soxhlet extraction using solvent Mix. 2. The 30 g of silica gel layer used in the column is placed in the lower part of the chromatographic column while the 10 g of alumina layer, in the upper part of the column. Measured quantity of 0.25 g of oil extract was added to the top of the column and eluted sequentially by 100 ml of hexane, 75 ml chloroform-hexane mixture (2:1), and 70 ml ethanol to separate aliphatic, aromatic and NSO fractions respectively.

2.4. Nuclear Magnetic Resonance Spectroscopy

High performance of digital NMR spectrometer in CDCl3, Model: Bruker 300 MHz/ Switzerland was used to study qualitatively the fractional composition of oil shale extract.

3. Results and Discussion

3.1. Material Characterization and Grain Size Distribution

The characterization of the studied oil shales; their mineralogy, composition, texture and quality are reported in Alnawafleh and Fraige [22] [23]. A brief summary is presented in Table 1. The studied oil shales differ in their organic matter content. Their

Table 1. Summary of the studied oil shale's properties. Table constructed based on data reported by Alnawafleh and Fraige [22].

<table>
<tr><th>Oil shale</th><th>Sample type</th><th>Organic matter %</th><th>Component summary</th><th>Internal texture summary</th><th>Fisher assay summary</th></tr>
<tr><td>Ash-Shoubak</td><td>Soft bituminous chalk marl</td><td>05.40</td><td rowspan="4">Significant amounts of organic matter; Calcite is the major mineral phase, minor quartz content, traces of fluorapatite and smectite</td><td rowspan="4">Very fine-grained matrix, strongly show flow structure and consists mainly of muddy material of cryptocrystalline micrite; Cretaceous forams are abundant. Brown organic matter fills pore spaces</td><td rowspan="4">Different oil yielding capacities; Highest for Lajjun and Sultani OS; Lowest for Ash-Shoubak and Jurf Ed-Darawish OS</td></tr>
<tr><td>Juf Ed-Darawish</td><td>Very soft bituminous marl</td><td>09.50</td></tr>
<tr><td>Sultani</td><td>Hard bituminous limestone</td><td>16.40</td></tr>
<tr><td>El-Lajjun</td><td>Very hard bituminous limestone</td><td>17.50</td></tr>
</table>

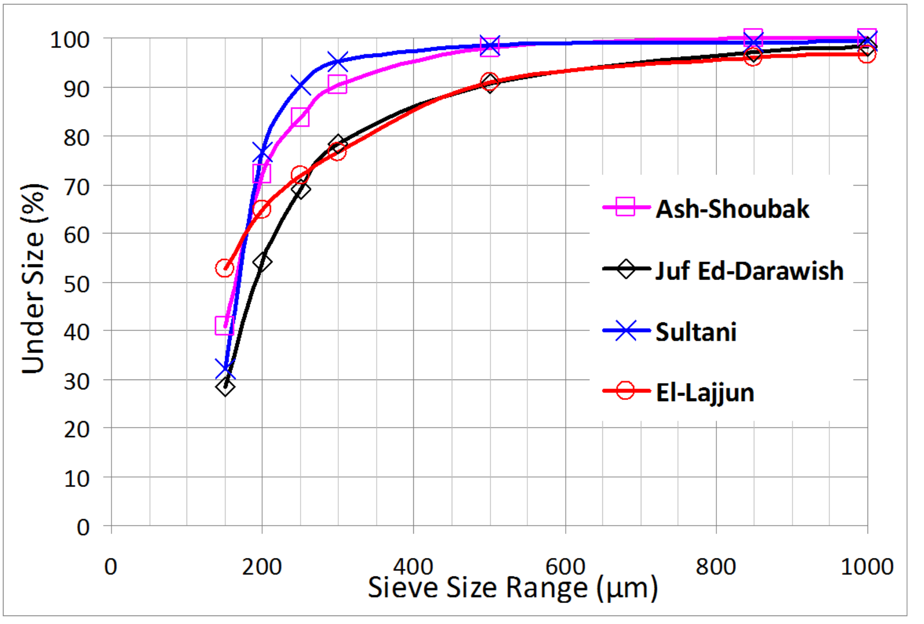

Figure 2. Grain size distribution curve for Jordanian oil shales from four different localities.

mineralogy and internal texture are quite similar. Slight differences are present from one location to another. Their oil yielding capacities are quite different.

Grain size distribution of OS samples from four OS deposits is shown in **Figure 2**. Results show that 80% of all studied samples sizes are less than 350 µm. All deposits reveal quite similar trend but different size distributions. This is normal due to their chemical and physical variability.

3.2. Elemental Composition

The average elemental composition % of the total solid samples calculated from duplicate analyses results is presented in **Figure 3**. All OS deposits show quite similar distribution for the determined four elements. Highest percentage is obtained from El-Lajjun deposit, whereas the lowest is for Juf Ed-Darawish OS deposit. The elemental composition values are higher than that reported for Egyptian OS by Al-Alla and Nassef [24] from Al-Quseir area. Quite high sulfur content in El-Lajjun OS may limit its future exploitation.

3.3. Solvent Type Effect

The effect of solvent type on the shale oil extractability is shown in **Figure 4** and **Figure 5**, respectively. The OM yields obtained from different solvents used are clearly unequal for the studied oil shales. The most effective extraction solvent is THF. Highest yield is obtained from polar solvents. This is consistent with the results reported by Shawaqfeh and Al-Harahsheh [14]. Solvation yield can be enhanced using solvent mixtures rather than using pure solvents [18]. The type of solvent used is reported to play a significant effect on the yield and the composition of the obtained oil [25]. The quantity of solvent used in the extraction is also very important factor [24]. A study by Tamimi and Uysal

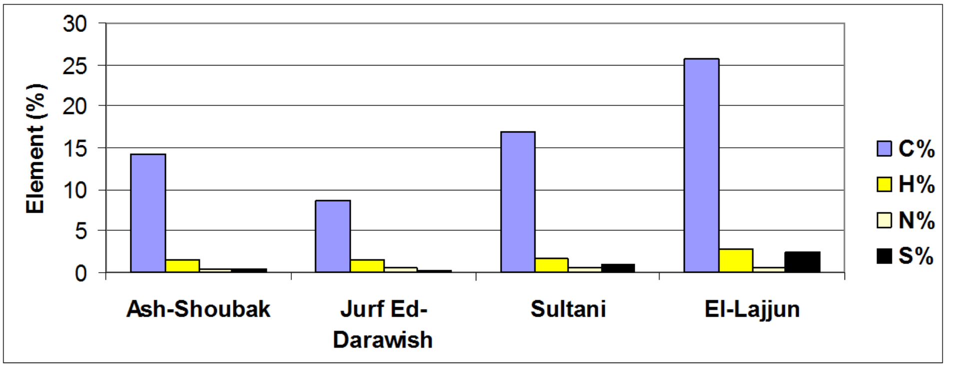

Figure 3. Average elemental composition % of the total solid samples.

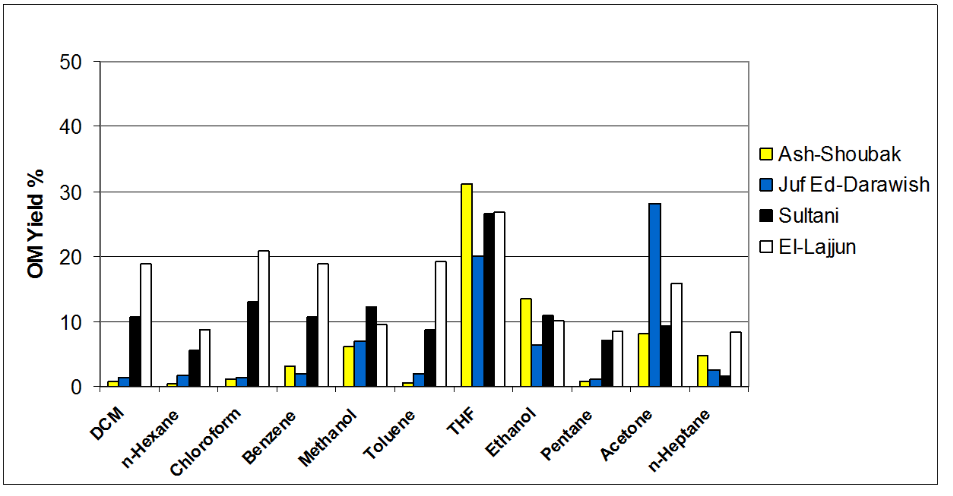

Figure 4. Organic matter (OM) yield % of different solvent types via Soxhlet extraction for 24 hrs; grain size < 150 µm.

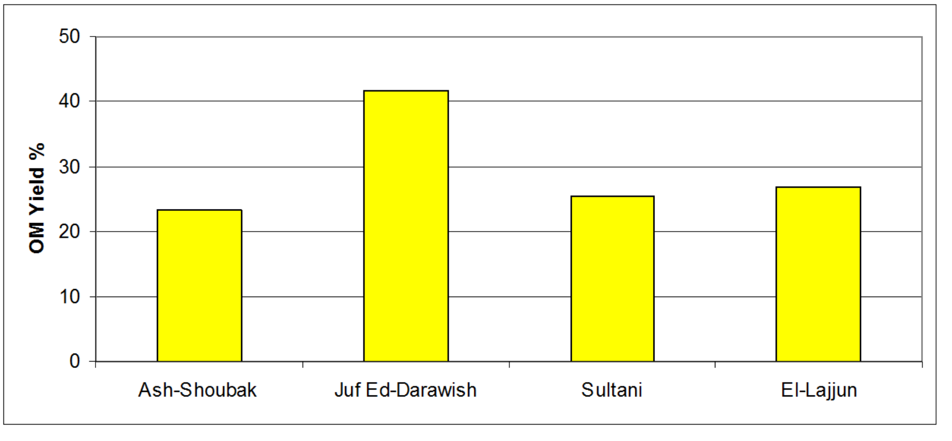

Figure 5. Organic matter (OM) yield % of solvent Mix. 2 (Chloroform (50%); Acetone (30%); Methanol (20%)) via Soxhlet extraction for 24 hrs; grain size < 150 µm.

[9] on Jordanian OS showed that the best extraction is obtained when the ratio of solvent to oil shale is in the order of 1:2. Since four OS deposits are studied, it is important to mention that the type of OS for each deposit as well as its original OM and type has

clear effect on the extraction yield.

3.4. Grain Size Effect

The effect of grain size on shale oil extractability is shown in Figure 6 and Figure 7, respectively. Results show that grain size has minor effect on OM yield. Results are consistent with that reported by Anabtawi and Uysal [15]. Grain size effect on shale oil extractability is indicated from the OM yield fluctuation on different grain sizes. The OM yield via soxhlet extraction is found to be high when compared with that of mixing and stirring extraction. The suitable size for extraction is reported to be depends on the extraction kinetics, dissolution thermodynamics, and the mode of mass transfer from the particles [9].

3.5. Mixing Time Effect

The effect of stirring time on shale oil extractability is shown in Figure 8. The OM yield

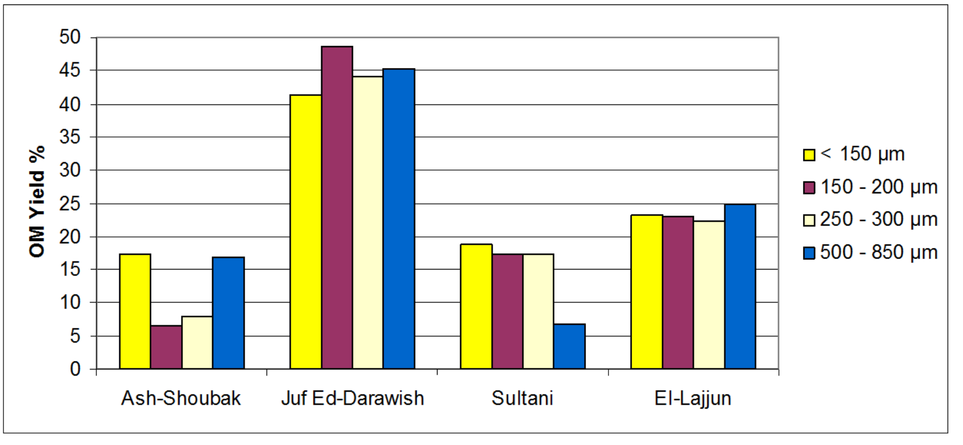

Figure 6. Effect of grain size on OM yield using solvent Mix. 1 via stirring for 10 mins at 50˚C and 1000 rpm.

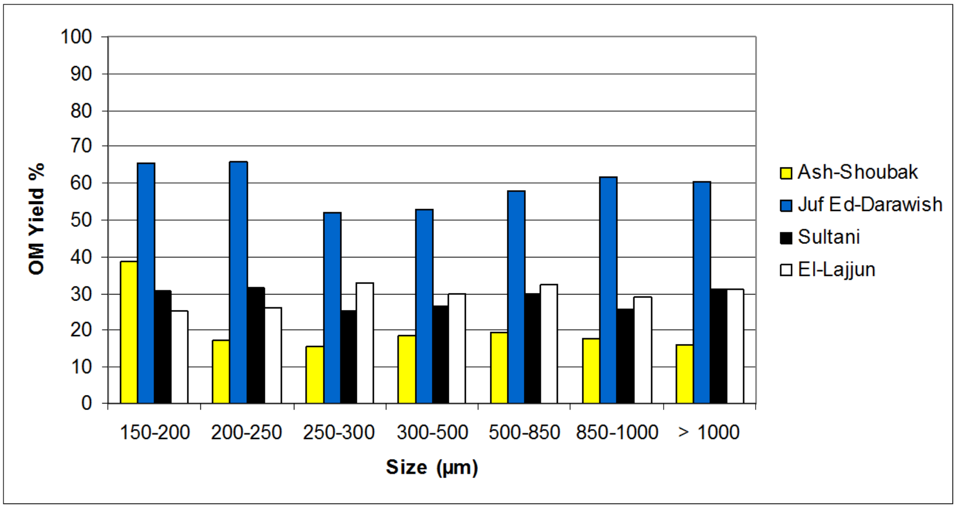

Figure 7. Effect of grain size on OM yield using solvent Mix. 1 via Soxhlet extraction for 24 hrs.

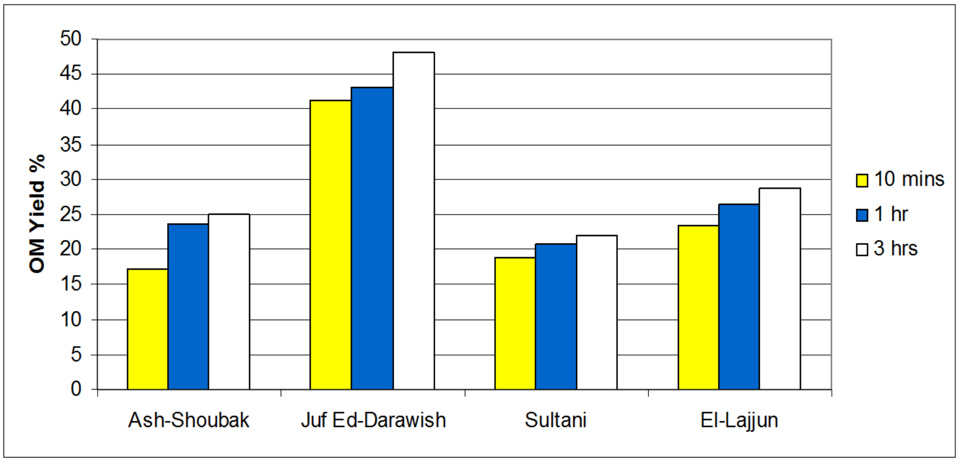

Figure 8. Effect of stirring time on OM yield using solvent Mix. 1 via stirring at 50˚C and 1000 rpm, grain size.

shows slight increase with the increase in mixing time. This is due to the dissolving of shale oil during the early stages of contact between solvent and OS material. After enough extraction time, the extraction completed and the ultimate yield will be achieved. Mixing improves the extraction yield due to increasing agitation and turbulence. The effectiveness of mixing on extraction depends on several factors include the rate of mixing, the design of the mixer, the mode of operation, and the solvent to oil shale ratio [9].

3.6. Heating Temperature Effect

The effect of extraction temperature on shale oil extractability is shown in Figure 9 and Figure 10, respectively. Generally, the OM yield increases with temperature increase. Significant OM yield is obtained using solvent mixtures under super-critical conditions for both El-Lajjun and Sultani OS deposits compared with the OM yield obtained from traditional methods of shale oil extraction (Figure 10). Super-critical conditions are preferred to be used in the field of shale oil extraction [9] [14] [17] [18].

3.7. Shale Oil Composition

Shale oil composition obtained from column chromatography fractionation is shown in Figure 11. Results show that shale oil composition differs from one deposit to another. The aliphatic hydrocarbons are obtained from El-Lajjun and Ash-Shoubak shale oils. With exception of that of Sultani, the aromatic fraction content is generally greater than aliphatic fraction content. All deposits are quite rich in the NSO in their shale oils. High residue fraction is obtained from Juf Ed-Darawish shale oil. The NMR analysis results are presented in Figure 12 and Table 2 respectively. Variability in shale oil composition is clearly indicated. The 1H NMR spectra of the extracted fraction from all OS deposits show saturated aliphatic and aromatic hydrocarbons. Unsaturated hydrocarbons (alkenes and alkynes) are found in shale oil obtained from Ash-Shoubak and Juf Ed-Darawish oil shales.

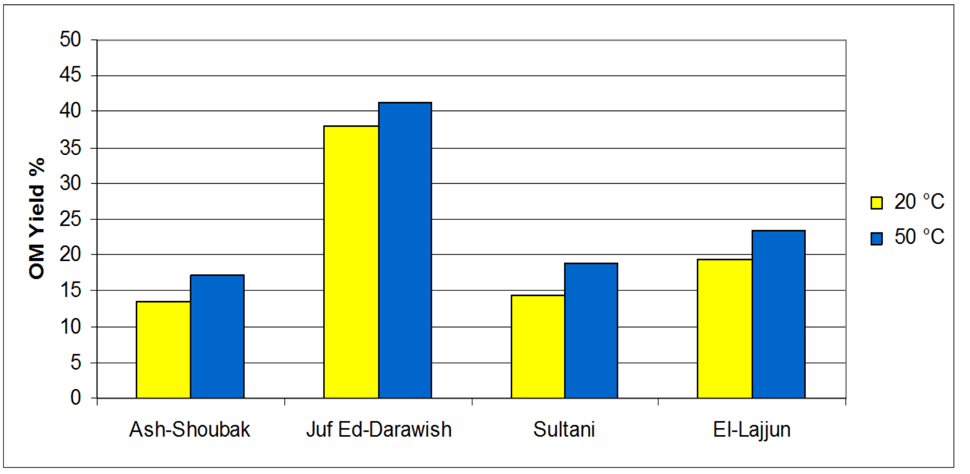

Figure 9. Heating temperature effect on OM yield using solvent Mix. 1 (THF-Acetone mixture 1:1) via stirring at 1000 rpm for 10 mins.

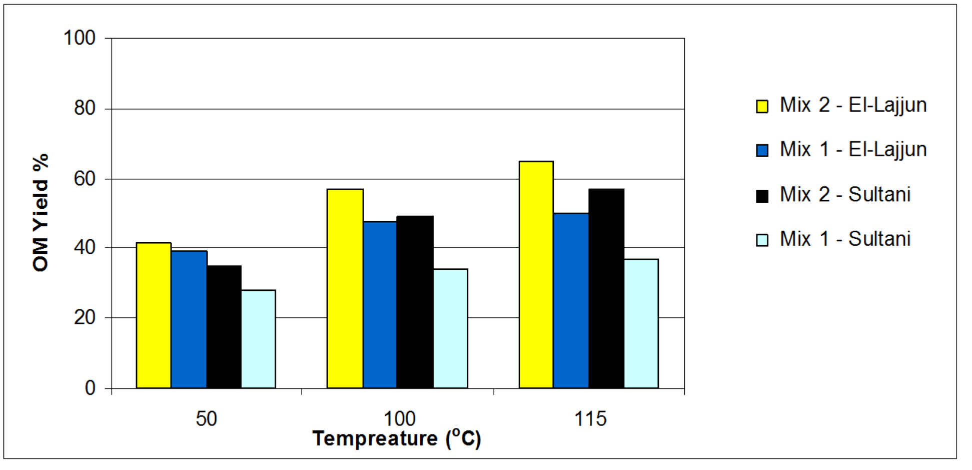

Figure 10. Shale oil yield increase under supercritical conditions via the designed reactor using solvent Mix. 1 and Mix. 2 at elevated temperature and increased mixing rate. Internal reactor pressure is 5 bars. Grain size < 150 μm. Extraction time: 10 mins.

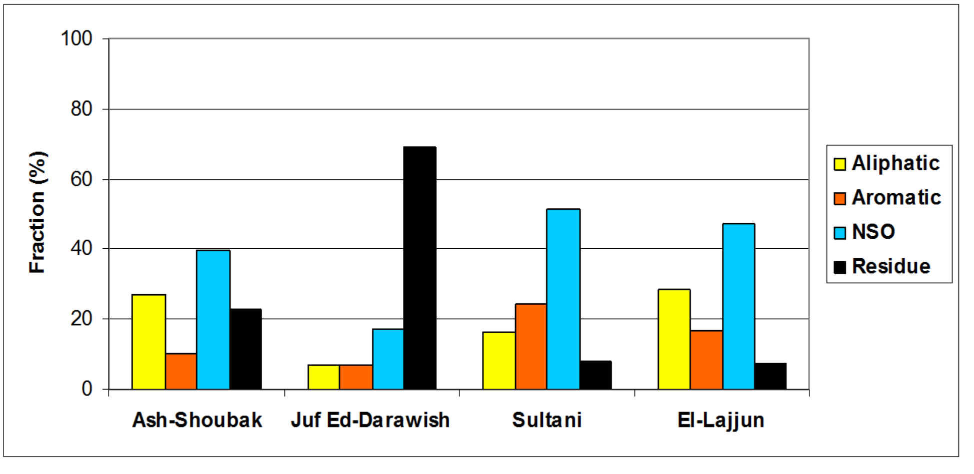

Figure 11. Shale oil content composition (%).

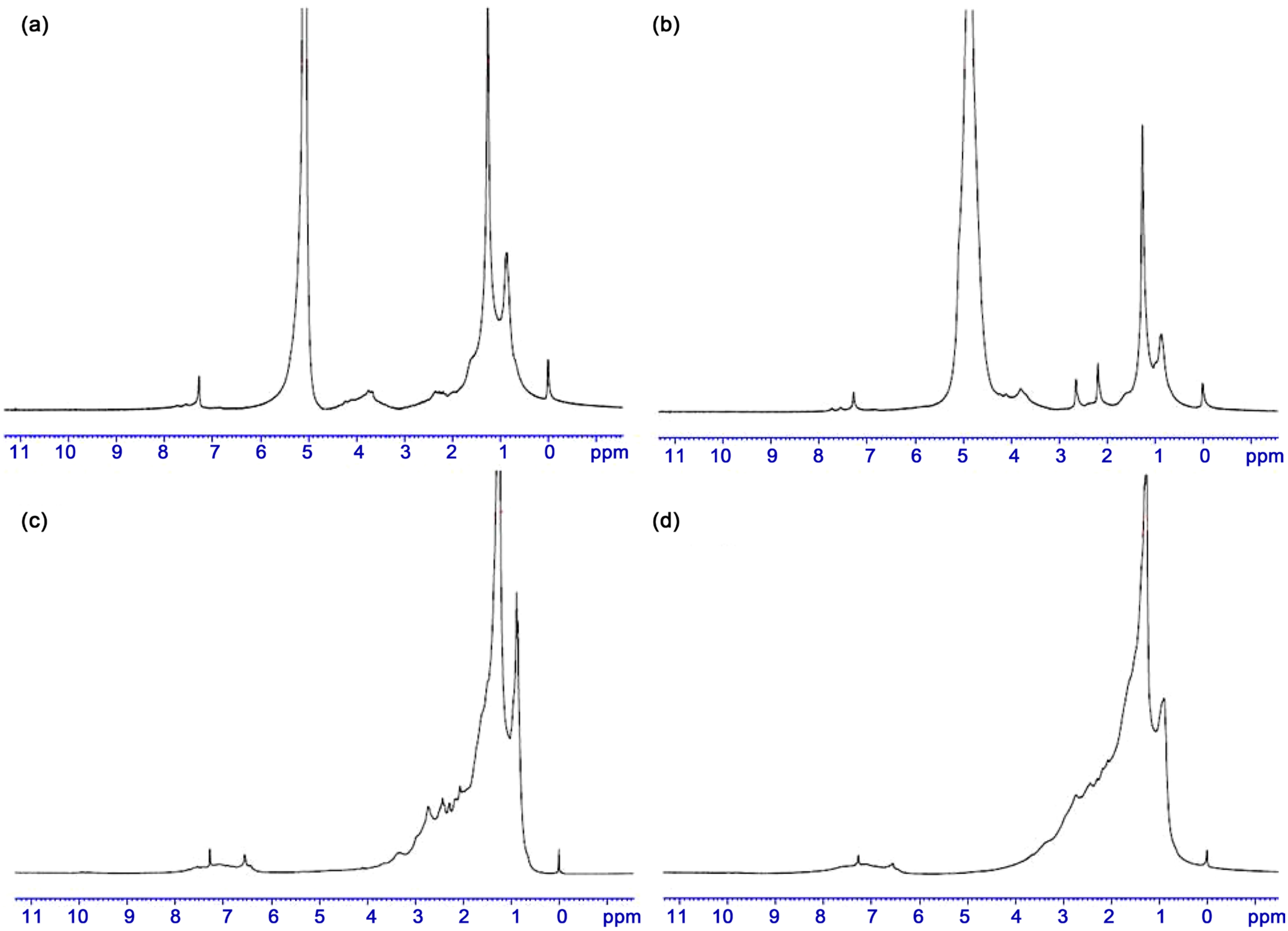

Figure 12. ^{1}H NMR spectra (CDCl3) of extracted shale oil by Soxhlet extraction: (a) Ash-Shoubak. (b) Juf Ed-Darawish. (c) Sultani. (d) El-Lajjun.

Table 2. Summary of the NMR analysis results.

Oil shale	Shale oil composition	Range on ^{1}H NMR spectra
Ash-Shoubak	Saturated (alkanes) and unsaturated hydrocarbons (alkenes and alkynes)—High	0.25 - 2.16 ppm for saturated hydrocarbons and at 4.80 - 5.85 ppm for unsaturated hydrocarbons
	Aromatic compounds—Trace	at 7.0 - 7.8 ppm
Juf Ed-Darawish	Saturated hydrocarbons and unsaturated hydrocarbons—High	At 0.45 - 2.24 ppm for saturated hydrocarbons and at 4.0 - 5.84 ppm for unsaturated hydrocarbons
	Aromatic compounds—Trace	At 7.0 - 7.5 ppm
Sultani	Saturated compounds (alkanes)	At 0.020 - 3.20 ppm
	Aromatic compounds—Trace	At 6.45 - 7.25 ppm
El-Lajjun	Saturated hydrocarbons only	At 0.21 - 3.65 ppm
	Aromatic compounds—Trace	At 6.57 - 7.50 ppm

Shale oil compositional variability results obtained from this study supported by the physical and chemical OS variability reported in literature, e.g. Alnawafleh *et al.* [4], indicate that different extraction techniques suit different OS deposits, and such variability should be considered in any future utilization of OS resources in Jordan. The extracted shale oil refinery, therefore, will require special facilities. Accordingly, the economic and environmental aspects of shale oil extraction in Jordan should be highly considered.

4. Conclusion

In this paper, a study of the fractional yield, shale oil composition and solvation variability from four OS deposits in Jordan is presented. Results show that the oil shales of Ash-Shoubak, Juf Ed-Darawish, Sultani, El-Lajjun from Jordan reveal quite similar trend in their size distributions and their elemental composition. These OS deposits have different solvation properties. Their solvation behavior is controlled by many factors such as OS type and OM content, extraction method and design, solvent type and quantity, heating temperature, and mixing rate and time. Particle size has minor role. They also show variation in their fractional yield and their shale oil composition. The extraction of Jordanian OS via solvation processes is promising under certain extraction conditions. Potential use of such methods is under super-critical conditions. High OS sulfur content, and the solvation variability should be considered in any future extraction techniques. The economic and environmental aspects of shale oil extraction in Jordan should be highly considered.

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