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COMPARISON STUDY FOR EXTRACTION OF OIL FROM OIL SHALE

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ABSTRACT

Oil shales are an important source of energy as the world's energy demand is increasing exponentially. In this study, use of mechanical agitation and ultra-sonication was investigated for the extraction of Quseir's oil shales by using different solvents such as tetrahydrofuran (THF), toluene, methylene dichloride, methanol and hexane and their yields were determined. Quseir's oil shales were characterized by elemental analysis, infrared spectroscopy, gas chromatography (GC), thermogravimetric analysis (TGA) and surface imaging techniques such as scanning electron microscope. GC and TGA analyses showed that the oil recovered from oil shale had higher percentages of hydrocarbons in comparison with other oil shale resources. THF, toluene and mixture of methylene dichloride with hexane resulted in better oil yields in comparison with hexane and methanol. In addition, 4 h of agitation time, 0.8 mm particle size of oil shale and 2:1 ratio of oil at refluxing conditions to solvent resulted in better yields in the mechanical agitation method. On the other hand, ultra-sonication yields results were superior up to 73% using THF in 15 min at ambient temperature. This showed that low frequency ultra-sonication is superior to the traditional mechanical stirring methods.

KEYWORDS: Shale oil, Oil shale, Solvents, Ultra-sonication, Mechanical agitation.

1. INTRODUCTION

Energy is paramount to all countries for their economic growth. World's energy demand in the last few decades is increasing exponentially, and the trend is expected to increase further. Main sources of energy are fossil fuels (coal, petroleum, and natural

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gas), nuclear and renewable energies (solar, hydro, and wind) contributing to 80%, 5% and 5% respectively of the world demand.

Oil shale is an alternative fuel source for petroleum. It is a rock containing significant amount of kerogen, which upon heating or ultra-sonication produces crude oil, which consists mainly of hydrocarbons [1]. Recently, oil shales, as an alternative source of energy, have become very attractive due to their wide availability Worldwide in addition to their booming processing technology development in the United States [2, 3]. Egypt has significant resources of oil shale [2, 3]. Extraction of oil from oil shale is challenging in contrast with shale oil or conventional petroleum crude. Traditional extraction of oil from oil shale is conducted via mechanical stirring using soxlet extraction with different organic solvents such as hexane, toluene, methylene dichloride, THF and methanol at elevated temperatures nearer to their boiling points [4, 5].

In this study, extraction of oil from Egyptian oil shales using traditional mechanical agitation as well as low frequency ultra-sonication will be investigated and compared with respect to their effectiveness in extraction using different types of non-polar solvents such as hexane and polar solvents such as methanol. Extraction parameters such as solvent quantity, extraction time and particulate oil shale size will be investigated. Oil shales will be characterized by elemental analysis, infrared spectroscopy (IR), scanning electron microscopy (SEM), and Thermogravimetric Analysis (TGA).

2. MATERIALS AND METHODS

The methodology of studying the different variables is conducted as one factor at a time (OFAT).

2.1 Materials

The solvents used for extraction of shale oil are tetrahydrofuran (THF), toluene (C_7H_8), methylene dichloride (CH_2Cl_2), chloroform ($CHCl_3$), n-hexane (C_6H_{14}). All solvents were purchased from El Gomhorya Company of Chemicals. The oil shale used in this research was obtained from Al-Quseir zone. The oil shales were powdered and sieved to the size distribution of 0.8-1 mm as shown in Fig. 1.

Fig. 1. Pulverized Oil Shale.

2.2 Method of Calculating the Percentage Yield of Extracted Oil

The yield was calculated according to the following equation:

*% yield =weight of oil produced (gm)/ weight of original shale sample (gm) (*100)* (1)

2.3 Methods of Extraction

2.3.1 Mechanical agitation method

In this method, a set up of three neck flasks provided with a heater, mechanical stirrer and a condenser was used for the extraction of oil from oil shale as shown in Fig. 2a.

2.3.2 Ultra-sonication method

Ultra-sonication of oil shale was conducted in a Branson Sonifier W-450 sonicator. The ultra-sonicator had a step horn of 13 mm in tip diameter and operates at 20 kHz ultrasonic frequency with a power of 200 W and is shown in Fig. 2b.

Fig. 2. (a) Experimental set-up for solvent extraction by mechanical agitation, (b) Ultrasonic apparatus

2.4 Experimental Procedures

2.4.1 Mechanical agitation method

In a three neck round bottom flask, 50 g of finely ground oil shale sample (0.8-1 mm) was placed with 100 g of the desired solvent (liquid-solid mass ratio of 2:1). The mixture was heated to the boiling point of corresponding solvent and stirred for 4 h. The slurry was then filtered under vacuum in a Buchner funnel fitted with a filter paper. The solvent was recovered using a rotary evaporator and the concentrate was analyzed by GC to determine its components as shown in Fig. 2a.

2.4.2 Ultra-sonication method

10 gm of finely ground oil shale sample (0.8-1 mm) was placed with 20 g of the desired solvent (liquid-solid mass ratio of 2:1) in a conical flask (120 ml) and sonicated

for 20 minutes. The slurry was then filtered under vacuum in a Buchner funnel fitted with filter paper. The solvent was recovered by using a rotary evaporator to the filtrate then the concentrate was analyzed by GC to determine its components as shown in Fig. 2b.

3. RESULTS AND DISCUSSION

3.1 Infra-Red (IR) Spectra of Oil Shale

The signals observed in IR spectra of oil shale are presented in Table 1. It represents the interpretation of absorption bands corresponding to the prominent functional groups present. The broad signals between 3000-4000 cm^{-1} represents the O-H bonds (3618.6 cm^{-1}) and N-H (stretching) bonds (3427.6 cm^{-1}) respectively. The signals at 2943.5 cm^{-1} and 2324.3 cm^{-1} represent the aliphatic C-H bonds (CH_2 and CH_3) and C≡C bonds respectively. The unique and sharp aromatic C=C-H stretching bonds were represented at 1437.0 cm^{-1} and 1624.1 cm^{-1} signals. The characteristically sharp N-H stretching vibrations were found at 1033.9 cm^{-1}. The wavenumber at 779.3 cm^{-1} represents the characteristics C-H aromatic vibrations (mono, di-substituted) and the wave numbers at 536.2 cm^{-1} represents the C-X bonds which could be chloroalkanes, bromoalkanes or iodoalkanes. The band at 459.1 cm^{-1} was responsible for clay and minerals in oil shale.

Table 1. Interpretation of absorption bands corresponding to the prominent functional groups present in oil shale.

Chemical bonds	O -H	C-H	C≡C	C=C-C	C-X	N-H	Clay and minerals
Wavenumber (cm^{-1})	3618.6	2943.5 (Aliphatic) 779.3 (Aromatic)	2324.3	1437.0 1624.1	536.2	2943.5 1033.9	459.1

3.2 Mechanical Agitation Method

This simple, low-cost method uses agitation or mixing to extract the PAHs from samples in a shake-flask placed onto a rotary shaker, or with a magnetic stirrer submersed into the flask directly. Agitation is an easy handling method with minimal glassware and smaller volumes of extraction solvent. Mechanical agitation extraction methods were carried out at the boiling point of corresponding solvents used.

3.2.1 Solvent selection and yield calculation

Figure 3 represents the a comparison of yields from the different solvents. A wide range of solvents with different polarities as well as a combination of solvents were utilized. THF gave the best yield of 22.8% and significantly higher than the other solvents used. This can be attributed to the coordinating/hydrogen bonding ability of THF with the kerogen structure and converting them into small molecules [6-8]. However, THF is not economically viable due to its high cost [6]. All these experiments were conducted in triplicate and the average values were taken (0.9 mm).

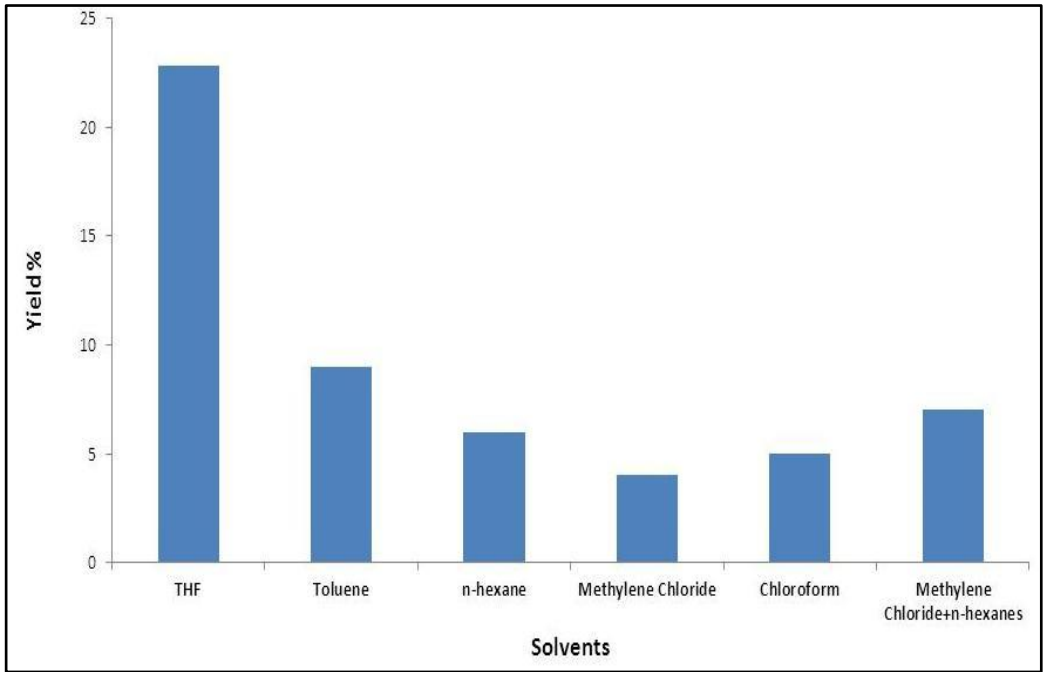

Fig. 3. Comparison of yields from different solvents used in extraction.

3.2.2 Effect of solvent to oil shale ratio

Figure 4 presents the extracted oil yields using different amounts of solvents. Toluene and a mixture of methylene dichloride and n-hexane (1:1 g/g) were taken as model solvents for this analysis. As the solvent ratio to shale oil increased from 1:1 to 2:1, yields of 44% and 42% were obtained for toluene and the mixture of methylene dichloride and n-hexane (1:1 g/g), respectively. However, further increase in the solvent to 1:3 and 1:4 resulted in no significant increase in yield for 0.9 mm particle size and for a duration of 4 hours.

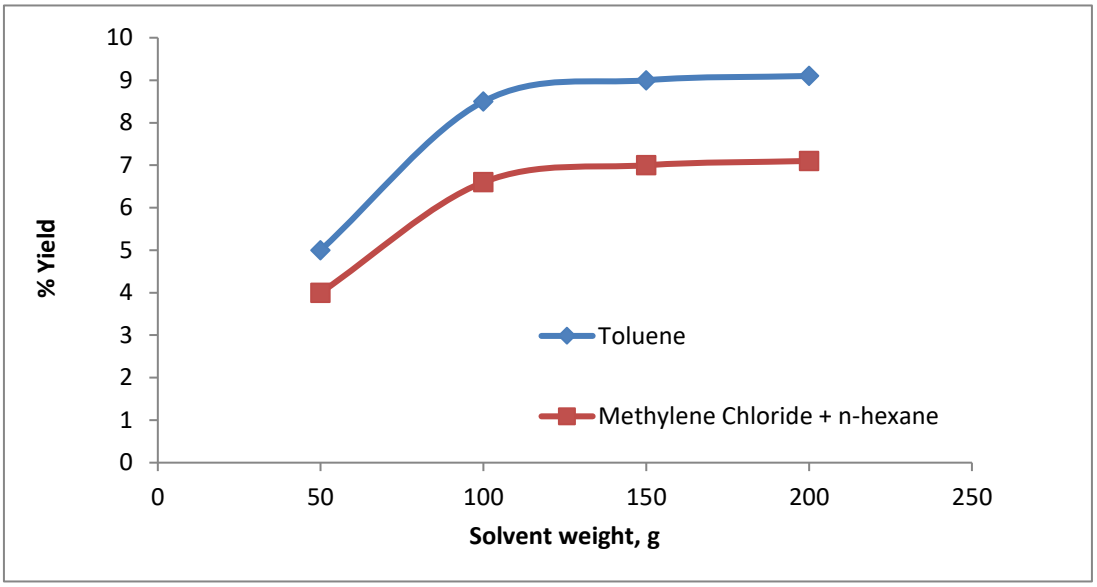

Fig. 4. Effect of solvent to oil shale ratio by weight.

3.2.3 Effect of extraction time on the yields

Figure 5 presents the effect of extraction time on the yields. Toluene was used as a model solvent. Solvent to oil shale ratio was 2:1 (g/g) and extraction was conducted under refluxing conditions. Up to 5 h the yields increased with the increase of extraction time and after 5 h the yields remained constant. These results affirmed that the transformation of shale with 0.8 mm particle size to oil was straight forward with no complex interactions and were consistent with the literature [8, 9].

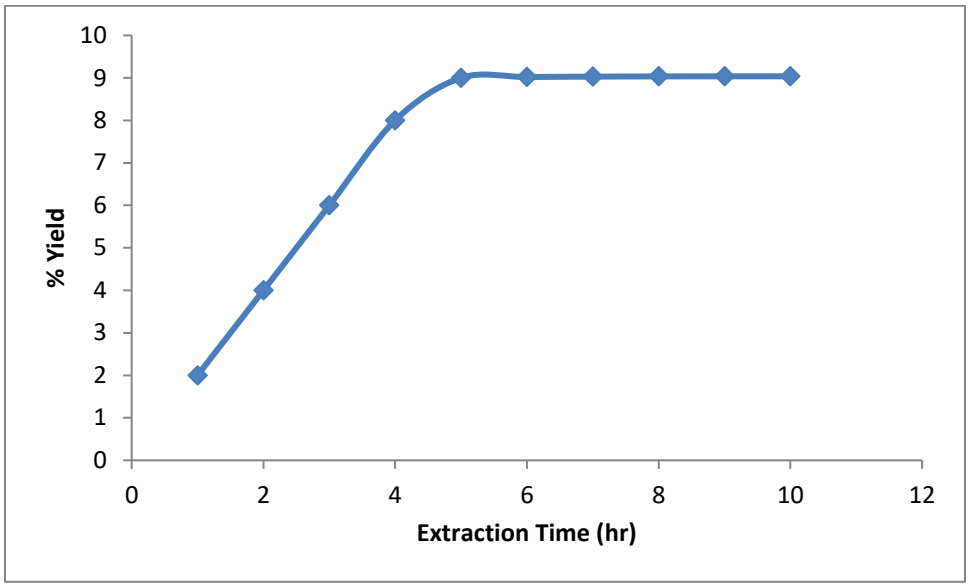

Fig. 5. Effect of extraction time on the yield.

3.2.4 Effect of particle size

Figure 6 presents the plot of particle size variation versus the yields from oil shale. Toluene and a mixture of methylene dichloride and hexane (1:1 g/g) were used a model solvent. Solvent to oil shale ratio was 2:1 (g/g) and extraction was conducted under refluxing conditions. There was a linear increase in the yield with the decrease in particle size from 4 mm to 1 mm with the latter particle size resulting in the best yields of 9% and 7% for toluene and the mixture of methylene dichloride and n-hexane (1:1 g/g) respectively. Smaller particle sizes prevented agglomeration and facilitated better mass transfer from oil shale to solvent during mixing. These results after 4 hours were consistent with the results reported by [9].

3.3 Solvent Extraction Assisted by Low Frequency Ultrasonication

Use of low frequency ultrasound has several advantages such as higher yields, short extraction time, minimal quantity of solvent requirement and ambient temperature operations [10]. However, the characteristics of oil including percentage of components,

boiling points, viscosities obtained after extraction remained the same irrespective of using mechanical agitation or ultra-sonication.

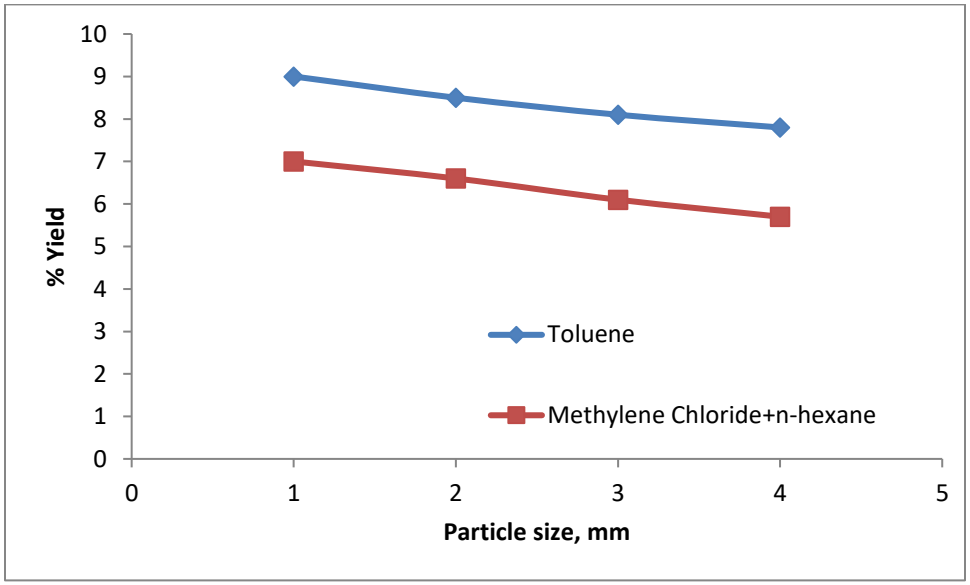

Fig. 6. Plot of yield versus variation in particle size, mm.

Ultra-sonication results in a phenomenon known as cavitation. On using ultra-sonication, sound waves are transmitted into the solvent, creating high-pressure and low-pressure cycles where the number of cycles depends on the frequency of ultra-sonication. Tiny vacuum bubbles are generated in the solvent system during the low-pressure cycle. The size/volume of a bubble increases during the ultra-sonication with the absorption of more energy. At certain volumes, the capability of the bubbles to absorb energy will be beyond its limitation, which leads to the spontaneous breakage. This happens especially in a high-pressure cycle. This cavitation phenomenon had a significant impact on the loosening of the kerogen structure in the oil shale leading to superior extraction of oil when compared with conventional mechanical agitation. The range of frequencies was reported for ultra-sonication of oil shales in the literature. Importantly, low frequency ultra-sonication led to better cavitation and thereby was effective in the oil shale extraction [10-13].

3.3.1 Effect of types of solvent on the ultrasonically assisted extraction

The comparison of oil yields obtained from low frequency ultra-sonication and mechanical agitation using different solvents was carried out. Figure 7 presents the plot of comparison of yields by ultra-sonication in different solvents. The solvent to oil shale ratio was 2:1. In ultra-sonication, THF gave the best yield of 73% and higher than all other solvents used and significantly higher than on using mechanical stirring. Overall in all solvents, ultra-sonication methodology resulted in superior yields when compared with mechanical stirring. The extraction enhancement by ultrasonic waves is a consequence of cavitation phenomenon. Ultrasounds cause oscillation of the hydrostatic pressure when applied to liquid medium and gas bubbles filled with vapor of the surrounding liquid are formed.

The collapse of the transient cavitation 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 radical formation by water sonolysis. This implosion of cavitation bubbles does the rough work of loosening the bitumens stuck on the oil shale and enhances the solid-liquid mass transfer [10-13].

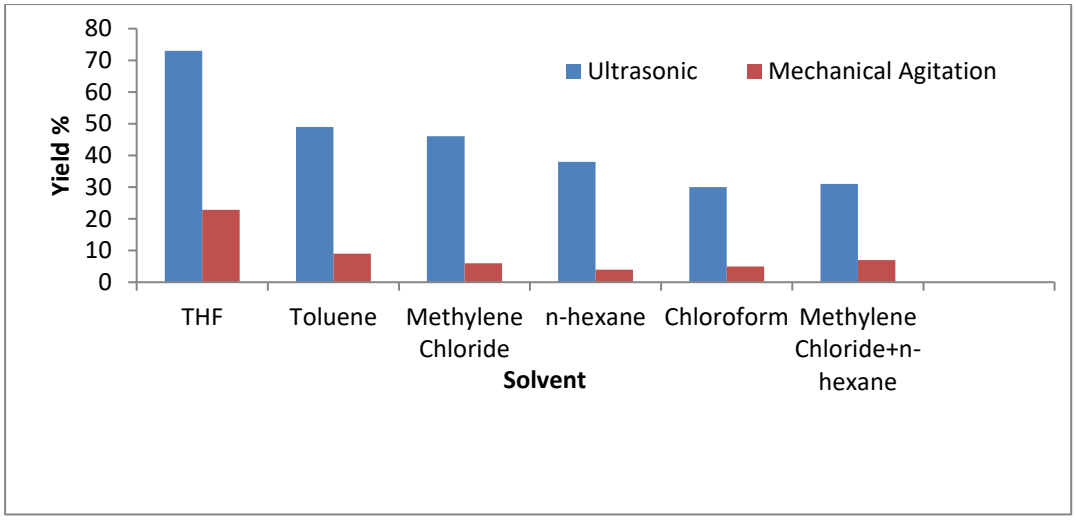

Fig. 7. Comparison of oil yields obtained between low frequency ultrasonication method and the mechanical stirring method from using different solvents.

3.3.2 Effect of extraction time

Figure 8 presents the effect of extraction time on the yields. THF, toluene, methylene dichloride, n-hexane, chloroform and a mixture of methylene chloride and n-hexane were used as solvents for a solvent to oil shale ratio of 2:1. The increase in yields were observed with the increase of extraction time up to 10 min after which the increase in yields were not significant. Low yields in the first 5 min can be attributed to the fact that the initial period of ultra-sonication effected the cavitation collapse near the oil shale particulates resulting in the permeation of the solvent into the oil shale. During the next 5 min, particle fragmentation in tandem with mass transfer took place resulting in higher yields. Particle fragmentation during ultra-sonication gradually increases the viscosity of the extracting mixture, which leads to the attenuation of ultrasonic waves. However, decrease in ultrasonic waves as well as solvent saturation takes place after 10 min and therefore no further significant increase in yields were observed with the increase of ultra-sonication time beyond 10 min.

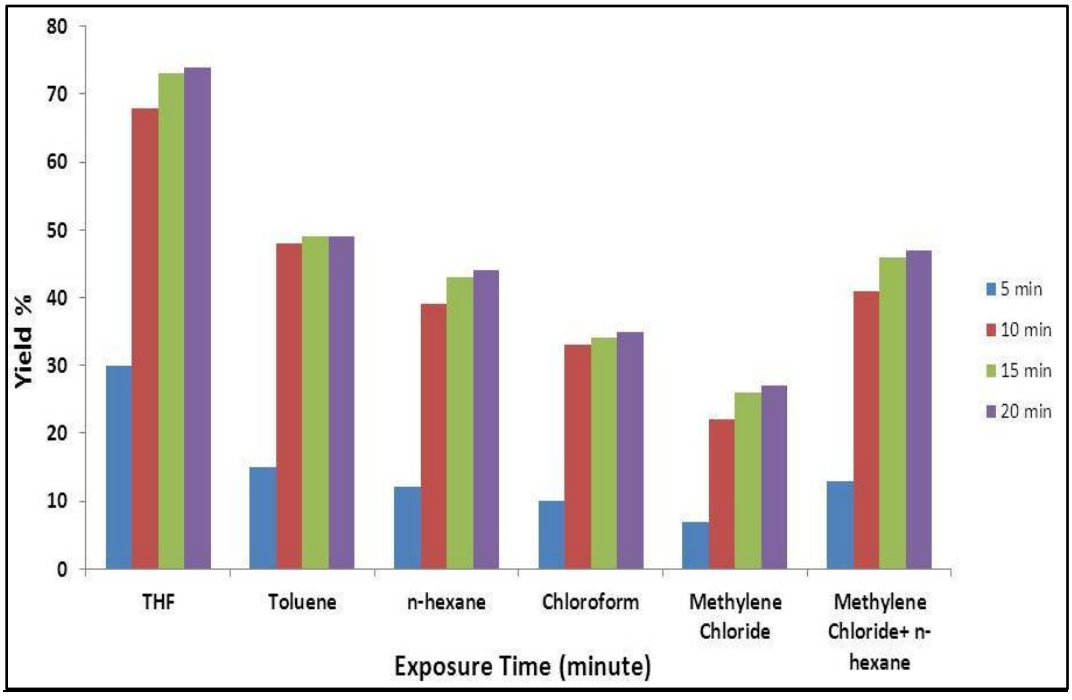

Fig. 8. The effect of ultrasonication time on the yield of Quseir oil shale.

3.4 Characterization of Shale Oil by Gas Chromatography (GC)

Figure 9 presents the GC analysis of extracted hydrocarbons using n-hexane, methylene dichloride, methanol and toluene respectively by both mechanical stirring as well as low frequency ultra-sonication (toluene only). Toluene was chosen as the second best choice since THF is more expensive. The hydrocarbon content in the extracted oil was higher with methylene chloride and toluene when compared with n-hexane. Methanol extracted oil showed near absence in hydrocarbon content in consistent with the literature [12, 13].

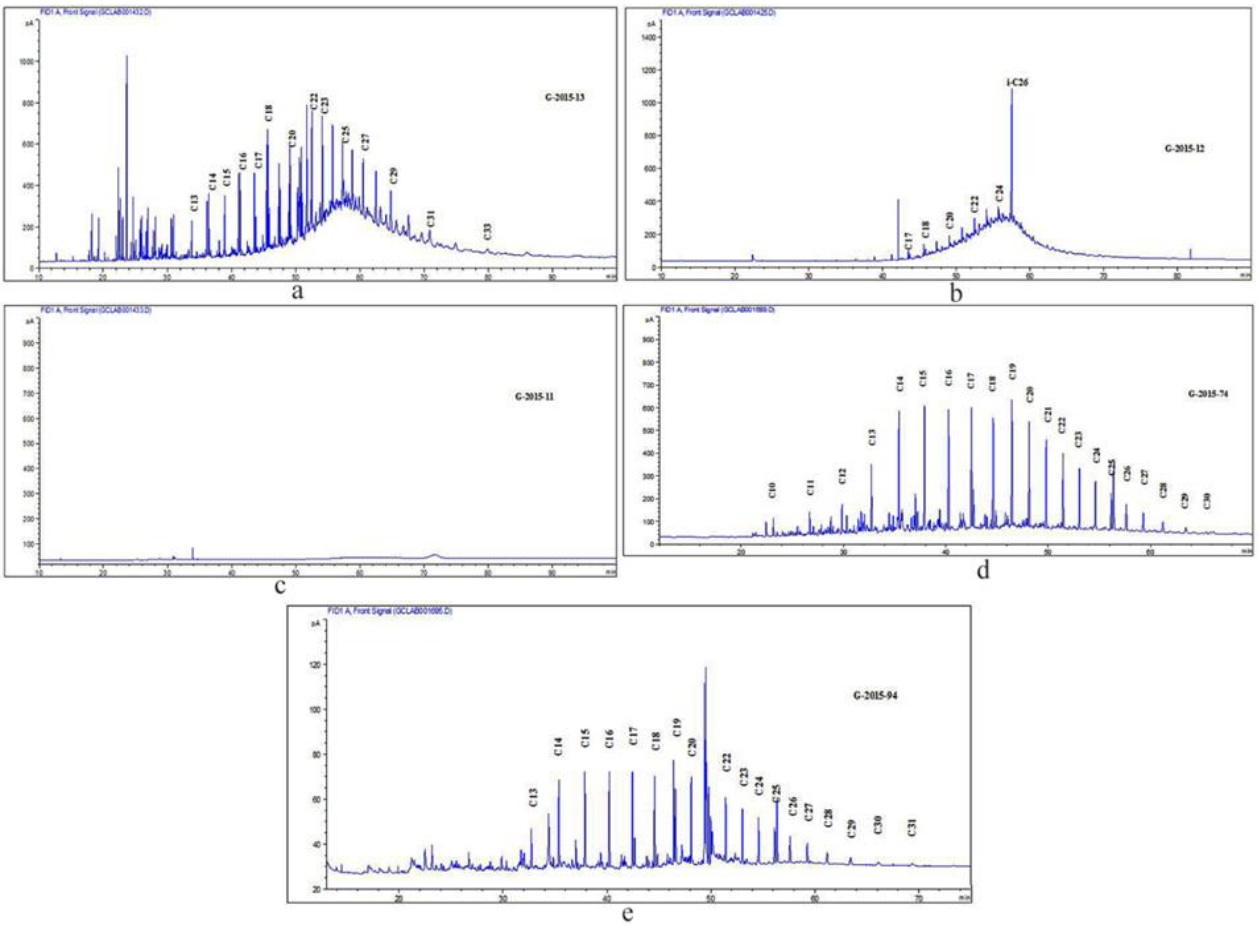

Fig. 9. (a) GC of oil using n-hexane as the extracting solvent, mechanical agitation (b) GC of oil using methylene dichloride as the extracting solvent, mechanical agitation (c) GC of oil using methanol as the extracting solvent, mechanical agitation, (d) GC of oil extracted using toluene as the extracting solvent, mechanical agitation (e) GC of oil using toluene as the extracting solvent, ultrasonication method

3.5 TGA of Shale Oil

Figure 10 presents the TGA for the crude oil shale rock, extracted oil from methanol and toluene respectively. TGA analysis clearly established that oil extracted by methanol composed mainly of the solvent whereas nearly no solvent is present in case of toluene extracted oil.

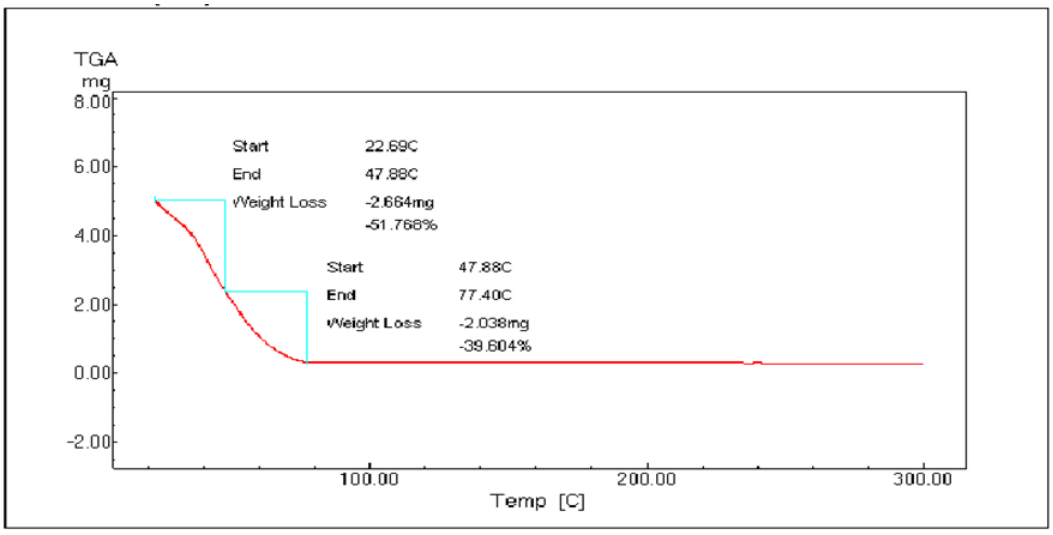

Fig. 10.a. TGA of extracted oil using methanol.

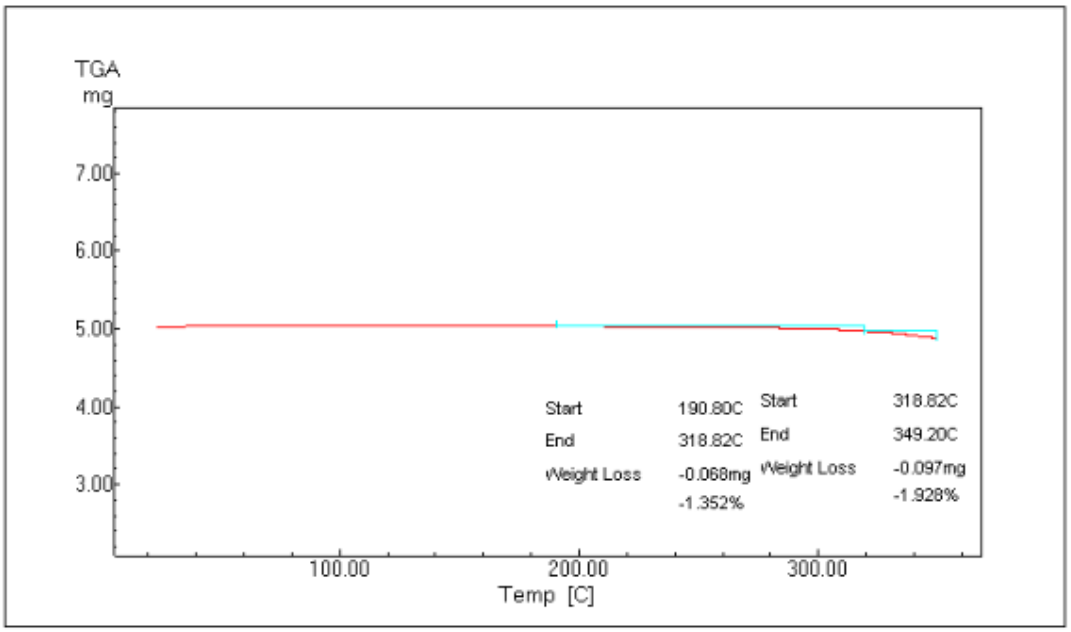

Fig. 10. b. TGA of extracted oil using toluene as the extracting solvent.

The observation of minuscule loss in weight in toluene extracted oil showed the absence of solvent present in the oil. Hence, toluene is a better solvent for extraction of oil and this is consistent with the literature [14, 15].

3.6 Physical Properties

3.6.1 Calorific value of oil shale

The calorific value of extracted oil under optimum conditions (toluene as a solvent with 2:1 solvent to oil shale ratio, stirred for 4 h at refluxing conditions) was 41201 kJ/kg. This was 10.5% lower than the calorific value of 46000 kJ/kg corresponding to the Egyptian standard gas oil [16]. Therefore, the consumption of the extracted oil from Egyptian oil shale will be higher than that of the Egyptian standard gas oil and thereby the increasing the operating costs of shale oil [16].

3.6.2 Viscosity

Viscosity of extracted shale under optimum conditions (toluene as a solvent with 2:1 solvent to oil shale ratio, stirred for 4 h at refluxing conditions) was 1.875 centistokes (cSt) which was comparable with the Egyptian standard gas oil (2 (cSt))[16].

3.6.3 Density

Density of extracted oil under optimum conditions (toluene as a solvent with 2:1 solvent to oil shale ratio, stirred for 4 h at refluxing conditions) was 830 kg/m^3 which was comparable with the Egyptian standard gas oil (820 kg/m^3) [16].

3.6.4 Cost analysis of the obtained shale oil

THF was more expensive than toluene with the prices of EGP 280 per liter and EGP 22 per liter respectively. Therefore, use of toluene as the extraction solvent was more economical than using THF though the yield from THF (79%) was superior to toluene (49%).

4. CONCLUSIONS

Since oil shale is a good alternative to petroleum fuels, the optimum conditions for extraction of oil from oil shale were obtained. It was observed that the polarity and coordinating ability of the solvent had a significant effect on the yields of recovered oil from oil shale. The yields were higher for THF, toluene and the mixture of (n-hexane and methylene dichloride) compared to methanol and hexane. Mechanical agitation required 4 h at refluxing conditions for optimum extraction whereas ultra-sonication required only 15 min. The solvent to oil shale ratio was 2:1(g/g) in both mechanical agitation as well as ultra-sonication methodologies. Increasing the solvent amount did not lead to higher yields. The optimum oil shale with particle size of 0.8 mm gave better yields. Ultra-sonication gave superior yields in comparison with mechanical agitation methods at lower temperature and shorter extraction time. The calorific value of the Egyptian oil shale was 41201 kJ/kg which is comparable with the Egyptian standard gas oil.

DECLARATION OF CONFLICT OF INTERESTS

The authors have declared no conflict of interests.

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دراسة مقارنه لاستخراج الزيت من الصخور الزيتية

استخدم البحث طريقة التقليب الميكانيكي وطريقة الموجات فوق الصوتية لفصل الزيت من الصخور الزيتية المستخرجة من القصير بمصر، باستعمال المذيبات العضوية: تتراهيدرو فيران والتولوين وثاني كلوريد الميثيلين والميثانول والهكسان، وحساب نتائج استعمالها كنسبه مستخلصه من الزيت، والتعرف على خصائص تلك الصخور بإجراء التحليل الأولي والتحليل الطيفي بالأشعة تحت الحمراء وكروماتوغرافيا الغاز والتحليل الحراري بالأشعة تحت الحمراء وتقنيات التصوير السطحي مثل مسح المجهر الالكتروني حيث تبين من نتائج التحاليل ان الزيت المستخلص يحتوي علي نسبه عالية من المواد الهيدروكربونية مقارنه بمثيلاتها من المناطق الأخرى وأن استخدام التتراهيدرو فيران والتولوين وخليط من ثاني كلوريد الميثيلين والهكسان يعطي نتائج افضل من استخدام الهكسان والميثانول، بالإضافة إلى تبين ان استمرار التقليب ٤ ساعات و ٠,٨ مم لحجم الجسيمات من الصخر الزيتي ونسبة ٢ الي ١ نفط الي المذيب أعطت نسب جيده من الزيت المستخلص بطريقه التقليب الميكانيكي بينما اعطت طريقه الاستخلاص بالموجات فوق الصوتية نتائج ونسب اعلي من الفصل التقليدي بالتقليب الميكانيكي وصلت إلى ٧٣ ٪ باستخدام المذيب العضوي تتراهيدرو فيران في فترة ١٥ دقيقة للتجربة وفي درجه الحرارة المحيطة.