POTENTIAL PRODUCTION OF SPECIALTY CHEMICALS FROM OIL SHALE IN THE UNITED STATES

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ABSTRACT

For the past 20 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 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. Historically, 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 products.

This study examined the historical experiences of oil shale industries around the world, with respect to making and selling specialty chemicals and byproducts rather than fuel products. It then considered the applicability of such experience to the modern-day United States industrial economy. It was found that, in contrast to the normal situation, there is an inverse economy of scale. That is, a small-size project can be more profitable than a large one, because small-volume specialty products can be sold for a higher price per ton of shale.

HISTORICAL REVIEW

A historical review of world oil shale industries reveals 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, cresylic acids, and other tar acids.

The review shows that all oil shale operations have been highly individualistic. The factors which allowed some industries to operate for long periods of time have never been exactly the same from one country to another. In Scotland, the industry which operated for the longest period of time in competition with petroleum managed to do so as a result of outstanding chemical and industrial leadership, carefully taking advantage of each product market opportunity which arose over a 100-year period. In the U.S.S.R., which maintains the strongest oil shale industry in the current era, the industry draws its

basis from an unusually rich resource which is burned directly in power plants.

There are many examples where the production and sale of byproducts made a crucial difference in the economic feasibility of a shale oil plant, at least for some period of time. The most common example in the early industry was the production of ammonium sulfate. Retort design and operations were often modified specifically to increase its production. Commercialization of the synthetic ammonia process eventually eliminated the values of byproduct ammonia.

In spite of the added value of byproducts, most oil shale companies expressed the need and desire to move to a single product stream. Because most byproduct streams were small, they were at the mercy of local and unreliable markets. Therefore most producers apparently thought that they could better compete with petroleum if their entire retorting output could be sold as a crude oil substitute. The evidence suggests, however, that whenever a shale oil industry was established strictly to compete with petroleum, it eventually succumbed to one of the periodic drops in petroleum prices. In few instances outside of Scotland was the industry large enough or possessing enough technical capability to undertake the development of alternative product slates. The major exception to this trend has been the U.S.S.R., where since the 1950's, emphasis has been placed on non-fuel uses for shale oil.

CHARACTERISTICS OF SPECIALTY CHEMICAL MARKETS

Many previous studies have shown the difficulties faced in producing large amounts (1,500 to 8,000 cubic meters per day) 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 cubic meter.

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 chemicals 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.

As a frame of reference, it may be noted that a United States shale oil project in the size range of 1,500 cubic meters per day would probably require a cash flow of more than $100,000,000 per year. The total United

States specialty chemicals market is estimated at $40,000,000,000, but there are only a few segments of that market which are large enough to provide a feasible target for entry by a new producer at $100,000,000 per year. The specialty chemicals business is very fragmented. Agricultural chemicals, the largest individual segment with sales of $5.5 billion, accounts for only about 14 percent of the total. The top five segments, which in addition to agricultural chemicals include oil field chemicals, industrial coatings, specialty lubricants, and industrial and institutional cleaners, account for only about half of total sales. On the bottom end, half (15) of the segments have less than a two percent share of the total.

If specialty chemicals are to provide a large fraction of the revenue for a United States shale oil plant, either the products will have to be sold into the five major markets, or else the products will have to have such outstanding price and performance characteristics that they can capture a major shale of some of the smaller market segments.

CHARACTERISTICS OF UNITED STATES SHALE OILS

There has never been a concerted effort to develop specialty products from United States oil shale resources. One company which produced small quantities of shale oil in the period of 1919 to 1924 experienced considerable difficulty in selling the byproducts from its product slate, which consisted of wax (15 percent), gasoline (5 percent), distillate fuel oil (41 percent) and lubricating oil (14 percent). The balance was made up of coke and refinery losses. The company attempted to sell the raw oil to the mining industry for use in ore flotation, but it was found to be unsatisfactory for this use. The wax product was also rejected by explosive companies, and the lubricating oil was of too low viscosity for use in automotive engines. All these defects could undoubtedly be cured by modern upgrading and refining methods.

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 hydrotreating.

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 satisfactory for reclaiming both natural and synthetic rubber scrap.

Tests were carried out on producing asphalt by air-blowing shale oil residuums. These tests indicated that asphalts of various grades could be produced.

In general, it was found that the concentrations of individual compounds in shale oil are too small for separation and purification to be practical. Shale oil is an extremely complex material. Hundreds or even thousands of individual compounds and isomers have been identified. Although many of these would be valuable as specialty chemicals, the concentrations (usually just parts per million) are too low to be of interest. It was concluded that the largest part of the shale oil must be sold in broad-cut products. Isolation and sale of individual chemical species will seldom be practical.

One possible exception to the preceding statement 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 the shale oil naphtha by simple distillation. This compound is used as a specialty solvent. Yield was estimated at 0.02 kilograms per ton of shale oil. Current prices for this material are about $7.00 per kilogram.

KEROGEN EXTRACTION

Researchers in the U.S.S.R. have studied the use of kerogen as a natural raw material for the synthesis of monomers by direct chemical processing. This is done by the scission of the native polymethylene chains in kerogen into mono- and, preferably, dicarboxylic acids. The technique used is to first beneficiate the kukersite until a kerogen concentration of 70-90 percent is obtained. Conventional industrial oxidants have been found to be suitable for direct oxidative conversion of the kerogen to saturated dicarboxylic acids. These fatty acids have a large number of uses.

Analyses of retorted shale oil in the United States have shown only trace amounts of dicarboxylic acids in the 370-535 degrees C distillate. This is because the carboxylic acids decarboxylate during the retorting processes used to produce shale oil. However, work carried out at the Western Research Institute has shown that large yields of carboxylic acids can be obtained by supercritical fluid extraction of oil shale with carbon monoxide and water, methanol and water, or toluene. Total yield of organic liquids with this procedure was higher than is obtained by retorting. Yields of as much as 90 percent of the organic matter (140 percent of Fischer Assay) were obtained. The products obtained in the first 15 minutes were almost entirely carboxylic acids amounting to 25 percent of the total organic matter in the oil shale.

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.

ASPHALT AND ASPHALT ADDITIVES

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 oliensis and modified oliensis 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 experiment station was still in good shape 30 years later.

Recent work at different institutions in the United States has shown that various shale oil fractions are highly effective in producing an 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 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.

A United States shale oil company has announced plans to carry out a pilot production program for asphalt from Colorado oil shale. Test strips will be laid down on various highways to compare the performance of shale-derived and petroleum-derived asphalts.

UNITED STATES MARKET POTENTIAL

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.

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. The small-volume specialty products markets offer a better opportunity for a small-scale oil shale operation. Some of the most attractive opportunities are listed in Table 1, along with the estimated size of the market in which a small oil shale facility would be competing. The size of the market is determined by the allowable shipping distance for the product. High-value products can be shipped large distances, and marketed throughout

the country. Low-value products are limited to regional markets because it would not be economical to ship them great distances.

TABLE 1

POTENTIAL PRODUCTS AND MARKET VOLUMES FOR NON-HYDROTREATED UNITED STATES SHALE OIL

Product	Market Location	Estimated Market Volume
Asphalt	Regional	1,200,000 metric tons/year
Fatty Acids	National	400,000 metric tons/year
Paraffin Wax	Regional	110,000 metric tons/year
Coal Dust Suppressant	Regional	40,000 metric tons/year
Phenolics	Regional	20,000 metric tons/year
Creosote	Regional	14,000 metric tons/year
Asphalt Additives	National	10,000 metric tons/year
Collidine	National	200 metric tons/year
Pyridines	National	Small

The data in Table 1 show clearly that a shale oil facility producing specialty chemical products will have to be quite small. It also appears that a process should be developed to separate polar from non-polar compounds in crude shale oil as a first refining step. The non-polar hydrocarbons in shale oil (which can be used to make waxes and fuels) carry no premium value over the same hydrocarbons in petroleum. Conversely, they should be of equal value if the nitrogen and metals content were comparable. Solvent extraction experiments have suggested that a non-polar hydrocarbon fraction consisting of about 60 percent of the raw shale oil can be obtained with low enough nitrogen levels to be fed directly to a catalytic cracker in a refinery. This would make it possible to sell 60 percent of the product to local refineries at a crude oil equivalent price without requiring expensive hydrodenitrogenation. The polar fraction will contain most of those constituents having possibilities for specialty markets.

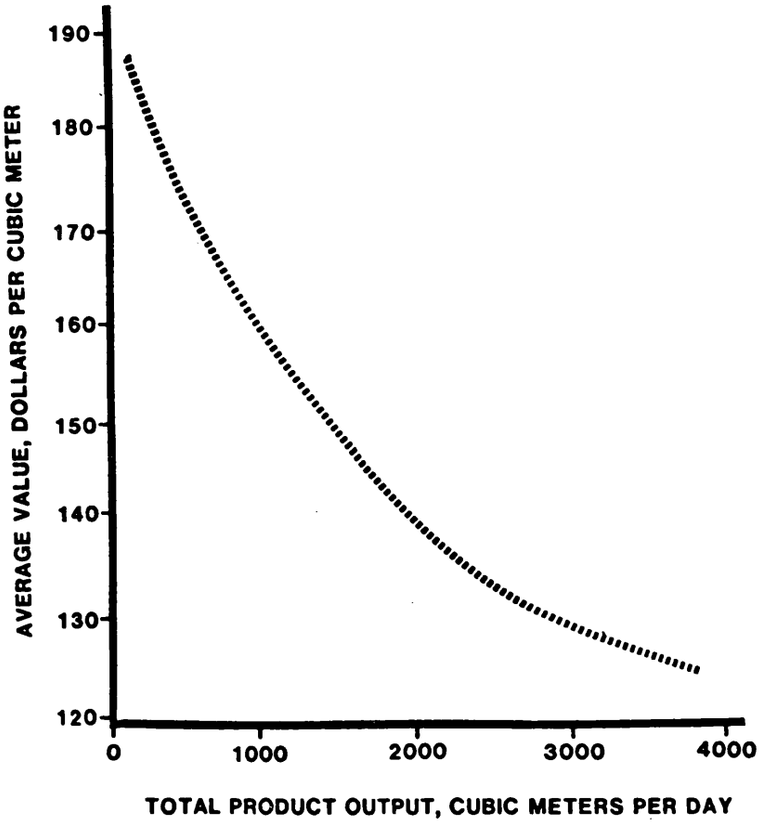
EFFECT OF PROJECT SIZE

This study found that producing some products for specialty markets can increase the market value of shale oil in the United States to more than the price for crude oil. By taking advantage of the unique characteristics of shale oil, rather than trying to force it into petroleum refining processes, unique products can be made. However, these products have only limited markets.

The optimum size for a shale oil facility making non-fuel products is probably no more than 800 cubic meters per day. In order to realize premium prices, production cannot exceed a reasonable share of the total available specialties market. When production exceeds that level, no further income from the specialties may be expected, and the average price obtained per cubic meter of product will decrease. This is illustrated in Figure 1. In constructing Figure 1, it was assumed that production volumes in excess of any specialty market demands would be dumped into the heavy fuel oil market.

FIGURE 1

EFFECT OF PROJECT SIZE ON ACHIEVABLE VALUE PER CUBIC METER



A typical high-value product slate is given in Table 2. The value of the products is about 70 percent higher than world prices for crude oil. The qualification of whole shale oil as an asphalt additive could result in far higher values. The numbers in Table 2 and Figure 1 are based on conservative assumptions for the percentage of shale oil which could be qualified as an asphalt additive. If the entire 40 percent polar fraction is tested and shown to be effective, the value of this fraction could be as high as $440 per cubic meter of raw shale oil.

TABLE 2

HIGH VALUE SPECIALTIES PRODUCT SLATE

Product	Yield, Percent	Value per Cubic Meter of Shale Oil
Cat Cracker Feed	52	$57.23
Paraffin Waxes	8	$1.07
Phenolics	0.2	$1.76
Carboxylic Acids	25	$69.37
Asphalt Anti-Strip	1	$12.89
Asphalt Recycler	3	$9.93
Creosote	2.5	$3.46
	Total	$185.71

It is concluded that research on extraction of polar materials from shale oil, on the direct extraction of carboxylic acids from kerogen, and on the use of shale oil as an asphalt additive would be the most profitable areas to pursue for a small oil shale facility in the United States.