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Solvent Extraction of Bitumen from Jordan Oil Shale Assisted by Low Frequency Ultrasound

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In this work, the efficiency of 20 kHz frequency ultrasounds *versus* the classical stirring procedure was investigated on the solvent extraction of Jordanian El-Lajjun oil shale by employing a horn type sonicator. The influence of sonication parameters (sonication time and ultrasonic power) and extraction parameters (extraction solvent and oil shale particle size) on the solubilization of organic matter (bitumen) from oil shale are reported here. The influence of seven individual solvents, namely: tetrahydrofuran, benzene, carbon tetrachloride, chloroform, kerosene, toluene, acetone and a mixture of methanol–acetone–chloroform on the fraction extracted was investigated and it was found that the fraction extracted was 90% after only ten minutes of sonication at 33 W when tetrahydrofuran was used as extraction solvent. It was found that the fraction extracted percentage is strongly influenced by the solvent extraction, ultrasonic power and exposure time and less influenced by the particle size. Under the current experimental conditions and using the tetrahydrofuran as extraction solvent, the extraction time was decreased by four folds while the fraction extracted percentage ($E\%$) was increased by three times.

Keywords

Jordanian oil shale, Low frequency ultrasound, Solvent extraction, Ultrasonically assisted extraction, Bitumen

1. Introduction

Jordan which owns over 50 billion tons oil shale is ranked as the 8th country among 37 countries in the world that possess this natural reserve. Oil shale is the major indigenous fossil-fuel in Jordan. The Jordanian oil shale is kerogen-rich, bituminous, argillaceous limestone that was deposited in shallow marine during the Maestrichtian–Danian periods. There are 24 known surface, near surface and deep deposits of oil shale distributed in many parts of the country but the major deposit, known as El-Lajjun is located south of Amman in central Jordan and is easily accessible from the desert highway¹⁾. The El-Lajjun oil shale are naturally bituminous marls and are varying shade of brown, grey or black with typical bluish light-grey color when weathered. Kerogen, the insoluble part of the organic matter, makes more than 80% of the total organic matter. Bitumen content, or the extractable organic matter, varies from few percent up to 20%²⁾. Several techniques that attempted to remove a different fraction of oil from shale have been employed, as reviewed by Robinson³⁾. The bitumens can be extracted from oil

shale by using organic solvents but the kerogens are completely insoluble. A mixture of two solvents, one polar and one nonpolar, is usually necessary for a complete extraction of bitumens by Soxhlet technique and it is important that the oil shale to be in the form of fine particle such as to ensure sufficient solid-solvent contact area⁴⁾. Many studies on solvent extraction have been reported, but they have been mostly by Soxhlet extraction^{5),6)} carried out using conventional solvents at temperatures near the boiling point of the solvent. Since the Soxhlet method have some drawbacks, namely: long extraction time, a minimal quantity of sample required for a complete run and the solvent boiling point, other extraction procedures have been reported, such as: supercritical fluids extraction⁷⁾, flash thermal desorption^{8)~10)}, and flow-bending¹¹⁾. Matouq and Alayed¹²⁾, reported a unique technique for oil shale extraction in the presence of a solvent and gamma ray radiations. They obtained good recovery yields (13–67%) for mixtures of: acetone–water, benzene–acetone, benzene–kerosene as well as for benzene, kerosene or water used separately. Various works on the oil shale ultrasonic assisted extraction alone or in combination with other techniques have been reported, also¹³⁾. Korth *et al.*¹⁴⁾, find that the solvent extracts of the shale oil from Duinga, Australia

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obtained after sonication were qualitatively identical with those from the traditional Soxhlet extraction but the extraction time was significantly decrease from several hours to only 1 h. Blanco *et al.*¹⁵, 1992, testing the efficiency of Soxhlet *versus* ultrasonic extraction on the immature Puertollano oil shale, reported that the ultrasonic extraction method is an excellent alternative to Soxhlet extraction in bitumen studies due to the short experimental time, low temperature and lack of transformation of the organic matter in the rock. However, the chromatograms of the whole extracts are similar, regardless of the solvent used for their extraction. They show that carbon disulfide and chloroform have similar yields in both extraction methods and also the standard deviation is lower and concluded that these two solvents are, with their low boiling point, the best for oil shale extraction. The extraction enhancement by ultrasonic waves is a consequence of cavitation phenomenon. Ultrasounds cause oscillation of the hydrostatic pressure when applied to a liquid medium and gas bubbles filled with vapor of the surrounding liquid are formed. The collapse of the transient cavitations during the compression phase of the ultrasonic wave causes very high instantaneous temperatures and pressures and generates physical effects such as the shock wave, microstreaming and chemical effects due to the OH· radicals formation by water sonolysis. This implosion of cavitation bubbles does the rough work of loosening the bitumens stuck on the oil shale and enhancing the solid-liquid mass transfer. Extraction by using ultrasonic cleaning bath is often reported in the oil shale extraction literature but nowadays the experimental work span a wide variety of ultrasonic devices. The intensity of the cavitation phenomenon is higher when sonication is performed at low frequency and the higher the ultrasonic intensity, the more pronounced are the cavitation effects. Therefore, an increasing in the intensity is more effective than an increase in the duration of exposure.

In this paper, the extraction of organic matter from Jordanian oil shale by low frequencies ultrasound *versus* classical stirring method with different solvents is reported. It is well known that the efficiency of any ultrasonic procedure it is influenced by the sonication parameters such as the exposure time, temperature, solid/liquid ration, and the ultrasonic frequency and intensity. Hereby, it is very important to identify the optimal values of the sonication parameters according to the targeted process. Thus, the influence of solvent extraction, exposure time, ultrasonic power and particle size of oil shale on the extraction process was investigated for the selected solvents.

2. Materials and Methods

Jordan oil shale obtained from Natural Resources

Table 1 Chemical and Physical Properties of El-Lajjun Oil Shale

Average oil content	[wt%]	10.5
Total organic matter	[wt%]	22.1
Calorific value	[kcal/kg]	1590
CaCO ₃	[wt%]	54.3
Sulfur	[wt%]	3.1
Density	[g·cm ⁻³]	1.81
Moisture	[wt%]	2.43

Source: Hamarneh *et al.*, 2006¹⁾.

Authority (NRA), mainly from El-Lajjun deposit was used in this experimental study. The oil content for all samples were measured and analyzed by NRA. The physical and chemical properties of the studied sample are given in **Table 1**. Prior to extraction experiments, the oil shale as received was crushed to particles of 1 mm and ground to particles ranging in size from 0.45 to 0.60 mm. Excepting the kerosene purchased from a local gasoline stand, all the solvents used were commercial pure chemical reagents (purity higher than 99.5%) and used without further purification as received: benzene, carbon tetrachloride and tetrahydrofuran from Wako Pure Chemical Industries, Ltd.; chloroform and methanol from Chameleon Reagent; toluene and acetone from Nacalai Tesque.

2.1. Classical Extraction Procedure

Mechanical stirring was employed as classical technique for comparing the results obtained by ultrasonically assisted extraction. A powerful magnetic mixer (Yamato, Mag-Mixer MD 800) was used for stirring experiments. The samples were stirred at approximately 700 rpm agitation speed for 10 min and the extraction period was the same as for ultrasonically assisted extraction. All experimental works were conducted at room temperature.

2.2. Sonication Procedure

In this work, sonication was carried out with a Branson Sonifier W-450 sonicator having a step horn with 1/2 inches (13 mm) in tip diameter operating at 20 kHz ultrasonic frequency. For each run, 20 g sample was placed in a 120 ml glass cell together with 100 ml of solvent. The ultrasonic power dissipated into the extraction medium was 33 W, excepting the experiments concerning the influence of ultrasonic power on the extraction were the ultrasonic power was 10, 23 and 33 W and the investigation regarding the influence of exposure time and particle size that were carried out at an ultrasonic power of 23 W. No any additional source of mixing and cooling was used during the sonication. The ultrasonic exposure time was 10 min, excepting the experiments regarding the influence of sonication time on the extraction efficiency when exposure times were 5, 10 and 20 min. The size of oil shale particle was approximately 1 mm but for experiments concerning the influence of particle size on the extraction process, particle smaller in size (ranging from 0.45

to 0.6 mm) were used as well. All experimental works here were conducted at room temperature.

2.3. Extract Quantification

After the extraction steps were completed, the extraction medium was transferred from the sonication glass into a Buckner funnel and filtered under vacuum through filter paper type Advantec nr. 5A (about 7 μm pore size). The solid remaining on the filter paper was exhaustively washed with a clean portion of extraction solvent. The extract collected in the Buckner flask was then concentrated in a rotary evaporator apparatus at normal pressure until a complete evaporation of the solvent was noticed. Moreover, in order to avoid the loss of volatile components, extracts were not dried to constant weights (a common step in the calculation of extraction yields). The fraction extracted percentage, $E\%$ was determined from the weight of the residue as shown in Eq. (1).

$$E\% = (\text{wt of dry extract/wt of extractible in original sample}) \times 100 \quad (1)$$

where weight of oil in the original sample was obtained and analyzed by NRA, using Fischer Assay Analysis, in which the oil shale was pyrolysed up to 520°C and the amounts of oil, water, gas and the residue (spent shale) were recorded.

3. Results and Discussion

This study focuses on the oil shale extractability in tetrahydrofuran (THF), carbon tetrachloride (CCL4), benzene (BEZ), chloroform (CHL), toluene (TOL), acetone (ACT), kerosene (KER), and a methanol-acetone-chloroform (MAC) mixed solvent (mixing ratio 1 : 1 : 1 by volume) under low frequency ultrasonic irradiation and the influence of ultrasonic exposure time, ultrasonic power and particle size.

3.1. The Effect of Solvent on the Ultrasonically Assisted Extraction

Figure 1 shows a comparison of $E\%$ for the selected solvents. Experimental results clearly indicate that under the described experimental conditions, THF is the most suitable solvent for achieving a high rate (90%) of extraction from oil shale while ACT is a weak solvent for the targeted material. The ultrasonic method produced significant differences in the $E\%$ for all selected solvents excepting ACT. This result is in contradiction with those concluded by Blanco *et al.*, 1992. The efficiency of the ultrasonic method is considerable in the case of CCL4 and MAC when the $E\%$ was increased 20 times by comparing with classical extraction. The fractional extracted percentage doubled in the case of BEZ and increased four times for TOL by comparing with classical method. KER and CHL have almost similar $E\%$ after ultrasonic treatment and only traces was noticed when classical extraction was employed.

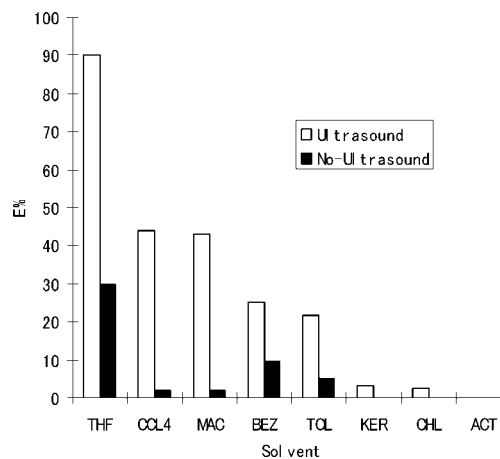


Fig. 1 Comparison of the Fraction Extracted Percentage ($E\%$) for Different Solvents, with and without Ultrasounds

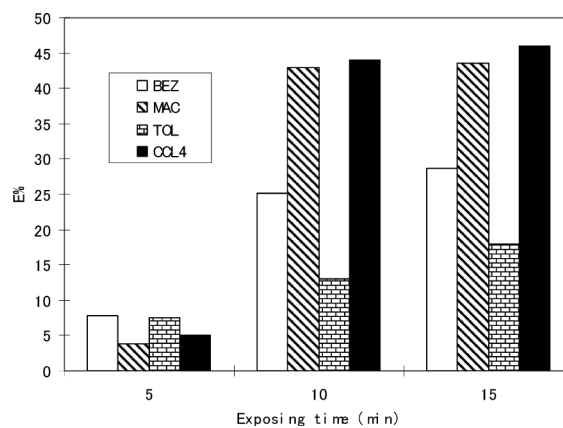


Fig. 2 The Effect of Ultrasonic Exposure Time on the Fraction Extracted Percentage ($E\%$) of Jordanian Oil Shale

Oil shale is often considered to be made by two parts: a solvent-insoluble fraction, consisting of a covalently cross-linked network, and solvent-soluble, low molecular weight substances trapped in this network. The nonpolar aliphatic and aromatic fractions are trapped or “protected” in this network. A high covalent bond density together with abundant relatively strong secondary interactions will result in low extractability. Our results suggest that THF, CCL4 and the mixed solvents MAC have stronger ability to disrupt these covalent bond interactions and give higher $E\%$.

3.2. The Effect of Exposure Time on the Ultrasonically Assisted Extraction

For any ultrasonically assisted process the sonication time is an important parameter that affects significantly the overall extraction cost as the sonicator is a highly energy consuming tool¹⁶. To investigate the influence of the ultrasonic exposure time on extraction efficiency, the extraction mixture was sonicated for 3 different periods of time: 5 min, 10 min and 15 min. As shown in Fig. 2, the fraction extraction percentage of bitumen

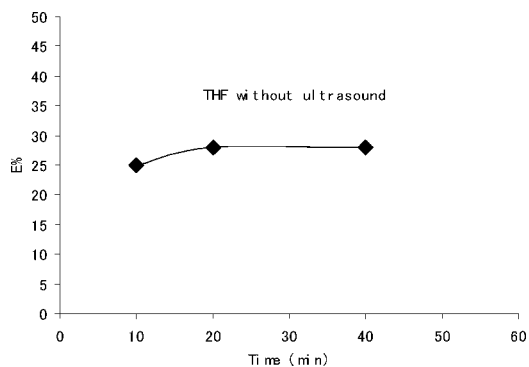


Fig. 3 The Effect of Extraction Time on the Fraction of Extracted Percentage ($E\%$) for THF in Silent Mode

from oil shale increased dramatically as the extraction time increased from 5 to 10 min for all of the following solvents selected for this experiment: CCL₄, BEZ, CHL, TOL and MAC, respectively. It was found that extending the sonication time to 15 min did not induce any significant enhancement in the extraction yield. Thus, in the first 5 min there is a slow extraction phase characterized by the penetration of the solvent into the oil shale as forced by the cavitation collapse in the vicinity of the extraction material. In the following 5 min that bring a dramatically increase in the extraction yield the second extraction stage take place as the cavitation induced phenomena such as material fragmentation and mass transfer progresses.

It is worth mentioning here that the oil shale is a weak material and an ultrasonically induced fine grinding process that takes place during sonication gradually enhance the viscosity of extraction medium. Any increase in the viscosity of the sonicated medium leads to ultrasonic wave attenuation. These data clearly indicate that the optimum extraction time is 10 min and any extension period is not in the benefit of extraction yield due to the ultrasonic wave attenuation and solvent saturation.

The ultrasonically assisted extractions are well known as being time saving methods. Thus, further experimental work was conducted in order to assess this issue for the material investigated here. **Figure 3** shows the extractability of oil shale in silent mode (agitation only) with THF as extraction solvent. By comparing these results with those shown in **Fig 2**, it is obvious that the extraction time was reduced four times and the yield was increased three times in the case of ultrasonically assisted extraction.

3.3. The Effect of Dissipated Ultrasonic Power on the Ultrasonically Assisted Extraction

The ultrasonic power dissipated into the sonication medium is of great importance when reporting the results in sonochemistry and associated fields such as ultrasonically assisted processing since the relationship between the electric power input to the transducer and

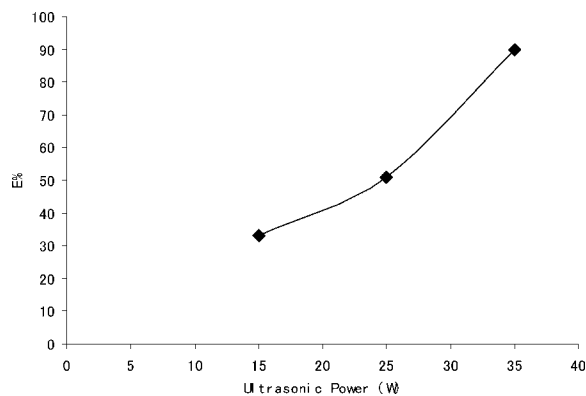


Fig. 4 The Effect of Ultrasonic Power on the Fraction Extracted Percentage ($E\%$) of Jordanian Oil Shale

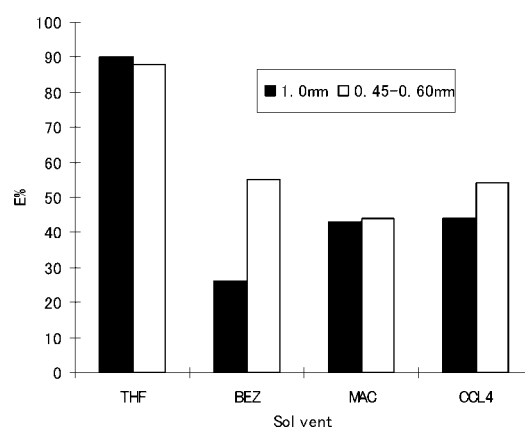


Fig. 5 The Influence of Particle Size on the Fraction Extracted Percentage ($E\%$)

the dissipated ultrasonic power shows a considerable dependence with the ultrasonic device employed¹⁷. Therefore, the influence of ultrasonic power on the extraction was examined for three power levels: 10, 23 and 33 W, using THF as extraction solvent and the experimental results are shown in **Fig. 4**. As it was expected, the extraction efficiency is increasing with increasing the ultrasonic power delivered to the extraction medium. The $E\%$ achieved at the highest intensity power was 90%, more than three times bigger as compared with the maximum value obtained in silent mode.

3.4. The Effect of Particle Size on the Ultrasonically Assisted Extraction

The experiment carried out to further evaluate the effects of particle size on the extraction shown that the extraction was most efficient for the particle size ranging from 0.45 to 0.60 mm, as compared with the 1 mm particle (**Fig. 5**). The present findings correspond to those reported by Haddadin¹⁸. It was noted that in the case of CHL the extraction yield almost doubled whereas THF and MAC extraction seemed to be less influenced by this parameter. This is a possible effect of the fact that, oil shale particle undergoes a significant crushing

process during ultrasonic exposure.

4. Conclusions

The efficiency of 20 kHz frequency ultrasounds on the solvent extraction of the oil shale have been investigated. It was found that the fraction extracted percentage is strongly influenced by the solvent extraction, ultrasonic power and exposure time and less influenced by the particle size. Among the solvents selected for this study, carbon tetrachloride, benzene, chloroform, toluene and MAC show good extraction yield whereas in the case of tetrahydrofuran the fraction extracted is 90%. The optimum ultrasonic power was found to be 33 W. Under the experimental conditions described here and using the tetrahydrofuran as extraction solvent, the extraction time was decreased by four folds while the $E\%$ was increased by three times. The ultrasonically assisted extraction of bitumen from oil shale is a time saving and yield enhancing technique that can be in the benefit of geological studies as well as of industrial processing. This study can help in the design of a large scale extraction technique with improved extraction yield of bitumen and kerogen and thus, promote a better utilization of oil shale.

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要 旨

ヨルダンオイルシェールからのピチューメン溶剤抽出に対する低周波超音波の照射効果

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ヨルダンの El-Lajjun オイルシェールを溶剤抽出することを目的とし、20 kHz ホーン型超音波発生装置を使用した場合と従来からの攪拌法の場合について、抽出効率を比較した。超音波の照射パラメーター（超音波の照射時間と出力）と、抽出操作のパラメーター（溶剤の種類とオイルシェールの粒径）が、オイルシェールから有機物（ピチューメン）を抽出する際に及ぼす影響について、それぞれ調べた。溶剤は7種類（テトラヒドロフラン、ベンゼン、四塩化炭素、クロロホルム、灯油、ト

ルエン、アセトン、メタノール/アセトン/クロロホルム混合物）を使用した。溶剤としてテトラヒドロフランを用い、出力 33 W の超音波を 10 分間照射すると、90% のピチューメンを抽出することができた。抽出効率に大きな影響を与える要素は、溶剤の種類、超音波出力、超音波照射時間の3項目であり、粒子サイズの影響は小さい。テトラヒドロフランを用いた現在の実験条件下では、マグネチックスターラーを用いた従来の抽出方法と比べ、抽出時間は1/4に、抽出物回収率は3倍になった。