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Hydrogenating Shale Oil at Low Space Velocity

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Hydrogenating Shale Oil at Low Space Velocity

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CONTENTS

ILLUSTRATION

TABLES

HYDROGENATING SHALE OIL AT LOW SPACE VELOCITY

by

C. M. Frost[1] and P. L. Cottingham[2]

ABSTRACT

Crude shale oil prepared by gas-combustion retorting of Colorado oil shale was hydrogenated over a cobalt molybdate catalyst at an operating pressure of 1,000 psig, temperatures of 781° and 761° F, and liquid hourly space velocities of 0.10 and 0.05 V_o/V_c/hr, respectively. The yields of total liquid products and the amounts of nitrogen and sulfur removed were comparable with those obtained at an operating pressure of 3,000 psig and a liquid hourly space velocity of 1.0 V_o/V_c/hr. Approximately 1.5 times as much gasoline was produced at the lower pressure and space velocities.

INTRODUCTION

Crude shale oils retorted from Colorado oil shale in N-T-U or gas-combustion retorts are heavy, viscous oils that contain little material boiling in the gasoline range. Crude shale oils retorted from Colorado oil shale have gravities in the range of 16° to 20° API, pour points of 70° to 90° F, sulfur content of nearly 1 pct, nitrogen content of over 2 pct, and oxygen content of 1 to 2 pct (1, 6-7).[3] The high percentages of nitrogen, sulfur, and oxygen compounds, which, for example, represent over 60 pct of one shale oil (1), render the raw oil unsuitable for refining to high-quality motor fuels by conventional refining processes.

Hydrogenation of crude shale oil at an operating pressure of 3,000 psig with space velocities near 1.0 volume of oil per volume of catalyst per hour (V_o/V_c/hr) has been shown to be an effective method for producing high yields of gasoline with low sulfur and nitrogen content (2, 4-5) and gas oil suitable for catalytic cracking (8). However, at operating pressures of 1,000 and 1,500 psig, some pretreatment of the crude shale is required, and considerably lower space velocities are used to achieve the same degree of denitrification and desulfurization (3).

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[1] Chemical research engineer.

[2] Project leader.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

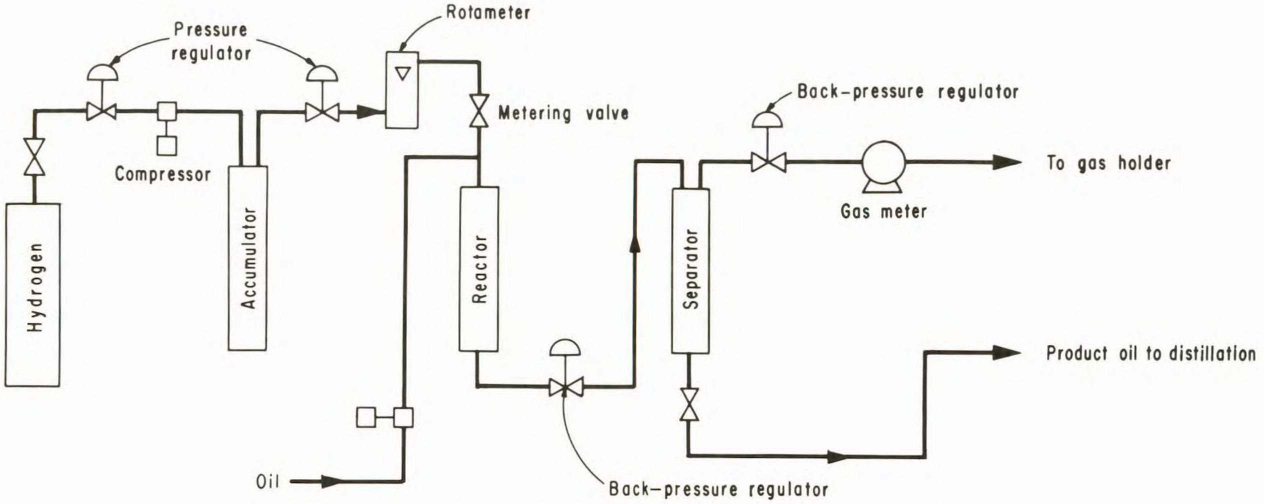

FIGURE 1. - Simplified Flow Diagram of Hydrogenation Unit.

The purpose of the present Bureau of Mines study was to investigate single-pass hydrogenation of crude shale oil at an operating pressure of 1,000 psig using very low space velocities. Tests were made at space velocities of 0.10 and 0.05 V_o/V_c/hr and operating temperatures of 781° and 761° F, respectively.

LABORATORY PROCEDURES

Apparatus and Operating Procedure

A simplified flow diagram of the hydrogenation equipment is shown in figure 1. The reactor was a type 347 stainless steel tube 40 in long (1-1/2-in ID by 2-1/2-in OD), which was charged with 300 ml of catalyst. The catalyst bed was 12-3/4 in long and was supported by a perforated, stainless steel plate 9-1/2 in from the bottom of the reactor. The upper 17-3/4 in of the reactor was filled with Alundum[4] granules and served as a preheater for oil and hydrogen. Temperatures were measured using five thermocouples placed in a concentric thermowell. These thermocouples were spaced at equal intervals from 1 in above the bottom of the catalyst bed to 5 in above the top of the catalyst bed. The recorded temperatures of the bottom four thermocouples were averaged to determine the operating temperatures. The reactor assembly was heated by a four-zone electric furnace, each zone of which was independently controlled.

Hydrogen (99.9+ pct purity) from standard shipping cylinders was used directly without further purification. At the beginning of each experiment, the catalyst was heated to reaction temperature while a stream of air was passing through the reactor. Then, the system was purged with helium and pressurized to 1,000 psig with hydrogen. To presulfide the catalyst, the hydrogen flow rate was adjusted to 2,000 ml/min, and a mixture of 1 vol thiophene in

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[4] Reference to specific products is made for identification only and does not imply endorsement by the Bureau of Mines.

4 vol n-hexane was pumped through the unit for 3 hr at the rate of 120 ml/hr. After the unit was flushed with hydrogen, the hydrogen feed rate was adjusted to that required for the particular experiment, and oil flow was started. Hydrogen was metered to the unit by a high-pressure rotameter and metering valve.

Products from the reactor passed through a back-pressure regulator into a separator maintained at 200 psig. Tail gas from the separator passed through a second back-pressure regulator and was metered and sampled. At the end of each 24-hr test period, the liquid product was drained from the separator and thoroughly mixed; then, a sample was taken for analysis. A portion of the sample was distilled through a column packed with stainless steel helices. The distillate collected with a vapor temperature below 400° F (760 mm) is reported as gasoline; material boiling above 400° F is reported as recycle oil.

Catalyst

The catalyst used was a commercial cobalt molybdate catalyst of the type used by Cottingham and Carpenter (3). The catalyst was received as 3/8-in pellets. The pellets were crushed and sized to pass a 6-mesh screen and be retained on an 8-mesh screen.

Analytical Methods

Standard American Society for Testing and Materials (ASTM) procedures were used whenever available. At the end of the experiment, catalyst deposit percentages were determined by burning the deposits in a stream of air passed through the reactor and collecting the combustion products. Hydrogen consumption was calculated from the ultimate analyses of feed and products.

Charge Stock

The crude shale oil used in this study was produced by retorting Green River shale in a gas-combustion retort at Rifle, Colo. The oil was filtered to remove any shale dust that otherwise would be deposited on the catalyst. Properties of the filtered crude shale oil are shown in table 1. For comparison, the properties of the crude shale oil used by Cottingham, White, and Frost (4) for hydrogenations made at 3,000 psig are included.

Experimental Procedures

One 10-day (240-hr) continuous run was made at a temperature of 781° F, a pressure of 1,000 psig, and a space velocity of 0.10 V_o/V_c/hr.

A second run was made at a temperature of 761° F, a pressure of 1,000 psig, and a space velocity of 0.05 V_o/V_c/hr. The second run was continued for 23 days (552 hr).

TABLE 1. - Properties of gas-combustion crude shale oils

Sample	Present work	Previous work[1]
Specific gravity....................60°/60° F..	0.9310	0.9393
API gravity....................................	20.5	19.2
Pour point.............................° F..	83	79
Viscosity.......................SUS at 100° F..	213	311
Analysis, wt pct:		
Sulfur....................................	0.60	0.67
Nitrogen..................................	2.18	2.10
Carbon....................................	84.93	84.90
Hydrogen..................................	11.32	11.32
Ash.......................................	0.08	0.03
ASTM distillation at 760 mm:		
Initial boiling point..................° F..	297	273
5 pct recovery.........................° F..	399	369
10 pct recovery........................° F..	430	427
20 pct recovery........................° F..	519	548
50 pct recovery........................° F..	625	695
90 pct recovery........................° F..	-	-
End point..............................° F..	670	733
Recovery...........................vol pct..	84.5	70.0

[1] Cottingham, White, and Frost (4).

RESULTS AND DISCUSSION

Table 2 summarizes operating conditions and product yields from the hydrogenation of gas-combustion crude shale oil at very low space velocities. Included in table 2 are data from a single-pass hydrogenation run made with gas-combustion crude shale oil at a pressure of 3,000 psig, a temperature of 784° F, and a space velocity of 1.0 V_o/V_c/hr (4).

Considerably more hydrocracking occurred at 1,000 psig than at 3,000 psig at similar temperature levels, as shown by the increase of more than 50 pct in both gasoline and gas yields. The increase in the occurrence of hydrocracking is reflected in the increased hydrogen consumption at the lower pressure. Catalyst deposit percentages of the oil were significantly less at the lower pressure and space velocities. However, the catalyst deposits as percents of the catalyst weights were about equal at comparable operating temperatures.

Properties of the liquid products are shown in tables 3-4. The data in table 3 show that the degree of denitrogenation and desulfurization attained at the lower pressure and space velocities was essentially the same as that attained at 3,000 psig and a space velocity of 1.0 V_o/V_c/hr. The gasolines obtained at 1,000 psig had slightly higher nitrogen content than that produced at the higher pressure, but the nitrogen contents of the recycle oils at 1,000 psig were lower.

TABLE 2. - Summary of operating conditions and product yields from hydrogenation of gas-combustion crude shale oil

Run data	Run 1	Run 2	Run 3[1]
Operating conditions:			
Temperature ° F	781	761	784
Pressure psig	1,000	1,000	3,000
Space velocity V_o/V_c/hr	0.1	0.05	1.0
Throughput V_o/V_c	23.5	27.2	5.9
Hydrogen feed rate scf/bbl	6,000	6,000	6,000
Hydrogen consumed scf/bbl	1,930	1,770	1,520
Product yields:			
Liquid product wt pct of charge	86.7	90.9	90.9
Gasoline wt pct of charge	27.5	28.0	18.4
Recycle oil wt pct of charge	59.2	62.9	72.5
Gas wt pct of charge	11.0	6.9	6.1
Methane wt pct of charge	2.6	1.6	1.6
Ethane wt pct of charge	2.1	1.7	1.3
Propane wt pct of charge	3.1	1.7	0.5
Butanes wt pct of charge	2.0	1.4	1.6
Pentanes wt pct of charge	1.2	0.5	1.1
Catalyst deposit wt pct of charge	0.4	0.2	1.5
Catalyst deposit wt pct of catalyst	10.2	5.2	10.0
Liquid product vol pct of charge	97.7	102.1	102.2
Gasoline vol pct of charge	33.4	33.9	19.3
Recycle oil vol pct of charge	64.3	68.2	82.9

[1] Cottingham, White, and Frost (4).

Rosenheimer and Kiovsky (9) have shown that with petroleum stock the denitrogenation reaction is first order with respect to nitrogen and that the concentration of nitrogen is related to the pressure and space velocity as follows:

$$\ln \left[\frac{C_n}{C_{n\,o}} \right] = -k_n \; P^2 \, \frac{60}{V}, \tag{1}$$

where C_n = final concentration of nitrogen,

$C_{n\,o}$ = initial concentration of nitrogen,

k_n = reaction rate constant,

P = hydrogen partial pressure,

and V = liquid hourly space velocity.

For crude shale oil at 785° F, the vapor pressure of the oil is very small compared with total pressures of 1,000 and 3,000 psig, and total pressure may be substituted for hydrogen partial pressure without great loss of accuracy in the equation.

TABLE 3. - Properties of liquid products from hydrogenation of gas-combustion crude shale oil

Run data	Run 1	Run 2	Run 3[1]
Total liquid product:			
Specific gravity..........60°/60° F..	0.8286	0.8294	0.8467
Sulfur..........wt pct..	0.02	0.02	0.01
Nitrogen..........wt pct..	0.20	0.20	0.25
Hydrogen..........wt pct..	13.24	13.36	13.38
Carbon..........wt pct..	86.28	86.56	86.36
Gasoline:			
Specific gravity..........60°/60° F..	0.7692	0.7694	0.7612
Sulfur..........wt pct..	0.02	0.01	0.01
Nitrogen..........wt pct..	0.10	0.10	0.07
Hydrocarbons:			
Saturates..........vol pct..	87	84	85
Olefins..........vol pct..	0	0	2
Aromatics..........vol pct..	13	16	13
Research octane numbers:			
Clear..........	45	51	47
+3 ml TEL[2]..........	69	77	72
ASTM distillation at 760 mm:			
Initial boiling point..........° F..	134	137	123
10 pct recovered..........° F..	191	191	189
50 pct recovered..........° F..	308	309	306
90 pct recovered..........° F..	378	379	371
End point..........° F..	400	400	393
Recovery..........vol pct..	98.0	98.0	97.5
Recycle oil:			
Specific gravity..........60°/60° F..	0.8564	0.8593	0.8761
Sulfur..........wt pct..	0.02	0.02	0.01
Nitrogen..........wt pct..	0.24	0.24	0.30
Viscosity..........SUS at 100° F..	43	43	-

[1] Cottingham, White, and Frost (4).
[2] Tetraethyllead.

Using different reaction pressures but the same temperature, the final concentration of nitrogen in the products from feedstocks with equal nitrogen content can be obtained by inserting the corresponding values in equation 1 and canceling equal terms, which would give the following equation:

$$\frac{V_1}{V_2} = \frac{P_1^2}{P_2^2}, \qquad (2)$$

where V_1 = space velocity at condition 1,

V_2 = space velocity at condition 2,

P_1 = pressure at condition 1,

and P_2 = pressure at condition 2.

TABLE 4. - Properties of products from hydrogenation of gas-combustion crude shale oil over cobalt molybdate catalyst

Days on stream	Total liquid product							Gasoline			Recycle oil			
	Gasoline content		Gravity, ° API	Nitrogen, wt pct	Sulfur, wt pct	Carbon, wt pct	Hydrogen, wt pct	Gravity, ° API	Nitrogen, wt pct	Sulfur, wt pct	Gravity, ° API	Nitrogen, wt pct	Sulfur, wt pct	Viscosity, SUS at 100° F
	Wt pct	Vol pct												
(RUN 1) TEMPERATURE 781° F; PRESSURE 1,000 PSIG; SPACE VELOCITY 0.10 V_o/V_c/HR														
1	32.65	34.77	39.0	0.17	0.10	85.60	13.10	52.0	0.11	0.05	33.6	0.20	0.06	42
2	32.50	34.56	39.8	.17	.04	86.18	13.11	51.6	.10	.02	34.6	.21	.03	43
3	31.90	34.21	40.2	.19	.03	86.24	13.21	52.0	.11	.04	34.4	.22	.02	43
4	31.50	33.82	39.6	.22	.02	86.58	13.18	52.0	.11	.03	33.8	.27	.02	43
5	34.50	36.57	39.4	.20	.02	86.16	13.34	53.0	.10	.01	34.0	.25	.04	42
6	29.50	31.80	39.0	.21	.04	86.06	13.20	53.0	.10	.01	33.4	.26	.01	43
7	29.40	31.70	39.0	.21	.01	86.68	13.34	53.0	.10	0	33.4	.26	.01	43
8	28.00	30.27	38.8	.23	0	86.20	13.32	53.0	.11	.01	33.4	.28	.03	43
9	28.10	30.36	38.6	.23	.04	86.34	13.26	53.0	.13	.04	33.2	.27	.01	43
10	31.20	33.53	39.2	.18	.01	86.52	13.24	52.0	.08	.03	33.4	.22	.02	43
(RUN 2) TEMPERATURE 761° F; PRESSURE 1,000 PSIG; SPACE VELOCITY 0.05 V_o/V_c/HR														
1	32.65	35.75	40.4	0.18	0.01	86.64	13.41	51.6	0.14	0.03	33.6	0.20	0.03	43
2	30.90	33.75	39.4	.22	.04	86.61	13.39	51.3	.16	.02	33.4	.25	.01	44
3	30.15	31.79	39.4	.22	.02	86.45	13.32	51.8	.14	.04	34.8	.25	.04	44
4	29.15	31.78	39.4	.21	.02	86.54	13.44	52.3	.14	.02	34.6	.24	.04	43
5	29.50	31.65	39.2	.19	.01	86.40	13.38	51.8	.11	.01	34.6	.22	.02	43
6	29.75	32.05	39.4	.17	.03	86.41	13.36	51.8	.11	.04	34.4	.19	.01	43
7	29.65	31.74	39.4	.20	.02	86.68	13.45	52.0	.12	.01	34.2	.23	.01	44
8	27.50	29.12	38.4	.22	.02	86.51	13.34	52.7	.11	.02	34.0	.26	.03	43
9	29.90	32.59	39.2	.22	.03	86.46	13.30	52.0	.12	.01	33.8	.26	0	44
10	31.55	34.00	39.6	.20	.01	86.60	13.32	51.6	.11	0	33.6	.24	0	44
11	30.55	34.26	40.9	.23	.02	86.30	13.42	51.3	.13	.01	32.5	.28	.01	45
12	30.10	32.41	38.2	.22	.02	86.54	13.39	51.8	.12	.01	33.0	.26	.02	43
13	29.80	32.36	38.2	.24	.01	86.77	13.45	51.8	.13	.02	33.0	.29	0	44
14	29.90	32.18	38.2	.22	0	86.70	13.22	51.6	.12	0	32.7	.26	.01	44
15	29.95	32.60	38.4	.23	0	86.46	13.18	51.8	.12	0	32.7	.27	0	43
16	31.10	34.00	39.2	.19	.02	86.68	13.34	52.0	.10	.01	32.8	.23	.01	43
17	32.00	34.72	39.2	.17	0	86.64	13.32	52.3	.08	.01	32.8	.21	.01	42
18	31.70	34.21	38.4	.18	0	86.51	13.32	51.8	.09	.03	32.8	.22	.01	43
19	31.60	35.05	38.6	.15	.02	86.35	13.24	52.3	.07	.02	31.0	.19	.01	42
20	32.15	35.04	39.4	.17	.02	86.80	13.44	51.8	.08	.01	32.8	.21	.01	43
21	32.50	34.93	38.9	.16	.02	86.54	13.49	52.0	.08	0	32.8	.20	.01	42
22	31.45	35.02	38.9	.16	.01	86.70	13.30	52.5	.08	0	30.2	.20	0	43
23	31.20	33.44	39.2	.17	.01	86.70	13.36	52.0	.09	.01	32.5	.21	0	43

From equation 2, it is calculated that the space velocity at 1,000 psig should be one-ninth that at 3,000 psig for the same degree of denitrogenation. The results obtained in our experiments agree with these calculations.

The data in table 4 show no evidence of a decrease in catalyst activity during either run. For example, in run 1 the maximum nitrogen content of the liquid product (0.23 wt pct) and minimum yield of gasoline (28.0 wt pct) occurred during the eighth day of operation. By the 10th day of operation, the nitrogen content of the liquid product had decreased, and the yield of gasoline had increased to approximately the levels attained on the first day of operation. In the second run, the maximum nitrogen content (0.24 wt pct) of the liquid product occurred on the 13th day of operation, and the minimum yield of gasoline was obtained on the eighth day. From the 16th day of operation until the conclusion of the run, the denitrification activity of the catalyst equaled or exceeded its activity at the beginning of the run. The fact that the denitrification and hydrocracking activity of the catalyst did not decrease appreciably during either run would indicate that long on-stream times could be expected when operating at low space velocities.

SUMMARY AND CONCLUSIONS

Hydrogenation experiments made at an operating pressure of 1,000 psig, temperatures of 781° and 761° F, and space velocities of 0.10 and 0.05 V_o/V_c/hr, respectively, showed that by using such low space velocities it is possible to produce gasoline and recycle oil with nitrogen contents as low as those produced by hydrogenation of crude shale oil at 3,000 psig and higher space velocities. The yields of total liquid product were comparable, and the yields of gasoline at 1,000 psig were approximately 1.5 times as great as that produced at the higher pressure. Nitrogen contents of the recycle oils produced at the low space velocity and pressure were lower than that of the recycle oil produced at the higher space velocity and pressure. Catalyst activity for denitrification at the end of the runs was at least as high as it was at the beginning of the runs.

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