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REFINING AND UPGRADING OF SYNFUELS FROM COAL AND OIL SHALES BY ADVANCED CATALYTIC PROCESSES

Quarterly Report for the Period
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I. Abstract

In this report, the pilot plant studies on the refining of two H-Coal syncrudes are summarized. This report shows that conventional transportation fuels (jet, diesel, and motor gasoline) can be refined from the H-Coal syncrudes. These syncrudes are relatively low boiling when compared to petroleum. As a consequence of this property, excellent yields of distillate fuels (jet and diesel) can be obtained from the syncrudes by simple hydrotreating with no subsequent cracking process. For the exclusive production of gasoline, a cracking process is needed.

Hydrotreating and, when necessary, hydrocracking appear to be suitable refining routes for converting the coal-derived syncrude to transportation fuels. This route gives a yield of transportation fuel almost equivalent to the original volume of the syncrude. In addition, the heteroatoms are ultimately removed as sulfur and salable ammonia.

The pilot plant studies have shown that modern commercial hydroprocessing technology can be used to refine the H-Coal syncrudes. However, they also show that high boiling impurities in the syncrudes can make these feedstocks difficult to refine in the downstream hydroprocessing units. Most of these impurities can be removed by redistilling the syncrude.

II. Contract Objectives and Scope of Work

The objective of the program as originally defined is to determine the feasibility and estimate the costs of hydroprocessing four synthetic crude feedstocks to distillate fuels, including high octane gasoline, using presently available technology. The first three feedstocks are: (1) Paraho shale oil; (2) solvent refined coal (SRC) in two forms, SRC-I and SRC-II; and (3) H-Coal process products from two different coals, Illinois No. 6 (Burning Star Mine) and Wyodak. DOE and Chevron have agreed that the fourth feedstock will be EDS process product from Big Brown Texas lignite, obtained from in the so-called bottoms recycle mode of operation.

According to the contract, the feasibility of hydroprocessing each of the synthetic liquids mentioned above will be compared through catalyst tests and evaluations from which commercial plant yields, hydrogen consumption, product distribution, and product inspection will be estimated. The necessary tests and evaluations for each feedstock will be done to support "process comparision"-type estimates for each of the major refining steps. The results of the contract, insofar as hydroprocessing is concerned, will be obtained with Chevron commercial catalysts.

Catalyst activity and stability information for each feedstock will be obtained as needed to define commercial operating conditions. These data will provide the basis for the overall refining plan, plant cost estimates, utility and hydrogen requirements, etc. If tests show that refining a particular feedstock using presently existing technology is not feasible, it is not intended under this program to conduct any research or development work to solve the problems encountered.

Tests will be conducted only to the extent needed to enable making reasonable estimates of commercial plant performance and only to the extent a commercial plant is feasible using presently existing technology, subject to the mutual agreement of DOE and Chevron Research. Tests will be made for each whole synthetic oil and, where appropriate, for the fractions derived therefrom. Tests will not be carried out for processes which can be reliably estimated.

III. Summary of Progress to Date

Studies of the processing of the first feedstocks, Paraho shale oil, are complete and are described in an interim report (FE-2315-25) issued in April 1978.

Experimental studies of the processing of the second feedstock, SRC, are also complete. This study was subdivided to include two types of SRC from the SRC process, SRC-I and SRC-II. The second interim report (FE-2315-45) describes the processing of SRC-I (November 1979). The third interim report describes the experimental program and the process engineering studies on the processing of SRC-II (FE-2315-47, March 1980). The fourth interim report (FE-2315-50) is an update of process engineering studies and costs for processing Paraho shale oil (June 1980).

The third feed, H-Coal process product, was supplied by Hydrocarbon Research, Inc., in two forms: (1) H-Coal process product derived from Illinois No. 6 coal, Burning Star Mine (Feed 3A), and (2) Wyodak H-Coal process product (Feed 3B). The experimental program is complete for both H-Coals. Work on Task VI (engineering design studies and processing cost estimates) is now in progress and we expect to complete this work during the first quarter of 1981. The fifth interim report on the refining of H-Coal syncrudes is in preparation.

Feed 4, selected by mutual agreement between Chevron and DOE, is to be EDS product from Big Brown Texas lignite produced in the bottoms recycle mode of operation. We have not yet received this feedstock.

DOE has also requested that our studies include an additional SRC-II syncrude which will be hydrotreated to provide DOE with product for biological studies. Contractual arrangements for inclusion of this feed as "Task 9" are being finalized, and we will start work on this task as soon as the feed is received.

IV. 1980 Papers and Presentations

The following papers were presented in 1980.

"Catalytic Upgrading of H-Coal Syncrudes," by D. J. O'Rear, R. F. Sullivan, and B. E. Stangeland, was presented at the Symposium on "Coal Liquids Upgrading" at the 179th National Amercian Chemical Society Meeting in Houston, Texas, March 23-28, 1980. This symposium was sponsored jointly by the Divisions of Fuel and Petroleum Chemistry. The cost of presentation of this paper was paid by DOE.

"Refining of Syncrudes," by R. F. Sullivan, D. J. O'Rear, B. E. Stangeland, and H. A. Frumkin, was presented in Houston, Texas, at the 45th American Petroleum Institute Midyear Refining Meeting Session on Feedstocks: Impact of Changing Quality, May 15, 1980. Cost of the presentation of this paper was paid by Chevron.

"Refining of Syncrudes," by R. F. Sullivan, D. J. O'Rear, B. E. Stangeland, and H. A. Frumkin, was presented to the California Energy Commission workshop on Strategic Energy Policy for California, July 17-19, 1980. Cost of the presentation of this paper was paid by Chevron.

"Catalytic Hydroprocessing of SRC-II and H-Coal Syncrudes for BTX Feedstocks," by R. F. Sullivan, D. J. O'Rear, and B. E. Stangeland, was presented at the 180th National ACS Meeting in Las Vegas, August 24-29, 1980, at the Symposium on Alternative Feedstocks for Chemicals. This symposium was sponsored jointly by the Divisions of Petroleum and Fuel Chemistry. Cost of the presentation of this paper was paid by Chevron.

"Downstream Processing of Colorado Shale Oil," by R. F. Sullivan, H. A. Frumkin, and B. E. Stangeland, was presented at the Morocco United States Shale Oil Colloquium held in Rabat, Morocco, October 3-10, 1980, and sponsored by the Moroccan Ministry of Energy and Mines jointly with the U.S. Departments of State and Energy and the U.S. Agency for International Development. Cost of the presentation of this paper was paid by Chevron.

"Cost Comparisons of Alternative Routes for Converting SRC-II Oil to Distillate Fuels," by H. A. Frumkin and R. F. Sullivan, was presented at the conference on "Synthetic Fuels: Status and Directions," sponsored by the Electric Power Research Institute and the Ministry of Energy of the Federal Republic of Germany, October 13-16, 1980, in San Francisco. Cost of the presentation of this paper was paid by Chevron.

V. Review of Pilot Plant Studies on the Refining of H-Coal Syncrudes

The first of two objectives of this program was to determine the technical feasibility of refining H-Coal syncrudes. To fulfill this objective, it was necessary to determine suitable operating conditions and yields from processes which refine H-Coal syncrudes to transportation fuels (motor gasoline, jet fuel, and diesel fuel). At the request of the DOE Technical Project Officer, the refining of H-Coal syncrudes to heating fuels was also evaluated. The second objective of this program was to estimate the cost of refining the syncrudes.

The program started with analysis of the syncrude. Based on the properties of the H-Coal syncrude, preliminary refining steps were selected. The results from these preliminary refining steps were used to select subsequent refining steps. In this way, the key refining steps were evaluated in pilot plants in accordance with the tasks of the program. After completion of the pilot plant program, process engineering studies were made. The estimation of the cost of refining the syncrude is based on the engineering studies which are still in progress.

A. Feed Preparation and Analysis

Two batches of H-Coal syncrudes used in this study simulated the expected liquid products from the commercial H-Coal process, as best could be determined at the time of selection. In the current proposed design for this process, all of the heaviest product from the liquefaction reactor is recycled or used to make the hydrogen which is needed in liquefaction. Therefore, the net liquid product from the proposed design and the batches of syncrude used in this study do not contain this heavy product and were blends of H-Coal atmospheric overhead and atmospheric bottoms.

H-Coal atmospheric overhead and atmospheric bottoms derived from Illinois No. 6 and Wyodak coals were received from Hydrocarbon Research, Inc. (HRI). The naphthas and atmospheric bottoms were blended in ratios recommended by HRI to form net whole liquid products from the H-Coal process. These net whole liquid products are referred to as Illinois H-Coal and Wyodak H-Coal syncrudes. The syncrudes were then analyzed by conventional methods which were developed for petroleum products.

Pilot plants were set up for three product slates: (1) the production of a maximum jet or diesel fuels, (2) the production of all gasoline,

and (3) the production of a maximum of heating fuel. Extensive pilot plant tests totaling more than 10,000 onstream hours were made to evaluate the catalysts needed to refine the H-Coal syncrudes to these three product slates.

B. Production of Maximum Jet and Diesel Fuel

Chevron's ICR 106 catalyst which contains nickel, tungsten, silica, and alumina was used to hydrotreat the Illinois H-Coal syncrude in a single stage to specification jet or diesel fuel. Typical conditions for the hydrotreating of the H-Coal and SRC-II syncrude to specification jet and diesel fuel are shown below.

Hydrotreater Operating Conditions and Yields	Illinois H-Coal		Wyodak H-Coal		SRC-II
	As Is	Rerun	As Is	Rerun	As Is
Temperature, °F	750	750	750	750	750
LHSV	0.5	1.5	1.0	1.5	0.5
H_2 Pressure, psia	2300	2300	2300	2300	2300
Max. Jet A Yield, LV %	88	84	75	72	85
Max. Diesel Yield, LV %	90	84	77	72	87
By-Product Naphtha Yield, LV %	21	23	29	32	25
H_2 Cons., SCF/Bbl	2150	2000	1230	1200	3100

The yields of jet, diesel fuel, and naphtha are excellent; but the hydrogen consumption can be large. These yields are from the hydrotreater alone and are not from the whole refinery. They do not allow for source of hydrogen or refining fuel. If these must be obtained from the syncrude, the net yield of these transportation fuels from the whole refinery will be less.

The jet and diesel fuels pass all stability tests, even without additives. When all the aromatic compounds in these syncrudes are converted to naphthenes, the jet fuel smoke point is about 22 mm (2 mm above the 20 mm ASTM minimum) and the diesel fuel cetane number is 40, which just meets the ASTM minimum.

For the manufacture of jet and diesel fuel, the H-Coal syncrudes were hydrotreated in two forms, either as the original blend or after rerunning (redistillation). The initial hydrotreating step is very sensitive to impurities in the H-Coal syncrude. These impurities,

which are insoluble in hot heptane, range from 469 ppm in the SRC-II syncrude to 3500 ppm in the Illinois H-Coal syncrude. The origin of these impurities is not known. They may be the result of aging of the syncrudes rather than original products of the coal liquefaction processes. These impurities boil at very high temperatures and can be readily separated from the syncrude by rerunning them. When this is done, the rates of the hydrotreating reactions increase.

	Illinois H-Coal		Wyodak H-Coal		SRC-II
	As Is	Rerun	As Is	Rerun	As Is
LV % of Whole Syncrude	100	87	100	96	100
Hot C_7 Insolubles, ppm	3500	54	680	<10	469
Max. LHSV for Jet Fuel Product	0.5	1.5	1.0	1.5	0.5
Relative Reactor Size of Hydrotreater	1	1/3	1/2	1/3	1

The size of the Illinois H-Coal syncrude hydrotreating reactor can be reduced by a factor of three when the syncrude is rerun and the concentration of heavy impurities is controlled. There were less impurities in the Wyodak H-Coal syncrude, but the size of the Wyodak H-Coal syncrude hydrotreating reactor can be reduced by a factor of 1.5 when the syncrude is rerun. Since these impurities severely hinder the refining of the syncrude, the amount of these impurities should be monitored and controlled during the production, transportation, and storage of the syncrude.

While these jet and diesel fuels have marginally acceptable smoke points and cetane numbers, they have very low freeze points and cloud points and are excellent fuels for cold climates. In addition, the cetane number of one diesel fuel was shown to be improved from 40.2 to 43.7 by the addition of only 0.1 vol % octyl nitrate. The addition of 0.3 vol % octyl nitrate improved the cetane number from 40.2 to 48.3.

C. Production of All Gasoline

If gasoline is the only desired product from these syncrudes, both hydrotreating and hydrcracking steps are needed. The Illinois H-Coal syncrude was hydrotreated in this all gasoline mode at 750°F, 2300 psia H_2, and 1 LHSV with ICR 106. The Wyodak H-Coal syncrude was hydrotreated at 785°F, 1850 psia H_2, and 1.5 LHSV with ICR 113 catalyst. ICR 113 contains nickel, molybdenum, silica, and alumina and is

both less active and less expensive than ICR 106. The hydrotreated product which boils above the naphtha was hydrocracked over ICR 202. The naphthas from these two steps are very rich in naphthenes and are excellent reformer feedstocks. If the end point of the naphtha is limited to 315°F, the concentration of dinaphthenes (potential reforming catalyst poisons) are reduced to an acceptable level.

	Typical 180-315°F Hydrocracked Naphtha Composition, LV %	
	Total Cyclic Compounds	Dinaphthenes
Illinois H-Coal	89	7
Wyodak H-Coal	85	4
SRC-II	89	3

These coal-derived syncrudes can also be refined to benzene, toluene, and xylene (BTX). The total yield of BTX precursors (naphthene analogues of BTX) are between 52 LV % and 59 LV %.

	BTX Precursor Yield, LV %
Wyodak H-Coal	52.5
Illinois H-Coal	55.6
SRC-II	58.9

The yield of BTX from a refinery which has only hydrotreating, hydrocracker, and reforming units could be nearly 50 LV %. If a dealkylation unit is included, the yield of BTX could be considerably higher.

D. Production of Heating Fuels

The specification jet and diesel fuels made from the H-Coal and SRC-II syncrudes can also be excellent heating fuels. However, in their preparation, these fuels have consumed a large amount of hydrogen; and the cost of refining these syncrudes is large. When the hydrotreating severity is reduced, a more aromatic and less costly heating fuel is produced. One selected set of fuels and conditions is shown below.

Hydrotreater Operating Conditions and Yields	Illinois H-Coal	Wyodak H-Coal	SRC-II
Catalyst	ICR 106	ICR 113	ICR 106
Temperature, °F	750	750	750
LHSV	1.5	1.5	1.5
H_2 Pressure, psia	1850	1850	1850
Max. Heating Fuel Yield, LV %	84	77	85
By-Product Naphtha Yield, LV %	19	23	21
H_2 Cons., SCF/Bbl	820	420	1720

These very aromatic heating fuels do not meet the ASTM specifications for API gravity or viscosity. Burner nozzles may have to be redesigned to accomodate this slightly denser and slightly less viscous heating fuel. In short-term tests, the minimum hydrogen pressure which is needed for the production of stable heating fuel from the Wyodak H-Coal syncrude was determined. At 400 psia, the product is unstable; and at 900 psia, the product is marginally stable. Above 900 psia, the product is stable in these short-term tests.

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