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Solvent and Supercritical Fluid Extraction of Oil Shale: A Literature Survey

Technical Note

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ABSTRACT

The current technology for the recovery of oil from oil shale is based on pyrolysis (retorting) at a high temperature of about 500°C. Although retorting is a relatively simple, well-studied method, it has certain limitations such as a high-energy requirement, low conversion of the organic matter to liquid, and the presence of heteroatoms and olefins in the product. In an attempt to eliminate or minimize all or some of these limitations, the Morgantown Energy Technology Center became interested in exploring alternative, nonpyrolytic methods. The literature search was undertaken to determine the state-of-the-art methodology for subpyrolytic extraction of oil shale. Most of the studies reported in the literature are based on extraction by solvents or supercritical fluids in the temperature range of 300 to 400°C under pressure. Kerogen, the insoluble organic matter in oil shale, needs to be thermally treated in order to solubilize it, and the above temperature range appears to be high enough to give satisfactory extract yields. Supercritical fluid extraction has definite separation advantages over solvent extraction for the recovery of shale oil. For the hydrogen-deficient eastern shale, the extraction needs to be carried out in the presence of hydrogen gas or a hydrogen-donor solvent. All the reported studies were conducted in laboratory-scale reactors, mostly batch-type and some semi-continuous. A complete process has not been reported, with the exception of a few patent disclosures. However, the published work does indicate that up to 90 to 95 percent of the organic matter can be recovered by these extractive methods at subpyrolytic temperatures under properly optimized conditions. There is a paucity of data for the development of an extraction process, and a suitable model is not available to predict the process performance.

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1.0 INTRODUCTION

The economic value of oil shale depends on its ability to yield oil on pyrolysis. The liquid product is normally obtained by retorting oil shale at about 500°C, but this is also accompanied by the evolution of gaseous products containing hydrogen and light hydrocarbons (C_1-C_4) and the formation of a coke-like residue. The cracking and coking reactions thus detract from the desirable liquid yield. The high-temperature retorting processes not only have a low liquid yield, but also suffer from a high energy requirement and undesirable components such as heteroatoms and olefins in the product. In an attempt to determine the merits of alternative, subpyrolytic recovery methods that may be free from these limitations, a literature search was undertaken. There are many favorable reports on the laboratory studies of the recovery of shale oil at subpyrolytic temperatures by solvent extraction and supercritical fluid extraction. This report summarizes the literature on solvent extraction and supercritical fluid extraction of oil shale at subpyrolytic temperatures.

As indicated later, it became apparent from the literature survey that any method to recover oil from oil shale would invariably include a thermal treatment step. Therefore, a brief description of oil shale kerogen, the U.S. deposits, and their thermolysis reactions is given as a preamble to the review of the literature on oil shale extraction.

1.1 Oil Shale and Kerogen Types

Oil shale is a shallow, sedimentary rock containing solid, insoluble, organic matter in a mineral matrix that yields oil in commercial amounts upon pyrolysis. The mineral matrix may vary from true shales, where clay minerals predominate, to marls and carbonates with subordinate amounts of minerals such as quartz, feldspar, and clay. Sandstone is the only lithology that is not associated with oil shales.

The organic matter in oil shale is mainly an insoluble, solid material called kerogen, which has a high molecular weight and a polymeric nature. There is no oil and little extractable bitumen naturally present in oil shale. However, when oil shale is destructively distilled (pyrolyzed) at about 500°C, a liquid hydrocarbon called shale oil with some gaseous products and a solid residue is generated. The rock is considered a potential energy source if it contains enough organic matter to give more than 10 gallons of oil per ton of rock (42 L/t).

When compared to the classification established for petroleum source rocks, oil shale kerogen is found to fall in Type I or II in the "van Krevelen diagram" (Figure 1). Type I refers to kerogen with a high hydrogen-to-carbon (H/C) atomic ratio (1.5 or higher) and a low oxygen-to-carbon (O/C) atomic ratio (usually below 0.1). Such kerogen comprises lipid materials with many aliphatic side chains and a low content of polyaromatic nuclei and hetero-atomic bonds. The small amount of oxygen occurs mainly in ester form. On pyrolysis, Type I kerogen shows higher conversion to oil (about 70 percent) than other types of kerogen.

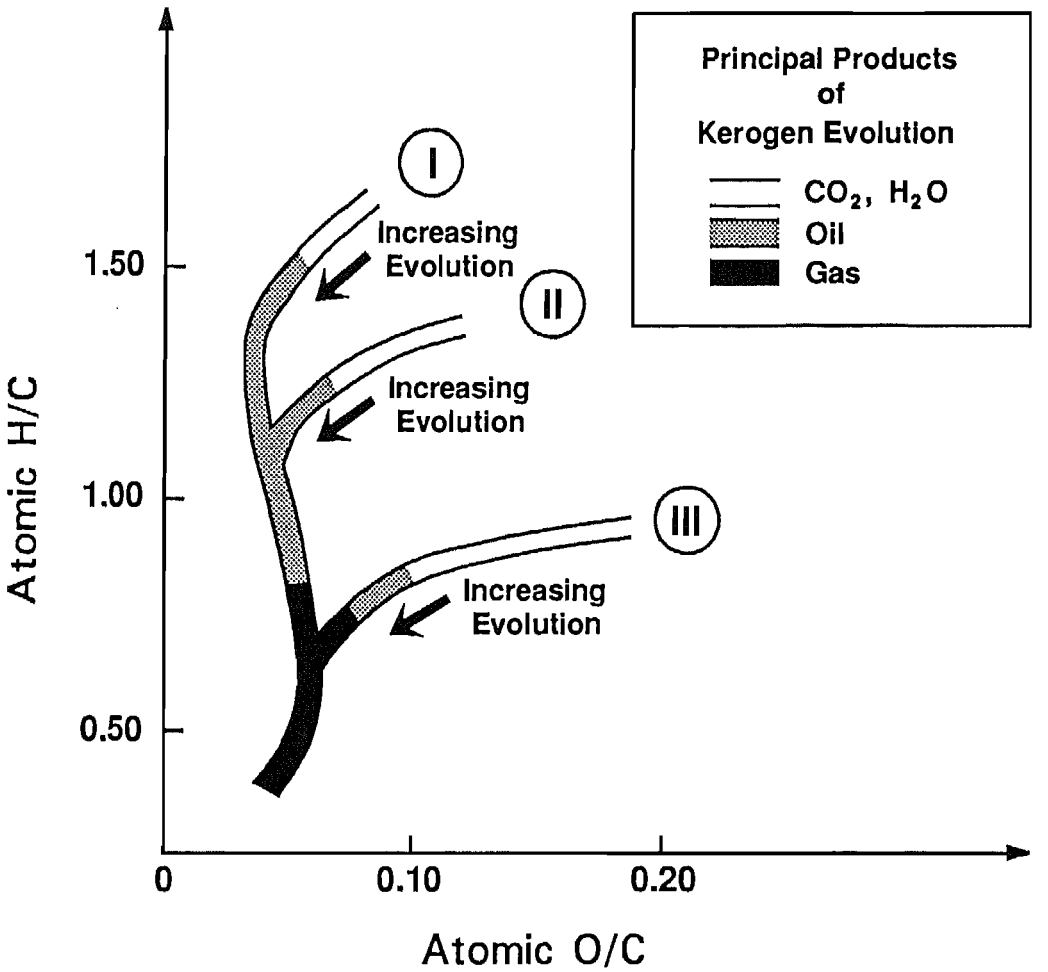


Figure 1. van Krevelen Diagram for Kerogen Types showing maturation pathways for Types I, II, and III kerogens as traced by changes in atomic H/C and O/C ratios. Adapted by Waples (1985) from Tissot et al. (1974); used with permission.

Type I kerogen is rather rare on a global scale because it is derived principally from lacustrine algae. The well-known example of Type I kerogen is the Green River formation oil shale. This enormous deposit of middle Eocene-age occurring in Colorado, Utah, and Wyoming is unique in organic-rich sediments (Smith 1983).

Type II kerogen occurs widely. This type has a hydrogen content (H/C ratio = 1.2 to 1.45) not quite as high as in Type I, and its oxygen content is slightly higher (O/C ratio = 0.10 to 0.20). The polyaromatic nuclei, heteroatomic ketone, and carboxyl groups are more common than in Type I. Ester bonds are comparable to that in Type I. In spite of increased aromatic content, there are still abundant aliphatic chains of moderate length as well as naphthenic (alicyclic) rings. Organic sulfur occurs in significant amounts as heteroatomic thiophenic rings and sulfide bonds.

Type II kerogen arises from autochthonous organic matter derived from a mixture of phyto- and zoo-plankton and microorganisms, and the lipid-rich residues of terrestrial spores and pollens. Most Type II kerogens are found in marine sediments deposited under reducing conditions. The vast deposits of Devonian-Mississippian black shales of the eastern United States represent Type II kerogens at various stages of thermal maturity. On pyrolysis, Type II kerogen shows lower conversion to oil (25 to 50 percent) than Type I.

Oil shale is not related to Type III kerogen, which is derived from higher plants and is classified as humic coal or carbonaceous shales accompanying coal. Further, on pyrolysis, Type III kerogen yields mostly gas and only a small amount of oil.

1.2 U.S. Oil Shale Deposits

The oil shale deposits of the United States are of two distinctly different types: the relatively young western oil shale deposits of tertiary Eocene age (about 40 to 55 million years ago) and the eastern oil shale deposits of Devonian-Mississippian periods (more than 300 million years ago). The two types of oil shale differ in both mineral content and organic chemical composition and, thus, require different approaches for process development. Western oil shales of the Green River formation are lacustrine deposits of marlstone, a mineral high in calcium and magnesium carbonates that has high compressive strength and tends to form large, chunky fragments when broken by explosives. The eastern oil shale deposits are of marine origin, and the mineral matrix is a true shale, high in aluminosilicate clay minerals that fractures readily along bedding planes (Morgantown Energy Technology Center 1986).

The western oil shale may contain up to 40 percent organic matter, which is made of Type I kerogen and a small amount (< 10 percent organic matter) of bitumen. The western oil shale of Green River formation is unique in organic-rich sediments. Some structural details of the kerogen have been elucidated by high resolution, solid-state nuclear magnetic resonance of carbon 13 by cross-polarization/magic angle spinning, i.e., by ^{13}C CP/MAS NMR studies (Trewella et al. 1986). These studies have revealed the following average structure:

- 18 to 20 percent aromatic carbon,
- 36 to 38 percent alicyclic carbon,
- About 26 percent carbon in long chain normal aliphatic structures,
- About 8 to 12 percent carbon linked to oxygen (e.g., esters, ethers, carboxylic acids), and
- About 5 percent carbon in methyl groups or methylene bridges bound to aromatic rings.

The eastern oil shale is leaner in organic matter and is made of Type II kerogen with less than one percent bitumen. The "richness" or "grade" of oil

shale is determined by the Fischer Assay (FA) oil yield. The FA is a standardized laboratory procedure (American Society for Testing and Materials D3904-80) based on pyrolysis of the substrate in an inert atmosphere at 500°C. The organic matter is said to be the continuous phase in rich shales (FA > 28 gal/ton) which are reported to respond well to extraction by solvent/supercritical fluid (Nowacki 1981).

For shales with a comparable organic matter, it has been observed that western oil shale yields two to three times more oil than eastern oil shale. (See Table 1.) However, retorting in a hydrogen atmosphere or in the presence of a hydrogen-donor solvent significantly improves the oil yield from eastern oil shale (Matthews and Feldkirchner 1983).

Table 1. Typical Data on U.S. Oil Shales

	Eastern	Western
Ultimate Analysis		
(Dry Basis) wt %		
Organic Carbon	13.7	13.6
Hydrogen	1.6	2.1
Sulfur	4.7	0.5
Carbon Dioxide	0.5	15.9
Fischer Assay		
Oil Yield, wt %	4.6 (~30% organic matter)	11.4 (~70% organic matter)
Assay, gal/ton	10.3	29.8
HYTORT Yields		
Oil Yield, wt %	9.1 (~59% organic matter)	Same as FA
Assay, gal/ton	23.2	Same as FA

1.3 Oil Shale Pyrolysis

The principal economic value of oil shale lies in its ability to generate oil by thermal decomposition. When heated to about 450 to 500°C, the polymeric structure of kerogen is broken down at its aliphatic and heteroatomic bonds, liberating lower molecular weight substances that are normally classified as oil and gas. The residual organic matter becomes progressively richer in aromatics with stronger bonds and, therefore, less susceptible to degradation. Graphitization of organic carbon is a thermodynamically favored process.

Miknis et al. (1982; Netzel and Miknis 1982) came to the following generalizations from an extensive study of pyrolysis (FA) and hydropyrolysis (Institute of Gas Technology HYTORT) of both western and eastern shales:

- Pyrolysis converts about two-thirds of the organic matter from western oil shale and about one-third of the organic matter from eastern oil shales to liquid products.

- Oil yield of a shale is directly related to its aliphatic carbon content. Eastern oil shales are twice as aromatic (carbon aromaticity, f^{C}_{ar}, the ratio of peak area under aromatic carbon to the total peak area under both aliphatic and aromatic carbon in ^{13}C Nuclear Magnetic Resonance (NMR) is about 0.5) as western shales ($f^{C}_{ar} \simeq 0.22$) and, therefore, yield half as much liquids on pyrolysis.

- Pyrolysis under hydrogen or a donor solvent increases the oil yield from eastern oil shales more than two-fold; western oil shales show only a slight increase (10 to 20 percent).

- The residual organic carbon is derived largely from the aromatic moieties of the starting shale, and by losing the aliphatic side chains (during pyrolysis), it can become fully aromatic ($f^{C}_{ar} \simeq 1.00$).

Nevertheless, the pyrolyzate shale oil may contain a significant amount of aromatics. This is probably derived from the scission of methylene bridges or heteroatomic bonds such as ether or ester-type linkages.

The thermal decomposition of oil shale has been studied by thermogravimetric (TGA) and other non-isothermal methods. These studies indicate two major regions of volatile release peaking near 460 and 740°C (Jeong and Kobylinski 1983). The products evolved at 350 to 500°C are a mixture of hydrogen and hydrocarbons (Campbell et al. 1980a; Campbell et al. 1980b). This temperature range is fundamentally important to oil shale processing, and the products formed may also contain heteroatoms. The high-temperature (700 to 800°C) volatiles evolution results from the decomposition and silication of carbonate minerals. Shale that contains pyrites show a shoulder at about 520°C in the differential thermogravimetric (DTG) plots. This has been ascribed to pyrite decomposition and pyrite-induced organic reaction (Jeong and Kobylinski 1983).

The majority of thermogravimetric weight loss below 200°C is believed to be caused by dehydration. However, certain carbonate minerals that decompose at low temperatures (e.g., nahcolite, $NaHCO_3$, decomposes at 90 to 200°C and dawsonite, $NaAl(OH)_2CO_3$, at 325 to 400°C) are also found to occur in certain strata of Green River formations (Campbell et al. 1980a; Cook 1970).

Hubbard and Robinson (1950) reported the thermal decomposition kinetics of Colorado oil shale samples of various richness (28, 53, and 75 gal/ton) at

350 to 525°C. By measuring the decomposition products (gas, oil, and bitumen), they were able to evaluate the rate law which was found to follow a first-order kinetics. At a given temperature, the rates were independent of oil shale richness. From the temperature dependence of rate constants, the following values for the parameters of the Arrhenius equation were calculated:

- $A = 1 \times 10^{13}\ min^{-1}$.
- $\Delta E = 192$ kJ/mol.

The product distribution curves appeared to suggest bitumen as the intermediate in converting kerogen to oil and gas.

The kinetics of oil shale pyrolysis has been studied rather widely, mainly from the standpoint of retorting process development (Nuttall et al. 1983; Shen et al. 1984; Hershkowitz et al. 1983; Campbell et al. 1978; Ekstrom and Callaghan 1987). The global kinetics of kerogen decomposition to oil appears to follow a first-order rate, and a three-parameter model proposed by Anthony and Howard (1976) provides a better fit for non-isothermal TGA data (Campbell et al. 1980b; Nuttall et al. 1983) than the two-parameter Arrhenius equation. Since the kerogen is a heterogeneous substance, its decomposition may involve a number of parallel reactions. Anthony and Howard's model assumes a Gaussian distribution of activation energies for the parallel reactions that may be occurring. Thus, an average activation energy and its associated standard deviation are the two parameters in this model. The frequency factor or the pre-exponential term of the Arrhenius equation is the third parameter.

Nuttall et al. (1983) studied the pyrolysis kinetics of oil shale samples from many formations in eight different countries. The pyrolysis rates among those diverse samples varied within a factor of 25. The three kinetic parameters varied as follows:

- $\Delta E = 98$ to 165 kJ/mol,
- $\sigma_{\Delta E} = 8.0$ to 18.3 kJ/mol, and
- $Z = 5.9 \times 10^{5}$ to 3.1×10^{10} 1/min.

However, other researchers reported higher values for activation energies and frequency factors (Campbell et al. 1978; Ekstrom and Callaghan 1987). The kinetic parameters were also found to depend on the heating rate; both parameters increase with decreasing rate of heating (Shadle 1988b).

Some approximate pyrolysis rates for a Utah oil shale sample are given in the following table.

Table 2. Pyrolysis Rates for a Utah Oil Shale

Temperature (°C)	Rate Constant, k (min^{-1})	Half Time, $t_{1/2}$ (min)
253	0.0003	2,166
300	0.0023	301
350	0.0130	53
400	0.06	11.5
425	0.106	6.6
500	0.9	0.77

1.4 Pyrolysis Mechanism

Although plenty of kinetics modeling work is reported in the literature, the mechanism of kerogen fragmentation has not been clearly established. However, the consensus among the researchers favors a two-step mechanism as given below (Campbell et al. 1978; Ekstrom and Callaghan 1987):

$$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} \xrightarrow{k_2} \text{Oil} + \text{Gas} + \text{Coke} \ .$$

When Campbell et al. (1980a) performed a mass spectrometric analysis of the gas stream evolved in a retorting experiment, they observed very little hydrogen and hydrocarbons (C_1-C_3) emission before oil evolution. They concluded that only traces of these gases are released during kerogen-to-bitumen reaction. It is also generally agreed that bitumen formation takes place at lower temperatures than that needed for oil generation. The rate of oil formation reaches a maximum at about 440°C, but it is also accompanied by a high rate of hydrogen and light hydrocarbon gas evolution.

From a slow heating-rate thermogravimetric analysis of oil shale, Allred (1966) observed that the critical temperature for complete pyrolysis of oil shale is about 475°C. He calculated that the heat of pyrolysis for the conversion of bitumen to volatile hydrocarbons is about 46 kJ/mol and an additional 39 kJ/ mol is required to vaporize the liberated hydrocarbons. Thus, a total of 85 kJ/mol is required to separate shale oil from the mineral matrix by pyrolysis. He also concluded that at temperatures below about 480°C, the conversion of kerogen to bitumen is rapid compared to bitumen conversion to oil. The enthalpy change for converting kerogen to bitumen in tetralin was determined indirectly by other researchers (Schnackenberg and Prien 1953) to be about 20 kJ/mol.

Miknis et al. (1987a; 1987b) conducted isothermal pyrolysis studies in the temperature range of 375 to 440°C on two oil shales from Colorado and Kentucky. From an analysis of evolved gas, oil, and bitumen, they concluded that the amount of extractable bitumen is inversely proportional to the [illegible]on aromaticity of the kerogen, and, for a given kerogen, it increases with [illegible]perature. The time dependence of bitumen yield shows a maximum that agr[illegible] with the suggested mechanism involving bitumen as an intermediate. The [illegible]mum bitumen yield was about 14 percent of the organic matter for the Kent[illegible]ky New Albany shale and about 58 percent for the Colorado oil shale. When added to the oil yield, these numbers give the total soluble yields of 38 and 95 percent, which are higher than the Fischer Assay values of 33 and 69 percent, respectively, for the two oil shales. The 95 percent conversion for Colorado oil shale occurs after 20 minutes of pyrolysis at 425°C. Prolonged heating at this temperature reduces the yield to less than 80 percent of the organic matter, probably because of the onset of coking.

The bitumen intermediate (also referred to as pyrobitumen) has recently been characterized (Chong et al. 1989). It is a highly polar material of variable composition: Its number average molecular weight (1,200-400) and H/C atomic ratio (1.7-1.2) decrease with temperature and time of pyrolysis, and the nitrogen content at each temperature increases to a maximum and then decreases with time to less than 10 percent of its value in the original kerogen.

The mechanism of oil shale decomposition has also been investigated at the Department of Energy's Morgantown Energy Technology Center under high heating rate conditions in a Xenon flash lamp reactor (Shadle et al. 1988a, 1988b). Flash lamp pyrolysis features extremely rapid rates of heating and quenching (on the order of 10^5 to 10^6 K/s). By applying a radiant energy pulse of a few milliseconds duration, the peak shale temperature is raised to above 1,000°C, which causes 80 percent or better conversion in less than 10 ms. Gases are a large portion of the flash products. The liquids are basically pyrobitumen with some differences. They are of high molecular weight ($\bar{M}_w$ = 700 - 1,000), containing a large amount of polars and a significant amount of polycyclic aromatic hydrocarbons. Heteroatomic functions that are eliminated under slow heating conditions are retained in the flash pyrolysis liquids.

Flash pyrolysis fragments macromolecular kerogen structure in a rather nonselective manner. The fragments undergo hydrogen rearrangements forming polycyclic aromatics. The mechanisms thus appears to be more complex than and different from that involved in slower heating pyrolysis.

2.0 RECOVERING OIL FROM SHALE

2.1 Retorting

Retorting is the simplest and most widely studied process for recovering oil from oil shale. This destructive distillation is normally carried out at a temperature of 480 to 510°C. At this temperature, the rate of kerogen pyrolysis is fast and complete decomposition occurs in minutes. However, cracking and coking also occur at this high temperature, leading to gas and solid formation that detracts from high oil yields. High-temperature retorting requires high energy cost and also has the additional limitation of generating olefins in the liquid. Since cracking and coking reactions do not become significant at temperatures below 410°C, recovery methods operating at lower temperatures will have not only lower energy requirements, but also better yield of oil with lower olefins content.

2.2 Low-Temperature Recovery

The low-temperature extraction of oil shale can be traced back to bitumen solubilization studies reported in the 1920's. The World War I boom period (1915 to 1930) for oil shale development saw the establishment of the Naval Oil Shale Reserve in Colorado and Utah and the involvement of the U.S. Bureau of Mines in oil shale research and development (Morgantown Energy Technology Center 1986). Although retorting was the principal method of interest (and it still is), several reports on solvent extraction were published during this period (Gavin and Aydelotte 1922; McKinney 1924). Using common solvents for petroleum such as benzene, acetone, chloroform, alcohol, carbon disulfide, carbon tetrachloride, etc., it was observed that a maximum of 7 to 12 percent organic matter of a Colorado oil shale (Gavin and Aydelotte 1922) and about 6 to 10 percent organic matter of a New Brunswick oil shale (McKinney 1924) could be extracted by solvents under reflux conditions. This low yield by Soxhlet extraction indicates that only the naturally occurring, soluble organic matter called bitumen is recovered by the solvent extraction of oil shale at or below reflux temperatures.

A natural extension of this finding was to determine the solvent extractability of oil shale at elevated but subretorting temperatures (< 400°C) under autogenous or exogenous pressure. Engler (1912) suggested that oil shale organic matter contained a material he referred to as "pyrobitumen," which was insoluble under normal conditions, but rendered soluble when heated to about 200°C. The enhanced solubility of oil shale kerogen in common organic solvents in the moderate temperature range of 200 to 400°C, referred to as "thermal solutions," was the subject of several patents in the 1920's (Ryan 1920; Day 1922; Hampton 1928; Ryan 1928; Hampton 1929). These patents described methods and apparatus for extracting oil shale by using shale oil and paraffin oil as solvents in the temperature range of 290 to 370°C.

The earliest American thermal-solution patents (Ryan 1920; Ryan 1928) were obtained by Ryan, who described a method of heating finely ground Green River oil shale by a heavy shale oil fraction at a temperature high enough

(315 to 370°C) to convert the kerogen to soluble material, but not so high as to volatilize too much of the solvent. Ryan's process was found to be inoperable at 400°C because of excessive vaporization and cracking of the solvent.

Day (1922) described a similar process, whereby oil shale crushed to -2 mesh (about 9 mm diameter) was digested in crude shale oil at 290 to 370°C under about 70 psi pressure for best results. Day claimed beneficial cracking of the shale oil during the treatment.

Hampton's patents (1928; 1929) described a process similar to Ryan's. However, Hampton used a heavy, paraffin-based oil and a kerosene fraction under pressure, and introduced steam, hydrogen, and inert gases.

The oil shale boom during World War I ended with the new discoveries of oil in California, Texas, and Oklahoma in the late 1920's. There was little interest in oil shale from 1930 to 1944 (Morgantown Energy Technology Center 1986). However, modest research activity was in progress overseas. Dulhunty (1942) described the extraction of Glen Davis (Australia) torbanite with benzene at 340 to 360°C with an extract yield of about 90 percent. At the elevated temperature, a molecular rearrangement was thought to be responsible for the increased solubility. Aromatic solvents were found to be more effective than aliphatic solvents. It was also observed that the organic matter was extractable by its own oily conversion product at 350 to 450°C.

In the 1940's, there were several Russian publications on the "thermal solution" of oil shale (D'yakova 1944a; D'yakova 1944b). Using about 1:1 ratio of shale (low sulfur, 48 percent organic matter) to solvent such as anthracene oil, fuel oil, diesel, primary shale-tar, and its hydrogenation products and distillates, gas oil, or tetralin, D'yakova observed 85 to 90 percent organic matter converted to liquid products in 10 to 30 minutes at 380 to 430°C under 20 to 40 atmospheres pressure. In the thermal solution process, 35 to 40 percent organic matter was made into gasoline-range products, and another 35 to 40 percent was converted into kerosene and heavy residue. The heavy residue could be hydrogenated to gasoline, or it could be used as asphalt for road construction. D'yakova also described a pilot plant handling 30 kg/h of the shale. Particle size of 0.3 to 5 mm was found to be satisfactory. Using a shale oil fraction (boiling range: 220 to 370°C) at equal weight ratio with shale, a 92 percent conversion was observed when the shale was processed for 20 minutes at 425 to 430°C under 470 to 500 psi pressure.

The post-war boom (1944 to 1968) started with the passage of the Synthetic Liquid Fuels Act of 1944. Serious efforts by both government and industry for oil-shale retorting development became noticeable (Morgantown Energy Technology Center 1986). However, reports on extraction were rather sporadic. Buchan (1949) described a semi-continuous process in which large lumps (+ ½ inch) of shale were treated with a hydrocarbon oil at 375 to 425°C for 2½ hours. A 60 percent conversion to liquid product was reported. Hubbard and Robinson (1950) reported a 50 percent conversion of a Colorado oil shale to benzene extractable at 350°C in 24 hours under a helium atmosphere. A significant process-development work based on thermal solution of Green

River oil shale was reported by Jensen et al. (1953). The investigators conducted extraction experiments in batch autoclaves, semi-continuous, and continuous bench-scale units in the temperature range of 380 to 460°C using shale oil, petroleum kerosene, anthracene oil, and quinoline as solvents. In the batch process, the conversion of organic matter to products (liquid and gas) reached a maximum of about 80 to 90 percent at 420 to 425°C in 1 hour. Although quinoline showed the highest yield, the shale-oil gas oil fraction was used in most of the flow experiments. In semi-continuous extraction for 3 hours, higher maximum yields (up to 95 percent) were observed at somewhat lower temperatures of 400 to 410°C. Although the reported yields were high, a significant portion of the product was gas, most of which was believed to have formed from solvent cracking. Solvent cracking was more conspicuous with the shale-oil gas oil fraction than with any other solvent.

Semi-continuous experimentation was very convenient and gave reproducible results. The investigators also studied the effect of particle size and shale grades on process efficiency and found that, for richer shales (FA > 20 gal/ton), extractability by thermal solution was independent of particle size below about a 2-inch diameter.

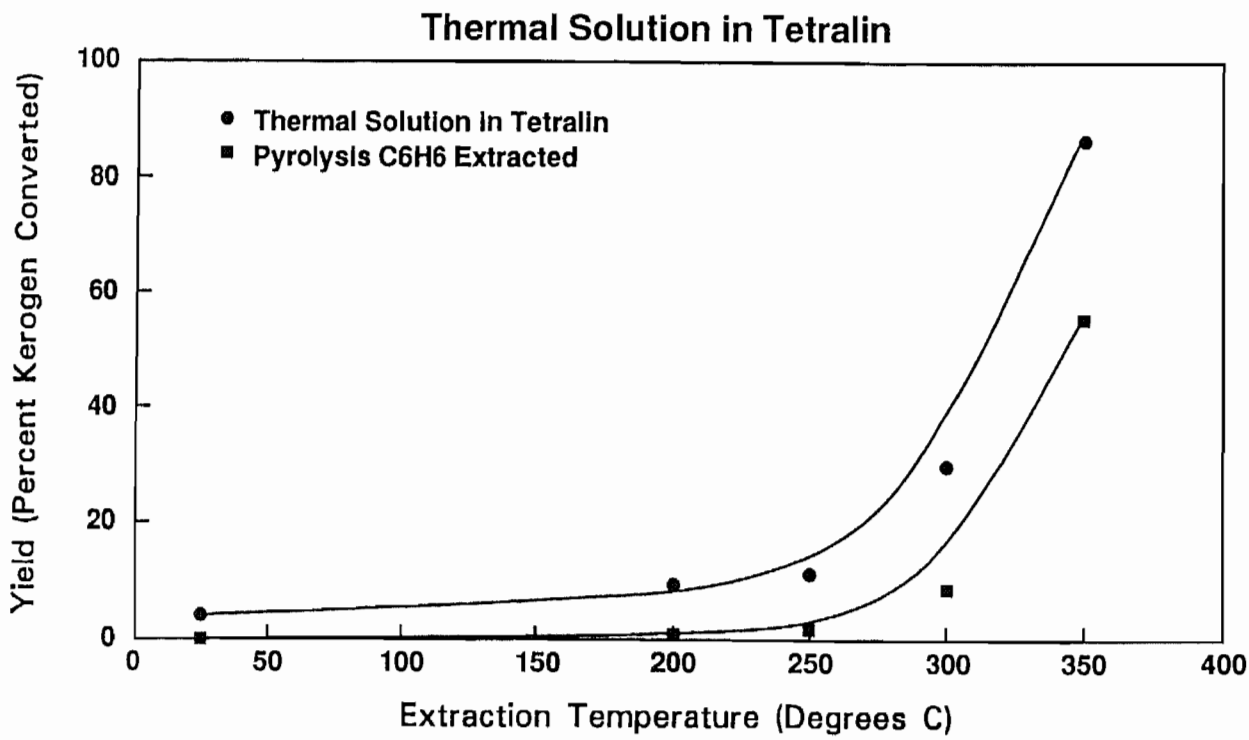
On the other hand, continuous extractions were conducted by using a slurry of finely-ground (-65 mesh) shale (FA = 27 gal/ton) in shale-oil gas oil at 400 to 450°C under 300 psi pressure. Although a high yield of 85 percent (gas and liquid) was observed in 10 minutes at 450°C and in 26 minutes at 430°C, severe cracking and coking of solvent was also noticed. To prevent coking and to improve the liquid product quality, thermal solution in hydrogen was also studied in the batch autoclave. Hydrogen pressure up to 500 psi was found to have no significant beneficial effect; catalytic or high-pressure hydrogenation was projected to be too costly.

The investigators also looked into the separation of solvent and product oil from the spent shale by flashing, steaming or heating, and filtration. Of these three methods, the filtration procedure was reported to offer the best possibility. After weighing merits and demerits of the thermal solution process, the authors concluded that it was not to be considered a practical shale-oil production process at that stage of technological development.

Schnackenberg and Prien (1953) studied the "thermal solution" of a 35-gal/ton Green River oil shale at 200°C in a dozen different solvents under autogenous pressure. The oil shale was finely ground to -30 mesh, and the substrate-to-solvent volume ratio was 1:5. The total run time under an inert atmosphere was 30 minutes, in addition to a 75-minute heating period to 200°C. Under such a mild condition and a short run time, the yield was low, 5 to 36 percent of FA values. In most of the solvents, namely water, methanol, acetone, dimethylsulfolane, phenol, benzene, cyclohexene, cyclohexane, and n-hexane, the oil yield was found to increase linearly with the molar volume of the solvent. However, in donor solvents such as tetralin and decalin, the yield was more than twice the value predicted from the above relationship. When plotted against the molecular weights of the solvents, the yield data showed an exponential increase of yield with molecular weight. Most of the oxygenates had low molecular weights and showed low yield; all the C_6 compounds, including phenol, had higher molecular weights and showed higher

yields that clustered around the cyclohexane value. The two H-donor solvents with the highest molecular weight showed the highest yields.

The high solubilizing power of tetralin on the thermal solution process of Green River oil shale kerogen led Robinson and Cummins (1960) to study oil shale extraction with tetralin at 25 to 350°C for 24 to 144 hours. When 2.3 ml of tetralin per g of shale was used, the amount of kerogen extracted in 48 hours varied from 4.4 percent at 25°C to 28.7 percent at 300°C and 84.9 percent at 350°C (Figure 2). At a constant temperature of 350°C, the yield was found to increase from 75.8 percent after 24 hours to 94.5 percent after 144 hours of extraction. From these and related data, the researchers speculated that a change in the mechanism of thermal solution process occurs at about 275°C. Since the principal focus of this study was to elucidate the kerogen structure, it revealed a wealth of information on the nature of extracts.



35% Organic Matter, 28.5% Organic Carbon, 66 Gal/Ton, 48 Hours

M90000639

Figure 2. Thermolysis of a Western Oil Shale

The 48-hour extracts obtained at various temperatures had fairly high average molecular weights (500 to 600 atomic mass units (amu)). These were considered bitumen that contained many of the original kerogen structures. At 350°C, the molecular weights of the extracts decreased from 625 to 400 when the extraction time was increased from 24 hours to 144 hours. The extracts could be resolved further into a number of fractions: asphaltene (molecular

weight (m.w.) 1,200 to 1,300), resins (m.w. 570 to 650), wax (m.w. 400 to 480), and oil (m.w. 340 to 375). At 350°C, the asphaltene content was found to decrease with time, whereas the other fractions increased. The oil fractions were further analyzed for paraffin, naphthene, aromatic, and polar contents, and it was observed that higher temperatures favored the aromatic and polar contents. Most of the heteroatoms were concentrated in asphaltene and resin fractions at all temperatures. From these findings the authors concluded that the Colorado oil shale kerogen is predominantly a heterocyclic material connected to or associated with smaller amounts of hydrocarbon materials consisting of straight- and branched-chain paraffin, cyclic paraffin, and aromatic groups.

In a long-term, low-temperature study, Cummins et al. (1972; 1974) determined the kinetics of the thermal decomposition of a benzene-extracted, 65-gal/ton Colorado oil shale in the temperature range of 150 to 350°C. The calculated Arrhenius parameters were:

- $A = 339\ min^{-1}$.
- $\Delta E = 79$ kJ/mol.

The products of low-temperature thermolysis were essentially bitumen and oil, the yields of which increased with time and temperature.

Tyler and coworkers (Kafesjian 1983; Leavitt 1987; Leavitt et al. 1987; Tyler et al. 1988) at the University of Utah conducted significant research into the thermal solution process using Utah oil shales and a Sunbury oil shale from Kentucky. For the Green River oil shale (Kafesjian 1983), temperatures from 275 to 380°C were used in isothermal extraction with cyclohexane and tetralin. The temperature range of 300 to 425°C was selected for the 5-hour extraction of Sunbury oil shale with methylcyclohexane, toluene, and tetralin (Leavitt 1987). The test conditions were such that tetralin extractions were subcritical solvent extractions and the rest were supercritical fluid extractions.

The yields of Green River oil shale in cyclohexane showed a broad maximum of about 90 percent conversion at 350 to 375°C. The decrease in the yield at higher temperatures is attributable to coking (radicals recombining to insoluble species). The yield in tetralin is lower than that in cyclohexane at low temperatures. However, it increases almost linearly with temperature and reaches a value of 92 percent at 382°C. Tetralin is a good hydrogen donor, and by scavenging radicals it inhibits the coking reaction (Tyler et al. 1988).

This difference in the temperature dependence of the yield can be explained in terms of physicochemical properties of the two solvents. Cyclohexane, being a supercritical fluid, possesses low viscosity and high diffusivity and enhances the solubility of low volatile solutes through favorable mass transport. On the other hand, tetralin has limited extracting power in the subcritical state, and its beneficial hydrogen donor effect is not realized until the temperature approaches 400°C.

An Arrhenius type of rate equation fits the yield data nicely. From a simulated distillation analysis (ASTM D2887-73), the authors observed that the boiling range of all extracts decreases with increasing extraction temperature, and the tetralin extracts boil at higher temperatures and show a narrower boiling range than cyclohexane extracts. From the extract characterization, Tyler et al. concluded that solvent extraction seems to be a "gentler" process in that fewer bonds are ruptured than supercritical fluid extraction, which is, in turn, gentler than pyrolysis (Kafesjian 1983).

From the extraction studies of a 21 gal/ton Green River oil shale with supercritical toluene at 330 to 450°C for 4 hours, Compton (1983) reached similar conclusions. Using a constant density of 0.53 g/cm^3 for the supercritical toluene, he observed an increase in the product yield from 34 percent at 330°C to 80 percent at 385°C, 88 percent at 393°C, and 92 percent at 450°C. The extracts at 450°C were shale oil with average molecular weight of about 300, but the lower temperature extracts had higher molecular weights.

The supercritical extraction of Colorado oil shale in a continuous flow experiment has been studied in a laboratory scale, fixed-bed reactor at the University of California at Davis (Estevez 1983; Triday 1987). In these experiments, 10 g of a 28 gal/ton oil shale placed in a 300 ml reactor were extracted at 370 to 400°C and 500 to 900 psi pressure by flowing 3.8 L toluene at 20 mL/ min. The effluent, after being depressurized and cooled to ambient conditions, was monitored by spectrophotometry at 400 nm. The higher temperature extracts (400°C or higher) showed a change in absorption pattern with time, and the spent oil shale was found to contain char deposits. At lower temperatures, the absorption spectrum of isothermal runs remained fairly unchanged. This indicated that the extracts' composition remained constant during supercritical fluid extraction of Green River oil shale at subpyrolytic temperatures. Beer-Lambert's law was applied to quantitate the extract yield, which was about 65 percent for 2.5 hours extraction at 377°C. The yield data were fitted in an extraction model with three adjustable parameters: activation energy, pre-exponential term, and the diffusivity of bitumen in toluene at its critical point. The calculated activation energy was much lower than the pyrolysis values, and this was interpreted as the ease with which kerogen is converted to the intermediate bitumen. However, no further supportive data were given regarding the nature of the extract.

In a recent patent (Pao et al. 1988), researchers at Duo-Ex Corporation have described a method and apparatus for extracting Green River oil shale with supercritical toluene at 400°C, 1,200 psi pressure, and up to 2 hours residence time. The patent also describes solvent recovery, product separation and upgrading, and solids-separation steps.

McKay and coworkers (McKay et al. 1983; McKay and Chong 1983; McKay and Blanche 1986a; McKay and Blanche 1986b; Chong and McKay 1987) at Western Research Institute have conducted significant research in the area of solvent and supercritical fluid extraction of both western and eastern oil shales. Most of these batch-type extractions were conducted at 400°C and under pressure up to 5,000 psi. Supercritical water, methanol, and mixtures were found to recover about 90 percent of the organic matter from Green River oil shale, although methanol was incorporated into the product as ester. The liquid

extracts have a high H/C atomic ratio of about 1.6 and a number average molecular weight of 500 to 800, which is more than twice as large as the amu of the shale-oil pyrolyzate. A group at the University of Oklahoma could not duplicate this high oil yield with water-methanal mixture (Ellington and Baugh 1987). However, by using ammonia in place of methanol (actually NH_4OH), this group obtained 90 percent yield in an hour of extraction at 390°C and 4,750 psi pressure.

Cummins et al. (1976; Chong et al. 1976; Cummins et al. 1978; Cummins et al. 1980) also studied thermal conversion of Green River oil shale in carbon monoxide and steam at 300 to 450°C under a pressure of 200 to 6,000 psi. The intent of these studies was to use the conducive effects of molecular or nascent hydrogen generated as a result of water-gas shift reaction:

$$CO + H_2O \rightleftarrows H_2 + CO_2.$$

The conversion of kerogen to liquid and gaseous products increased with temperature as expected: 30 percent at 350°C, 50 percent at 375°C, 78 percent at 400°C, and almost 98 percent at 450°C, with most of the conversions occurring in 1 hour or less. Increasing the CO pressure above a certain minimum, e.g., 200 psi, reduced the yield of the liquids. At lower pressure and higher temperature (greater than 400°C), the liquid product contained a volatile oil fraction.

The liquid product can be fractionated into polars (acids, bases, and neutral nitrogen compounds) and nonpolars (n-alkanes, branched and cyclic alkanes, and aromatics). At higher temperatures (greater than 375°C), the relative amount of acid fraction decreases and hydrocarbon and base increases. Increasing extraction temperature also lowered the molecular weight of the extracts.

In water alone (supercritical in most cases), comparable total yields of liquids and gases were observed. However, the evolution of large amounts of gases (three to nine times the amount with CO and steam) at all temperatures, and the appearance of carbon residue at the highest temperature used (450°C) bear an indirect evidence that, in CO and steam, some hydrogen is added to the products formed, minimizing gas and coke formation.

Although the laboratory results of the high-pressure CO and steam process were encouraging, subsequent cost analysis of a simulated commercial process showed them to be uneconomical. High-pressure operation and insufficient gas production for CO makeup were cited as the major factors raising the cost of oil (Parkinson and Merson 1982).

Kesavan and coworkers (1988) reported the supercritical fluid extraction of a Stuart oil shale sample from Australia with carbon dioxide. Although the product yield was disappointingly low at lower temperatures, they obtained 85 percent or higher conversion at 400 to 500°C under about 2,000 psi pressure in 1- to 2-hour extractions. The liquid products had a wider boiling-point distribution, mostly at the heavier end, than that of the product obtained by

retorting in nitrogen or subcritical carbon dioxide. Analysis of the extract by gas chromatography/mass spectrometry (GC/MS) indicated the presence of C_{12} to C_{35} compounds, mostly hydrocarbons but some with oxygen and some with nitrogen functionality.

2.3 Extraction of Eastern Oil Shales

The Eastern oil shales are relatively hydrogen-deficient and contain more ring structures than the Green River oil shale. Leavitt et al. (1987) reported much lower oil yields for the solvent and supercritical fluid extraction of a Sunbury oil shale. In supercritical fluid extraction the maximum yields were 49 percent in toluene and 58 percent in methylcyclohexane at 375 to 400°C. These values, although much lower than Green River oil shale yields, compare favorably with FA oil yield of only 27 percent. In tetralin, the yields were lower than supercritical fluid extraction values at temperatures below 350°C. At higher temperatures, the yield increased significantly and leveled off at a value of about 80 percent at 400°C.

McKay and Chong (McKay and Chong 1983a; McKay and Chong 1983b) also studied the extraction of eastern oil shale at 400°C and pressures up to 5,000 psi. By using binary mixtures of water with methanol, toluene, octanol, and tetralin, they observed an increase in oil yield from 25 to 92 percent for 1 hour extraction of Chattanooga oil shale. The ancillary effect of tetralin on the liquid product yield has also been demonstrated with other samples of eastern oil shale. The number-average molecular weight of the liquid products is 500 to 700, which is much higher than that of retorted shale oil.

The importance of hydrogen donors in the solvent conversion of eastern oil shales was also studied at Gulf (Cronauer et al. 1983; Cronauer and Solash 1985). Using a Cleveland member of Ohio shale and tetralin as the hydrogen donor, these researchers observed a 60 percent conversion to toluene solubles at 400°C after 30 minutes. They also reported that a sizeable portion of tetralin was lost due to adduction with residue, isomerization to methylindan, and cracking-type reaction leading to alkylbenzenes.

From a similar study on the hydroliquefaction of eastern oil shales, Das and Hamrin (1982) also observed the beneficial effects of donor solvents like tetralin and 1,2,3,4-tetrahydroquinoline. By conducting hydroliquefaction of Sunbury and Cleveland oil shales in a "tube-bomb" reactor under unspecified pressure at 395°C and a shale-to-solvent weight ratio of 1:2, they observed the maximum conversion of two-thirds organic matter in 30 to 50 minutes in tetralin (cf. FA = 38 percent); tetrahydroquinoline showed even better yields. For the Cleveland oil shale in tetralin, a cobalt molybdate catalyst was shown to increase the yield by about 50 percent.

Since significant progress has been made in the production of syncrude by the HYTORT (Schora et al. 1982) process (which is based on retorting at 480 to 600°C in a countercurrent flow of hydrogen gas under 250 to 500 psi pressure), the effect of hydrogen treatment on the supercritical fluid extraction of a Kentucky oil shale has also been studied. At 375 to 410°C and a hydrogen pressure of 1,200 to 2,000 psi, the hydrogen pretreatment followed by

supercritical fluid extraction with n-heptane gave an 84-percent increase in extract yield over supercritical fluid extraction alone (Scinta and Ewert 1983). The following extract yields were reported for this example: FA = 13.2 gal/ton, supercritical fluid extraction = 15.0 gal/ton, and H_2/supercritical fluid extraction = 27.6 gal/ton.

The beneficial effect of hydropyrolysis of a Kentucky oil shale in supercritical toluene has been studied at the Colorado School of Mines (Baldwin et al. 1983; Baldwin and Manley 1988). These experiments, which were conducted at 380 to 460°C under 2,200 to 3,000 psi pressure, showed that carbon conversions and oil yields in excess of 185 percent FA values can be obtained at a short residence time by the proper selection of final temperature, heating rate, and hydrogen pressure. Low hydrogen pressures were found to be adequate for supercritical fluid extraction in toluene. The reported observation that hydrogen consumption was the same in both donor and non-donor solvents needs further clarification.

Triad Research, Inc., a subsidiary of Addington, Inc., of Ashland, Kentucky, reported the development of a liquid donor-solvent process for the extraction of oil from eastern oil shales (Addington et al. 1984; Greene and Damukaitus 1985). The technique is similar to the Exxon Donor Solvent process for coal liquefaction and involves the cyclic use of a hydrogen-transfer solvent. This is a process-derived fraction, which boils in the middle distillate or gas-oil range and transfers hydrogen noncatalytically to the oil shale kerogen. The spent solvent is separated, catalytically hydrotreated, and recycled. The process, called the Hydrogenation-Extraction process, operates at 400 and 450°C under 220 to 295 psi and produces high-quality oil with yields more than twice the FA. The composition of the solvent and its reactions and regeneration conditions are proprietary. Based on the promising results of bench-scale tests and on technological and economic evaluation, Triad Research has undertaken the construction of a pilot plant facility.

Cha and coworkers (1988) have recently described a thermal solution method known as the recycle oil pyrolysis and extraction (ROPE) process, which recovers oil from eastern oil shale. The process involves three principal steps: pyrolysis in the presence of recycled product oil at temperatures less than 400°C, pyrolysis of the residue at temperatures greater than 400°C, and combustion of the solid residue and pyrolysis gas to generate process heat. The process has been developed in 2-inch diameter and 6-inch diameter screw reactors. The oil yields approached or exceeded FA and the product was high quality. The light fraction (boiling point less than 177°C) could be used as recycled oil or for producing gasoline and heavy product oil (boiling point 177 to 371°C) as a feedstock for benzene-toluene-xylene (BXT) or high-density fuels.

3.0 SUMMARY

- Only bitumen, the small amount of soluble organic matter in oil shale, is extractable at ambient conditions. Kerogen, the insoluble organic matter in oil shale, needs to be thermally treated in order to solubilize it or make it extractable by supercritical fluids.

- Recovery of shale oil at subpyrolytic temperatures can be accomplished by solvent extraction or supercritical fluid extraction.

- As measured by the liquid product yield, the rate of solubilization increases with temperature. In the temperature range of 300 to 400°C, the thermolysis appears to be fast enough to give appreciable yield in a reasonable time (hours to minutes).

- Most of the studies reported in the literature were conducted in batch-type reactors at about 400°C under pressure (up to 5,000 psi). Coking becomes significant at higher temperatures and longer reaction time.

- Supercritical fluid extraction of Green River oil shale at 370 to 400°C with cyclohexane, toluene, aqueous ammonia, water alcohol, etc., shows a 90 percent conversion of organic matter to liquid products (Fischer Assay = 60 to 70 percent). The yield decreases at higher temperatures.

- Solvent extraction of Green River oil shale with a donor solvent (tetralin) gives lower yields at lower temperatures, but the yields approach or exceed supercritical fluid extraction values at temperatures over 380°C. A mixture of carbon monoxide and water has also been tried as a donor solvent and proved somewhat successful.

- For eastern oil shales, solvent extraction or supercritical fluid extraction improves the yield by about 50 percent over FA, but significant improvement (more than twice the Fischer Assay yield) is observed only in a donor solvent or in hydrogen.

- Solvent extraction/supercritical fluid extraction of eastern oil shale with a mixture of water, methanol, or toluene with a hydrogen donor (tetralin) appears to be the method of choice, although a sizeable portion of tetralin will be lost.

- Process severity on liquid products as determined by molecular weight or simulated distillation is in the order:

  Pyrolysis > Supercritical Fluid Extraction > Solvent Extraction .

  The product of pyrolysis is oil with an average molecular weight of about 300 and that of solvent extraction is bitumen with an average molecular weight of about 700.

- Particles as large as a few centimeters in size appear to respond well to solvent extraction. The particle size effect gets less stringent in supercritical fluid extraction because of favorable transport properties of supercritical fluids.

4.0 ADVANTAGES AND DISADVANTAGES

The literature survey indicates that solvent and supercritical fluid extraction of oil shale may have a number of advantages over the conventional recovery methods based on pyrolysis:

- Operations at lower temperatures (380°C versus 500°C) and in the presence of a fluid will give a more energy-efficient process.

- The yield of the liquid product is much higher, e.g., 90 percent conversion as opposed to 60 to 70 percent in Fischer Assay (FA) for western oil shales and 50 to 60 percent versus 30 percent in FA for eastern oil shales.

- Lower temperature products obtained in the presence of a fluid may be better quality. The oil may contain less olefins and heteroatoms. Supercritical fluid extraction extracts are reported to have higher H/C ratio. However, the product characteristics may depend on the nature of the extracting fluid.

- The solvent extraction/supercritical fluid extraction process works better with richer shales. Beneficiation and extraction steps may be designed to be complementary. Research has not been reported in this area.

- In solvent extraction, utilizing a process-derived fraction appears to be the economic solution for solvent selection, but the concept is still at the developmental stage.

- Solid-liquid separation has been a problem in oil shale processing. As the organic matter is extracted, the shale matrix is deconsolidated eventually to silt-size particles (2 to 20 μm in diameter). In a supercritical fluid, these particles readily separate. Therefore, solid fluid separation will be most efficient in supercritical fluid extraction.

- "Destraction" (a coined antonym for extraction) by pressure letdown may prove to be an efficient method for the recovery of supercritical fluid from the product stream.

- In supercritical fluid extraction, the extraction and separation steps are expected to be faster and more efficient than in solvent extraction. Further, the selectivity of extraction by supercritical fluids can be controlled by regulating the pressure.

When compared with retorting, the following disadvantages of solvent extraction/supercritical fluid extraction of oil shale will become apparent:

- The use of a solvent or supercritical fluid incurs additional chemical and processing costs. Solvent recovery, purification, recycling, and compression needed for supercritical fluid extraction will add to the process complexity.

- Longer residence time at lower temperature and higher pressure for supercritical fluid extraction may adversely affect the process economics.

- The product of solvent extraction/supercritical fluid extraction will have a higher molecular weight (and also a higher H/C ratio) than pyrolyzate and may well be a heavy crude or bitumen. However, it may be advantageous to upgrade the heavy crude in a downstream step.

- The effect of fluid loss due to adsorption on shale matrix can be tremendous.

From a technological standpoint, the advantages of solvent extraction/supercritical fluid extraction appear to outweigh their disadvantages. Moreover, the disadvantages mentioned above are only estimates and may not be as severe as they sound when quantitatively evaluated. A systems analysis may provide the necessary answer. However, from a separation standpoint, supercritical fluid extraction appears to be more advantageous than other processes.

5.0 RECOMMENDATIONS

For the development of an oil shale recovery process based on supercritical fluid extraction, the following R&D activities need to be focused:

- Determine the feasibility of continuous and semi-continuous extraction and set up a laboratory-scale supercritical fluid extraction system to screen new fluids and generate data necessary for process development.

- Conduct continuous or at least semi-continuous extraction experiments. Using various types and grades of oil shales, optimize process parameters such as temperature, time or flow rate, pressure, solvent power, substrate/solvent ratio, particle size, etc.

- Determine yield and characterize products as a function of time. These data will be used for the evaluation of rate parameters and optimization of the extraction process for a specific product type.

- Determine how the attendant physical changes such as swelling and deconsolidation of shale affect the process performance.

- Design and develop equipment for carrying out continuous or semi-continuous extraction, solid-supercritical fluid separation, and supercritical fluid recovery from the product stream by "destraction."

- Develop predictive models for the oil-shale extraction processes. In addition to an Arrhenius-type equation, which is commonly used in oil-shale extraction, the model should also incorporate the concepts of solvent strength and transition enthalpy, diffusion, phase behavior, and other fluid properties as predicted by a suitable equation of state.

- Investigate new catalysts for upgrading to a specific product type.

- Establish a data base on the recovery of oil shale and coordinate Government and industry efforts in the development of a supercritical fluid extraction-based pilot or process development unit.

- Investigate new solvent systems that have shown promise in other industries.

- Conduct systems analysis to guide researchers as to the significance of parameters such as pressure, yield, hydrogen requirement/cost, solvent loss/cost, etc.

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