

Hydrogenated COED Oil

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Introduction

The COED process converts coal by fluidized-bed pyrolysis into gas, oil and char. Under Project COED, which is sponsored by the Office of Coal Research of the Department of the Interior, a 30 B/D fixed-bed catalytic hydrogenation pilot plant was constructed and operated for the hydrogenation of COED oils. This facility operates with a 36 T/D coal pyrolysis pilot plant. The Central Research and Development Department of the FMC Corporation conducts this work.

As would be expected, COED oils as produced have a high density and a low hydrogen content. In addition, they have a high concentration of heteroatoms--oxygen, nitrogen and sulfur. Hydrogenation is necessary to produce a synthetic crude oil from the COED oil to fit in with conventional refinery processing. The raw COED oil must be filtered before fixed-bed hydrogenation to remove fines. The fines content of the raw oil is reduced from about 3.0 percent to less than 0.1 percent by weight prior to hydrogenation.

The hydrogenation pilot plant was started up in May, 1971 after resolution of a number of mechanical problems. Except for recurrence of several minor mechanical problems, operation has proceeded satisfactorily.

Pilot Plant Design

The pilot plant is, in general, of conventional refinery hydro-treating design. The major equipment consists of downflow reactors with makeup and recycle hydrogen compressors and heaters. No downstream or upstream distillation equipment is included. Details were published in a project report to the Office of Coal Research¹.

One somewhat unusual feature is the use of a guard chamber-type reactor ahead of the main reactors. This was installed because it was feared that residual fine solids or the caking characteristics of the charge stock might plug the main reactors. All reactors are in series. To date no difficulty has been experienced with plugging of the guard chamber.

The design feed to this hydrotreating unit was 30 B/D of filtered COED oil with a gravity of less than zero °API. The total reactor design was for a 1.0 hourly space velocity on a weight basis. The catalyst charged to the reactors was HDS-3 catalyst produced by American Cyanamid Co. This is a 1/8-inch extrudate with 3 percent NiO and 15 percent MoO₃ on alumina. The compressors were designed to recycle enough hydrogen to produce a ratio of 18,000 scf/bbl. The maximum temperature and pressure were designed to be 950°F. at 3300 psig.

Hydrogenation Results

All of the runs reported in this study were made with a COED oil produced from the pyrolysis of a Colorado coal from the Bear Mine. This is a high-volatile B bituminous coal. The analysis of the feed oil is shown in Table I.

Demetalization

Unlike most petroleum crudes, there were very few major metallic ingredients in the COED oil. The analyses of the feed and product oil after hydrogenation are shown in Table II.

Treatment with hydrogen over a hydrogenation catalyst effectively removed iron, aluminum and silicon. Only minor effect was noted on the boron, sodium and vanadium concentrations.

Heteroatom Removal

Several long-term runs were made on the hydrogenation pilot plant. These were mainly at lower-than-design temperatures and space velocities while maintaining high recycle hydrogen rates. The results of these runs are shown in Table III.

The results shown in Table III are presented graphically in Figures 1 and 2. Because of the exothermic nature of the reaction and the spacing of the thermocouples, the reactor temperatures varied. The average throughout the beds was 650-750°F. Additional runs at higher temperatures and higher space velocities are planned and will be reported later.

As is noted on Figure 1, the heteroatom removal of sulfur, nitrogen and oxygen compounds is essentially complete at the lower space velocities and at the reactor conditions prevailing. Nitrogen was the most difficult component of the COED oil to remove on hydrotreating. Sulfur and oxygen were less difficult and almost identical, not only in the relative difficulty of removal, but also in the effect of changes in space velocity.

The effect of space velocity, other conditions nearly constant, upon API gravity of the heavy oil product is shown in Figure 2. As would be expected, the lower the space velocity, the higher the API gravity.

Because of the few runs so far from this hydrotreating pilot unit, no direct comparison can be made to previous studies^{2, 3}. In general, however, the results presented here from the hydrotreating pilot unit tend to confirm the earlier bench-scale studies from the AtlanticRichfield studies. They also prove that adequate heteroatom removal in commercial units is possible at modest severities.

Product Inspections

A sample of the hydrotreated COED oil from Run H3D (maximum heteroatom removal) was distilled into several fractions. These fractions represent the conventional distillation ranges for gasoline, middle distillates, gas oil and bottoms produced in conventional

petroleum refining. The approximate yields of these various cuts are shown in Table IV. The distillation curves for the raw COED oil and for the hydrotreated COED oil are presented in Figure 3.

The results of the product inspections on these various cuts are presented in Table V. Also, an ASTM distillation of the gasoline boiling-range material is presented in Figure 4.

From these petroleum-type inspections it can be readily seen that hydrotreated COED oil is a satisfactory crude oil charge to a petroleum refinery. These inspections show that these cuts can be adequately blended into conventionally produced refinery streams. The gasoline and middle distillate stocks exhibit a high gum content. This gum can be virtually eliminated by any number of conventional refinery treating processes.

The middle distillates fraction is somewhat low in gravity, as would be suspected. It would be anticipated, however, that it would be very high on a Btu per volume basis. No attempt was made to evaluate the special properties of such middle distillate fractions as jet fuel, kerosene, diesel fuel or No. 2 fuel. Color and color stability are excellent.

The higher boiling cuts also appear to be adaptable to conventional refining techniques. The gas oil fraction has a low carbon residue of 0.03 wt. percent and metals of less than 0.2 ppm nickel and vanadium. From the ultimate analysis it would appear that the residue boiling higher than 800°F. would make excellent feedstock for a carbon-black plant. From these analyses there is an indication of concentration of the nitrogen-containing molecules in the gas oil and residue fractions; no similar concentration of sulfur or oxygen is noted. The gas oil fraction should make excellent feed for either a catalytic-cracking or hydrocracking unit.

References

- ¹ "Char Oil Energy Development" - Project COED, Final Report; J. F. Jones, F. H. Schoemann, J. A. Hamshar, and R. T. Eddinger; Period of Performance: October 1966 - June 1971; Contract No. 14-01-0001-498.
- ² White, P. J. (ARCO Chemical Co.), Jones, J. F., and Eddinger, R.T., "To Treat and Crack Oil from Coal", Hydrocarbon Processing, 47, No. 12, pp. 97-102, December 1968.
- ³ Jacobs, H. (AtlanticRichfield), Jones, J. F., and Eddinger, R. T., "Hydrogenation of COED Process Coal-Derived Oils", Ind.Eng.Chem. Process Des.Develop., 10, No. 4, October 1971.

TABLE I
Analysis of Feed Oil

Oil Source	Colorado Bear
Moisture, wt. %	0.20
Quinoline Insoluble, wt. %, dry	0.00
<u>Ultimate Analysis, wt. %, dry</u>	
Carbon	83.05
Hydrogen	8.35
Nitrogen	1.10
Oxygen ¹	0.35
Sulfur	7.15
Ash	0.00
°API Gravity, 60°F./60°F.	-4 to -5
Pour Point, °F.	118
Flash Point, °F.	350
Viscosity, SUS ²	1090

¹ Oxygen determined by difference.

² Viscosity determined at 210°F.

TABLE II

Special Analyses of Feed and Product Oil

Run No.	Feed	Product
<u>Metals Analysis, ppm</u>	-	H3D
Iron	350	<1
Lead	<1	<1
Copper	<1	<1
Chromium	<1	<1
Aluminum	60	<1
Nickel	<1	<1
Silver	<1	<1
Tin	<1	<1
Silicon	23	<1
Boron	9	5
Sodium	6	2
Phosphorus	<100	<100
Zinc	<100	<100
Calcium	<100	<100
Barium	<100	<100
Vanadium	7	6
Magnesium	2	<1
Titanium	<1	<1
Conradson Carbon, wt. % ¹	-	0.31

¹ On a 10% ASTM distillation residue.

TABLE III
Analysis of Heavy Oil Product

Run No. ¹	H3	H4	H3D	H5
Feed Rate, lb./hr.	183.7	298.2	199.6	499.0
Space Velocity, lb. oil/hr./ lb. catalyst	0.24	0.38	0.26	0.64
Moisture, wt. %	0.31	1.42	0.00	0.90
Quinoline Insoluble, wt. %, dry	0.03	0.01	0.00	0.00
<u>Ultimate Analysis, wt. %, dry</u>				
Carbon	88.12	87.49	88.00	86.90
Hydrogen	11.76	10.88	11.60	10.00
Nitrogen	0.02	0.40	0.01	0.90
Sulfur	0.02	0.04	0.01	0.10
Oxygen ²	0.08	1.19	0.38	2.10
Ash	0.00	0.00	0.00	0.00
°API Gravity, 60°F./60°F.	24.4	15.1	24.5	9.1
Pour Point, °F.	55	60	60	70
Flash Point, °F.	95	140	168	182
Viscosity, SUS ³	46	182	44	1041
<u>Heteroatom Removal, %</u>				
Sulfur	94.3	88.6	97.1	71.4
Nitrogen	98.2	63.6	99.1	18.2
Oxygen	98.9	83.4	94.7	70.6

¹ All runs made at 2500 psi at temperatures between 650-750°F. with American Cyanamid AERO HDS-3 catalyst.

² Oxygen determined by difference.

³ Viscosity determined at 100°F.

TABLE IV
Product Yields

	<u>Vol. % of</u> <u>Hydrotreated Oil</u>
Gasoline, IBP-400°F.	17
Middle Distillates, 400-600°F.	36
Gas Oil, 600-800°F.	31
Residual, Above 800°F.	16

TABLE V
Analyses of H3D Cuts

Run No. Cut, °F.	H3D			Residue
	IBP-400	400-600	600-800	
Moisture, wt.%	0.2	<0.2	<0.2	<0.3
Quinoline Insoluble, wt.%, dry	0.0	0.0	0.0	0.0
Ultimate Analysis, wt.%, dry				
Carbon	86.20	87.20	88.39	88.94
Hydrogen	13.74	12.40	11.51	10.89
Nitrogen	0.02	0.06	0.10	0.16
Sulfur	0.02	0.01	0.00	0.01
Oxygen ¹	0.00	0.33	0.00	0.00
Ash	0.02	0.00	0.00	0.00
°API Gravity, 60°F./60°F.	45.1	28.9	20.1	0.926 ²
Pour Point, °F.	-	-121	-31	-
Flash Point, °F.	-	148	-	-
Freezing Point, °F.	-	-	-	-
Cloud Point, °F.	-	<-60	-	-
Smoke Point	-	10	-	-
Viscosity, SUS @100°F.	<32	32.4	52.0	56.8 ³
Color	-	lighter than 1.0	-	-
Conradson Carbon, wt.% ⁴	-	0.02	0.03	-
Reid Vapor Pressure, @100°F., psi	1.1	-	-	-
Copper Strip	1B	-	-	-
Gum, mg./100 ml.	63.0	2026	-	-
Octane No.	Too much	gum for analysis	-	-
Aromatics	15.7	47.5	-	-
Olefins	1.4	1.4	-	-
Saturates	82.9	51.1	-	-

¹ Oxygen determined by difference.
² Specific gravity at 210°F.
³ SUS @210°F.
⁴ On a 10% ASTM distillation residue.

FIGURE 1

SPACE VELOCITY VS HETEROATOM REMOVAL
(TEMP. 650-750°F, PRESSURE 2500 PSIG)

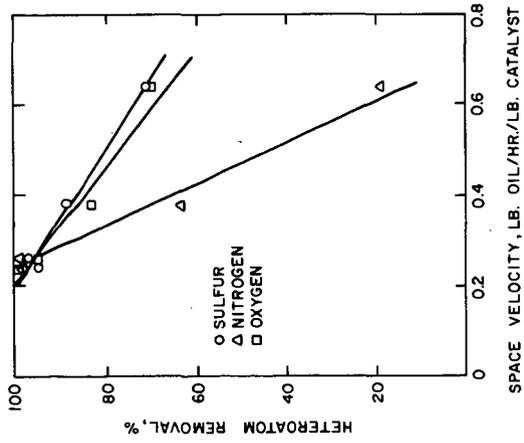


FIGURE 2

SPACE VELOCITY VS API GRAVITY
(TEMP. 650-750°F, PRESSURE 2500 PSIG)

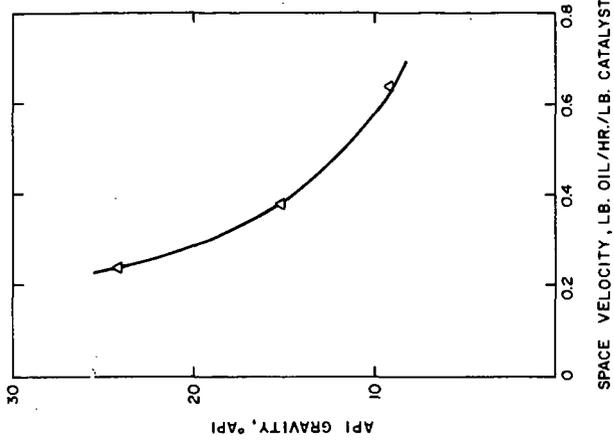


FIGURE 4
ASTM DISTILLATION
H-3D IBP-400°F CUT

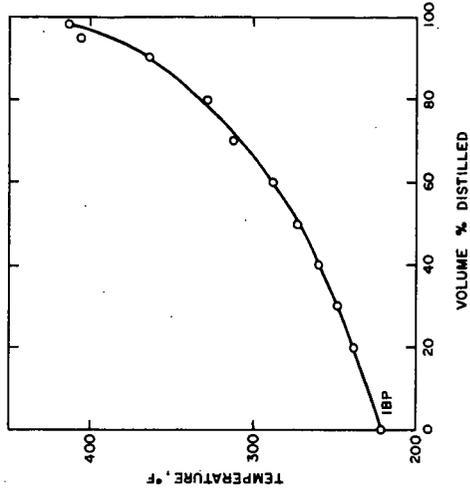


FIGURE 3
ASTM DISTILLATION
FEED OIL & H-3D HEAVY OIL PRODUCT

