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# Extraction of El-Lajjun Oil Shale

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## ABSTRACT

Extraction of the bitumen fraction of El-Lajjun oil shale was carried out using 17 different solvents, pure and combined. Out of all the solvents used, toluene and chloroform were found to be the most efficient for extraction of the bitumen to perform the major part of the experiments. This selectivity was based on the quality and quantity of the yield and on the quantity of solvent recovered. Extraction was carried out using a Soxhlet extractor. For complete recovery of solvent the extract phase was subjected to two stages of distillation, simple distillation followed by fractional distillation, where different cuts of oil were obtained. It was found that an optimum shale size of 1.0 mm offered better solvent recovery. One hour was the optimum time needed for complete extraction. The yield of oil was determined from the material balance gained from fractional distillation after testing for the existence of any traces of solvent trapped in the different cuts by using a gas chromotography technique. When chloroform was used, it was found that the average amount of bitumen extracted was 0.037 g/g of shale, which corresponds to 98% of the actual bitumen trapped in the oil shale (by assuming the bitumen represents 15% of the organic matter) and 84.1% of solvent recovered. When toluene was used, it was found that the average amount of oil extracted was 0.0293 g/g of shale, which corresponds to 78% of the actual bitumen trapped in the oil shale (by assuming bitumen represents 15% of the organic matter) and 89.9% of solvent for extraction with toluene.

*Key Words.* Oil shale; Extraction; Solvent selection

## INTRODUCTION

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. The organic matter should not exceed 25% (1). The organic matter in oil shale is composed of bitumen [about 10–20% and rarely exceeding 20% (2)] and kerogen (about 80–90%). Bitumen is a heteroatomic polymer soluble in many organic solvents and therefore can be extracted for hydrocarbon recovery. Kerogen is a heteroatomic polymer having a molecular weight greater than 3000 and is insoluble in most organic solvents; therefore, it cannot be extracted for oil utilization. El Lajjun oil shale, previously geochemically analyzed by one of the authors (3), and was found to consist of the following groups: organic matter, biogenic calcite, calcite and apatite, detrial clay minerals, and quartz. Kerogen and bitumen are thermally unstable. With the application of heat, 250°C, they decompose to form gaseous and liquid products (1). Kerogen is decomposed in a batch retort operation into gas oil and solid residue whereas the light hydrocarbons of the bitumen fraction and the gaseous hydrocarbon product from the kerogen fraction may be lost. It is therefore important to investigate the extractability of the bitumen prior to the retort operation. The extraction process is a mass transfer process in which the solvent dissolves the solute on the surface of the particles and changes its phase from solid to liquid by dissolution. This is followed by solvent diffusion, first forward through the pores of the large particles, where dissolution takes place inside the pores, then by backward diffusion and mass transfer of this solution to the main bulk of solution flow (4, 5). Any of these three steps can control the process. The first step is favored by using a powerful solvent, the second step is favored by applying extraction to particles with large pore sizes, whereas the third step may control the process if turbulence is enhanced so that the convective mass transfer is increased (5). Bitumen is usually extractable by organic solvents at a moderate temperature where these solvents extract the hydrocarbons and the more complex products which are heteroatomic. The kerogen, which is the insoluble fraction left in the rock, is retorted and collected as the yield. The main problem that arises from the extraction operation is the loss of a large quantity of solvent by adsorption, and therefore a good distillation technique is needed to reduce these solvent losses. It is thus the objective of this study to investigate several solvents used for the extraction of oil shale and to recommend the most suitable solvent based on the quantity and quality of the yield extracted and the quantity of solvent recovered.

## EQUIPMENT AND EXPERIMENTAL PROCEDURES

A Soxhlet extractor was employed for the leaching experiment. For each run, 50 g of 1.0 mm mesh oil shale was charged into the Soxhlet extractor and 200 mL solvent was used. Extraction was carried out at the boiling point of each solvent used until a clear liquid came from the shale, which indicated complete extraction of the extractable oil. The shale was then measured using a sensitive scale and from the difference between the weight of the spent shale after extraction, the original weight of the sample, and the amount of oil extracted, the weight of the adsorbed solvent can be determined. The extracted phase was then distilled in two stages to separate the oil. The first stage was a simple distillation followed by a second stage which was a fractional distillation as shown in Fig. 1.

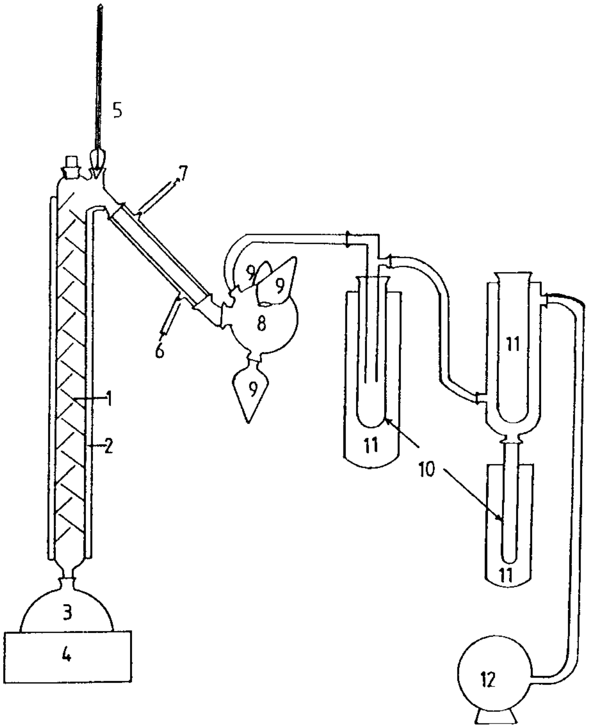

FIG. 1 Fractional distillation apparatus: 1) Vigreux column, 2) insulation, 3) round-bottom flask, 4) heater, 5) thermometer, 6) water in, 7) water out, 8) cow, 9) receivers, 10) traps, 11) liquid nitrogen, 12) vacuum pump.

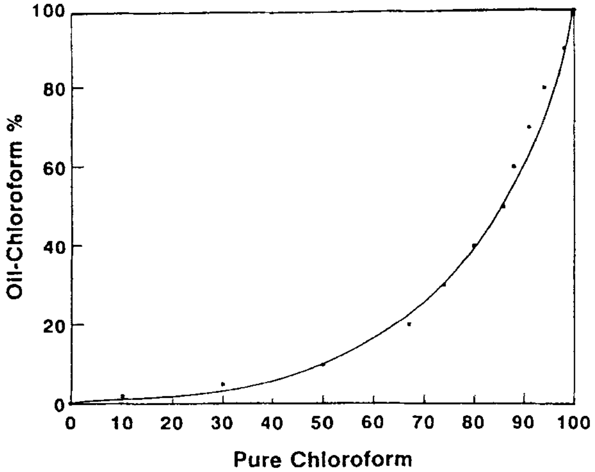

FIG. 2 Calibration chart for chloroform.

The total amount of solvent recovered was taken as the the sum of 1) solvent recovered from the extraction process in the Soxhlet extractor, 2) solvent recovered from first stage of distillation, 3) solvent recovered from the second stage of distillation (mainly the major quantity of solvent recovered in the trap and some traces of solvent trapped in cuts 1, 2, 3, and

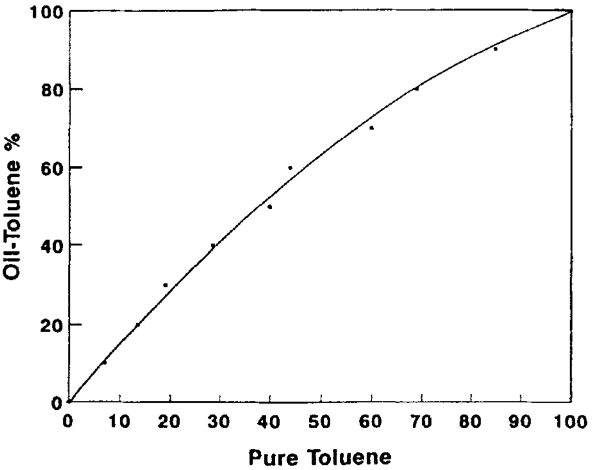

FIG. 3 Calibration chart for toluene.

in the residue, by the GC calibration chart), 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 the pure solvent (Figs. 2 and 3). A sample of the oil shale was placed in a furnace at 1000°C for 45 minutes, and the compositions for both the inorganic and organic matter were determined.

## RESULTS AND DISCUSSION

### Selectivity of Solvent

Dissolution of bitumen into the organic solvent is considered to be the limiting step in the oil shale extraction process. This is a result of the chemical and physical interaction which takes place through direct contact of the solvent and the solid accommodating the bitumen. If the force of attraction between the bitumen and the solvent is greater than that between the solvent molecules or of 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 the pores and the power of the solvent used for dissolving the oil.

Solvents are usually classified by the number of functional groups present in the molecule, which affects the interaction of either or both types of physical and chemical interactions between the solute and the solvent (6, 7). Seventeen different organic solvents (pure and combined) commonly used for extraction were used for the leaching operation. Table 1 shows the properties of these solvents.

Comparison among these solvents and selectivity of the best solvents for further investigation were made qualitatively based on observation and on the physical properties of the solvents used, quantity and quality of yield, and quantity of solvent recovered. A test on a sample retorted using the Fisher Assay showed that a solvent used for extracting bitumen should not have a temperature higher than 153°C, so the solvents selected for our investigation were limited by that boiling point.

Xylene was the solvent with the highest boiling point, 144°C. Some solvents were rejected on the basis of their color, viscosity, amount of yield, amount of the solvent recovered, boiling point, and the effect of high temperature on the stability of the hydrocarbons obtained.

Carbon tetrachloride gave a high yield, but the amount of solvent recovered was very small and the yield was nonviscous, had a yellowish color, and a strong solvent odor. The high yield obtained seemed to be at the expense of inefficient extraction because a large quantity of solvent was left with the extracted oil, and so it was rejected.

TABLE 1
Compounds Tested as Solvents

| | | | Solvent recovery | | Solvent adsorbed | | | |
|---|---|---|---|---|---|---|---|---|
| Solvent[a] | bp (°C) | Density (kg/m$^3$) | mL | % | mL | % | Yield (mL) | Color |
| CTC | 77 | 1595 | 155 | 77.5 | 23.0 | 11.5 | 18.5 | Brown |
| Benzene | 80 | 879 | 171.6 | 85.8 | 18.3 | 9.2 | 2.9 | Black |
| TCE | 87 | 1466 | 183 | 91.5 | 14.7 | 7.4 | 1.8 | Yellow |
| Xylene | 144 | 881 | 173 | 86.5 | 17.1 | 8.6 | 10.5 | Black |
| *n*-Heptane | 98.5 | 684 | 181 | 90.5 | 14.6 | 7.3 | 0.2 | Yellow |
| Isopropanol | 82.5 | 789 | 158 | 79.0 | 36.8 | 18.4 | 4.0 | Yellow |
| *tert*-Butanol | 83 | 779 | — | — | 23.1 | 11.6 | — | |
| Cyclohexane | 80 | 779 | 175 | 87.5 | 10.3 | 5.2 | 0.2 | Yellow |
| *n*-Butanol | 117 | 810 | 177 | 88.5 | 16.1 | 8.1 | 2.0 | Black |
| Benzene–toluene | 94 | — | 150 | 75.0 | 13.8 | 6.9 | 3.5 | Black |
| Benzene–*n*-butanol | 94 | 895 | 170 | 85.0 | 19.0 | 9.5 | 10.5 | Black |
| TCE–CTC | 88 | 1531 | 163 | 81.5 | 14.4 | 7.2 | 14.7 | Black |
| Benzene–xylene | 97 | 880 | 173 | 86.5 | 16.5 | 8.3 | 7.7 | Black |
| Toluene | 110.6 | 867 | 170 | 85.0 | 19.2 | 9.6 | 9.4 | Black |
| Benzene–TCE | 90 | 1173 | 179 | 89.5 | 14.5 | 7.3 | 4.0 | Black |
| Chloroform | 61 | 1492 | 147 | 73.5 | 22.0 | 11.0 | 6.1 | Black |
| TCE + *n*-butanol | 98 | 1138 | 170 | 85.0 | 19.4 | 9.7 | 9.0 | Black |

[a] CTC = carbon tetrachloride; TCE = trichloroethylene.

Cyclohexane has also produced a nonviscous, yellow-colored yield with a negligible amount of oil, so it was also rejected.

*n*-Heptane and isopropanol as two separate solvents produced very low yields of a light yellowish color, so these two solvents were eliminated. *tert*-Butanol was not a suitable solvent because some crystals formed in the Soxhlet extractor at high temperature, which resulted in clogging of the pipes, so it was rejected.

Mixtures of benzene–toluene 1:1 by volume and of trichloroethylene–carbon tetrachloride 1:1 by volume gave viscous yields of oil but with low solvent recovery, which may be due to the high volatility of the solvents. These mixtures were eliminated.

Trichloroethylene was a powerful solvent with high solvent recovery, but the yield was fairly low and so it was eliminated.

*n*-Butanol was also a powerful solvent which produced a highly viscous yield, but during distillation thermal cracking occurred regularly, so it was eliminated.

Xylene was a powerful solvent which produced a high yield but the solvent recovery was not very high, which reflected inefficient extraction.

Also, the solvent has a very high boiling point (144°C), which makes the separation of oil from solvent difficult with the possibility of thermal cracking of the oil produced. This may also be responsible for loss of some of the light hydrocarbons, so this solvent was eliminated.

Benzene–*n*-butanol (1 : 1 by volume) and xylene–benzene (1 : 1 by volume) were good solvents which gave a reasonable amount of yield and solvent recovery. However, both combinations of solvents required high temperatures to complete distillation, which resulted in a higher loss of light hydrocarbon, so both were eliminated.

The mixture of trichloroethylene–*n*-butanol (1 : 1 by volume) was a good solvent which gave a very high yield with very high solvent recovery. The main disadvantage of this combination was the formation of tar during the distillation process at a temperature close to the boiling boil of the mixture, so it was eliminated.

In general, benzene, toluene, chloroform, and the benzene–trichloroethylene mixture gave fairly high yields and very reasonable amounts of solvent recovery. The benzene–trichloroethylene mixture was eliminated because trichloroethylene is an expensive chemical to be used for extracting oil shale. Benzene was also eliminated based on the purity of the yield obtained based on gas chromotography.

Chloroform and toluene were found to be the best solvents for extracting El-Lajjun oil shale and so were chosen for the second stage of investigation. The main criteria for their selection were the quality and quantity of the yield and the quantity of solvent recovered. When chloroform was used as a solvent, the time taken to complete the leaching operation was much less than that of toluene. Chloroform also has a lower boiling point temperature, which leads to easier separation. However, toluene has better solvent recovery than chloroform but the disadvantage of a higher boiling point and therefore is more difficult to separate.

## Calculation of the Yield

Before the effects of different variables on the rate of extraction for both chloroform and for toluene were studied, calibration charts were produced for both solvents by using the gas chromotographic technique. These charts were produced to test for the amount of solvent still trapped with the yield after conducting the second stage of distillation as follows. First a pure sample of solvent was injected in the gas chromotograph column at a certain setting of initial temperature. Temperature rate, chart speed, and the retention time for the pure solvent were recorded and corresponded to 100% GC area. Then a mixture of pure oil and 10% increments of solvent was added and tested in the same column and at the same setting as that of the pure solvent. The areas which corresponded to the solvent at the same retention time were recorded, and the pure solvent against the oil solvent mixture was plotted (Figs. 2 and 3). When fractional distillation was conducted on both solvents separately, the products of different cuts were tested by GC, and the amount of solvent was calculated from the charts and their magnitudes were subtracted from the yield. The mass of the yield was found by taking the different fractions obtained from fractional distillation minus the amount of the solvent that was detected from the calibration chart in the trap, cuts 1, 2, and 3, and the residue. This total yield volume was multiplied by the density of oil (0.92 g/cm$^3$). After extraction of oil using several runs, two samples of 50 mL oil each, obtained using chloroform and toluene, were subjected to first stage and second stage distillations. Tables 2 and 3 show the results obtained. The amount of oil obtained by extraction using chloroform was 3.7% and the amount of solvent recovered was 84.1%, whereas the amount of oil obtained using toluene was 2.93% and the amount of solvent recovered was 89.9%. In both cases we believe that still more solvent can

TABLE 2

Distillation Result of 50 g Oil Extracted from 900 g Oil Shale Using Chloroform. First Stage Distillation Gave 4.685 g Solvent. Second Stage Distillation of 41.667 g Oil Gave the Following:

| Cuts | Weight (g) | Temperature range (°C) | Color |
|---|---|---|---|
| Trap | 12.666 | 80 | Brownish |
| 1 | 0.726 | 80–120 | Black |
| 2 | 1.450 | 120–160 | Black |
| 3 | 1.875 | 160–180 | Black |
| Residue | 24.950 | >180 | Black |

TABLE 3

Distillation Result of 50 g oil Extracted from 1280 g oil Shale Using Toluene. First Stage Distillation gave 1.42 g Solvent. Second Stage Distillation of 43.79 g Oil Gave the Following:

| Cuts | Weight (g) | Temperature range (°C) | Color |
|---|---|---|---|
| Trap | 11.79 | 80 | Brownish |
| 1 | 2.688 | 80–120 | Black |
| 2 | 3.75 | 120–160 | Black |
| 3 | 3.76 | 160–180 | Black |
| Residue | 22.813 | >180 | Black |

be recovered by improving the fractional distillation conditions. From the test conducted for the determination of the composition of the oil shale, the results showed that the sample contained 75% inorganic matter and 25% organic matter. If the amount of soluble bitumen was taken as 15% of the organic matter, then the amount of extractable bitumen using chloroform can be considered to be 98% compared to that extracted by toluene (78%).

## Effect of Particle Size

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 the rate of transfer of material. The shorter the distance the bitumen has to diffuse within the solid, and the shorter the distance for the bitumen to travel to reach the surface of the solid. But since there was no agitation in this study, the area may not be effectively used with very fine shale, and separation of particles from the liquid becomes disadvantagous (8). To test for the best particle size for maximum extraction rate, several experiments were conducted using both toluene and chloroform (Fig. 4). It was found that the oil yield decreases with increasing particle size from 1.0 to 4.0 mm. However, the decrease was not very significant. It was also noticed that the larger the particle size, the smaller the amount of solvent adsorbed and the lower the extraction

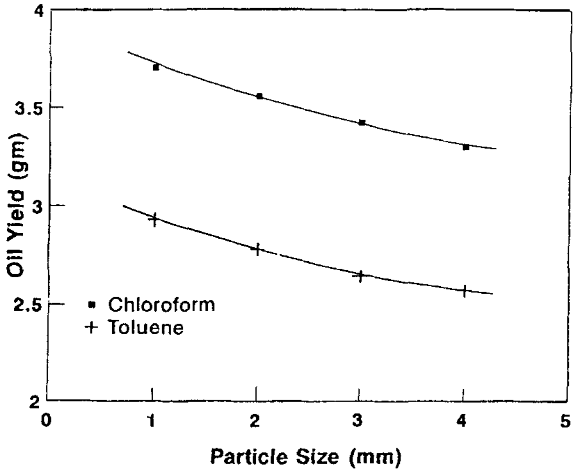

FIG. 4 Effect of particle diameter on the yield.

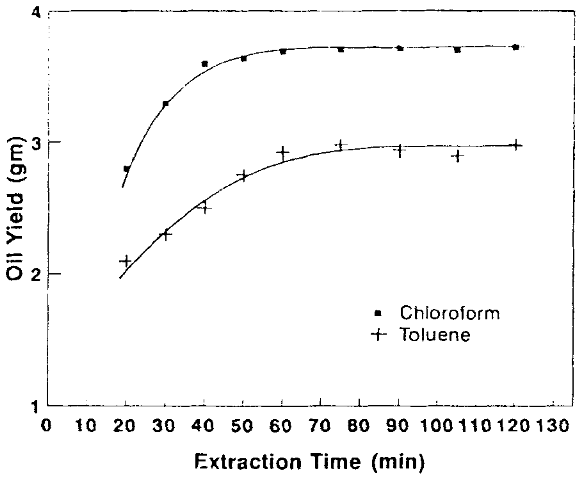

FIG. 5 Effect of extraction time on the yield.

rate, so the optimum particle size was taken as 1.0 mm. This is in agreement with Williams and Martin (9) who recommended an optimum particle size of less than 1.5 mm. Other experiments were conducted at particle sizes below 1.0 mm, but there were some difficulties with running a smooth extraction process, mainly due to clogging in the return line in the Soxhlet extractor and a slower rate of extraction.

### Effect of Extraction Time

The effect of extraction time on yield is shown in Fig. 5. The figure shows that as the time of extraction increases, the yield increases up to a time of 1 hour. Beyond that time, the effect of time is not very significant, which indicates that the extraction process is almost complete. Tamimi and Uysal (10) showed that the effect of extraction time is more significant for particles of larger diameter, greater than 2.0 mm. However, in this investigation the bulk of the work on the solvents chloroform and toluene was conducted on particles of 1.0 mm.

## CONCLUSIONS

Seventeen organic solvents were used to extract the bitumen fraction of El-Lajjun oil shale. Chloroform and toluene were the best solvents based on the quality and quantity of the yield and the amount of solvent recovered. The amount of bitumen fraction extracted by toluene was found to be 0.0293 g/g shale, which is 78% of the total bitumen available in the shale, and the amount of toluene recovered was 89.9%. The amount of bitumen fraction extracted by chloroform was found to be 0.037 g/g shale, which is 98% of the total bitumen available in the oil shale, and the amount of chloroform recovered was 84.1%. The percentages of bitumen recovered are based on 15% of the organic matter in the shale being bitumen. It was found that a shale size of 1.0 mm offers the best yield and solvent recovery, and a time of 1 hour was the optimum needed for complete extraction.

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