Parametric Investigation of Oil-Shale Extraction with Organic Solvents

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Abstract

Oil-shale deposits at El-lajjun, a rich oil-shale area south of Jordan, were extracted with organic solvents. The amount of extracted oil depends on the operating conditions and parameters which affect the process. The effects of particle size, extraction time, extraction temperature, mixing rate, solvent-to-oil-shale ratio, and type of solvent were investigated.

INTRODUCTION

The organic material in oil shale is called kerogen. It is a heterogeneous mixture of organic minerals that can be dissolved by organic solvent and extracted from the oil shale. Generally, the extraction process takes the following path: first, the solvent dissolves the kerogen (solute) on the surface of the particle and change its phase from solid to liquid by dissolution. Second, there is forward diffusion of solvent through the pores of large particles, where dissolution takes place inside the pores. Third, there is backward diffusion and mass transfer of this solution to the main bulk of the solution flow (*1*). These steps are illustrated in Fig. 1.

Any one of these three main steps can be a limiting process. The first step is usually fast if the proper solvent is used. The second step is also fast if the particles have large pores and the solvent viscosity and surface tension are quite low. The third step will be fast if turbulence and agitation are high enough to increase the mass transfer convection processes (*2*).

Porosity and pore size distribution greatly affect the rate of oil extraction because the solvent must flow or diffuse in and out of the pores, and sometimes the solute moves through the pores to the particle surface by diffusion (*3*).
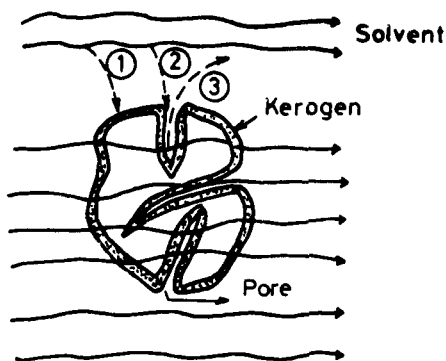
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FIG. 1. Solvent–kerogen interaction.

SYSTEM DESCRIPTION

Oil shale was crushed and screened into several ranges of particle size that covered a range of 0.1–3 mm in diameter. Every batch of a specific particle size was processed into a CSTR-type extractor. The extractor was a cylindrical vessel with a conical false bottom packed with steel wool and supplied with a regulating valve at the outlet line. The crushed oil-shale batches were dumped into the extractor to a certain depth. Organic solvents were poured into the extractor with agitation.

Operating parameters include particle size, extraction time, extraction temperature, mixing rate, solvent-to-oil-shale ratio, and type of solvent used. In each experiment, one parameter was varied and the others were kept constant. At the end of each experiment the extract was allowed to percolate and flow through the bed of the crushed oil under gravity, where it was filtered by the steel wool. The extract was collected in a collecting tank and separated into solvent and oil by means of a rotary evaporator. The organic solvent was recycled for use as a fresh solvent. The system assembly is shown in Fig. 2.

Several batches of a certain particle size were extracted with a solvent mixture of 75% benzene and 25% cyclohexane at the same operating conditions of temperature, contacting time, mixing rate, and solvent-to-oil-shale ratio.

EFFECT OF PARTICLE SIZE

Particle size is a significant parameter in the washing extraction of oil shale. It is a direct function of the total surface area available for extraction. The process is favored by increasing the surface area per unit volume of
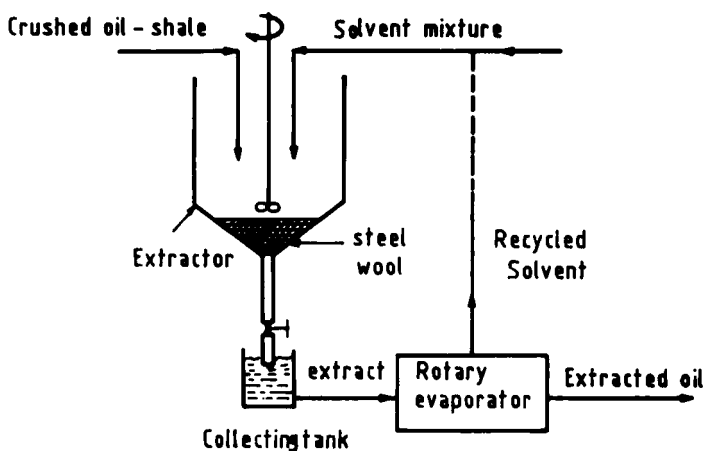
FIG. 2. Batch extraction of oil shale by organic solvents.

solids. This permits the soluble kerogen to be washed out easily from the rock matrix.

Solid–liquid interfacial tension is a strong function in the pore diameter, viscosity, and surface tension of the solvent–solute–solution combination. Also, thermodynamics indicates that solubility of very small particles should be larger than that for large particles.

The extract was separated into solvent and oil. The yield was reported as grams of oil separated per kilogram of fresh oil shale fed to the extractor. All experiments indicated that the range of particle size suitable for extraction was 0.2–2 mm in diameter. This depends on the type of oil-shale deposits and the operating conditions of the extraction process.

If the particle size is less than 0.2 mm, the problems of agglomeration and coagulation impede agitation, hinder dissolution, and obstruct the percolation process. The solution drainage or settling velocity will be small due to the high resistance to solvent flow inside the extractor under gravity settling conditions.

For particles larger than 2 mm, the extraction rate is essentially constant and slow. Under a given set of conditions, mass transfer from small pores becomes a limiting factor for particles larger than 2 mm. Experimentation on El-lajjun oil shale indicated that transition occurs at a particle size that covers a range of 1.6–2.0 mm. The exact size depends on the extraction kinetics, dissolution thermodynamics, and the mode of mass transfer from the particles. Particles larger than 2.0 mm in diameter offer more resistance

to the solvent for flow inside their pores and for the extract to flow outside to the bulk solvent (solution). The extraction yield from fine particles exceeded that from coarse particles by an amount which decreased with increasing residence time, as shown in Fig. 3.

The particle size effect on yield has not yet been built into an explicit model that can predict the limiting particle size. All data were generated from direct experimentation.

EFFECT OF TEMPERATURE

The extraction yield from cold oil shale (unpreheated) is small but increases substantially when the oil shale is preheated. Preheating the oil shale to a temperature less than the boiling point of the solvent increases the oil solubility and extractability (4). The higher the temperature, the
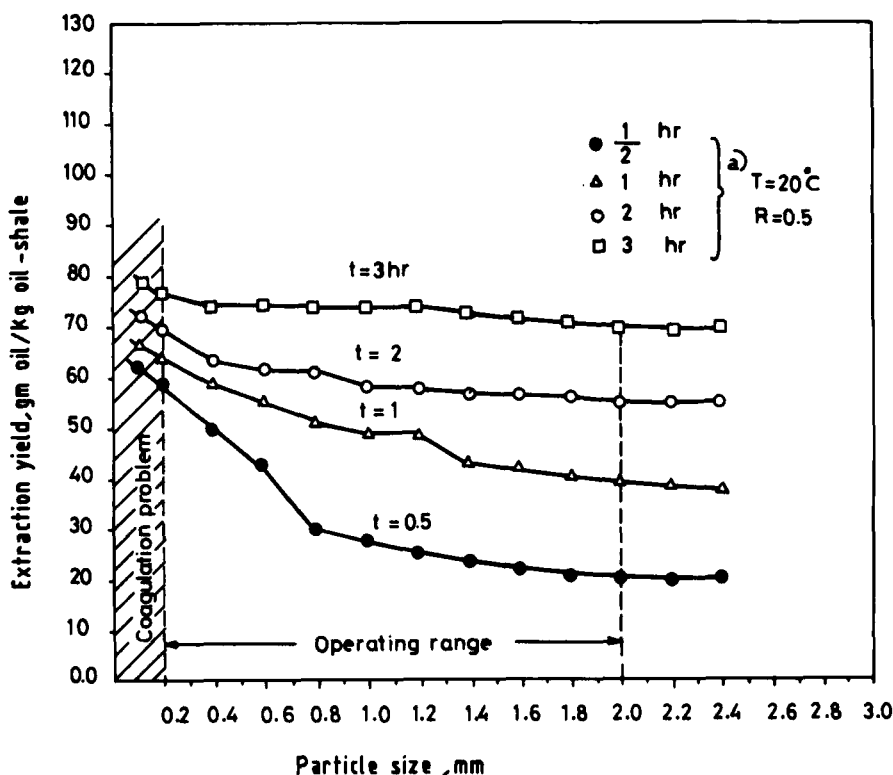

FIG. 3. Effect of particle size and time on yield at $T = 20°C$.

higher the extraction yield. Increasing the temperature decreases the adhesiveness, viscosity, and surface tension of the oil contained in the shale but increases its diffusivity; that is, increases its mobility from the shale. After a certain temperature the yield asymptotically approaches that obtained by complete devolatilization at high temperature and combustion.

This suggests that substantial extraction in a relatively short time may be observed by heating the oil shale to a temperature of 50°C. This suggestion seems reasonable since the net time required for a given degree of extraction is much less at higher temperatures. Different batches of oil shale were preheated to certain temperature, then soaked with the solvents mixture for a fixed time with agitation. The experiments were repeated at different temperatures for the same residence time. The extraction yields from these experiments are shown in Fig. 4.
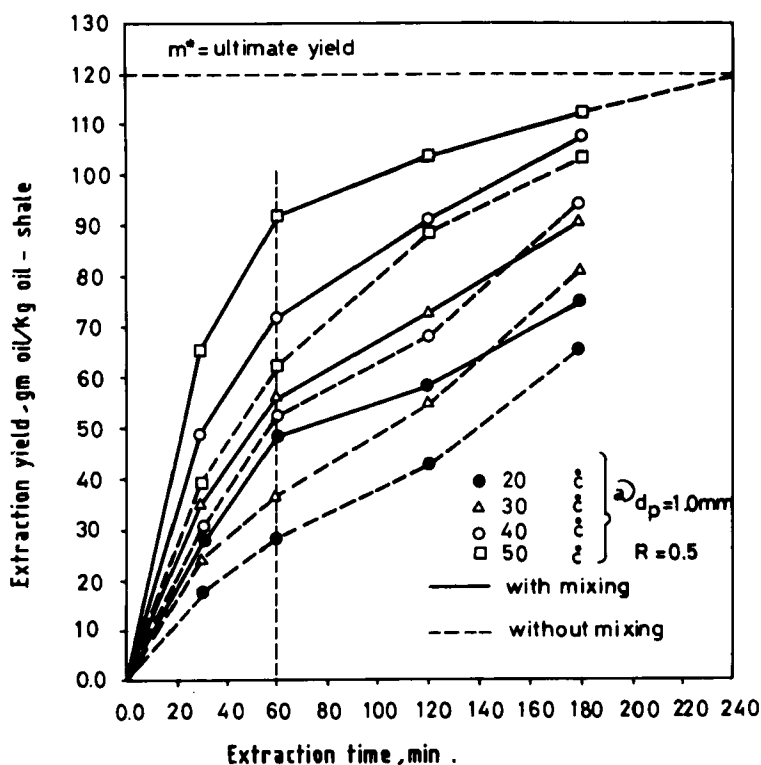

FIG. 4. Effect of extraction time and mixing on yield at various temperatures.

Higher temperatures (above 50°C) may cause fires due to the flammability of the solvents mixture. The extraction process should be carried out under a vented hood in a closed extractor. The extracted oil may also undergo thermal cracking and carbon deposition. This might reduce the extraction yield to a value less than that achievable at lower temperatures and smaller contact times. However, more work is needed to determine the asymptotic value behavior at high temperatures with various solvents.

EFFECT OF EXTRACTION TIME

The effect of extraction time on yield is much stronger for large particles ($d > 2.0$ mm) than for small particle ($d < 1.0$ mm). The extraction of particles smaller than 1.0 mm in diameter is a weak function of the residence time because most of the extractable oil is exposed to the solvent. Thus, the oil is dissolved between the solvent and the oil shale during the early stages of contact as shown in Figs. 3 and 4.

Generally, as time increases, the effect of temperature on extraction yield becomes less apparent since the extraction eventually approaches completion. Given enough time, the extraction yield versus temperature would presumably be the horizontal line approximated in practice by the yield obtained from complete devolatilization and combustion. This yield is defined as the ultimate yield, m^*, as shown in Fig. 4. The behavior of the temperature–time history reflects the fact that the amount of extraction yield occurring at a given temperature depends on the time spent at that temperature. The rate of extraction is high in the early stages of the process (i.e., the first hour) and then slows down. This is indicated by the slopes of the curves which represent the rate of dissolution and removal of oil from the shale at the experiment conditions.

EFFECT OF MIXING

Mixing increases the extraction yield due to increasing agitation and turbulence (2). This improves convection and the solubility of the oil by the solvent. The effectiveness of mixing on dissolution and extraction depends on the rate of mixing, the design of the mixer, the mode of operation, and the solvent to oil shale ratio. The net effect of mixing is presented in Fig. 4 as dashed curves. More work is needed to generate a model that can predict the effect of mixing rate on extraction yield.

EFFECT OF SOLVENT TYPE

Oil-shale extraction is considered to be a dissolution process of a solute (kerogen) into an organic solvent. The process involves contact of a liquid and a solid where a chemical-physical interaction takes place upon one or

more solute components in the solid matrix. If the force of attraction between solute molecules (kerogen) is greater than that between solvent molecules, or if solvent–solvent interactions are stronger than solute–solid interactions, there will be no incentive for the formation of solute–solvent links. Either the solute or the solvent will prefer self-association. The ease of dissolution will depend on the degree of interaction of solute and solvent species. This depends on the nature of kerogen deposits inside the shale and the type of kerogen–solid bonds (5).

Organic solvents are generally classified by the functional groups present in the molecules. Such distinctive groups give an indication of the type of physical or chemical interaction that can occur between solute and solvent, that is, the solvation capacity or solubility parameter (6). There are also other factors in selecting an organic solvent such as cost, recovery, and ease of handling and operation. In this study a solvent mixture of 75% benzene and 25% cyclohexane was found suitable under these considerations.

EFFECT OF SOLVENT TO OIL-SHALE RATIO, R

The weight of solvent used per kilogram of oil shale is denoted by R. It is a key factor in this process. The solvent quantity should be enough to impregnate all the oil-shale particles with solvent. This allows contact of the solvent with all possible accessible kerogen in the shale so as to render it soluble. This ratio was found to be 0.5 kg solvent per 1 kg oil shale. Increasing the solvent quantity beyond this limit has little effect on the extraction yield, as shown in Fig. 5.

Reducing the solvent amount below this ratio has drastic effects. Also, solvent retention reaches a fixed value, depending on the particle size, but the average value was found to be 200 g solvent per 1 kg oil shale as shown in Fig. 5.

CONCLUSIONS

The use of organic solvents to extract oil from shale deposits seems to be a potential method for technical production when it is done under the proper conditions. Solvent retention was found to be 200 g solvent per 1 kg shale. This can be recovered by heating the residue above the boiling point of the solvent, condensing the formed solvent vapors, and recycling the condensed solvent used for extraction.

Oil recovery by this method was found to be 73.3 wt% based on 12 wt% kerogen in the raw oil shale. In supercitical fluid extraction with organic solvents, the yield percent of oil extracted by toluene was found to be 19.6
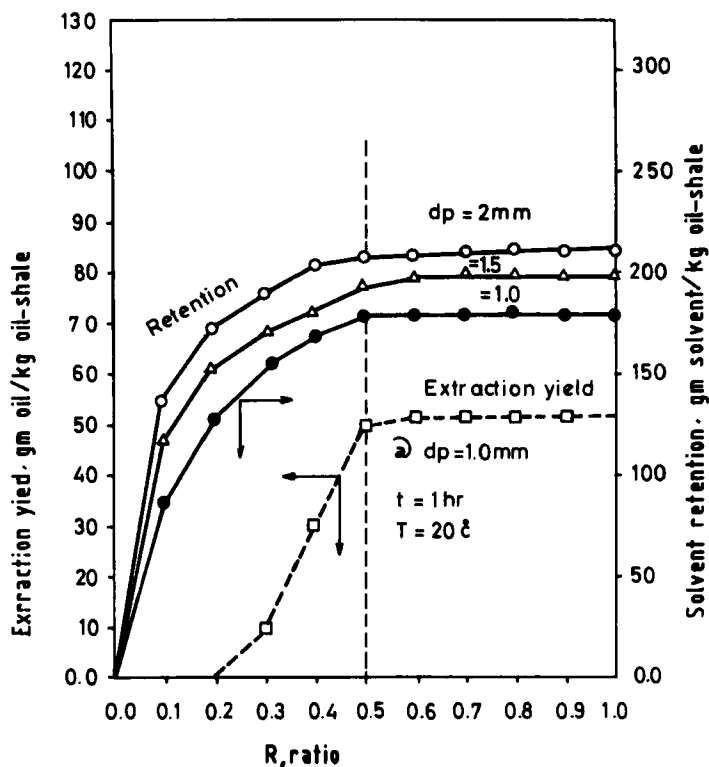
FIG. 5. Effect of solvent–oil shale, R, on extraction yield and solvent retention.

wt%. The operating conditions were 673 K, 23 MPa, 1.8 h, and 0.8 mm particle diameter (7).

Acknowledgment

REFERENCES

1. P. Schweitzer (editor-in-chief), *Handbook of Separation Techniques for Chemical Engineers*, McGraw-Hill, New York, 1979.
2. C. Geankopolis, *Mass Transfer Phenomena*, Holt, Rinehart and Winston, New York, 1972.
3. J. Coulson and J. Richardson, *Chemical Engineering*, Vol. 2, Pergamon, England, 1986.
4. T. Yoshii and F. Yoshimura, "Variation in Extraction Yields from Coal Caused by Pre-heating," *Fuel*, *49*(1), 122–133 (1970).

5. T. Yashii and F. Yoshimura, "Mechanism of Solvent Extraction from Coal and Its Chars with Chloroform," *Ibid.*, *49*(1), 133–141 (1970).
6. M. R. Dack, *Solutions and Solubilities, Part II*, Wiley-Interscience, New York, 1976.
7. T. Funazukuri, S. Yokoi, and N. Wakao, "Supercritical Fluid Extraction of Chinese Moaoming Oil-Shale with Water and Toluene," *Fuel, 67* (1988).