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Mohammed Z. Anabtawi[a]
[a] CHEMICAL ENGINEERING DEPARTMENT, UNIVERSITY OF BAHRAIN, ISA TOWN, BAHRAIN

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Comparison between Continuous Stirred Tank Reactor Extractor and Soxhlet Extractor for Extraction of El-Lajjun Oil Shale

MOHAMMED Z. ANABTAWI
CHEMICAL ENGINEERING DEPARTMENT
UNIVERSITY OF BAHRAIN
P.O. BOX 32038, ISA TOWN, BAHRAIN

ABSTRACT

Extraction of El-Lajjun oil shale in a continuous stirred tank reactor extractor (CSTRE) and a Soxhlet extractor was carried out using toluene and chloroform as solvents. Solvents were recovered using two distillation stages, a simple distillation followed by a fractional distillation. Gas chromotography was used to test for the existance of trapped solvent in the yield. It was found that extraction using a CSTRE gave a 12% increase in yield on average compared with the Soxhlet extractor, and an optimum shale size of 1.0 mm offered a better yield and solvent recovery for both techniques. It was also found that an optimum ratio of solvent to oil shale of 2:1 gave the best oil yield. The Soxhlet extractor was found to offer an extraction rate of 1 hour to complete extraction compared with 4 hours in a CSTRE. The yield in a CSTRE was found to increase an increase of stirring. When extraction was carried out at the boiling point of the solvents in a CSTRE, the yield was found to increase by 30% on average compared to that of extraction when the solvent was at room temperature. When toluene was used for extraction, the average amount of bitumen extracted was 0.032 g/g of oil shale and 85.8% of the solvent recovered, compared with 0.0293 g/g of oil shale and 89.9% of the solvent recovered using a Soxhlet extractor. When chloroform was used for extraction, the average amount of bitumen extracted was 0.039 g/g of oil shale and 76.4% of the solvent recovered, compared with 0.037 g/g of oil shale and 84.1% of the solvent recovered using a Soxhlet extractor.

Key Words. Oil shale; Extraction; CSTRE; Soxhlet extractor

INTRODUCTION

Jordan is rich in oil shale resources. The El-Lajjun oil shale deposit has an estimated reserve of over 1.3 billion metric tonnes (1, 2). This area is considered one of the world's richest in oil reserves (2). Oil shales are geologically classified as marlstones because of their large percentage of carbonates. Oil shale is composed of about 86% mineral matter and 14% organic matter; however, the organic matter should not exceed 25% (2, 3). Oil shale was also geochemically analyzed (4) and was found to consist of organic matter, biogenic calcite and apatite, detrital clay minerals, and quartz, and its calorific values were correlated as a function of different operating conditions. The organic matter in the oil shale is composed of bitumen, about 10–20% and rarely exceeding 20% (3), and kerogen, about 80–90%. Bitumen is a heteroatomic polymer which is soluble in many organic solvents but has a high percentage of sulfur content and therefore can be extracted for hydrocarbon recovery and sulfur retention. Kerogen is a heteroatomic polymer and is insoluble in most organic solvents; therefore, it cannot be extracted for oil utilization. If retorting is carried out without being preceded by extraction, the sulfur content of the bitumen will be released and will cause major pollution problems. Kerogen and bitumen are thermally unstable. At 250°C they decompose to form gaseous and liquid products (2). Kerogen is decomposed into gas oil and solid residue in a batch retorting operation whereas the light hydrocarbons of the bitumen fraction and the gaseous hydrocarbon product from the kerogen fraction may be lost. The extraction process is a mass transfer process in which the solvent dissolves the solute on the surface of the particles and change its phase from solid to liquid by dissolution (5, 6). Bitumen is usually extractable by organic solvents at moderate temperature. The kerogen, which is an insoluble fraction left in the rock, is retorted and collected.

The objective of this study was to compare two different techniques for the extraction of El-Lajjun oil shale, a continuous stirred tank reactor (CSTRE) and a Soxhlet extractor, using toluene and chloroform as solvents. It also aimed at recommending the best techniques for extraction based on the quality and quantity of yield and solvent obtained, and on other operating parameters that affect extraction.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

A CSTRE and a Soxhlet extractor were employed for leaching experiments (Figs. 1 and 2). In the CSTRE 75 g of 1.0 mm mesh oil shale was

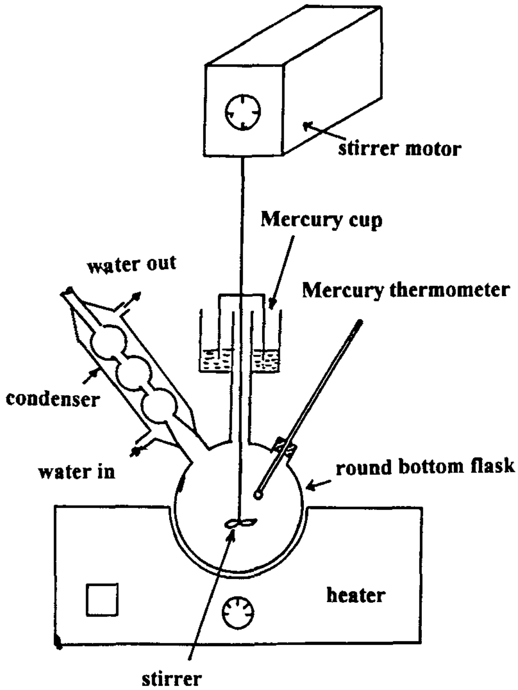

FIG. 1 Schematic diagram of the continuous stirred tank reactor extractor.

charged into the extractor and 150 mL of solvent was used for each run. In the Soxhlet extractor 50 g of 1.0 mm mesh size oil shale was charged into the extractor and 200 mL of solvent was used for each run. Extraction was carried out at the boiling points of the solvent used. The shale was then measured, and from the difference between the weight of the spent shale, the original weight of the sample, and the amount of oil extracted, the weight of the adsorbed solvent could be determined. The extracted phase was then distilled in two stages. The first stage was a simple distillation followed by a second stage which was a fractional distillation. The total amount of solvent recovered was taken as the sum of 1) the solvent recovered from the extraction process in the extractors, 2) the solvent recovered from first stage of distillation, 3) the solvent recovered from fractional distillation, and 4) the solvent adsorbed on the shale surface. The oil produced was tested by GC for the presence of traces of solvent and was compared with the CG chart for pure solvents (3, 7).

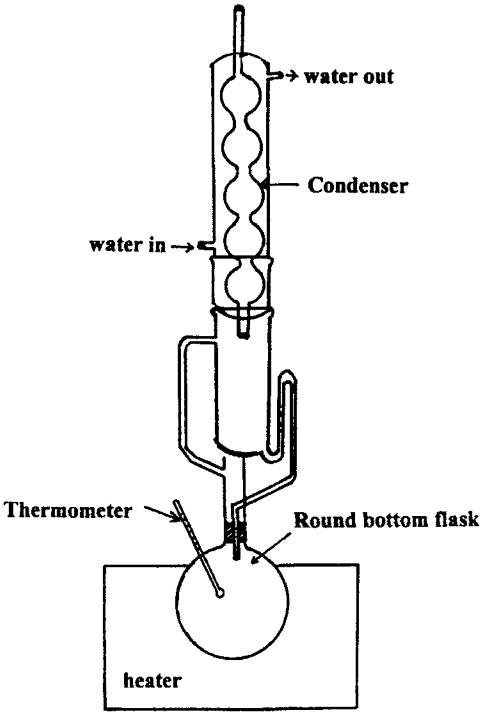

FIG. 2 Schematic diagram of the Soxhlet extractor.

RESULTS AND DISCUSSION

The dissolution of bitumen into the organic solvent is considered to be the limiting step in the oil shale extraction process. This is the result of direct contact of the solvent and the solid accommodating the bitumen at the point where chemical and physical interaction takes place. If the force of attraction between the bitumen and the solvent is greater than that between the solvent molecules or the dissolution of the bitumen, then the bitumen can be easily extracted. The degree and speed of extraction and the quantity of oil recovered depend on both the nature of the oil trapped in pores and the power of the solvent used for dissolving the oil. Solvents are usually classified by the number of functional groups present in a molecule which affect the interaction of physical and/or chemical interactions between the solute and the solvent (8, 9). In previous work Anabtawi and Uysal (3, 7) showed that both chloroform and toluene are the best solvents among the common solvents usually used for oil shale extraction. This selection was based on both yield and solvent recovered. When chloroform was used for extraction, the time taken to complete the leaching operation was much less than that of toluene, and it also had a lower boiling point temperature, which gave easier separation. However, the use of toluene resulted in better solvent recovery, but it had the disadvantage of a higher boiling point than chloroform and was therefore more difficult to separate.

Calculation of the Yield

The mass of the yield and solvent recovered were calculated by using calibration charts developed by Anabtawi and Uysal (2) for both toluene and chloroform and based on a gas chromotography technique. These charts were produced for testing the amount of solvent still trapped in the yield after extraction was completed. After extractions using both solvents and both extraction techniques, two samples of 50 mL of oil were subjected to two stages of distillation. The quantity of solvent trapped in the yield was tested using the calibration charts and subtracted from the amount of oil used initially in the two stages of distillation. The mass of the yield was found by taking the different fractions obtained from fractional distillation minus the amount of solvent detected from the calibration chart in all cuts and residues from fractional distillation. The total volume of the yield was multiplied by the density of oil (0.92 g/cm^3). The results showed that the amount of oil obtained by extraction using chloroform was 3.9% and the amount of solvent recovered was 76.4% whereas the amount of oil obtained using toluene was 3.2% and the amount of solvent recovered was 85.8%. The values reported by Anabtawi and Uysal (3) for a Soxhlet extractor were 3.7% for chloroform and the amount of solvent recovered was 84.1% whereas for toluene it was 2.93% and the amount of solvent recovered was 89.9%.

Effect of Particle Size

Particle size is an important parameter in washing extraction of oil shale. It is a direct function of the total surface area available for extraction. The diffusion of bitumen through the pore structure of the residual solids is the controlling factor for the extraction of oil. The smaller the size of the particles, the greater is the interfacial area between the solid and the liquid, and therefore the higher is the rate of transfer of the material. The smaller the distance the bitumen has to diffuse within the solid, the smaller will be the distance the bitumen has to travel to reach the surface of the solid. Since there is agitation in a CSTRE, the area may be effectively used with very fine shale but the separation of particles from the yield becomes difficult. The effect of particle size on the yield for both a CSTRE and Soxhlet extractor is shown in Fig. 3. It was found that the yield decreases with increasing particle size from 1.0 mm to 4.0 mm. It was also found that the a CSTRE produced a higher yield than did a Soxhlet extractor. Both a CSTRE and a Soxhlet extractor have shown lower adsorption rates with an increase of particle size. It was found that the optimum particle size that provides sufficient mass transfer area without agglomeration of particles (which, in turn, ensures the free mass transfer mechanism) is 1.0 mm. The optimum size of 1.0 mm is in agreement with Williams and Martin (10) who recommended an optimum particle size less than 1.5 mm. Other experiments were conducted at particle sizes below 1.0 mm but there were some difficulties in obtaining smooth extraction, mainly due to clogging in the side line in the extractor and operation at a slower rate of extraction.

Effect of Extraction Time

The effect of extraction time on the yield in a CSTRE and in a Soxhlet extractor are shown in Fig. 4. Figure 4 shows that as the time of extraction increases, the yield increases to 4 hours in the CSTRE compared to 1

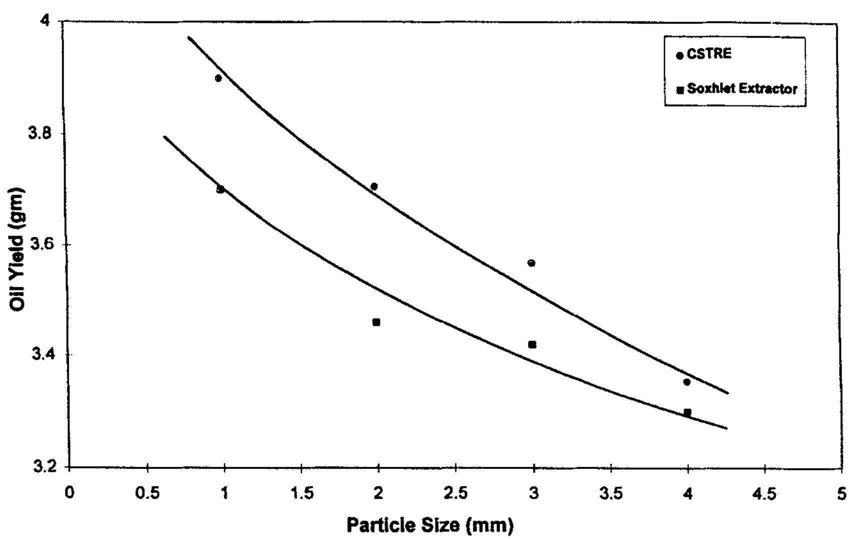

FIG. 3 Effect of particle size on the oil yield for extraction using chloroform.

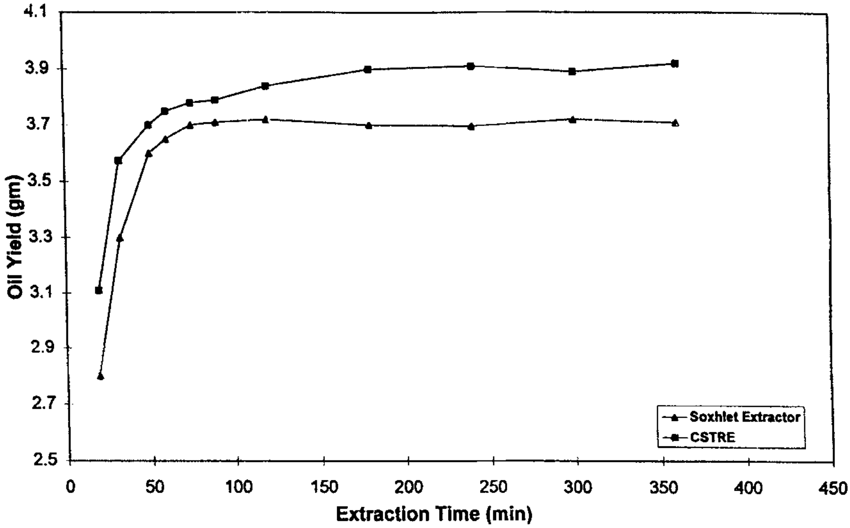

FIG. 4 Effect of extraction time on the oil yield using toluene.

hour in the Soxhlet extractor (3). Beyond this time the effect of time on yield became less apparent because the extraction approaches completion. This may be explained as follows: At a short time of extraction, the driving force for mass transfer between the concentrations of the oil-rich shale phase and the solvent phase was very high, which resulted in a rapid increase in the yield. As the time exceeded 15 minutes for the Soxhlet extractor and 90 minutes for the CSTRE, the driving force was reduced because the concentration of oil in the shale phase compared to the oil in the solvent became smaller and the rate of extraction tended to decrease and approached a constant value with an optimum time of 4 hours in the CSTRE and 1 hour in the Soxhlet extractor. These times were an indication that the extraction process had almost reached completion. Tamimi and Uysal (11) showed that the effect of extraction time was more significant for particle diameters greater than 2.0 mm. However, in this work most experiments were conducted with particles sizes of 1.0 mm. In the CSTRE most experiments took place at a constant rate of stirring of 200 rpm and at the boiling point of the solvent.

Effect of Temperature

The effect of operating temperature on yield was investigated in the CSTRE and is shown in Fig. 5. Figure 5 shows that as the temperature

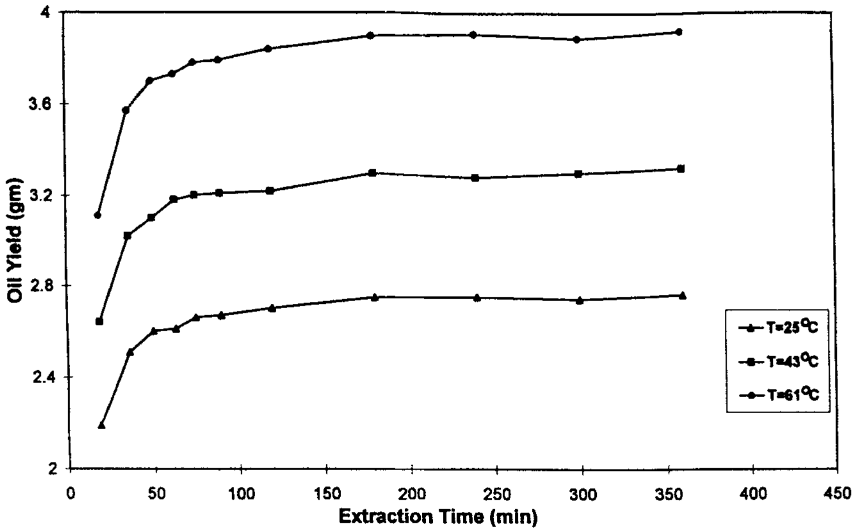

FIG. 5 Effect of solvent temperature on the oil yield using chloroform.

of the solvent increases, the yield increases until the solvent reaches its boiling point where the yield was about 30% higher than that obtained when extraction was carried out at room temperature. This effect of temperature on extraction is expected because increasing the temperature decreases the adhesiveness, viscosity, and surface tension of the oil trapped in the shale. At the same time, the diffusivity of the oil into the solvent increases. This increase in diffusivity is due to the reduction of the attraction of solvent molecules for each others and thus enhances the transport of these molecules. Tamimi and Uysal (11) showed that preheating oil shale to a temperature just under the boiling point of the solvent increases oil solubility and extractability.

Effect of Solvent to Oil Shale Ratio

The quantity of solvent used for extraction should be large enough to impregnate all the oil shale particles with the solvent. The quantity of solvent should be high enough to allow contact of the solvent with all possible accessible soluble hydrocarbons in the oil shale. Several runs were carried out at solvent-to-oil-shale ratios of 0.5:1.0 to 3.0:1.0 (a 10% increase of solvent). The results showed that the yield increased with an increase of the solvent-to-oil-shale ratio up to 2.0:1.0. Beyond that limit,

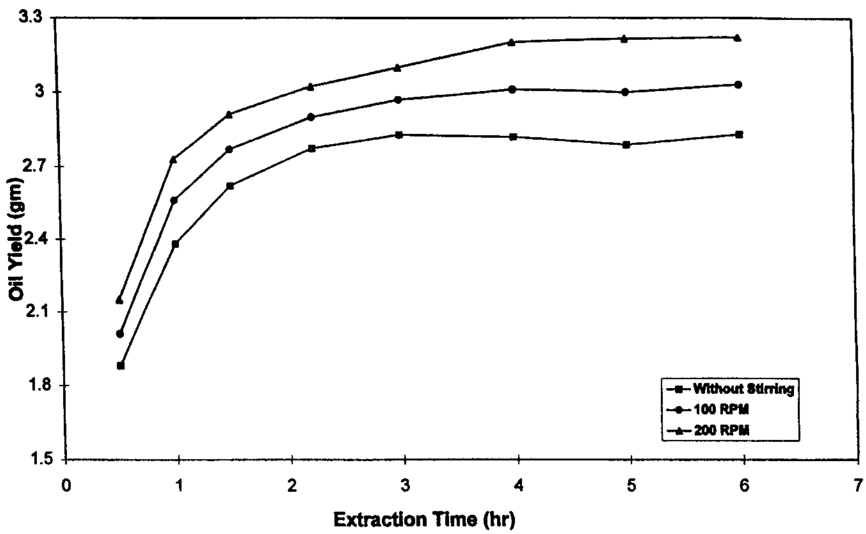

FIG. 6 Effect of stirring speed on the oil yield using toluene.

any increase in the ratio had a negligible effect. This findings is in agreement with that reported by Williams and Martin (10).

Effect of Stirring

Mixing increases the turbulence and hence increases the rate of extraction (9). This enhances the solubility of oil by solvent. The effect of stirring on the yield is shown in Fig. 6. Figure 6 shows that as stirring speed increases, the yield also increases. At a stirring speed of 200 rpm the yield was increased by 12% on average compared to that of an unmixed sample in a CSTRE. When the speed was increased beyond 200 rpm the particles were disturbed and started to interfere with the extraction process. The degree of mixing and its effect on the yield depend on several parameters, mainly the type of mixer, the rate of mixing, and the solvent-to-oil-shale ratio. Further work is needed to relate these parameters.

CONCLUSIONS

Extraction of El-Lajjun oil shale was carried out in both a CSTRE and Soxhlet extractor using chloroform and toluene as solvents. It was found that 1.0 mm was the optimum shale size and an optimum solvent-to-oil-shale ratio of 2:1 gave the best conditions for extraction for both techniques based on the yield and solvent recovered. It was found that a stirring speed of 200 rpm in a CSTRE increased the yield by 12% on average compared to that in the Soxhlet extractor. It was found that the Soxhlet extractor required 1 hour to complete the extraction compared to 4 hours in the CSTRE. It was also found that the yield increased with an increase in the temperature of the solvent from that of room temperature to 30% higher on average when extraction was carried out at the boiling point of the solvent. The amount of bitumen fraction extracted in the CSTRE using chloroform was found to be 0.039 g/g of oil shale and 76.4% of solvent recovered compared to 0.037 g/g of oil shale and 84.1% solvent recovered in the Soxhlet extractor. However, the amount of bitumen fraction extracted in a CSTRE by using toluene was found to be 0.032 g/g of oil shale and 85.8% of solvent recovered compared to 0.0293 g/g of oil shale and 89.9% of solvent recovered in a Soxhlet extractor.

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