ABSTRACT

The large decline in oil prices which began in 1985 has rendered un-economic all conventional schemes for producing shale oil as a substitute for petroleum-derived fuels. While continuing advances in production technology may be expected, such advances will be incremental in nature and are unlikely to reduce the cost of production by one half or more, as would be required to be competitive at today's conditions.

If all oil shale development is deferred until such time as oil prices increase greatly, it will not be possible to respond to needs for alternative fuels in a timely fashion. It would therefore be extremely beneficial if a self-supporting shale oil facility of any type could be built and operated in the near future. One way in which this might be possible is to build a small-scale facility to manufacture products which are more valuable than fuels.

In examining the potential for producing specialty products from oil shale, a marketing assessment was carried out for a small facility which would be located in the western oil shale region. Interest has been expressed in the apparent beneficial effects of shale oil when used as an additive or blending agent in asphaltic concrete for highway paving. A life-cycle paving cost analysis was used to estimate the value of shale oil as an asphalt blend at 1988 prices for asphalt. This showed that prices of over $60 per barrel for shale oil are feasible. A study of the asphalt market in the western oil shale region then showed that a shale oil plant producing on the order of 2,000 barrels per day for this market would be possible.

THE NICHE MARKET CONCEPT

For the past 25 years, most oil shale development efforts in the United States have been focused on large projects, with a potential production of 8,000 cubic meters (50,000 barrels) per day or more. With projects of this size, only the markets for petroleum fuels are large enough to accept the shale oil production. Therefore, the emphasis has been on upgrading and refining shale oil to fit those markets. However, shale oil industries which were established in other parts of the world were able to find or maintain a market position by providing a variety of specialty products.

A historical review of world oil shale industries revealed that non-fuel products or byproducts have been essential features of the most important oil shale industries which existed in the past. Byproducts accounted for up to 60 percent of total income (Sweden). Major byproducts which have been produced include bricks from spent shale, ammonia, sulfur, ammonium sulfate, waxes, lubricants, wood preservatives, liquefied petroleum gases, coke, solvents, medicinal products, cement, asphalt, creosolic acids, and other tar acids.

Many previous studies have shown the difficulties faced in producing large amounts of shale oil in the United States. Raw shale oil is not an acceptable feedstock to petroleum refineries and there are not enough users of heavy fuel oil in the western oil shale region to provide a dependable market. The only alternatives are to hydrotreat the oil, or else ship it long distances to a larger market area. Either of these alternatives results in a cost penalty of several dollars per barrel. The net price received for raw shale oil at the plant would be several dollars per barrel less than the world price for crude oil.

A different approach was proposed for this study. Instead of attempting to enter the large-volume petroleum products market, it was hypothesized that a small shale oil facility might be able to produce specialty products with a high enough average value to absorb the high costs of shipping small quantities to distant markets and still provide a higher netback to the plant site than sales to the conventional petroleum products market. This approach, rather than attempting to refine shale oil or to modify its characteristics to satisfy the specifications for petroleum feedstocks or products, focuses instead on those particular characteristics which distinguish shale oil from petroleum, and attempts to identify applications which would justify a premium value for those distinctive characteristics.

A historical example of a niche market, or specialty market, was the early development of the oil shale industry in New South Wales, Australia. In about 1865, torbanite from New South Wales was studied and it was discovered that only a five percent addition of this unusually rich shale (180 gallons per ton) to coal would increase the luminosity of producer gas by a factor of six. Producer gas was being widely used for illumination at that time.

As a result, an industry developed in New South Wales, mining and selling the richest shale (80 to 200 gallons per ton), called 'export shale,' to the United States and Europe. The lower quality shales (less than 80 gallons per ton) were retorted locally for production of liquid fuels and related products. The torbanites of Australia became known as kerosene shales. Eventually the invention of the incandescent mantle, in 1911, ended the export market for raw oil shale.

A niche market, by definition, is a small market requiring product specifications or characteristics which can be met only by a particular producer or product. That product can then command a premium price.

SHALE OIL AS ASPHALT BLENDING MATERIAL

Early work by the United States Bureau of Mines byproducts group showed that vacuum distillation of crude shale oil would produce a residue meeting most asphalt specifications. It failed the oiliness and modified oiliness spot tests, which are an indication of previous cracking. It contained more wax but less sulfur than most petroleum asphalts. Experiments with air blowing of crude shale oil showed that asphalt could also be
produced in this way. An asphalt roadway laid down at the Anvil Points experiment station was still in good shape 30 years later.

More recent work at different institutions in the United States has shown that various shale oil fractions are highly effective in producing asphalt which is resistant to moisture damage during freeze/thaw cycles. Shale oil has also been tested as an asphalt pavement recycling agent.

It has been found that shale oil asphalt can be produced by conventional methods in acceptable grades for highway paving mixtures. The adhesive properties of the shale oil asphalt compare favorably with those of petroleum asphalts, and it is much more resistant to damage by water. Hardening of the shale oil asphalts due to heating during mixing and compacting was about the same as that of petroleum asphalt, and the stiffness of the mixtures was not greatly different.

The superior resistance to moisture damage which is exhibited by shale oil asphalts appears to be related to the nitrogen-containing compounds, but to date it has not been possible to identify a specific fraction.

VALUE OF SHALE OIL AS AN ASPHALT BLEND

Work with shale oil at Texas A & M University as early as 1977 pointed to basic nitrogen compounds in the shale oil as being responsible for improved resistance to moisture damage. The Texas A & M work was later extended by Western Research Institute (WRI). WRI specifically investigated the strength of the nitrogen compound-aggregate bond and its resistance to water-induced weakening. One of the major causes of asphalt pavement failure is moisture induced damage. Moisture and repeated freeze-thaw cycles tend to break apart asphalt pavement. WRI has been granted United States Patent 4,325,738 "Tertiary Nitrogen Heterocyclic Material to Reduce Moisture-Induced Damage in Asphalt Aggregate Mixture."

A comparison of the number of freeze-thaw cycles in the Water Susceptibility Test required to induce failure clearly showed the superiority of shale oil over petroleum. Briquets made from petroleum-derived asphalt failed in a maximum of seven freeze-thaw cycles, while the shale-oil-derived briquet showed no signs of failure after 100 cycles.

If the life of asphalt paving can be extended by using a shale oil blend, then the incremental value can be assigned to the shale oil.

Asphaltic concrete used in highway construction consists of about four to six percent bitumen and 94 to 96 percent aggregate. Typical laid-down costs in Colorado in 1988 were $21 per ton for hot-mix asphaltic concrete and $150 per ton for bitumen. Thus the bitumen accounts for about 36 percent of the total laid-down cost.

Therefore, if an improved bitumen blend results in a 10 percent longer pavement life, then the value of the bitumen is increased by 28 percent. If the improved blend was achieved by blending 20 percent shale-derived bitumen with 80 percent conventional bitumen, then the value assigned to the shale-derived material could be three times that of the petroleum-derived material. The results of a series of such calculations are presented in Figure 1. It shows that shale asphalt values of over $70 per barrel can be achieved for a five percent pavement life increase with a 10 percent blend.

Figure 1 VALUE OF SHALE OIL IN ASPHALT BLENDS

The value assigned in Figure 1 is actually very conservative because it considers only the material cost of the asphaltic concrete. Other large benefits will arise from longer pavement life. They include less frequent interruption of traffic for pavement resurfacing, and less wear and tear on vehicles due to pavement being in good condition for a larger fraction of its total lifetime. The cost to the public of traffic delays for resurfacing has been calculated to be equal to or greater than the material cost of the paving itself in many cases. This means that the true value to society of a shale oil blend could be even much higher than the $70 per barrel quoted earlier.

ASPHALT MARKET FOR A WESTERN OIL SHALE PROJECT

By far the greatest end use for asphalt, 75-80 percent, is asphaltic concrete for roads and streets. The points of consumption for asphalt are constantly changing and geographically widely distributed. Because it must be transported hot and in batches, transportation costs are high, and shale-derived asphalt is likely to be used only within a radius of a few hundred miles from the plant. For a shale oil project located in northwestern Colorado, the total asphalt market as a function of distance from the plant is indicated in Figure 2. A large jump to about 45,000 barrels per day occurs at a radius of around 900 miles, but this is outside the practical marketing radius.

Figure 2 ASPHALT MARKET VERSUS DISTANCE
Shale oil will never be a complete replacement for petroleum bitumen. If it were used as a complete replacement, its value over petroleum would only be in direct proportion to the increase in pavement life. As illustrated earlier, sale as a byproduct makes it possible to achieve much higher values. If only the three-state Colorado, Utah, Wyoming market is considered, then Figure 3 gives the size of a shale oil asphalt plant which could be built, as a function of the amount of shale oil in the blend. This assumes that the entire asphalt market could be captured, but of course not all of the market is life cycle cost sensitive. If it is assumed that half the total market would be sensitive to life cycle cost analysis, and that about 50 percent of the raw shale oil could be converted to an asphalt blendstock, then Figure 3 gives the maximum crude shale oil production which would be feasible as a function of blending level in asphalt. The latter assumption depends upon the retorting process used, and upon the material with which the shale oil is blended. Although the fraction of total shale oil meeting asphalt viscosity specifications can be increased by oxidative procedures such as air blowing, this is not generally recommended. If the petroleum bitumen base stock is a deeper than normal refinery cut, such as AC-40 grade, then a less viscous (and therefore larger fraction of the total) cut of shale oil can be blended in. Although asphalt-producing refineries in the Rocky Mountain region do not normally produce an AC-40 grade, it is believed that they could do so if the market were present. Then a retort which produces a heavy product, such as the inclined fluid bed retort being developed by WRI, could probably convert 50 percent of its output to asphalt blendstock.

It may be concluded that 2,000 barrels of raw shale oil per day would provide most of the asphalt blendstock which could be marketed in the three-state region.

![Figure 3 PLANT SIZE FOR BLENDS](image)

**EXTRACTION OF SPECIALTY CHEMICALS**

Research has shown that many specialty products can be derived from shale oil. However, none of these represent a true niche market opportunity for shale oil, because the resulting products are usually inferior to existing products unless expensive refining and upgrading procedures are used.

The United States Bureau of Mines carried out a program of byproduct research in the early 1950's which showed that paraffin wax could be extracted from the gas oil fraction by selective organic solvents. The crystal structure of the shale-oil microcrystalline wax was found to be almost identical with petroleum microcrystalline wax, but the wax contained excessive amounts of olefins. These could be removed by hydrocracking.

From the tar acids, it was found that phenols and their homologs could be extracted which were useful for cresylic acids, insecticides, disinfectants, drugs, and synthetic resins and plastics. From the tar bases, the extraction of pyridine homologs was expected to be useful for making insecticides, detergents, rubber compounds, and other chemicals.

A formula for rubber reclaiming oil that contained phenolic sulfides made from shale oil phenolics and carboxylic acids was found to be suitable for reclaiming both natural and synthetic rubber scrap.

Researchers in the U.S.S.R. have obtained from kukersite large quantities of saturated dicarboxylic acids. These fatty acids have a large number of uses. One of the largest market areas for fatty acids is oil well drilling fluids. Fatty acid derivatives provide corrosion resistance, lubrication for bentonite drilling muds, and foaming action to remove particles from the hole under extreme heat and pressure. Analyses of retorted shale oil in the United States, however, has shown only trace amounts of dicarboxylic acids in the 370-535 degrees C distillate. This is because the carboxylic acids decarboxylate during most retorting processes used to produce shale oil.

In general, it is found that the concentrations of individual compounds in shale oil are too small (usually just parts per million) for separation and purification to be practical. One possible exception is 2,4,6-trimethylpyridine. This compound was found to be an unusual artifact of shale oil produced from western United States oil shale. It could be separated in high purity from shale oil naphtha by simple distillation. This material is used as a specialty solvent. Potential yield is estimated at 0.2 pounds per barrel of shale oil. Since total United States demand is estimated at about 100 tons per year, this could be satisfied completely by a plant producing 2,600 barrels of shale oil per day. This approximately matches the maximum feasible plant size estimated for the asphalt market.

**SPLIT STREAM PROCESSING**

The production of large-volume petrochemical products from oil shale is unlikely to be competitive with petroleum for the near future in the United States. The relatively low cost of producing crude petroleum, and the economies of scale which are possible in converting crude petroleum to large-volume products, make it unlikely that shale oil can compete in this arena.

After comparing the characteristics of shale oil to United States markets for specialty chemicals, it was concluded that there probably is no single market in which the entire raw shale oil stream could bring a price above that of crude petroleum. Therefore, it would be best to separate out any fractions which could be sold regionally for near crude oil prices, and ship only the higher-valued fractions or derivatives to long-distance markets to capture premium values which may exist.

Broadly speaking, the chemical constituents of shale oil can be classified as either polar or non-polar compounds. The non-polar compounds are for the most part, hydrocarbons. We have not found any application in which the hydrocarbon compounds in shale oil would appear to be significantly more valuable than the corresponding boiling point range
hydrocarbons found in petroleum. On the other hand, the polar compounds, mostly the heterocycles, are not only the ones which decrease shale oil's value as a refinery feedstock, but are also the ones which might possibly have premium values in some applications.

These considerations make it obvious that a low-cost way to separate raw shale oil into polar and non-polar fractions would be an ideal step in a shale oil refining process. The non-polar fraction, presumably greatly reduced in nitrogen concentration, could be sent directly to a refinery where it should command a price equivalent to crude oil. Since there is little prospect of the hydrocarbons qualifying for significantly higher prices than crude oil, this would be the most efficient market option for this fraction. The high cost of hydrotreating would be avoided.

It appears that such a polar/non-polar separation is feasible. For instance, work carried out at Occidental Research Corporation, (Stover, United States Patent 4,209,385) showed that a combination of an organic acid, such as acetic acid, and a mineral acid could cleanly separate polar and non-polar phases. The organic acid acts as a selective solvent which, with the addition of a strong acid makes a greater quantity of acidic protons available for ionization of the heterocyclic compounds for extraction into the more polar solvent phase. Extraction could be performed in batch or continuous extraction processes using either co-current or countercurrent extraction techniques. Following the contact phase of the extraction process, separation is possible by decanting. The selective solvent can be recovered in another extraction process or by distillation.

The non-polar phase produced by this procedure can have a nitrogen content of less than 0.2 percent and would make an acceptable cat cracker feedstock without further upgrading. About 60 percent of the raw shale oil might be split to the non-polar fraction and 40 percent to the polar fraction.

Although techniques such as the above are known, they have not been considered to be of value for large-scale shale oil facilities. The reason is quite simple. If 40 percent of the raw shale oil is separated as a polar fraction, it is too large a fraction to discard, and it is too large a stream to find an outlet in specialty markets. For a small-scale project, however, this becomes a practical approach. The non-polar hydrocarbons can be sold directly to a refinery, without the need for hydrodenitrogenation, and the polar stream is small enough that it may be possible to sell it into specialty markets.

Polar/non-polar separation processes have not been developed far enough to be able to estimate the economics. However, it will be a simple, low temperature, atmospheric pressure process, and should be less expensive than hydrodenitrogenation.

INTEGRATED SYSTEM

Assembling the individual processing steps discussed above into an integrated whole, a complete liquids processing scheme for a small-scale shale oil plant might appear as in Figure 4.

The major products are a low-nitrogen feedstock for local refineries and a shale oil asphalt for regional asphalt plants. In winter, the asphalt operation would probably be shut down and a heavy fuel oil or bunker fuel produced.

Figure 4 INTEGRATED PROCESSING SCHEME

Because the shale oil asphalt is expected to be the most valuable fraction, the facility would be designed to produce the maximum amount of this stream possible. Thus all of the raw shale stream boiling above the minimum acceptable cutoff temperature would go to asphalt. Additional asphalt cut might be obtained by oxidative treatment of some lower boiling material followed by ROSE extraction.

Following the distillation, an acid extraction step would separate the distillate into polar and non-polar fractions. The non-polar fraction might be processed to recover specialty waxes before being used as conventional refinery feedstock.

Products of secondary importance from the polar fraction could include creosote, asphalt additives, and collidine. Minor products might include phenols, cresols, xylene, cresylic acids, and carboxylic acids.

One of the major problems with conventional acid extraction techniques in refining is disposal of the acid sludge. The proposed polar/non-polar separation process using weak organic acids is much different, and produces very little or no acid sludge. The scheme in Figure 4 shows the use of burst shale to neutralize the sludge, which is then recycled back to the retort to reclaim residual organic values. This step may not be required.

BUILDING MATERIALS FROM SPENT SHALE

Every oil shale industry which has existed on a commercial basis for any length of time has made some use of retorted shale for building materials. The simplest application is merely to use the crushed, retorted shale as aggregate in construction fill or in building road bases.

Studies of the compressive strength of spent (burned) Colorado shale have shown that rich oil shale, in which kerogen forms a continuous phase, loses a large part of its compressive strength in retorting. Lean shales were found to retain good compressive strength after retorting. This indicates that the lean spent shale could be recommended as road base material.

When using the spent shale as aggregate in asphaltic concrete mixtures, it was found that the porosity of the particles (created by retorting the kerogen) apparently absorbed some asphalt, so that the asphalt requirement per cubic foot of asphaltic concrete was about 50 percent above normal.

A high asphalt requirement and low abrasion resistance suggest that spent shale would not be a desirable aggregate for surface layers of pavement. The light weight, flexibility and strength suggest that it would perform adequately in base and sub-base courses or in flexible pavement structures.
Bricks were manufactured from spent shale at a number of locations in the past. The manufacture of shale-lime bricks was carried out profitably for many years by Scottish Oils Ltd. at their Pumperston works. Producing acceptable bricks for the market was very dependent on achieving the right color, and this varied, depending on the age and amount of oxidation which had occurred in the spent shale piles.

Portland cement is produced by burning a lime-containing material (such as limestone, shell, or chalk) with shale, slate or clay. The raw materials are proportioned to supply correct ratios of lime, silica, aluminum oxide and iron oxide, then heated to around 2,700 degrees F. Grinding the resulting clinker produces cement.

Colorado oil shale, having a high calcium content, exhibits cement-forming characteristics on its own if heated to sufficient temperatures.

At Dotternhausen, Germany, the Rohrbach process produces a Portland cement from oil shale in an integrated process. Raw oil shale is burned in a fluidized bed to produce heat and power. Additional raw shale provides both feedstock and energy in the production of clinker, and the clinker is combined with the residue of fluidized bed combustion to make the final cement mixture.

In summary, decarbonized spent shale can be and has been used to make a variety of products for the construction and building industry. However, the areas in which this has been done are highly developed areas with a large population and large demand for building materials. All of the materials produced, such as aggregate, bricks, cement, etc., are heavy and very sensitive to freight rates. Therefore, they cannot be shipped long distances to compete with products from other sources unless they have some outstanding product characteristics or production economics.

The major economic advantage of course, is that mining costs can be assigned a value of zero. Even so, the costs of mining competing sand, gravel, clay, limestone, etc., in most parts of the country is quite low. Using a figure of $4 per ton for mining, and two cents per ton-mile for freight, the cost advantage due to no mining cost would only extend for a radius of 200 miles from the oil shale plant. For the Colorado-Utah oil shale area there is not enough population within this range to create any significant market.

It may be concluded that the manufacture of byproducts from retorted shale for the building material industry cannot be a significant factor in the overall economics of even a small oil shale plant located in the West. We estimate a maximum potential market of less than 400 tons of spent shale per day, with net revenues of less than $4 per ton.

FLUIDIZED BED DESULFURIZATION AGENT

The Electric Power Research Institute (EPRI) has sponsored studies to investigate oil shale as a sulfur sorbent in a circulating fluidized-bed combustor. These studies were intended to determine the shale requirement as a function of coal sulfur content for acceptable sulfur retention, and compare the effectiveness and cost of oil shale as a sorbent to that of limestone. They found that oil shale is an effective absorbent for sulfur dioxide at fluidized bed temperatures of 1,650 degrees F and below. Sulfur dioxide emissions can be maintained below federal and Colorado standards at operating temperatures below 1,625 degrees F and absorbent/sulfur molar ratios of 1:24:1 or greater. Under these conditions, oil shale can be economically competitive with limestone or dolomite in fluidized bed coal combustion units where transportation costs can be equalized.

Raw oil shale contains appreciable energy, which can add about $5 per ton to its value when used as a sulfur sorbent in a coal combustor. A major significance of this fact is that oil shale removed during mine development operations could be sold, creating early cash flow for an oil shale mining and retorting project.

Unfortunately, the only existing coal-fired fluidized bed power plant within economical shipping distance of northwest Colorado is the Colorado-Ute facility at Nucla, about 150 miles away. Transportation costs are estimated to be approximately $10 per ton. With limestone as the competing product for sulfur sorption at $15 per ton, there is a potential net-back price of $10 per ton for oil shale at the mine site.

The Nucla facility is a 110 megawatt power plant burning coal with about 0.8 percent sulfur. At a typical ratio of 0.05 tons of shale per ton of coal, the plant could consume only about 100 tons of oil shale per day for sulfur absorption.

Thus, although the sale of raw shale as a desulfurization agent could make a modest contribution to the overall economics of a small oil shale facility, it will not exert any significant effect on the size of mine which would be feasible. Retorted (but noncombusted) shale could still be effective as a desulfurization agent, but loss of the $5 per ton credit for fuel value would render the economics borderline.

CONCLUSIONS

It appears that the most promising niche market for western oil shale is an asphalt blending material. Market distance considerations suggest an upper facility size of about 2,000 barrels of shale oil per day. Total revenues of around $30 per barrel of raw shale oil may be possible. Data demonstrating a quantitative improvement in asphaltic concrete pavement life when made with shale oil are urgently needed.

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