COMBINED BENEFICIATION AND HYDRORETORTING OF OIL SHALE

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ABSTRACT

The Mineral Resources Institute (MRI) of The University of Alabama and Institute of Gas Technology subsidiary, HYCRUDE Corporation, are evaluating the potential benefits of combining pre-concentration of oil shale by froth flotation followed by hydroretorting to recover the oil. Exploratory laboratory testing of several oil shales has been completed in a continuing research program. To date the testing includes a sample of Upper Devonian New Albany shale from Indiana, an upper Chattanooga shale from Alabama and a Permian Irati shale from Brazil.

Results of flotation tests of the three samples showed that the oil content in the beneficiation concentrates was increased by a factor of 2 to 3 with recoveries up to 90 percent. After briquetting the products, the MRI beneficiated oil shales were submitted to HYCRUDE and subjected to bench scale HYTORT processing. The yield was improved further through hydroretorting by a factor between 3 and 5.5.

INTRODUCTION

Until recent years most of the research and development work directed toward establishing a domestic oil shale industry has focused on the shales of the Green River Formation of Eocene age occurring in Colorado, Utah, and Wyoming. This is largely because the Western shales are relatively rich (in the range of 25-30 gal/ton) and respond favorably to oil production by simple thermal treatment, yielding 75-85% of their organic content (kerogen) as oil when pyrolyzed.

Recent developments in innovative retorting and fine particle technologies have altered this situation significantly. The HYTORT process, developed by HYCRUDE Corporation utilizes hydrogen rich gas during retorting to enhance oil yields from certain types of oil shales. It has provided a key to processing the Devonian-Mississippian shales of the Eastern United States to achieve oil yields comparable to those from Colorado shales. This technique permits the fullest possible recovery of oil from the kerogen present in the shale.

The range of potential oil shale resources available to HYTORT processing can be expanded by combining hydroretorting with The University of Alabama Mineral Resources Institute's (MRI) physical beneficiation process. The MRI process involves fine grinding the oil shale matrix followed by selective froth flotation of the kerogen. During flotation up to three quarters of relatively kerogen-free inorganic matter is rejected as waste.

By combining the HYTORT and MRI processes, the economics of treating oil shales can be improved, and the range of oil shales which can be processed is extended. Descriptions of the MRI and HYTORT processes, and typical results obtained on oil shales of low and moderate kerogen content are presented in this paper.

BACKGROUND

The HYTORT Process

Oil shales vary significantly in their ability to produce oil. For example, the Green River oil shales of the Western U.S. contain a high hydrogen content in proportion to organic carbon, and exhibit relatively complete conversion of kerogen to oil. When retorted by conventional thermal processes. However, many other oil shales including the Eastern U.S. Devonian shales, contain lesser amounts of hydrogen relative to organic carbon as shown in Table 1. This deficiency in hydrogen reduces the fraction of the kerogen which can be converted to hydrocarbon products by conventional retorting (1,2). Oil yields from these shales can be substantially improved by supplying hydrogen during retorting. Thus a significant larger fraction of the kerogen is converted to hydrocarbon products rather than remaining in the spent shale in the form of coke. The degree of oil yield enhancement for each particular oil shale depends upon the partial pressure of hydrogen used.

In 1980 HYCRUDE Corporation was formed to commercialize the HYTORT process. HYTORT is a process which utilizes a hydrogen-rich gas for the hydroretorting of oil shale kerogen to produce a synthetic crude oil. The hydroretorting is carried out in a hydrogen-rich atmosphere at elevated pressure, and enables attainment of the maximum possible oil yields from most oil shales. As a result of a Development Agreement with Phillips Petroleum Company, a feasibility study was conducted by HYCRUDE Corporation, Phillips Petroleum Company, Bechtel Group, Inc., and the Institute of Gas Technology. The HYTORT process development work during the feasibility study was divided into three basic areas:

- Chemistry of hydroretorting
- Experimental development work to support mechanical design of HYTORT reactors
- Process design, reactor mechanical design, and cost estimation work.

The HYTORT experimental work and process economics were completed in May 1983 and details are available in other publications (3,4).

Throughout the course of the feasibility study, the HYCRUDE Corporation and Bechtel Group, Inc. continually reviewed the experimental efforts to assure that the experimental programs addressed areas important to the design of commercial reactions (5). This study resulted in a conceptual commercial plant design for Eastern U.S. Devonian shale processing based on the results of the experimental program. The conceptual HYTORT plant flow diagram is shown in Figure 1. The plant contains all the process areas necessary to produce upgraded shale oil including by-product recovery of sulfur and ammonia. As designed, the HYTORT reactors can be constructed using currently available equipment. All other processes are within the sizing and operating constraints of commercial facilities. Implementation of the plant design can be achieved with current process technology.

Natural gas is utilized in the production of hydrogen and as an indirect heat source for hydroretorting. This is an economic optimum for areas such as the Eastern United States where inexpensive sources of natural gas area available. For plants located in areas lacking an inexpensive natural gas source, the HYTORT process conditions would be selected to provide sufficient by-product gas as a substitute.

Although most of the HYTORT process development effort has concentrated on Eocene oil shales of the Western U.S. and on Eastern U.S. Devonian oil shales (1,2), HYCRUDE Corporation in cooperation with the U.S. Geological Survey is conducting work on other oil shales from various locations worldwide. The primary goal of this on-going work is to determine the extent of oil yield enhancement which can be obtained using HYTORT processing. Test work is conducted in a Hydroretorting Assay unit (6), which is designed to serve the same function for HYTORT processing that the ASTM D3904-80 Fischer Assay test serves for conventional thermal retorting processes. Table 2 gives results of Hydroretorting Assay tests on some of the samples. The data show that HYTORT processing had a wide range of effects on the shales tested, with oil yield enhancements varying from no improvement to oil yields over four times those obtained in Fischer Assay tests. No trend of behavior with geological age is evident. Further details of these test results are available in a previous publication (4).

The MRI Oil Shale Beneficiation Process

Physical beneficiation techniques have long been used in the mineral and coal industries to obtain a product more enriched in the economical mineral than the run-of-mine ore. A prerequisite for physical separation is to free the valuable constituent from the associated impurities. This is normally achieved by comminution of the raw material to sizes finer than their natural particle size consist. The degree of grinding may dictate certain separation approaches. This is particularly important in the case of oil shales, which are fine grained sedimentary rocks composed of 10 micron particles (7). Thus ultrafine grinding of the shale is required to achieve reasonable liberation of oil-bearing kerogen from the intimately associated inorganic mineral matter.

Ultrafine grinding and physical beneficiation of finely disseminated ores were once considered impractical. This is because of the general belief that the grinding costs are prohibitive and that most separation techniques at sizes finer than 74 microns (200 mesh) are ineffective (8). However, this belief has been dispelled with the continuing engineering advancement in beneficiation equipment and recent advances in fine particle technology. This is evidenced by the non-magnetic taconite flotation plant of the Cleveland-Cliffs Iron Company in the Lake Superior Region (9). In this large tonnage plant the hard taconite ore is ground to a particle size finer than 30 microns (500 mesh) prior to flotation to recover high grade iron oxide products. The technical practicality and economic feasibility of extremely fine grinding of the hard, tough taconite suggests that fine grinding and flotation of the oil shale should be equally effective.

During the past six years of continuing research, MRI has developed a beneficiation process which successfully concentrates the Devonian oil shales of the Eastern U.S. The MRI process involves wet grinding the raw shale to minus 20 microns followed by froth flotation to recover a kerogen rich concentrate. Details of the development of this process are available in previous publications (10-12).

MRI test results have been used to formulate a process flowsheet for an oil shale beneficiation plant (Figure 2). The plant is designed to recover concentrates yielding 2 to 3 times as much recoverable oil per ton as can be obtained from the raw untreated shale. Unit operations of this plant are within the limits of current commercial practice. In the process, at least 50% to as much as 70% of the raw shale will be rejected as a substantially barren waste which need not be retorted.

The beneficiation plant includes the following standard mineral processing unit operations:

- Fine grinding of shale to mineral particle liberation size
- Classification
- Kerogen flotation
- Thickening and filtration
- Agglomeration or briquetting of the flotation concentrate
- Disposal of the flotation tailing

Most of the beneficiation research investigations has been directed to the Eastern oil shale deposits, particularly the Devonian shales outcropping in Northern Alabama, but several samples from the Western United States and foreign countries also have been tested in a cursory way. Typical results are shown in Table 3. Plans are to evaluate additional types of oil shales as they become available.

EXPERIMENTAL

The combined beneficiation and hydroretorting studies were conducted on two Eastern oil shale samples (Alabama and Indiana) and one foreign sample (Brazil). The Indiana sample was collected by HYCRUDE Corporation from the Upper Devonian New Albany shale formation near Henryville, Indiana. The Alabama shale sample was part of a 5-ton lot of Upper Chattanooga shale collected by MRI from the Hester Creek area in Madison County, Alabama. The Brazilian oil shale represents a typical shale from the Irati formation in the south of Brazil. Analyses and Fischer Assay oil yields from the three samples and a Western shale are shown in Table 1.

Procedures and Techniques

The beneficiation tests were conducted at the Mineral Resources Institute at the University of Alabama. In these tests the raw shale samples were stage crushed dry to minus 2 mm (10 mesh) and wet ground in a 20 x 30 cm stainless steel rod mill operated at 78% of critical speed using 26 stainless steel rods of 1.7 cm diameter as the grinding medium. A 500-gram charge of each flotation test sample was ground at 50% solids in Tuscaloosa tap water for two hours to reduce the particles to 90% minus 10 microns. Bench scale flotation tests were conducted using a Denver Model D-12 laboratory flotation machine for the conditioning, roughing and cleaning steps. The flotation products were filtered, dried at 50°C, weighed and assayed for oil yield using the modified Fischer Assay method. Samples for hydroretorting were produced from the flotation concentrate using a uniaxial compression briquetting unit to make 1.25 cm diamter by 1 cm high specimens.

Hydroretorting tests were conducted at the Institute of Gas Technology at Chicago, Illinois under the sponsorship of HYCRUDE Corporation using a Hydroretorting Assay unit designed to evaluate the hydroretorting characteristics of oil shale samples. Details of the apparatus and the test procedure have been previously published (6). In this unit a 100-gram sample of material is reacted with hydrogen gas under the following conditions.

- 1000 psig pressure
- 1000°F temperature
- 4 SCF/hr gas flow
- 25 degree/minute heat-up rate
- 30 minutes reaction time

RESULTS AND DISCUSSION

Beneficiation of Raw Oil Shale

Response of the oil shale samples to beneficiation by ultrafine grinding and flotation are given in Table 4. All three samples responded favorably to beneficiation. Good flotation of the kerogen-enriched fractions was obtained from the ground shale which indicated that reasonable liberation of the kerogen and the mineral components was achieved. As compared to the flotation feed, the concentrates recovered from the Alabama and Indiana samples were upgraded in kerogen by factors of 2.4 and 2.8, respectively. Flotation of the Brazilian shale yielded a concentrate assaying 33.5 gallons per ton, but the ratio of concentration (1.7) was less than that of the American oil shale samples. The variations in the response of the samples to flotaton are attributed to differences in their origin, mineral substrate, and composition. The oil recoveries in all cases were comparable. Only the Alabama oil shale has been investigated extensively at MRI and improvements in the flotation results of the other shales would be expected by further research. Even with the limited number of samples evaluated, it appears reasonable to assume that beneficiation of oil shales can be accomplished with good results.

Experimental testwork is continuing on this research program at The University of Alabama to further define the beneficiation variables in an effort to optimize the process. The goal of the research is to establish the technical parameters of the process in a continuous pilot plant operation to define the process economics. The pilot testing will also produce a reasonably large quantity of kerogen enriched concentrate which will be used in more extensive hydroretorting tests.

Hydroretorting of Raw Oil Shale

Results of Hydroretorting Assay tests on the three raw shale samples are given in Table 5. Results of the tests of the U.S. samples indicate that the HYTORT process can produce oil yields of 222 to 226% of those obtained by conventional thermal retorting. The oil yeild from the Brazilian sample was less, only 156%. The hydroretorting data shows that oil yields of 27 to 29 gallons per ton can be produced from oil shale resources which would be considered too lean for commercialization by conventional retorting.

Combined Beneficiation and Hydroretorting of Oil Shale

Combined MRI beneficiation-HYTORT processing was tested on a laboratory scale by hydroretorting the flotation concentrates of three oil shale samples. Test results are shown in Table 6. The concept proved to be technically successful in substantially increasing the extraction of oil. The data indicate that the combined technique can improve the overall level of oil yield from the raw shale by a factor of 2.9 to 5.6.

CONCLUSIONS

Based on the above results, the potential of the combined beneficiation-hydroretorting approach is evident in the following areas:

-- Reduction in the capital and operating costs for oil shale production should be possible by substituting atmospheric pressure, ambient temperature, grinding and froth flotation equipment for some of the elevated pressure and temperature HYTORT reactor units. Further, because of the enhanced shale oil yields, energy savings should result in a lower cost per barrel of shale oil.

-- Pre-retorting concentration of kerogen from lean shales should extend the range of oil shales which can be considered for commercial processing.

-- Rejection of inorganic sulfur (i.e., pyrite) may be possible either by flotation or high-intensity magnetic separation. By removing the pyrite, not only will the kerogen content increase but the overall quality of the concentrate will be enhanced.

-- During grinding, trace elements are solubilized into the process water. As a result, the tailings rejected during beneficiation and the spent shale produced by HYTORT processing should be less prone to the natural leaching of harmful metals and elements. Thus, surface and groundwater contamination after disposal should be substantialy reduced.

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Table 1. Analysis and Fischer Assay Oil Yield of Selected Oil Shales

Oil Shale Sample	Alabama	Indiana	Brazil	Colorado
ULTIMATE ANALYSIS (wt. %)				
Organic Carbon	14.20	12.53	13.70	13.60
Organic Hydrogen	1.03	0.93	1.37	2.10
Sulfur	8.02	4.41	4.98	0.50
Carbon Dioxide	2.90	2.30	N.A.	15.90
Nitrogen	0.48	0.48	0.44	0.50
Ash	79.70	77.83	80.00	66.80
Atomic H/C Ratio	0.87	0.94	1.2	1.85
FISCHER ASSAY				
Yield (wt. %)	4.9	4.6	7.1	11.4
Yield (gal/ton)	11.6	12.0	18.6	29.8
Carbon Conversion (%)	31.2	32.9	50.0	84.0

Table 2. Selected Hydroretorting Assay Test Results

Oil Shale Sample	Oil Yield (gal/ton)		
	Fischer Assay	Hydroretorting Assay	Percent of Fischer Assay
Sweden - Billingen	3.8	17.5	440
Sweden - Naerke	10.9	32.3	300
Sicily	4.4	12.2	280
Indiana - New Albany	12.5	28.2	230
Montana - Heath Formation	16.2	33.6	210
Canada - Kittle	10.0	21.1	210
Jordan - El Lajjun	32.8	57.0	170
Brazil - Lower Irati	19.4	32.7	170

Table 3. Selected Beneficiation Test Results				
Oil Shale Sample	Fischer Assay (gal/ton)		Percent Oil Recovered	Ratio of Concentration
	Flotation Feed	Flotation Concentrate		
Eastern U.S.				
Alabama	12	37	87	3.1
Kentucky	17	31	81	1.8
Indiana	12	35	81	2.9
Western U.S.				
(Lo-grade)	14	34	90	2.4
(Hi-grade)	46	88	80	1.9
Canadian	8	16	52	2.0
Brazil	20	34	89	1.7

Table 4. Flotation Response of Raw Oil Shales				
Oil Shale Sample	Flotation Products	Weight Percent	Fischer Assay Yield (gal/ton)	Distribution of Oil (%)
Alabama Chattanooga Shale	Concentrate	27.0	34.3	80.0
	Reject	73.0	3.2	20.0
	Feed	100.0	11.6	100.0
Indiana New Albany Shale	Concentrate	35.5	27.2	79.0
	Reject	64.5	4.4	21.0
	Feed	100.0	12.5	100.0
Brazil Irati Shale	Concentrate	48.9	33.5	88.2
	Reject	51.1	4.3	11.8
	Feed	100.0	18.6	100.0

Table 5. Hydroretorting Assay Test Results of Raw Oil Shales			
Oil Shale Sample	Original Sample Fischer Assay (gal/ton)	Hydroretorted Sample Assay (gal/ton)	Oil Yield Percent of Fischer Assay
Alabama - Chattanooga	11.6	27.8	220
Indiana - New Albany	12.5	27.2	230
Brazil - Irati	18.6	29.0	160

Table 6. Combined Beneficiation - Hydroretorting of Oil Shales				
Oil Shale Sample	Oil Yield (gal/ton)			Overall Percent of Fischer Assay
	Original* Sample	Flotation* Concentrate	Hydroretorted Concentrate**	
Alabama - Chattanooga	11.6	34.3	65.0	560
Indiana - New Albany	12.5	27.2	54.4	430
Brazil - Irati	18.6	33.5	53.3	290

* Fischer Assay
** Hydroretorting Assay

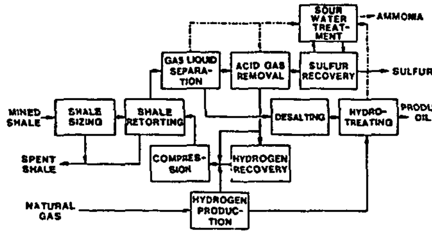

Figure 1. CONCEPTUAL COMMERCIAL HYTORT PLANT BLOCK FLOW DIAGRAM

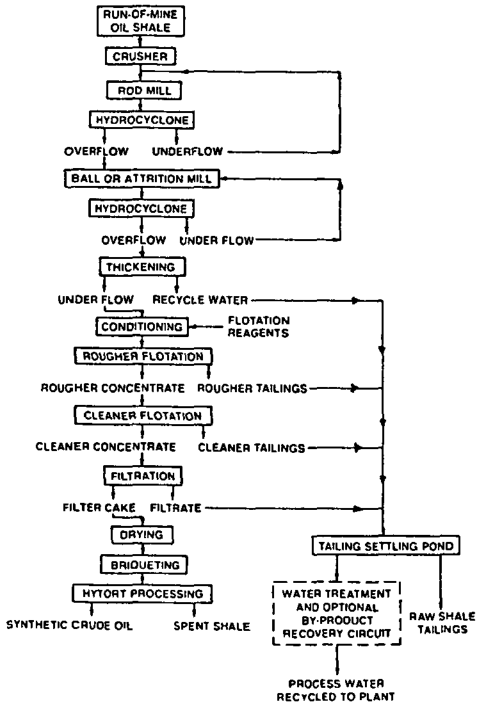

FIGURE 2. SCHEMATIC FLOWSHEET FOR MRI OIL SHALE BENEFICIATION PLANT