

# OIL SHALE

## 1. Introduction

Oil shale is a sedimentary mineral that contains kerogen, a mixture of complex, high molecular weight organic polymers. The solid kerogen is a three-dimensional polymer that is insoluble in conventional organic solvents. Upon heating, kerogen decomposes to form gas composed of hydrogen (qv), low molecular weight hydrocarbons (qv), and carbon monoxide (qv); liquids, composed of water and shale oil; and a solid char residue.

Oil shale deposits were formed in ancient lakes and seas by the slow deposition of organic and inorganic remains. The geology and composition of the inorganic minerals and organic kerogen components of oil shale vary with deposit locations throughout the world (1) (see also FUEL RESOURCES; PETROLEUM).

## 2. Reserves

Estimates of oil shale deposits by continent are given in Table 1 (2). Characteristics of many of the world's best known oil shales are summarized in Table 2 (3,4). Oil shale deposits in the United States occur over a wide area (Table 3). The most extensive deposits, covering ca 647,000 km<sup>2</sup> (250,000 mi<sup>2</sup>), are the Devonian-Mississippian shales of the eastern United States (5). The richest U.S. oil shales are in the Green River formation of Colorado, Utah, and Wyoming. Typical mineral and organic analyses for Green River oil shale are given in Table 4.

The Green River formation includes an area of ca 42,720 km<sup>2</sup> (16,500 mi<sup>2</sup>), and in-place reserves are ca  $(0.5 - 1.1) \times 10^{12}$  m<sup>3</sup>  $((3 - 7) \times 10^{12}$  bbl) of which ca 80% are federally owned. The richest portion (85% of the reserve) of the Green River formation is in the Piceance Basin of Colorado. The deposits in Utah and Wyoming contain 10% and 5% of the reserves, respectively (6).

The Parachute Creek member contains the majority of the oil shale in the Piceance Creek Basin and is ca 580 m thick at the depositional center of the basin. The members of the Green River formation and the thickness of the various zones are indicated in Figure 1. Organic and saline mineral contents increase toward the depositional center of the basin. The rich Mahogany zone extends across the Piceance Basin and into the Uinta Basin in eastern Utah. In addition to its high contents of organic matter, the Parachute Creek member contains large reserves of nahcolite[15752-47-3], NaHCO<sub>3</sub>, and dawsonite [12011-76-6], NaAl(OH)<sub>2</sub>CO<sub>3</sub>, which are present in the deepest parts of the basin (see ALKALI AND CHLORINE PRODUCTS, SODIUM CARBONATE).

## 3. Analytical and Test Methods

Sample preparation for the modified Fischer assay technique, a standard method to determine the liquid yields from pyrolysis of oil shale, is necessary to achieve reproducible results. A 100-g sample of >230 μm (65 mesh) of oil shale is heated in a Fischer assay retort through a prescribed temperature range, eg,

ca 25.5–500°C, for 50 min and then soaked for 20 min. The organic liquid which is collected is the Fischer assay yield (7). The Fischer assay is not an absolute method, but a qualitative assessment of the oil that may be produced from a given sample of oil shale (8). Retorting yields of greater than 100% of Fischer assay are possible.

A total material balance assay is a Fischer assay in which the retort gases are collected. A complete material balance closure and yields in excess of those expected from Fischer assay results are achieved. More complete descriptions of both the Fischer assay and the Tosco material balance assay methods have been reported (9).

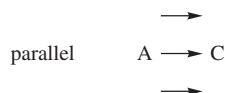
## 4. General Properties

**4.1. Kerogen Decomposition.** The thermal decomposition of oil shale, ie, pyrolysis or retorting, yields liquid, gaseous, and solid products. The amounts of oil, gas, and coke which ultimately are formed depend on the heating rate of the oil shale and the temperature–time history of the liberated oil. There is little effect of shale richness on these relative product yields under fixed pyrolysis conditions, as is shown in Table 5 (10).

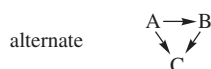
Numerous kinetic mechanisms have been proposed for oil shale pyrolysis reactions (11–14). It has been generally accepted that the kinetics of the oil shale pyrolysis could be represented by a simple first-order reaction (kerogen  $\rightarrow$  bitumen  $\rightarrow$  oil), or



This sequential first-order reaction adequately describes the kinetics of pyrolysis of the Green River oil shale in western United States. Additional kinetic studies (15,16) indicate that sequential reactions are inadequate to describe the kinetic reactions for the thermal decomposition of oil shales worldwide. First, there is no well-defined chemical induction time as predicted by first-order reactions. Secondly, kerogen decomposition is a complex array of thermal reactions involving a variety of organic materials, water, and gases, such as CO and CO<sub>2</sub>, as well as hetero-atom reactions involving nitrogen, sulfur, and oxygen. It is impossible to define the process using simple individual reactions. The kinetic reactions can best be described using a global approach that encompasses the sequential first-order reaction (eq. 1) as well as



and



**4.2. Temperature and Product Yields.** Most oil shale retorting processes are carried out at ca 480°C to maximize liquid product yield. The effect of increasing retort temperature on product type from 480 to 870°C has been studied using an entrained bed retort (17). The oil yield decreased and the retort gas increased with increased retorting temperature; the oil became more aromatic as temperature increased, and maximum yields of olefinic gases occurred at about 760°C. Effects of retorting temperatures on a distillate fraction (to 300°C) are given in Table 6.

**4.3. Carbonate Decomposition.** The carbonate content of Green River oil shale is high (see Table 4). In addition, the northern portion of the Piceance Creek basin contains significant quantities of the carbonate minerals nahcolite and dawsonite. The decomposition of these minerals is endothermic and occurs at ca 600–750°C for dolomite, 600–900°C for calcite, 350–400°C for dawsonite, and 100–120°C for nahcolite. Kinetics of these reactions have been studied (19). Carbon dioxide, a product of decomposition, dilutes the off-gases produced from retorting processes at the above decomposition temperatures.

## 5. Retorting

Oil shales are solid minerals, impervious to the flow of fluids, and are generally situated in deposits below the earth's surface. Therefore, several process steps must be undertaken to produce crude shale oil. In the case of the commonly used above-ground retorting (AGR), these steps involve mining, crushing, and heating (see MINERALS RECOVERY AND PROCESSING). The grade (volume of oil per weight of rock) of most oil shales is low (see Table 2), and large amounts of the oil shale rock must be processed to produce crude shale oil. Depending on the grade, 2 to 25 metric tons of oil shale must be processed to produce one cubic meter of crude shale oil (0.4–4.6 short tons per barrel of crude shale oil). In order to eliminate the costs of mining and material handling, direct underground retorting (*in situ* retorting) has been considered as an alternative to the conventional AGR.

Historically, direct combustion has been employed in which some of the organic matter of the kerogen is combusted to provide the heat necessary for retorting. Although these direct heat (DH) processes do not require a supplemental source of fuel, some of the kerogen is consumed and the gaseous products of the kerogen decomposition are diluted with the products of combustion. In order to obviate these shortcomings, indirect heat (IH) processes were developed in which the heat required for retorting was supplied by hot gases or solids that were heated externally. However, the IH processes do not utilize any of the solid residual carbon or char resulting from kerogen decomposition and they do require an external source of fuel.

There are numerous means of classifying the many processes that have been employed to retort oil shale. In addition to the types of retorting, the retorting process can be classified by the type of feed used and by the flows within the retort. Types of oil shale feed can be classified as coarse, >5 mm (>0.25 in.) or fine, <65 mm (<0.25 in.). The flows within the retort can be classified as concurrent, ie, all materials flowing in the same direction, or countercurrent, ie, the

solid oil shale flowing in one direction, the air and gases in the opposite direction. The coarse feed systems usually result in the disposal of the raw shale fines as waste. The fine feed systems obviate the latter problem but result in increased crushing costs and greater environmental impacts from particulate emissions during the material handling operations. A list of most of the oil shale retorting processes in use worldwide since the 1940s is provided in Table 7.

Retorting processes consist of several well-defined steps, or zones, within the retort, as shown in Figure 2 for the batch-process Nevada-Texas-Utah (NTU) retort, the forerunner of most of the technologies listed in Table 7. For DH systems the zones are the oil shale preheating or off-gas oil-mist cooling zone; the pyrolysis zone, where the solid organic kerogen is converted into gases, oil mists and vapors, and residual carbon; the combustion zone, where carbon is burned to provide heat; and the shale cooling zone, where the retorted shale is cooled and the incoming air is preheated.

**5.1. Above-Ground Retorting.** AGR processes can be grouped into DH or IH processes. Numerous design configurations as well as a variety of heat-transport mediums have been used in the indirect heated processes (Table 7).

**5.2. Gas Combustion Retort.** The continuous gas combustion retort (GCR) has been modeled after the earlier batch-operation NTU retort. Although the term "gas combustion" has been applied to this process, it is a misnomer in that, in a well-designed and properly operated system, the residual char on the retorted shale supplies much of the fuel for this process. The GCR is the forerunner of most continuous AGR processes (Table 7).

**PETROSIX.** The PETROSIX technology is operated in the IH mode using hot recycle gas as the heat-transport medium. The PETROSIX retort has only one level of heat input, uses countercurrent flows, and uses a circular grate to control the flow of solids (Fig. 3). The PETROSIX has been operated by Petrobras (Brazil) since the 1950s and is one of the few retorting processes producing shale oil in 1995.

**Paraho.** The Paraho retorting technology is similar to the PETROSIX technology except that it can be operated in the direct heat (DH) mode. The unique feature of the Paraho technology is the two levels of heat input (Fig. 4). In the IH mode, the air blower shown in Figure 4 is replaced by a recycle gas heater. The Paraho DH operation has been carried out near Rifle, Colorado since the 1970s; operations to produce asphalt (qv) from shale oil are continuing.

**Tosco II.** The Tosco II retorting technology, developed by The Oil Shale Corporation, represents IH technology employing concurrent flow using fine-sized feedstock. It was tested in Colorado from the late 1950s until the early 1980s. The unique feature of the Tosco II process is the use of ceramic balls as the heat-transport medium (Fig. 5). These 125-mm (0.5-in.) balls, larger than the finely crushed shale feed, are separated from the retorted shale, recycled, reheated, and reused in the process.

**UNISHALE B.** The UNISHALE process, like the Paraho process, uses lump feed and countercurrent flows, and can be operated in either the DH or IH mode. The UNISHALE B process is an IH process that uses hot recycled gas as the heat-transport medium (Fig. 6). The unique feature of the UNISHALE processes is the rock pump. The solids move upward through the retort as the vapors are moving downward. The rock pump was used in the UNISHALE

technology at Parachute, Colorado to produce more than  $0.64 \times 10^6 \text{ m}^3$  (four million barrels) of crude shale oil. Operations were shut down in 1991.

**Lurgi.** The Lurgi process, developed by Lurgi-Ruhrgas GmbH for mild gasification of coal, has been tested as an oil shale retort. The Lurgi process is similar to the Tosco II process in that it uses finely divided oil shale as a feedstock and employs indirect heating and concurrent flows. The unique feature of the Lurgi process is the use of hot combusted retorted shale as the heat-transport medium (Fig. 7) and retorting is carried out by mixing the hot combusted shale and raw oil shale in a screw conveyor. Because a portion of the retorted shale is combusted to supply the process heat, the Lurgi process utilizes more of the organic matter in the oil shale than other IH processes (see Table 7).

**Superior.** The Superior retort is different from all the other AGR processes in that it consists of a slowly rotating circular grate instead of the vertical shafts, rotating drums, or screw conveyors used by other technologies (Fig. 8). The Superior technology is an adaptation of the circular grate system used to calcine limestone (see LIME AND LIMESTONE). Raw oil shale is loaded onto the rotating circular grate which transports the solids through the same zones as shown in Figure 2: solids preheat, retorting, char combustion, shale cooling, and air preheating. Because the gas composition varies within each of these zones, each zone is separated by a baffle screen as the solids are transported around the circle. The Superior retort was tested in Colorado in the late 1970s.

**5.3. In Situ Retorting.** True *in situ* retorting has been considered as a means of avoiding the costs of mining, crushing, and surface disposal of spent shale, and the associated environmental impacts of AGR. However, the impervious nature of the oil shale formation and the overburden pressures have prevented true *in situ* operations. Shale oil yields, the amount of oil produced divided by the theoretical amount estimated to be in the oil shale rock, for *in situ* retorting are usually half that experienced with AGR retorting. A true *in situ* experiment, using drilling and resource fracturing procedures typical of conventional petroleum development, was tried by the Energy Research Development Administration (a forerunner of the U.S. Department of Energy) in 1975 in Rock Springs, Wyoming. No significant yields of shale oil were produced (22). Other true *in situ* tests were conducted using the Equity BX superheated steam process in Colorado, and Dow hot air process in Michigan; neither produced significant yields of oil shale. It appears that true *in situ* retorting is not a practical approach for the thick strata of oil shale normally situated deep below the surface.

**LOFRECO.** The LOFRECO process, developed by Geokinetics, Inc. (Utah) is a true *in situ* process. It is limited to relatively thin deposits of oil shale situated beneath a relatively thin overburden (Fig. 9). The LOFRECO process has been successful because the oil shale is rubblized in place by raising the overburden. Retorting consists of direct combustion horizontally through the rubblized formation, similar to that shown for the NTU retort (see Fig. 2). Although the costs of mining and materials handling are obviated, the LOFRECO process causes significant surface disturbance and results in oil yields significantly lower than those obtained in the better controlled AGR processes.

**VMIS.** The Vertical Modified *in situ* (VMIS) process consists of constructing an underground retort of rubblized oil shale within the deep, thick deposits situated in the Piceance Basin in western Colorado. In order to provide space for the rubblization without upheaval of the overburden, a portion of the oil shale is mined out and taken to the surface (Fig. 10). Retorting is carried out in the DH mode exactly as shown in Figure 2. Steam and air are pumped into the top of the VMIS retort, combustion proceeds down through the rubblized bed, and oil and gas are pumped out from the bottom. Although yields are significantly lower than those attained by AGR processes, the VMIS has demonstrated that modified *in situ* can produce shale oil from thick deposits situated deep below the surface. These operations have resulted in approximately one-fifth of the oil shale being mined out to provide space for the VMIS rubblizing and retorting. A project involving both VMIS and AGR processing, to utilize the mined-out shale, had been planned, but was canceled in 1991 (24).

## 6. Crude Shale Oil

**6.1. Properties.** The composition of shale oil has depended on the shale from which it was obtained as well as on the retorting method by which it was produced. Properties of shale oils from various locations are given in Table 8. A comparison of a Green River shale oil and a Michigan Antrim shale oil, retorted under similar conditions, is given in Table 9.

Shale oil contains large quantities of olefinic hydrocarbons (see Table 8), which cause gumming and constitute an increased hydrogen requirement for upgrading. Properties for crude shale oil are compared with petroleum crude in Table 10. High pour points prevent pipeline transportation of the crude shale oil (see PIPELINES). Arsenic and iron can cause catalyst poisoning.

The primary difference in shale oils produced by different processing methods is in boiling point distribution. Rate of heating, as well as temperature level and duration of product exposure to high temperature, affect product type and yield (28). Gas combustion processes tend to yield slightly heavier liquid products because of combustion of the lighter, ie, naphtha, fractions.

Carbon-to-hydrogen weight ratios for typical hydrocarbon fuels are natural gas (methane), 3; gasoline, 6; crude oil, 6–7; shale oil, 7–8; Green River kerogen, 7; diesel and fuel oil, 8; residual oil, 10; and coal and coke, 12. A typical Green River shale oil contains 40 wt% hydrocarbons and 60 wt% organic compounds which contain nitrogen, sulfur, and oxygen. The nitrogen occurs in ring compounds such as pyridines and pyrroles, as well as in nitriles, and these materials comprise 60 wt% of the nonhydrocarbon organic components. Another 10 wt% of these components is comprised of sulfur compounds which exist as thiophenes and some sulfides and disulfides. The remaining 30 wt% is oxygen compounds occurring as phenols and carboxylic acids (1).

**6.2. Upgrading Shale Oil.** Crude shale oil has a high (~2 wt%) content of organic nitrogen which acts as a catalyst poison, contains a large (20–50 wt%) atmospheric residuum fraction, and has a high (>5°C) pour point (29,30). Prerrefining crude shale oil to produce a synthetic crude that is compatible with typical refineries generally is necessary (31–33). Prerrefining to reduce

organic nitrogen content to low levels consists usually of either a delayed coking step of the crude shale oil or residuum fraction, followed by one or more hydrogenation steps, or a more severe direct hydrogenation of the crude shale oil. Conditions for the hydrogenations are ca 400°C, 13.8 MPa (2000 psi) hydrogen partial pressure, and up to 356 standard cubic meters of hydrogen uptake per cubic meter of shale oil (2000 ft<sup>3</sup> at STP/bbl) (34). The nitrogen and sulfur are converted to ammonia and elemental sulfur, and the hydrogen content of the oil is increased. Upgraded shale oil is a desirable refinery feedstock. It is paraffinic and characterized by low residuum, nitrogen, and sulfur (see FEEDSTOCKS).

Shale oil has been refined to produce gasoline, kerosene, jet fuel, and diesel fuel (33). Different procedures have been tested to produce different product states, eg, hydrotreating followed by hydrocracking for jet fuel production, hydrotreating followed by fluid catalytic cracking for gasoline production, and coking followed by hydrotreating for diesel fuel production. Production of military fuels from the refining of 1590 m<sup>3</sup> (10,000 bbl) of Paraho crude shale oil at the Gary Western refinery in Colorado has been reported (35) and 15,900 m<sup>3</sup> (100,000 bbl) of Paraho shale oil has been processed under a U.S. Navy contract, at Sohio's Toledo refinery (33).

At the Parachute Creek Project, Unocal designed and operated an oil shale upgrading unit to prerefine crude shale oil into syncrude, ie, upgraded shale oil (36). The unit was designed to handle 1600 m<sup>3</sup> (10,000 bbl) of crude shale oil per stream day. More than 650,000 m<sup>3</sup> (four million barrels) of syncrude were produced. Results of the Unocal shale oil upgrading process are given in Table 11. The syncrude is compared with Arabian light crude oil in Table 12. Although Arabian light is considered a premium crude oil among petroleum refiners, the Unocal shale oil syncrude shows improvements in each of the characteristics listed. Production of the conventional fuels and lubricants using Unocal shale oil syncrude as the refinery feedstock is less difficult and less costly than using Arabian light crude oil (see LUBRICATION AND LUBRICANTS).

## 7. Alternative Uses

Oil shale is an energy resource that produces a liquid fuel that can be used to replace conventional crude oil or petroleum. However, the costs associated with processing oil shale into conventional refined products are significantly greater than that of processing conventional crude oil. In order to develop the oil shale resource, other uses have been considered. These functions include direct combustion to produce process heat for power generation (qv), direct gasification of the oil shale geological deposit, and special petrochemical production.

**7.1. Direct Combustion.** Direct combustion of oil shale has been used to produce heat for power generation at specific sites and is being carried out in Estonia and Israel.

In Estonia, most of the rich oil shale, 209 L/t kukersite, is burned as a solid fuel to produce electric power (37). The kukersite, although technically an oil shale, is actually similar to a high ash, low grade coal (qv) ideally suited for this use.

In the remote Negev desert region of Israel, oil shale is being burned in a fluidized-bed combustor to supply process heat and produce electric power. Unlike the Estonian kukersite, this oil shale is lean, about 63 L/t, but is being mined to access an underlying phosphate deposit (26).

**7.2. Gasification.** For significant conversion of shale oil or oil shale to gaseous products, considerable hydrogen must be used. Hydrogasification is the main process under consideration for gasification of oil shale. Hydroretorting of oil shale has been studied extensively (38,39). Gasification of Colorado oil shale in hydrogen and synthesis gas has been carried out at 524–760°C and at up to 38.3 MPa (5540 psig). Another study involves conventional oil shale retorting followed by gasification of the resulting shale oil in a fluidized bed (40). The hydrogen is supplied by gasification of the coke on the spent shale and from the gasifier. Other hydrogasification work includes the processing of Green River and eastern Devonian oil shales (41,42). Because of their character, the eastern Devonian shales produce less product oil, ca 35 wt% Fischer assay, than do Green River shales. The hydrogasification process is claimed to recover about 90 wt% of the kerogen content. Additional oil shale gasification research at the Laramie Energy Technology Center (U.S. DOE) has been reported (43–45).

**7.3. Petrochemicals Production. Early Consideration.** In the 1950s, the U.S. Bureau of Mines studied pyrolysis of both oil shale and shale oil for the production of light olefins. High temperature retorts were used to determine the effect of continuing the cracking, which is begun when the kerogen is converted to shale oil (46). Low temperature shale oils are low in aromatic content, thus one goal has been the production of an aromatic-rich naphtha. High temperature retorting of this type on Green River oil shales has the disadvantage of the additional energy requirements of the endothermic carbonate decomposition, with over 50 wt% decomposition occurring at 815°C. This effect has little importance for low carbonate oil shale, eg, the eastern U.S. Antrim oil shales (41). Comparison of thermal cracking of conventional shale oil to high temperature retorting under the same conditions illustrates that naphtha production is enhanced considerably by high temperature retorting (46).

Utilization of shale oil products for petrochemical production has been studied (47–51). The effects of prerefining on product yields for steam pyrolysis of shale oil feed and the suitability of Green River shale oil as a petrochemical feedstock were investigated. Pyrolysis was carried out on the whole oil, vacuum distillate, and mildly, moderately, and severely hydrogenated vacuum distillates.

**Specialty Chemicals.** Specialty chemicals have been considered an economically attractive means of using the oil shale resource. These specialty chemicals consist of high value, niche market items (52) that utilize the high concentration of heteroatoms (nitrogen, sulfur, and oxygen) found in most crude shale oils (see Table 8). The use of shale oil with its complex, high molecular weight, low pour point resid materials, and high concentration of various functional groups could be used to produce waxes, aromatic lubricating oils, sulfonate feeds, substitutes for coal-tar acids and bases, resins, and special organic intermediates (53). Revenue that may be achieved from shale oil would be greatly enhanced if used in their production.

**Shale Oil Asphalt.** The New Paraho Corporation has been producing asphalt (qv) made from crude shale oil (54,55). This shale oil asphalt, SOMAT,



represents a specialty product that utilizes many of the properties of crude shale oil that would reduce its value as a refinery feedstock, ie, low pour point, high boiling point, and large quantities of heteroatoms and organic functional groups, especially basic nitrogen groups. These properties reduce the value of crude shale oil as a refinery feedstock, but tend to produce an improved asphalt. SOMAT is superior to conventional petroleum asphalt (AC-10) in terms of tensile strength retained after freeze–thaw cycles (Table 13).

Shale oil asphalt also meets or exceeds the performance of the improved, but more costly, polymer-based asphalt. Since 1989, more than 8 km (5 mi) of test strips of SOMAT have been placed on various roadways in seven U.S. states. The SOMAT has demonstrated marked improvement over conventional petroleum-based asphalt. These assessments are continuing. As of this writing (ca 1995), Paraho is preparing preliminary designs for an oil shale facility to produce about 325 m<sup>3</sup>/d (2000 bbl/d) of the shale oil modifier used to produce SOMAT (56).

## 8. Environmental Issues

The plans to develop a commercial oil shale industry in the three-state region of Colorado, Utah, and Wyoming in the 1970s raised the possibility of significant adverse environmental, health, safety, and socioeconomic (EHSS) impacts. Processing oil shale to produce oil on a large-scale commercial basis requires a large amount of mining, crushing, material transport, and disposal operations.

Adverse EHHS impact could result from uncontrolled, or inadequately controlled, large-scale oil shale operations. Without controls, significant amounts of dust, ie, particulates, would be produced. Because the gas produced from kerogen breakdown contains significant amounts of hydrogen sulfide and ammonia, uncontrolled release, or direct combustion with no control technology, could pose adverse health impacts and air pollution. The liquids produced from retorting operations, ie, process water and crude shale oil, contain significant levels of toxic metals, suspected or known carcinogens, and other hazardous materials. Discharge of this water would thus require treatment. Combusting and/or refining the crude shale oil would also require adequate treatment and environmental controls. The large quantities of materials involved in oil shale development means that disposal of the retorted shale poses special problems. Proper controls are needed to avoid significant air pollution from dust emissions, and surface and groundwater contamination from leaching and runoff. The amount of water required for commercial oil shale operations poses water quality impact on the semiarid region of Colorado, Wyoming, and Utah. Engineering technology was thus developed for oil shale operations. Most predictions of significantly adverse EHHS impacts (Table 14) were based on assumptions from earlier foreign operations and impacts from similar industries (57–61), and were not realized during the 1975–1990 oil shale boom.

**8.1. Air Pollution.** Particulates and sulfur dioxide emissions from commercial oil shale operations would require proper control technology. Compliance monitoring carried out at the Unocal Parachute Creek Project for respirable particulates, oxides of nitrogen, and sulfur dioxide from 1986 to 1990 indicate

a +99% reduction in sulfur emissions at the retort and shale oil upgrading facilities. No violations for unauthorized air emissions were issued by the U.S. Environmental Protection Agency during this time (62).

**8.2. Water Quality.** All commercial oil shale operations require substantial quantities of water. All product water is treated for use and operations are permitted as zero-discharge facilities. In the Unocal operation, no accidental releases of surface water have occurred during the last four years of sustained operations from 1986 to 1990. The Unocal Parachute Creek Project compliance monitoring program of ground water, surface water, and process water streams have indicated no adverse water quality impacts and no violations of the Colorado Department of Health standards (62).

**8.3. Solids.** Proper handling and disposal techniques can obviate potential problems associated with the solid waste-retorted shale. Retorted shale disposal and revegetation have posed no adverse environmental impacts at the Unocal Parachute Project (62). Earlier studies carried out using Paraho and Lurgi retorted shales indicated that these materials behave as low grade cements (63,64) and can be engineered and compacted into high density materials (Fig. 11) and water impervious structures (Table 15).

**8.4. Health and Safety.** Much of the adverse health issue publicity involving risks of exposures to carcinogens, such as benzo- $\alpha$ -pyrene, have been based on recorded exposures of Scottish oil shale workers that took place nearly 100 years ago. It is believed that the increase in cancer was due more to poor personal hygiene than exposure to shale oil. Industrial hygiene monitoring and health surveys indicate no significantly increased health risks among oil shale workers (62).

**8.5. Socioeconomics.** Impact from recurring boom-and-bust cycles typified many of the earlier mining developments in the western United States (65). However, this and the Oil Shale Trust Fund, established by the legislation that set up the Federal prototype leases (C-a, C-b, U-a, and U-b), has provided funds to local towns and counties to assist in the construction and upgrading of infrastructures. These infrastructures are needed to accommodate the work force needed to construct and operate the large oil shale processing facilities. Further, companies such as Unocal have provided socioeconomic grants to these counties (66).

## 9. Economic Aspects

As of 1995, there were only a few commercial oil shale facilities operating in the world. These facilities are located in countries where the economic, political, and environmental requirements for commercial oil shale development are met. There are commercial oil shale facilities in Brazil, China, Estonia, and Israel. No commercial oil shale facilities have existed in the United States because the costs of shale oil processing exceed those associated with conventional petroleum crude processing.

In the United States, estimates of oil shale retorting have ranged from \$113/m<sup>3</sup> (\$18/bbl) to \$567/m<sup>3</sup> (\$90/bbl). The lower estimate is based on using the actual costs of constructing a commercial oil shale retorting facility and

using a high grade ( $>25$  L/t ( $>30$  gal/short ton)) of oil shale (3). The higher estimate is based on conservative estimates utilizing unproven or noncommercial oil shale retorting technology.

The estimated costs for upgrading crude shale oil range from  $\$38/\text{m}^3$  ( $\$6/\text{bbl}$ ) to  $\$63/\text{m}^3$  ( $\$10/\text{bbl}$ ). However, the resulting upgraded shale oil is superior to most conventional crude petroleum and is more valuable as a refinery feedstock (67). The costs for upgrading crude shale oil depend on the upgrading techniques, ie, hydrotreating and coking or hydrotreating and fluid catalytic cracking. However, the greatest economic factor in oil shale upgrading is the amount of hydrogen required as reflected in the concentration of heteroatoms such as nitrogen, sulfur, and oxygen.

The commercial production of shale oil as an alternative energy source has not been economically feasible. As of 1995, all commercial oil shale operations in the world (Petrobras, Brazil; PAMA, Israel; The Chinese Petroleum Corporation, Fushun and Maoming, China; Kivioli Oil Shale Processing Plant, Kohtla-Jarve, Estonia) receive some sort of economic incentives or assistance from the countries in which they are operating.

The first stage of the Stuart oil shale project near Gladstone, Australia, 6000 t/d (6600 short tons/d), is scheduled to be constructed by Southern Pacific Petroleum. Financial assistance from the Australian government, consisting of special depreciation incentives and exemption of gasoline taxes equivalent to about U.S.  $\$1.91/\text{m}^3$  of crude shale oil ( $\$12.00/\text{bbl}$ ) has been assured (68).

As a result of the 1980 Energy Security Act, the United States Synthetic Fuels Corporation (USSFC) was established to provide financial assistance in the development of alternative energy sources to reduce the dependence on foreign petroleum to meet the needs for liquid fuels. More than  $\$15$  billion was authorized for financial assistance to those projects having the potential for producing about 318,000  $\text{m}^3/\text{d}$  of crude shale oil (two million bbl/d) by 1992. Whereas letters of intent to negotiate for assistance were authorized by USSFC for three oil shale projects, ie, Cathedral Bluffs, Occidental Oil Shale, Inc. (Rio Blanco, Colorado); Seep Ridge, Geokinetics, Inc. (Vernal, Utah); and Parachute Creek, Union Oil Company (Parachute, Colorado) (69), the only oil shale project to receive financial assistance from the USSFC was the  $\$654$  million Parachute Creek project which received about  $\$114.5$  million assistance in the form of a price guarantee of  $\$56\text{--}73/\text{bbl}$  from July 1983 until Union Oil Company ceased operations in Parachute in June 1991. Less than one-third of the available funds had been utilized (70).

The Deficit Reduction Act of 1984 significantly curtailed the available funding for the USSFC, which ceased operations in 1985.

## 10. Commercial Operations

The number of commercial oil shale operations worldwide has decreased significantly since the decade 1975–1985 and are producing only a fraction of the world's liquid fuels' needs. Most commercial oil shale operations have been scaled back.

**10.1. PETROSIX Operations in Brazil.** Petroleo Brasileiro (Petrobras) has a dedicated facility to produce crude shale oil from the Irati formation in southern Brazil. The facility is called the Oil Shale Industrialization Superintendency (SIX) and uses the PETROSIX retorting technology (see Table 7 and Fig. 3).

During its 40-year development, three different sizes of PETROSIX retorts have been operated on a continuous basis: a 1.83-m (6-ft) diameter demonstration plant; a 5.49-m (18-ft) diameter Prototype Unit (UPI); and a 10.97-m (36-ft) diameter Industrial Module (MI). Within the SIX facility are numerous pilot plants available for retorting coarse-sized oil shale, fines utilization, and oil shale upgrading (3,67).

The UPI and MI retorts are processing 7000 t/d (7700 short tons/d) of Irati shale to produce 24,381 m<sup>3</sup>/d (3870 bbl) of shale as well as 80 t (55 short tons) of LPG, 132 t (145 short tons) of clean fuel gas, and 98 t (108 short tons) of sulfur. The SIX plant has reached its design rate (Table 16) in an energy efficient manner with a high on-stream (operating) factor.

Pilot-plant studies have been conducted by Petrobras on many of the different oil shales from around the world. Tests indicate that many oil shales could be processed using the PETROSIX retorting technology (67) (Fig. 12).

**10.2. Oil Shale Operations in Israel.** Oil shale, the only fossil fuel resource in Israel, is being used to generate electric power. The oil shale feed stock, typical of the low grade Israeli oil shale (see Table 2), is situated in a deposit overlying phosphate ore. The oil shale operations are being carried out because the oil shale has to be mined to obtain the phosphate ore.

A circulating fluidized-bed boiler, using raw shale oil as a feedstock, is being used to supply process heat for the phosphate operations and to operate a 100-MW power plant. Scale-up in the 1990s should increase the electric power generation to 1000 MW (71).

**10.3. United States.** In 1980, Unocal began constructing the Parachute Creek Project, designed to produce 1600 m<sup>3</sup> (10,000 bbl) of upgraded shale oil per day. The project included a conventional underground room-and-pillar mine, the Unishale B (see Table 7) retort, and a special Unocal upgrading facility. Plant startup occurred in 1986, and daily shale oil production reached 1100 m<sup>3</sup>/d (7000 bbl/d). By 1991, total production exceeded  $0.6 \times 10^6$  m<sup>3</sup> (four million barrels). However, the Parachute Creek Project was shut down in mid-1991 for economic reasons.

The New Paraho Corporation has been conducting research on asphalt derived from shale oil, SOMAT, at its pilot plant (Rifle, Colorado) (54,55). It is the only active oil shale operation in the United States as of 1995. New Paraho is continuing its pilot operations while designing a commercial facility to produce SOMAT. The economics appear promising (56).

**10.4. Other Oil Shale Operations.** As of this writing, commercial production of shale oil is still being conducted in the People's Republic of China and Estonia. However, production rates continue to dwindle owing to the availability of conventional petroleum and other sources of energy as well as continued worldwide energy conservation.

Commercial shale oil production in the People's Republic of China is still being carried out in Fushin and Maoming. However, production in both areas

is declining because of continued emphasis on conventional petroleum and coal. Annual shale oil production in China is about  $10 \times 10^6 \text{ m}^3$  ( $1.6 \times 10^6$  barrels) (72).

Shale oil production in the former Soviet Union is also declining. The only significant shale oil operations are in Estonia. Most of the rich (208 L/t (50 gal/short ton)) Estonian oil shale is combusted directly as fuel.

Plans are underway to develop commercial shale oil operations in Australia. Southern Pacific Petroleum, N.L. is planning a commercial oil shale project utilizing the Stuart deposit (Brisbane, Australia). Favorable economics are attained by tax incentives to the Stuart project in the form of increased depreciation writeoffs and exempting excise tax for gasoline produced from shale oil. In Stage 1 of the Stuart project, expected to be operational in 1996, surface mining is to be used with AGR Taciuk retorting (see Table 7) to produce about  $675 \text{ m}^3$  (4250 barrels) of hydrotreated naphtha and fuel oil per stream day. In the full-scale, Stage 3 of the Stuart project, daily production is estimated to be nearly  $10,000 \text{ m}^3$  (about 60,000 barrels) of upgraded shale oil syncrude (73).

## BIBLIOGRAPHY

"Shale Oil" in *ECT* 1st ed., Vol. 12, pp. 207–221, by B. Guthrie and H. M. Thorne, Bureau of Mines, U.S. Dept. of the Interior; in *ECT* 2nd ed., Vol. 18, pp. 1–20, by R. E. Gustafson, Cameron and Jones, Inc.; "Oil Shale" in *ECT* 3rd ed., Vol. 16, pp. 333–357, by P. F. Dickson, Colorado School of Mines.

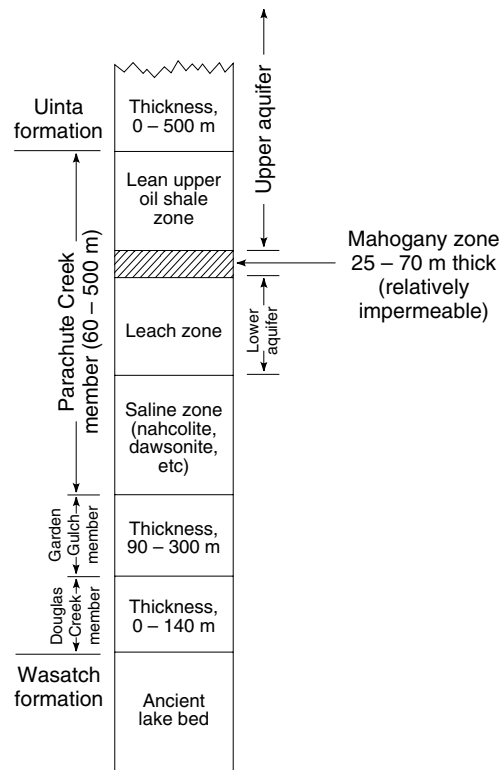
## CITED PUBLICATIONS

1. S. Siggia and P. Uden, eds., *Analytical Chemistry Pertaining to Oil Shale and Shale Oil*, National Science Foundation Grant Number GP 43807, June 24–25, 1974, 11–13.
2. D. C. Duncan and V. E. Swanson, *U.S. Geol. Surv. Circ.* **523**(7), 9 (1965).
3. D. L. Bachman and co-workers, *1993 Eastern Oil Shale Symposium*, Lexington, Ky., Nov. 16–19, 1993.
4. H. M. Thorne and co-workers, *U.S. Bur. Mines Inf. Circ.* **8216**, 6 (1964).
5. G. L. Baughman, ed., *Synthetic Fuels Data Book*, 2nd ed., Vol. 4, Cameron Engineers (Division of The Pace Co.), Denver, Colo., 1978, 67–104.
6. *Oil Shale and the Environment*, EPA-600/9-77-033, U.S. Environmental Protection Agency, Washington, D.C., Oct. 2, 1977.
7. ASTM D3904, American Society for Testing and Materials, Philadelphia, Pa., 1980.
8. R. N. Heistand, *Am. Chem. Soc. Div. Fuel Chemis. Preprint* **21**(6), (1976).
9. L. Goodfellow and M. T. Atwood, *Colo. Sch. Mines Q.* **69**, 205 (Apr. 1974).
10. K. E. Stanfield, *U.S. Bur. Mines Rep. Invest.* **4825**, (1951).
11. V. D. Allred, *Colo. Sch. Mines Q.* **62**, 657 (1967).
12. J. J. Cummins and W. E. Robinson, *U.S. Bur. Mines Rep. Invest.* **7620**, 1 (1972).
13. R. L. Braun and A. J. Rothman, *Fuel* **54**, 129 (Apr. 1975).
14. J. H. Campbell and co-workers, paper presented at *The 10th Oil Shale Symposium Proceedings*, Colorado School of Mines Press, July 1977, 148–165.

15. A. K. Burnham and co-workers, *Comp. Stud. Various Oil Shales* **34**(1), 36–42 (Mar. 1989).
16. A. K. Burnham, *Relationship Between Hydrous and Ordinary Pyrolysis*, UCRL-JC-114130, Lawrence Livermore National Laboratory, Livermore, Calif., June 1993.
17. S. S. Tihen, *Ind. Eng. Chem.* **47**, 464 (1955).
18. G. U. Dineen, "Effect of Retorting Temperature on the Composition of Shale Oil," *AIChE Meeting*, Denver, Colo., Aug. 1962.
19. J. H. Campbell and A. K. Burnham, paper presented at *The 11th Oil Shale Symposium Proceedings*, Colorado School of Mines Press, Golden, Colo., Nov. 1978, 242–259.
20. E. M. Piper, *6th IIASA Resource Conference*, Luxemborg, Austria, Colorado School of Mines Press, Golden, Colo., 1981.
21. J. B. Jones, Jr. and R. N. Heistand, *Proceedings, 12th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1979, 184–195.
22. Energy Development Consultants, "Oil Shale in the United States, 1981," *EDC*, Golden, Colo., 1980.
23. A. Stevens and R. L. Zahradnik, *Proceedings, 16th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1983, 267–268.
24. L. Dockter, *Colo. Sch. Mines Q.* **83**(4), 120–122 (1988).
25. R. F. Crane, in Ref. 21, 1–16.
26. A. H. Pelofsky and co-workers, in Ref. 21, 32–42.
27. A. Long, Jr., N. W. Merriam, and C. G. Mones, in Ref. 15, 120–135.
28. N. D. South and co-workers, *Colo. Sch. Mines Q.* **71**, 153 (Oct. 1976).
29. R. E. Poulson, C. M. Frost, and H. B. Jensen, *ACS Div. Pet. Chem. Prepr.* **17**(2), 175 (1972).
30. M. T. Atwood, paper presented at *The ACS Symposium: Fuels of the Future*, Dallas, Tex., Apr. 4–13, 1973.
31. C. M. Frost, R. E. Poulson, and H. B. Jensen, *ACS Div. Pet. Chem. Prepr.* **17**(2), 156 (1972).
32. D. P. Montgomery, *Ind. Eng. Chem. Prod. Res. Dev.* **7**, 274 (1968).
33. R. F. Sullivan, B. E. Stangeland, and H. A. Frumkin, *ACS Div. Pet. Chem. Prepr.* **22**, 998 (1977).
34. V. F. Yesavage, C. F. Griswold, and P. F. Dickson, paper presented at *The 180th National ACS Meeting*, San Francisco, Calif., Aug. 25–29, 1980.
35. H. Batrick and co-workers, *Final Report—The Production and Refining of Crude Shale Oil into Military Fuels*, Applied Systems Corp. for Office of Naval Research, Washington, D.C., Aug. 1975.
36. C. P. Reeg, A. C. Randle, and J. H. Duir, *Proceedings, 23rd Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1990, 68–95.
37. J. D. Baker and C. O. Hook, in Ref. 21, 26–31.
38. H. F. Feldman and co-workers, *Inst. Gas Technol. Res. Bull.* **36** (Aug. 1966).
39. S. A. Weil and co-workers, paper presented at *The 167th National ACS Meeting*, Los Angeles, Calif., Apr. 1974.
40. U.S. Pat. 3,703,052 (1972), H. R. Linden (to Institute of Gas Technology).
41. F. C. Schora and co-workers, *Hydrocarbon Process.* **56**(4), 107 (1977).
42. F. C. Schora, "The Application of the IGT Hydroretorting Process to Eastern Shale," *Energy Topics—a Supplement to IGT Highlights*, Institute of Gas Technology, Chicago, Ill., May 9, 1977.
43. E. L. Burwell and I. A. Jacobson, Jr., "Concurrent Gasification and Retorting of Oil Shale—a Dual Energy Source," *Rocky Mountain Regional Meeting*, SPE 5535, Society of Petroleum Engineers (SPE), AIME, Denver, Colo., Apr. 7–9, 1975.
44. E. L. Burwell and I. A. Jacobson, Jr., *U.S. Bur. Mines Tech. Prog. Rep.* **85**, 1 (Nov. 1974).

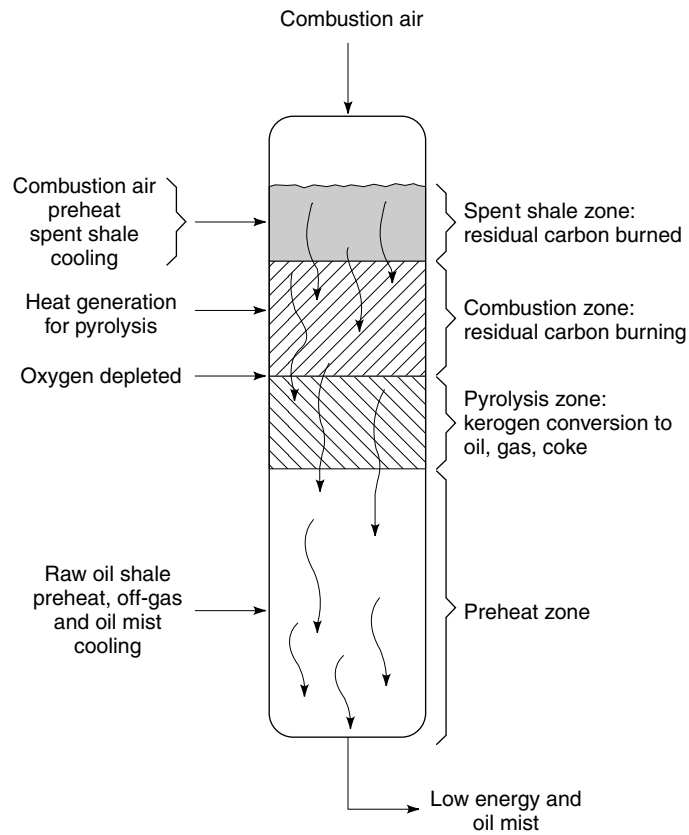
45. E. L. Burwell and I. A. Jacobson, *Colo. Sch. Mines Q.* **71**, 139 (Oct. 1976).
46. H. W. Sohns and co-workers, *Ind. Eng. Chem.* **47**, 461 (1955).
47. C. F. Griswold, V. F. Yesavage, and P. F. Dickson, *ACS Div. Fuel Chem. Prepr.* **21**, 207 (1976).
48. E. A. Fritzler, V. F. Yesavage, and P. F. Dickson, *Proceedings, The Second Pacific Chemical Engineering Conference*, American Institute of Chemical Engineers, New York, 1977, p. 542.
49. P. D. Smith, P. F. Dickson, and V. F. Yesavage, *ACS Div. Pet. Chem. Prepr.* **23**, 756 (1978).
50. C. F. Griswold, A. Ballut, H. R. Kavianian, P. F. Dickson, and V. F. Yesavage, *Chem. Eng. Prog.* **75**(9), 78 (1979).
51. C. F. Griswold, A. Ballut, H. R. Kavianian, P. F. Dickson, and V. F. Yesavage, *Energy Commun.* **6**(2), 153 (1980).
52. J. E. Sinor, "Niche Market Assessment for a Small Western Oil Shale Project," Final Report, DE-FC-86MC11076, U.S. Dept. of Energy, Washington, D.C., 1979.
53. J. E. Bunger and A. V. Deveni, *Proceedings, 25th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1992, 281–294.
54. L. A. Lukens, *Proceedings, 22nd Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1989, 196–206.
55. L. A. Lukens and M. A. Plummer, *Colo. Sch. Mines Q.*, 108–114 (1988).
56. L. A. Lukens, *Col. Sch. Mines Q.*, 115–119 (1988).
57. *An Environmental Impact Analysis for a Shale Oil Complex at Parachute Creek, Colorado*, Vol. I, II, III, Colony Development, Denver, Colo., 1974.
58. *Detailed Development Plan*, Vol. 1 and 2, Oil Shale Lease Tract C-b, C-b Shale Oil Project, 1976.
59. *Modifications to Detailed Development Plan*, Oil Shale Tract C-b, C-b Shale Oil Venture, 1977.
60. *Project Independence Oil Shale Task Force Report*, FEA, Washington, D.C., 1974, p. 154.
61. T. L. Thoem and E. F. Harris, in Ref. 19, 1–9.
62. J. B. Benton, *FUEL* **71**, 238–242 (Feb. 1992).
63. J. P. Fox, *Proceedings of the 13th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1980, 131–139.
64. R. N. Heistand and W. G. Holtz, in Ref. 63, 140–150.
65. A. Gulliford, *Boomtown Blues: Colorado Oil Shale, 1885–1985*, University Press of Colorado, Boulder, 1989.
66. J. Evans, *Colo. Sch. Mines Q.*, 103–105 (1988).
67. E. M. Piper and co-workers, *Proceedings of the 25th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1992, 221–242.
68. *1992 Annual Report*, Southern Pacific Petroleum N.L., 1993.
69. *1984 Annual Report*, United States Synthetic Fuels Corp., 1985.
70. *Oil Gas J.*, 38 (Apr. 8, 1991).
71. J. Yerushalmi, *Proceedings of the 1992 Eastern Oil Shale Symposium*, IMMR Press, Lexington, Ky., 1993, p. 367.
72. C. Du, *Proceedings of the 18th Oil Shale Symposium*, Colorado School of Mines Press, Golden, Colo., 1985, 210–215.
73. B. C. Wright, *Alternate Energy '89 Proceedings*, Council on Alternate Fuels, Washington, D.C., 1989, 175–194.

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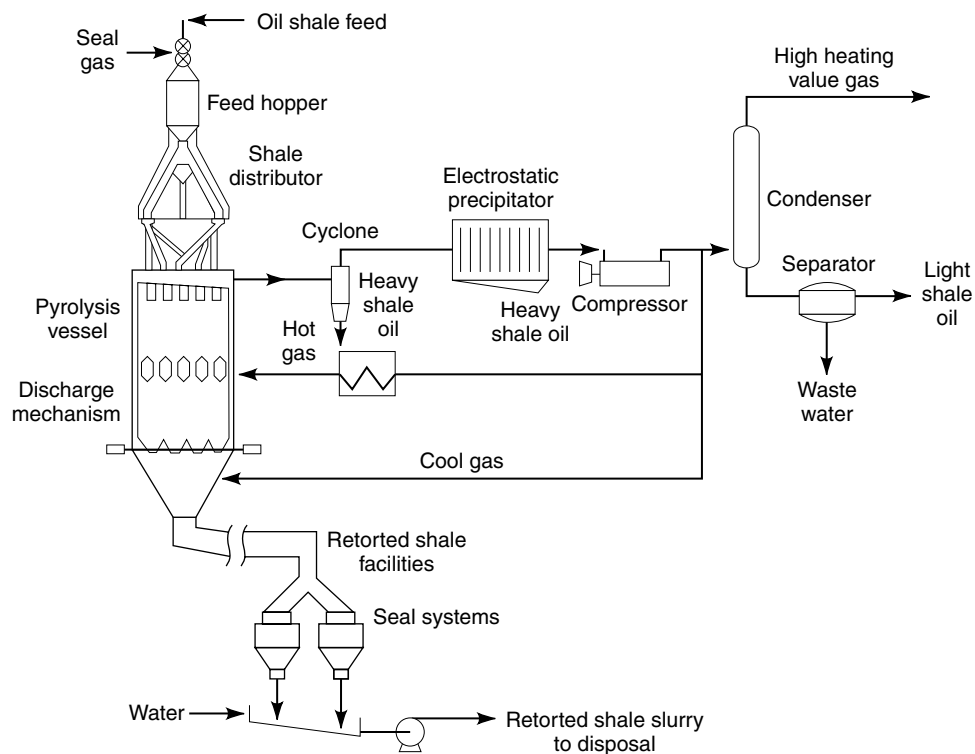


**Fig. 1.** Green River formation, Colorado.

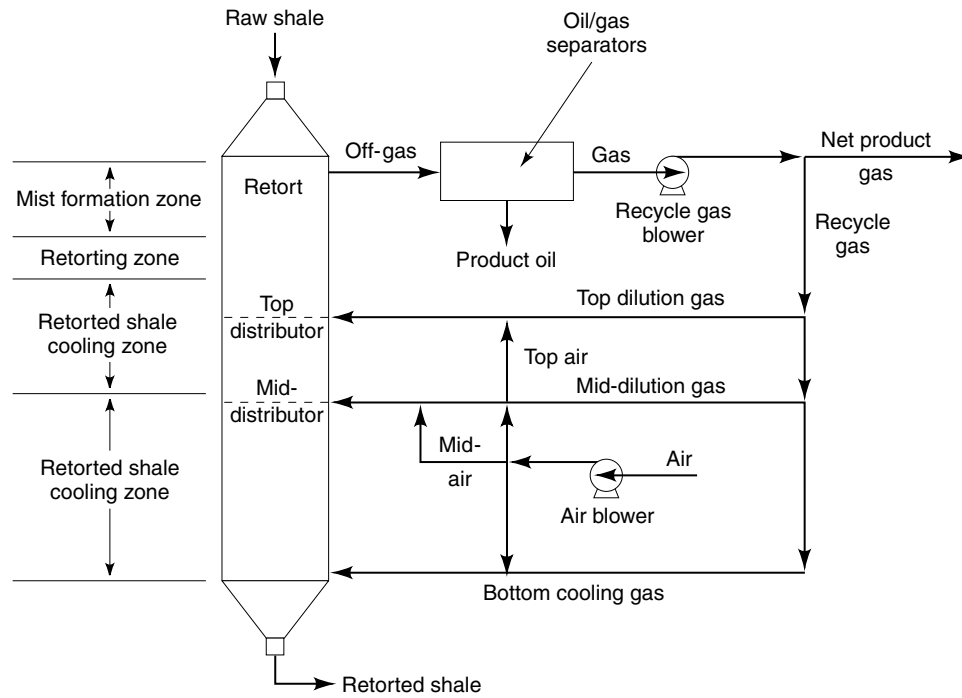




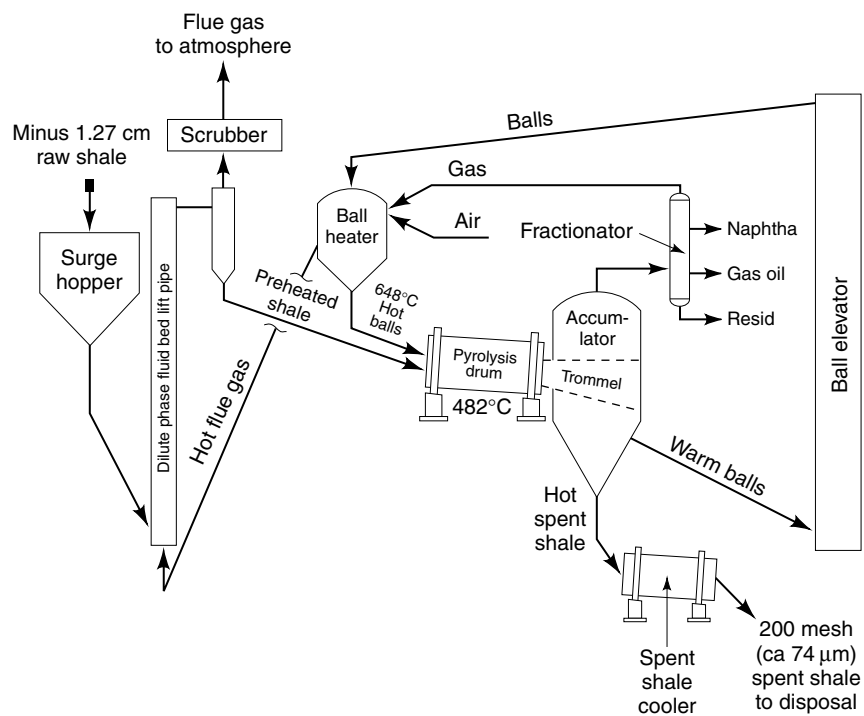
**Fig. 2.** Nevada-Texas-Utah (NTU) retort schematic.



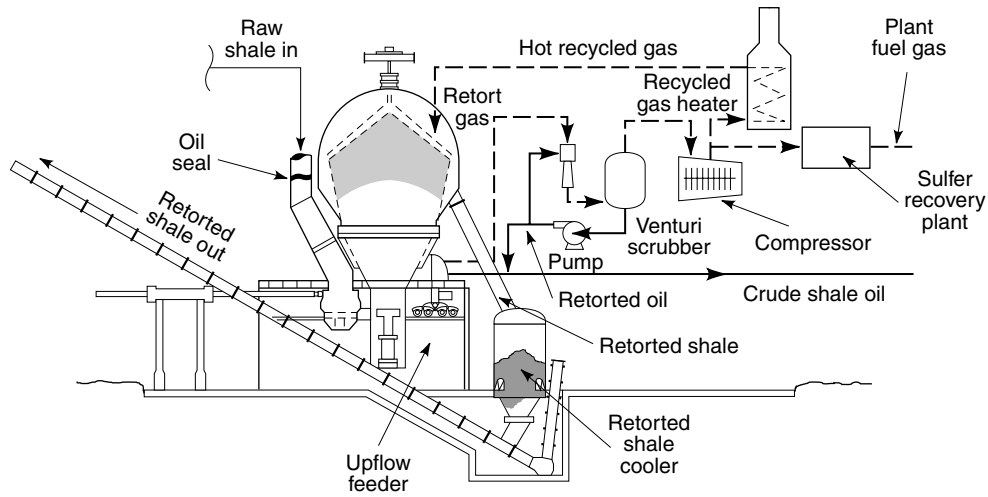
**Fig. 3.** PETROSIX process (20).



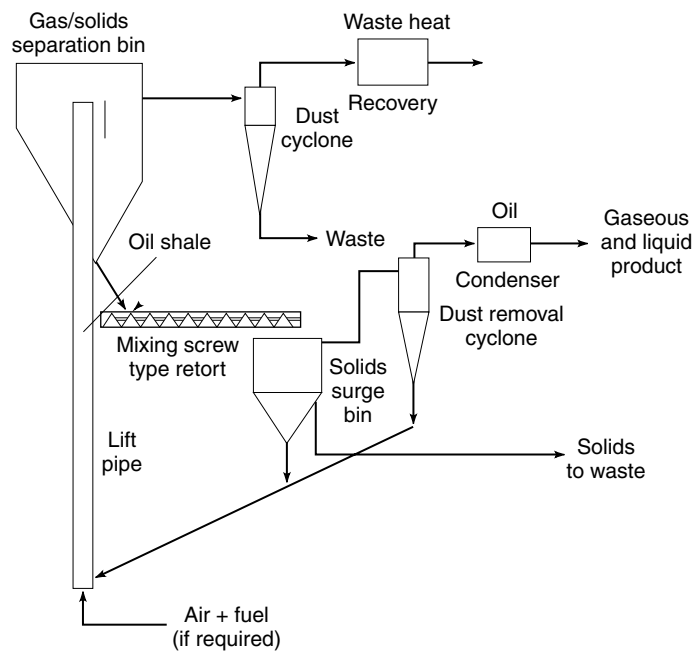
**Fig. 4.** Paraho DH process (21).



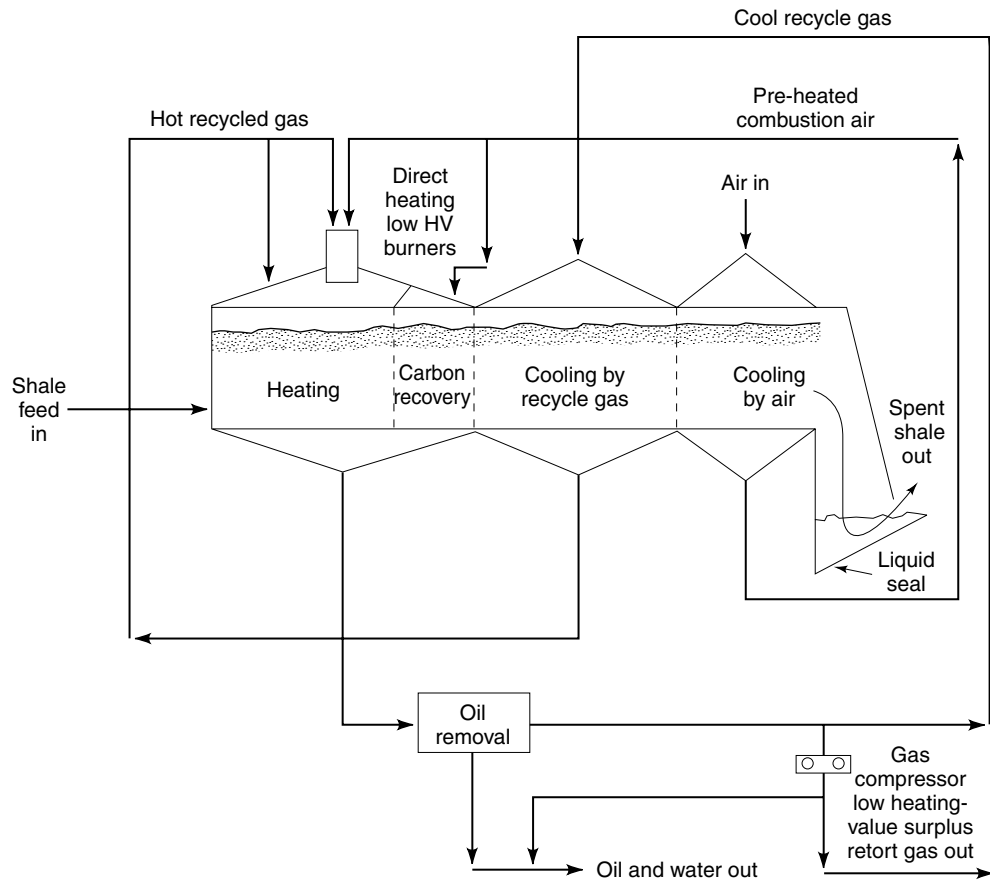
**Fig. 5.** Tosco II process (20). The resid is residual oil.



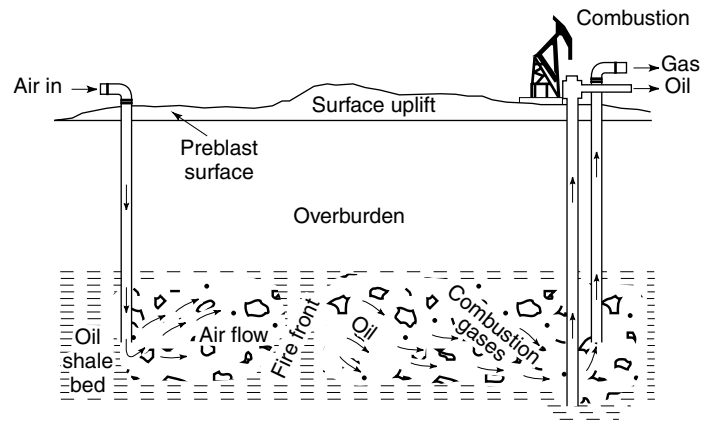
**Fig. 6.** UNISHALE B process (20).



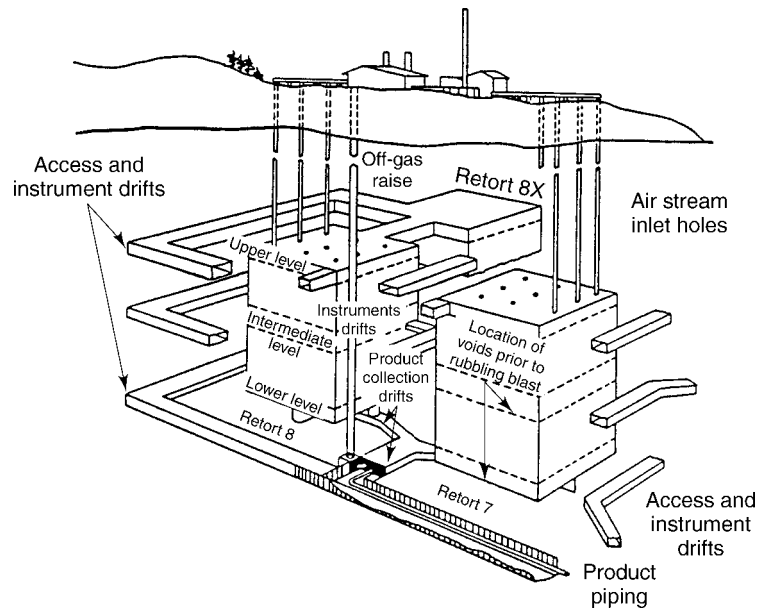
**Fig. 7.** Lurgi process (20).



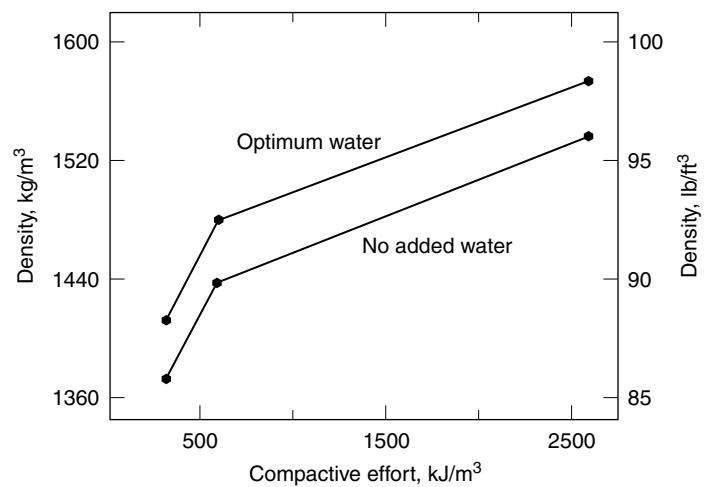
**Fig. 8.** Superior process (20). HV = heating value.



**Fig. 9.** LOFRECO process (20).

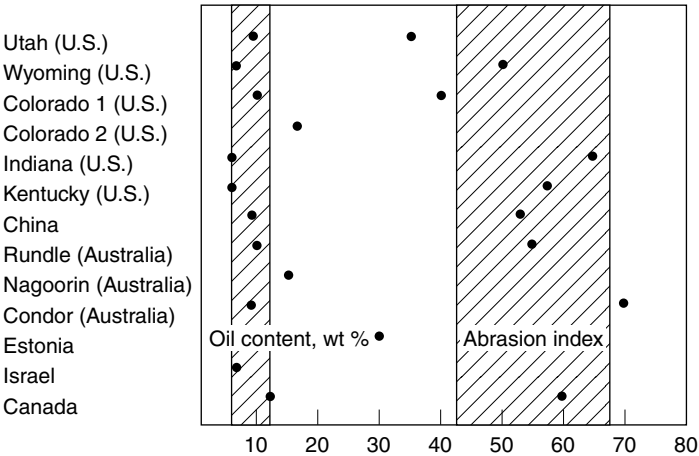


**Fig. 10.** VMIS process (23).



**Fig. 11.** Density of retorted shale vs compactive effort (64).





**Fig. 12.** Shale oil characteristics compared to Irati oil shale (3).

Table 1. Shale Oil Resources<sup>a</sup>, 10<sup>9</sup> m<sup>3b,d</sup>

Geographic area	Total resource <sup>c</sup>			Marginal or submarginal resources <sup>d</sup>		
	21–42	42–104	104–417	21–42	42–104	104–417
Africa	71,500	12,700	636	small	small	14
Asia	93,800	17,500	874		2	11
Australia and New Zealand	15,900	3,200	159		small	small
Europe	22,260	4,100	223		1	6
North America	41,400	8,000	477	350	254	99
South America	33,400	6,400	318		119	small
<i>Total</i>	<i>278,260</i>	<i>51,900</i>	<i>2,687</i>	<i>350</i>	<i>376</i>	<i>130</i>

<sup>a</sup> Ref. 2.<sup>b</sup> To convert m<sup>3</sup> to bbl, divide by 0.159.<sup>c</sup> Includes oil shale in known resources, in extensions of known resources, and in undiscovered but anticipated resources.<sup>d</sup> Numbers represent shale oil yield range in L/t. To convert L/t to gal/short ton, multiply by 0.2397.

Table 2. Properties of World Wide Oil Shales<sup>a</sup>

Property	Timahdit	Irati	Nagoorin	Kentucky	Maoming	Colorado	Condor	Alpha	New Brunswick	Israeli Kunkersite
<i>Fischer assay, %</i>										
oil weight	6–9	6–12	14.1	5.3	9.7	16.5	6.3	52.0	6–12	28.6
water, bound	2.1–2.7	0.2–2.1	6.9	1.9	3.8	1.0	1.9	4.0	0.9–1.4	2.5
spent shale	85–88	83–90	72.4	90.0	82.0	78.6	87.3	33.0	91.1–84.5	62.7
gas + loss	2.8–3.7	2–4	6.6	2.8	4.5	3.8	4.5	11.0	2.0–2.1	6.2
<i>Other properties</i>										
moisture, wt%	6.7–9.8	0.2–6	23.2	2.8	11.3	0.7	7.7	2.8	5.4–6.7	5.8
specific gravity	1.88–1.99	1.9–2.1	1.47	2.22	1.73	1.94	2.05	1.16	2.32–1.97	1.57
gross heating value, J/g <sup>b</sup>	5.230–6.904	5.439–6.987	11.950	5.791	8.577	9.113	4.728	30.669	3.766–6.908	4.209
total carbon, wt%	14.78–19.46	12–17	25.67	12.82	18.74	23.45	10.50	70.54	10.75–16.58	15.5
total hydrogen, %	1.9–2.0	0.9–2.4	3.7	1.5	2.9	2.9	1.7	8.39	1.4–2.2	1.6
total sulfur, %	2.1–2.7	3.9–5.6	1.0	4.4	1.6	1.1	0.9	1.4	0.9–1.0	2.9
nitrogen, %	0.46–0.63	0.3–1.9	0.3	0.3	1.3	0.6	0.3	1.0		0.1
loss on ignition, at 950°C, %	31.4–38.9	20–24	41.9	21.3	32.1	38.0	18.6	91.7	21.1–28.5	56.2
<i>Ash composition, wt%</i>										
SiO <sub>2</sub>	31.6–37.5	5.0–5.6		64.8	57.2	45.2	73.2	53.4	54.8–55.7	33.2
Fe <sub>2</sub> O <sub>3</sub>	3.5–5.8	7.6–9.8		10.7	12.2	5.5	8.1	9.9	6.8–5.7	6.6
Al <sub>2</sub> O <sub>3</sub>	8.6–13.0	9.8–12.6		12.5	19.5	2.3	12.1	24.3	17.9–15.0	8.9
CaO	15.7–26.7	1.3–3.9		1.9	1.1	18.9	2.0	3.4	8.9–13.8	33.7
MgO	5.6–7.4	2.0–3.7		0.6	0.8	17.4	1.0	4.1	6.1–3.7	9.5
<i>Fischer assay oil</i>										
specific gravity, 20°C	0.962	0.906	0.918	0.926	0.890	0.902	0.895	0.905	0.880	0.958
total carbon, wt%	78.73	84.60	83.40	84.95	84.81	84.21	84.72	84.32	85.6	83.4
hydrogen, %	9.69	12.50	11.37	11.85	11.65	11.29	12.54	11.89	12.3	10.7
sulfur, %	6.33	1.10	1.16	1.40	0.52	0.92	0.46	1.72	0.6	0.7
nitrogen, %	1.52	0.90	1.18	1.12	2.60	1.78	1.30	0.69	1.1	0.1
gross heating value, J/g <sup>b</sup>	40.074	42.547	43.070	41.773	42.447	42.723	42.677	42.539	43.932	39.748
										39.790

<sup>a</sup> Ref. 3.<sup>b</sup> To convert J to cal, divide by 4.184.

Table 3. Shale Oil Resources of the United States<sup>a</sup>, 10<sup>9</sup> m<sup>3b</sup>

Geographical area	Total resource <sup>c,d</sup>			Marginal or submarginal resources <sup>d</sup>		
	21-42	42-104	104-417	21-42	42-104	104-417
Green River Formation, ie, Colorado, Utah, and Wyoming	636	445	191	318	223	83
central and eastern United States	318	159		32	32	0
Alaskan deposits	large	32	40	small	small	small
other	21,300	3,537	80		small	small
<i>Total</i>	<i>22,254</i>	<i>4,173</i>	<i>311</i>	<i>350</i>	<i>254</i>	<i>83</i>

<sup>a</sup> Ref. 2.<sup>b</sup> To convert m<sup>3</sup> to bbl, divide by 0.159.<sup>c</sup> Includes oil shale in known resources, in extensions of known resources, and in undiscovered but anticipated resources.<sup>d</sup> Numbers represent shale oil yield range in L/t. To convert L/t to gal/short ton, multiply by 0.2397.

Table 4. **Composition of Green River Oil Shale**<sup>a,b</sup>

Material	Composition, wt%
mineral (inorganic, 85 wt% of total)	
carbonates	40.8
feldspars	17.8
quartz	12.8
clays	11.0
pyrite and analcite	2.6
kerogen (organic, 15 wt% of total)	
carbon	11.7
hydrogen	1.5
nitrogen	0.3
sulfur	0.15
oxygen	1.35

<sup>a</sup> Ref. 1<sup>b</sup> Shale oil yield of 104 L/t (25 gal/short ton).

Table 5. Conversion of Kerogen by Fischer Assay<sup>a</sup>

Component	Grade of shale, L/t					
	43.8	111.4	151.5	238.3	257.9	312.9
oil, wt%	51	65	69	66	69	71
gas, wt%	14	12	11	12	12	11
organic residue, wt%	35	23	20	22	19	18

<sup>a</sup> Ref. 10.

Table 6. Effect of Retorting Temperature on Product Type<sup>a,b</sup>

Retorting temperature of distillate (reduced to 300°C)	Saturates, vol%	Olefins, vol%	Aromatics, vol%
537°C	18	57	25
649°C	7.5	39.5	53
760°C	0	2.5	97.5
871°C	0	0	100
gas combustion	30	50	20
simulated <i>in situ</i>	41	37	22
<i>in situ</i>	59	16	25
median U.S. crude	60–100	<5	0–40

<sup>a</sup> Ref. 18.<sup>b</sup> Colorado oil shale.

Table 7. **Retorting Technologies**

Technology	Country	Heating process <sup>a,b</sup>	Feed	Flow <sup>c</sup>
<i>Above-ground retorting</i>				
Chevron	United States	DH	fine	
FBC	Israel	DH	fine	CC
Fuschun	China	DH	coarse	CC
Galoter	Russia	IH	coarse	CO
Gas combustion	United States	DH	coarse	
Kiviter	Russia	IH and DH	coarse	CO and CC
LLNL/HRS	United States	IH (ash)	fine	CO
Lurgi	United States	IH (ash)	fine	CO
Paraho DH	United States	DH	coarse	CC
Paraho IH	United States	IH (gas)	coarse	CC
Petrosix	Brazil	IH (gas)	coarse	CC
Superior	United States	IH (gas)	coarse	
Taciuk	Australia	IH (gas)	fine	CC
TOSCO II	United States	IH (solids)	fine	CC
Unishale A	United States	DH	coarse	CC
Unishale B	United States	IH (gas)	coarse	CC
<i>In situ retorting</i>				
Equity BX	United States	IH (steam)		
IGT	United States	IH (H <sub>2</sub> /steam)		CO
LOFRECO	United States	DH		
MultiMineral	United States	DH		
RISE	United States	DH		
VMIS	United States	DH		

<sup>a</sup> DH = direct heat; IH = indirect heat.<sup>b</sup> Heat-transfer medium is given in parentheses.<sup>c</sup> CC = countercurrent; CO is concurrent.



Table 8. Properties of Oils Produced from Shales

Country or company	Retort	Sp gr	°API	N, wt%	S, wt%	Analysis of distillate, wt% <sup>a</sup>		
						Saturates	Olefins	Aromatics
Australia, Glen Davis <sup>b</sup>	Pumpherstons	0.828	27.9	0.52	0.56	42	39	19
Brazil, Tremembe <sup>b</sup>	gas combustion	0.919	22.5	1.06	0.68	23	41	36
France <sup>b</sup>								
Autun	Pumpherstons	0.931	20.5	0.90	0.51	33	36	31
Severac	Marcecaux	0.925	21.5	0.53	3.0	30	32	38
Severac	Petit	0.959	16.0	0.65	3.40	25	20	55
St. Hilaine	Lantz	0.908	24.3	0.54	0.61	31	44	25
Scotland <sup>b</sup>	Pumpherstons	0.874	30.4	0.77	0.35	42	39	19
South Africa, Ermelo	Salerno	0.906	24.7	0.85	0.64	35	44	21
Spain, Puertollano <sup>b</sup>	Pumpherstons	0.901	25.6	0.68	0.40	51	27	22
Sweden, Kvarntorp <sup>b</sup>	Rockesholm	0.977	13.3	0.68	1.65	12	24	64
United States								
Colorado	gas combustion	0.943	18.6	2.13	0.69	27	44	29
Colorado	Pumpherstons	0.900	25.7	1.57	0.77	30	38	32
Superior Shale Oil <sup>c,d</sup>		0.630	0.93	2.0	0.8	25	25	50
Rundle Shale Oil <sup>c,e</sup>		0.636	0.91	0.99	0.41	48	2	50
Israeli Shale Oil <sup>f</sup>		0.623	0.955	1.2	7.1			

<sup>a</sup> Boiling at 315°C.<sup>b</sup> Ref. 4.<sup>c</sup> Ref. 25<sup>d</sup> Initial boiling point to 204°C.<sup>e</sup> Whole oil.<sup>f</sup> Ref. 26. Also contains 79.8 C, 9.7 H, and 2.2 wt% O.

Table 9. Comparison of Colorado and Michigan Antrim Shale Oils<sup>a</sup>

Property	Colorado	Michigan
naphtha, vol%	6.8	3.5
light distillate, vol%	24.9	41.1
heavy distillate, vol%	43.6	38.6
residuum, vol%	23.9	16.3
specific gravity (°API)	0.911 (23.8)	0.934 (20.0)
pour point, °C	10	−15
hydrogen, wt%	12.5	11.1
carbon, wt%	84.7	83.6
nitrogen, wt%	1.6	0.7
sulfur, wt%	0.8	3.5

<sup>a</sup>Ref. 27.

Table 10. Comparison of Green River Crude Shale Oil and Median U.S. Crude<sup>a</sup>

Property	Tosco II	U.S. Bureau of Mines		Simulated <i>in situ</i>	Union Oil Co. A	Median U.S. crude
		Gas combustion	<i>In situ</i>			
distillation boiling point, °C <sup>b</sup>						
ibp <sup>c</sup> 200	18	6	11–15	7	5	30
200–315	24	19	41–48	31	20	22
315–480	34	38	27–35	46	40	28
>480	24	37	9–14	17	35	20
pour point, °C	–1 <sup>d</sup> , 15 <sup>e</sup>	21–28	–1 to 5	10–15	32	<–15
specific gravity	0.927	0.934	0.892	0.910	0.940	0.850
°API	21	20	27	24	19	35
nitrogen, wt %	1.9	1.5–2.1	1.4–1.8	1.6	2.0	0.09
sulfur, wt %	0.7	0.8	0.7	0.6–0.9	0.9	0.6
oxygen, wt %	0.8	1.7			0.9	
viscosity, mm <sup>2</sup> /s (=cSt)						
at 37°C	22	59	8–15	21	46	6
100°C	04	07			06	
saturates, vol %		30	59	41		60–100
olefins, vol %		50	16	37		<5
aromatics, vol %		20	25	22		0–40
carbon-to-hydro- gen ratio		7–8				5–7
arsenic, ppm		40				<0.03

<sup>a</sup> Refs. (1,27).<sup>b</sup> Values represent % of product.<sup>c</sup> ibp = initial boiling point.<sup>d</sup> After a patented heat treatment which temporarily reduces pour point.<sup>e</sup> No heat treatment.

Table 11. Properties of Shale Oil during the Unocal Upgrading Process<sup>a</sup>

Raw shale oil from retort	After particulates removal	After arsenic removal	After unicracking	Syncrude
gravity, °API	22	22	25	38
pour point, °C	23.9	23.9	26.6	<3.9
particulates, ppm	300	0	0	0
arsenic, ppm	25	25	0	0
distillation, °C				
initial	65.5			433
maximum	590			538

<sup>a</sup>Ref. 36.

Table 12. Properties of Shale Oil Syncrude and Arabian Light Crude<sup>a</sup>

Property	Syncrude	Arabian Light
gravity, °API	40	34
sulfur, ppm wt	5	17,000
nitrogen, ppm wt	60	800
carbon residue, wt%	0.05	3.6
heavy metals, ppm wt		20
distillation, vol%		
X-538°C	100	85
538°C+		15

<sup>a</sup>Ref. 36.

Table 13. **Tensile Strength Retained, %<sup>a</sup>**

Asphalt	Number of freeze–thaw cycles			
	1	3	5	9
AC-10	85	79	72	48
SOMAT	85	96	87	84

<sup>a</sup> Ref. 56.

Table 14. Estimate of Colony Oil Shale Project Emissions Production, kg/h<sup>a,b</sup>

Source	SO <sub>2</sub>	NO <sub>x</sub>	Solid particulates	Hydro-carbons	Carbon monoxide
crushing and conveying					
primary crusher dust collection system	0	0	27	0	0
final crusher dust collection system	0	0	136	0	0
fine-ore storage dust collection system	0	0	27	0	0
pyrolysis and oil recovery unit					
preheat systems	529	2172	51	128	17.4
steam superheater ball circulation systems	9	56	103	0.2	1.0
processed shale moisturizing systems	0	0	116	0	0
hydrogen unit					
reforming furnaces	146	244	4.9	0.8	4.6
gas-oil hydrogenation unit					
reactor heaters	10	54	1.1	0.4	0.45
reboiler heater	2.7	17.7	0.4	0.04	0.3
naphtha hydrogenation unit					
reactor heater	2.2	4	0.09	0.01	0.09
sulfur recovery unit					
sulfur plants with common tailgas plant	29				
delayed coker unit					
heater	21	35	0.7	0.14	0.64
utilities					
boilers	51	246	5.4	1.8	1.4
<i>Total</i>	<i>799.9</i>	<i>2828.7</i>	<i>472.59</i>	<i>131.39</i>	<i>25.88</i>

<sup>a</sup> Ref. 57<sup>b</sup> Using no control technology.

Table 15. Permeability of Retorted Shale<sup>a</sup>

Compaction	Loading, kPa <sup>b</sup>	Permeability cm/s $\times 10^{-6}$	
		No water	Optimum water
standard, 593 kJ/m <sup>3c</sup>	345	43.0	6.8
	690	29.3	1.4
	1380	19.1	0.8
heavy, 2693 kJ/m <sup>3c</sup>	345	38.1	1.1
	690	32.4	0.6
	1380	25.2	0.1

<sup>a</sup> Ref. 64.<sup>b</sup> To convert kPa to psi, multiply by 0.145.<sup>c</sup> To convert kJ to kcal, divide by 4.184.



Table 16. **MI-Main Operation Data**<sup>a</sup>

energy consumption/energy produced	0.38
oil yields, %	87–90
gas yields, %	140–150
operation factor, %	88–90
retorting rate, kg/(h·m <sup>2</sup> )	2300–2900

<sup>a</sup> Ref. 3.