

PRODUCTION OF SYNTHETIC CRUDE FROM CRUDE SHALE OIL
PRODUCED BY IN SITU COMBUSTION RETORTING

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INTRODUCTION

Among the considerations associated with the development of a shale oil industry are the costs and environmental hazards of disposing of the spent shale that inherently is produced if any mining and aboveground retorting approach is involved. For several years the Bureau of Mines has been engaged in research in recovering shale oil by in situ combustion retorting, an approach that avoids spent shale disposal. Both actual underground (1-3) and simulated in situ retorting (4-7) are being investigated.

Crude shale oils produced by in situ combustion retorting of Green River oil shale normally have higher API gravities and lower viscosities and pour points than do crude shale oils produced in N-T-U or gas combustion retorts (8). In situ crude shale oils also contain a much higher percentage of material boiling below 1,000° F. While the nitrogen contents of in situ crude shale oils may be somewhat lower than those of crude shale oils produced in N-T-U or gas combustion retorts, they still contain more than twice as much nitrogen as high-nitrogen petroleum crudes.

Since existing refineries would not be able to cope with the high nitrogen content of raw shale oil if it were a substantial part of the refinery feed, the National Petroleum Council (NPC) (9) has suggested that crude shale oil be upgraded at the retorting site by a process of catalytic hydrogenation to produce a premium feedstock called "syncrude." In this process, the crude shale oil would be distilled to produce naphtha, light oil, heavy oil, and residuum. The residuum would be processed in a delayed-coking unit to produce petroleum coke, and a vapor stream containing gas, naphtha, light oil, and heavy oil. Vapor from the coking unit would flow back to the crude distillation facilities for separation into various fractions. The naphtha, light oil, and heavy oil would be subsequently hydrogenated to remove nitrogen and sulfur and to reduce the viscosity and pour point of the finished syncrude.

There is some disagreement in the literature as to which type of hydrotreating catalyst is the most effective for removing nitrogen from crude shale oil and/or shale oil coker distillates. Carpenter and Cottingham (10) found that, of 17 catalysts tested, a cobalt-molybdate-on-alumina catalyst was superior for removing nitrogen from crude shale oil. Benson and Berg (1) reported that of 12 catalysts tested an HF-activated cobalt-molybdate catalyst was superior for removing nitrogen from shale oil coker distillates. On the other hand, Montgomery (12) reported that catalysts containing high concentrations of nickel and tungsten were best for hydrodenitrogenation. These investigators did not report any work with nickel-molybdenum or nickel-cobalt-molybdenum catalysts.

The purpose of the present study was to test various modern hydrogenation catalysts for their effectiveness in removing nitrogen from in situ crude shale oil fractions and to determine the feasibility of producing a synthetic crude oil that would meet the specifications for syncrude suggested by the National Petroleum Council. Six modern hydrogenation catalysts were tested to compare their efficiencies in removing nitrogen from a heavy (600° to 1,000° F) in situ gas oil. The best catalyst, nickel-molybdenum-on-alumina, was used in preparing fractions of a synthetic crude using the methods suggested by NPC.

PROPERTIES OF IN SITU CRUDE SHALE OIL

The crude shale oil used in this study was obtained from an in situ combustion retorting experiment at Rock Springs, Wyo. (1-2), during the last week of the experiment and is considered a representative "steady state" oil. Properties of the in situ crude shale oil are shown in table 1.

TABLE 1. - Properties of in situ crude shale oil

Gravity.....	° API...	28.4
Nitrogen.....	wt-pct...	1.41
Sulfur.....	wt-pct...	.72
Pour point.....	° F...	40
Viscosity.....	SUS at 100° F...	78
Carbon residue.....	wt-pct...	1.7
Ash.....	wt-pct...	.06

EXPERIMENTAL PROCEDURES AND RESULTS

Apparatus and Operating Procedure

A simplified flow diagram of the hydrogenation unit is shown in figure 1. The reactor used in these experiments was a 1-inch-outside-diameter by 9/16-inch-inside-diameter, type 316, stainless steel tube 40 inches long. The catalyst bed was supported by a stainless steel screen 11 inches from the bottom of the reactor. A second screen was placed at the top of the catalyst bed, and the upper part of the reactor was filled with quartz chips and served as a preheater for oil and hydrogen. The reactor was surrounded by a 3-inch-outside-diameter by 1-inch-inside-diameter aluminum block and was heated by a four-zone electric furnace, each zone of which was independently controlled. Temperatures were measured by five thermocouples placed in a groove in the aluminum block adjacent to the reactor and spaced at equal intervals along the length of the catalyst bed and preheater. With proper adjustment of the heating elements, the recorded temperatures could be maintained within 5° F of each other.

At the beginning of each experiment the catalyst was heated to 700° F with air passing through the reactor at the rate of 1.1 standard cubic feet per pound of catalyst per hour (scf/lb/hr). Steam was then introduced at the rate of 0.41 pound per pound of catalyst per hour (lb/lb/hr), and these conditions were maintained for 16 hours. The reactor was then cooled to 500° F, the steam was cut off, and, after the system cooled to 350° F, the air flow was stopped. The reactor was then purged with helium and pressurized to 250 psig. A hydrogen stream containing 5 weight-percent hydrogen sulfide was passed through the reactor at a rate of 1.0 scf/lb/hr for 3 hours to sulfide the catalyst. The temperature, pressure, and hydrogen flow rate were adjusted to those required for the particular experiment, and the oil flow was started. Hydrogen (99.9 percent purity) was used directly from standard shipping cylinders without further purification.

Products from the reactor passed through a back-pressure regulator into a separator maintained at 75° F and 200 psig. Tail gas from the separator passed through a second back-pressure regulator and was metered and sampled. Liquid products were drained from the separator after each 24-hour period of operation and washed with water to remove ammonia and hydrogen sulfide before a sample was taken for analysis. At the conclusion of each experiment the oil and hydrogen flows were stopped, the reactor was depressurized, and steam was introduced at the rate of 0.41 lb/lb/hr while the reactor was cooled to 700° F. Air was then introduced at the rate of 1.1 scf/lb/hr, and these conditions were maintained until the coke burnoff was completed.

Catalyst Screening Tests

The catalysts used in these tests were obtained from commercial sources. Table 2 shows the manufacturer, manufacturer's number, active metals, and catalyst designation for each of the catalysts tested. Three of the catalysts were received in the form of 1/16-inch extrusions and were used as such. The other catalysts, obtained in larger sizes, were crushed and sized to 10-20 mesh.

TABLE 2. - Catalysts tested

<u>Manufacturer^{1/}</u>	<u>Manufacturer's No.^{1/}</u>	<u>Active metals</u>	<u>Catalyst designation</u>
American Cyanamid Co.	Aero HDS-2A	Co Mo	I Co-Mo
American Cyanamid Co.	Aero HDS-3A	Ni Mo	II Ni-Mo
Harshaw Chemical Co.	Ni 4301-E	Ni W	III Ni-W
Harshaw Chemical Co.	Ni 4303-E	Ni W	IV Ni-W
Nalco Chemical Co.	NM-502	Ni Mo	V Ni-Mo
Davidson Chemical Co.	NICOMO	Ni Co Mo	VI Ni-Co-Mo

^{1/} Reference to specific manufacturers or trade names does not imply endorsement by the Bureau of Mines.

Charge stock for the catalyst testing experiment was prepared by topping a sample of the in situ crude shale oil to 600° F in a batch still equipped with a column having 35 trays, and then separating the 600° to 1,000° F fraction in a vacuum flash distillation unit. Properties of the 600° to 1,000° F fraction of in situ crude shale oil are shown in table 3.

TABLE 3. - Properties of 600° to 1,000° F distillate from in situ crude shale oil

Gravity.....	° API...	23.3
Nitrogen.....	wt-pct...	1.66
Sulfur.....	wt-pct...	.51
Viscosity.....	SUS at 100° F...	111
Carbon residue.....	wt-pct...	.5
Distillation		
Initial boiling point.....	° F...	579
5 pct recovered.....	° F...	611
10 pct recovered.....	° F...	620
20 pct recovered.....	° F...	648
30 pct recovered.....	° F...	666
40 pct recovered.....	° F...	681
50 pct recovered.....	° F...	699
60 pct recovered.....	° F...	732
70 pct recovered.....	° F...	768
80 pct recovered.....	° F...	809
90 pct recovered.....	° F...	867
95 pct recovered.....	° F...	914
End point.....	° F...	995

All catalyst tests were run at an operating temperature of 800° F, a space velocity of 1.0 weight of oil per weight of catalyst per hour ($W_o/W_c/hr$), and a hydrogen feed rate of 5,000 standard cubic feet per barrel of feed (scf/bbl). Eighteen grams of catalyst were charged to the reactor in each test. Five of the six catalysts were

tested at an operating pressure of 1,000 psig, and all six were tested at an operating pressure of 1,500 psig. Each test was continued for 96 hours.

In figure 2 the first order denitrification rate constants at 1,000 psig expressed as the logarithm of the ratio of nitrogen in the feed to nitrogen in the liquid product ($\ln N_0/N_t$) are plotted against days on stream to show the effect of operating time on catalyst activity. These curves show that the activities of all the catalysts tested decreased quite rapidly with time on stream. The catalyst with the highest denitrification activity at an operating pressure of 1,000 psig was catalyst I Co-Mo and the one with the lowest denitrification activity was catalyst IV Ni-W.

Figure 3 shows a plot of the first order denitrification rate constants versus time on stream at an operating pressure of 1,500 psig. The catalysts with the highest initial denitrification activity at 1,500 psig were catalyst II Ni-Mo and catalyst I Co-Mo. However, catalyst V Ni-Mo showed the highest activity after 96 hours, and its activity decreased very little with time on stream. Catalyst VI Ni-Co-Mo also had a high resistance to deactivation but had a much lower initial activity. Catalyst IV Ni-W again showed the lowest denitrification activity.

Composite samples of the total liquid product from each test were fractionated to determine the degree of hydrocracking attained with each catalyst. Distribution of the various distillate fractions are shown in figure 4. The distributions shown are for the tests made at 1,500 psig. Yields of naphtha and light oil were uniformly lower for tests made at 1,000 psig. The highest volume-percent yields of liquid product were attained with catalysts I Co-Mo and V Ni-Mo and the lowest yields with catalysts III Ni-W and IV Ni-W. The highest conversion--i.e., material converted to products boiling below 550° F--was attained with catalyst VI Ni-Co-Mo. The lowest conversion was attained with catalyst IV Ni-W, a hydrocracking catalyst. The highest yields of naphtha and light oil were attained with catalysts I Co-Mo and VI Ni-Co-Mo. Because of its high sustained denitrification activity, catalyst V Ni-Mo was selected for use in the preparation of syncrude by hydrogenation of the in situ distillate fractions.

Preparation of Synthetic Crude

The overall flow diagram for upgrading crude shale oil is shown in figure 5. A sample of in situ crude shale oil was fractionated in a Podbielniak Hypercal distillation unit to obtain a 350° F end point naphtha, a 350° to 550° F light oil, a 550° to 850° F heavy oil, and a vacuum residuum. Residuum from the fractionation was coked at atmospheric pressure in a laboratory coking unit, and the liquid product from the coker was mixed with a proportionate amount of fresh in situ crude shale oil. The mixture of crude shale oil and coker distillate was then fractionated to obtain fractions similar to those from the first distillation. Residuum from the second distillation was coked and liquid product from the coker again mixed with a proportionate amount of crude shale oil. The mixture of coker distillate and crude shale oil was fractionated to obtain a 350° F end point naphtha, a 350° to 550° F light oil, and a 550° to 850° F heavy oil to be used as charge stocks for the preparation of synthetic crude oil. Yields from the first and third distillations and coking are compared in table 4. Properties of the liquid products are shown in table 5.

The 550° to 850° F heavy oil from the third distillation was hydrogenated in a continuous 174-hour run. No deactivation of the catalyst was evident from analyses of samples of the liquid product taken during the run, and yields of liquid and gaseous products as well as hydrogen consumption were constant with time throughout the total test. Operating conditions and yields of products are shown in table 6. Approximately 40 weight-percent of the heavy oil was converted to products boiling below 550° F, of which 23.75 weight-percent was light oil boiling between 350° and 550° F, and 9.25 weight-percent was material boiling between 175° and 350° F.

TABLE 4. - Yields of products from distillation and coking

Percent of crude.....	First distillation		Final distillation	
	Weight	Volume	Weight	Volume
IBP - 350° F.....	6.20	6.86	6.30	7.00
350° - 550° F.....	43.71	45.50	37.58	39.24
550° - 850° F.....	28.89	28.60	34.62	33.50
850° F+.....	21.20	18.94	21.50	19.26
Coker distillate.....	17.21	17.50	17.30	17.47
Coke.....	2.83		3.08	
Hydrogen.....	.01		.02	
Methane.....	.26		.27	
Ethane.....	.17		.16	
Ethylene.....	.02		.03	
Propane.....	.22		.20	
Propylene.....	.11		.09	
Isobutane.....	.06	.09	.03	.05
Butane.....	.09	.14	.10	.15
Butenes.....	.09	.13	.10	.14
Carbon monoxide.....	.02		.03	
Carbon dioxide.....	.03		.02	
Hydrogen sulfide.....	.08		.07	

TABLE 5. - Properties of fractions from distillation of in situ crude shale oil

	Original crude	Final distillation
C ₅ - 350° F naphtha:		
Gravity..... ° API...	45.4	45.8
Nitrogen..... wt-pct...	1.16	1.09
Sulfur..... wt-pct...	.52	.70
350° - 550° F light oil:		
Gravity..... ° API...	34.9	35.0
Nitrogen..... wt-pct...	1.24	1.29
Sulfur..... wt-pct...	.52	.54
550° - 850° F heavy oil:		
Gravity..... ° API...	26.8	27.2
Nitrogen..... wt-pct...	1.53	1.61
Sulfur..... wt-pct...	.46	.46
850° F+ residue:		
Gravity..... ° API...	11.3	11.2
Nitrogen..... wt-pct...	1.93	1.91
Sulfur..... wt-cpt...	.60	.56

The 350° to 550° F light oil obtained from hydrogenation of the 550° to 850° F heavy oil was combined with the 350° to 550° F light oil from the third distillation of the in situ crude shale oil and coker distillate. The combined light oils were hydrogenated in a continuous 75-hour run. Operating conditions and products yields are shown in table 7. Approximately 39 weight-percent of the 350° to 550° F material was converted to products boiling below 350° F, of which 15.7 weight-percent was naphtha boiling between 175° and 350° F.

TABLE 6. - Hydrogenation of 550° to 850° F heavy oil

Operating conditions:

Temperature.....	° F...	800
Pressure.....	psig...	1,500
Space velocity.....	W ₀ /W _c /hr...	1.0
Hydrogen feed.....	scf/bbl...	5,000
Hydrogen consumed.....	scf/bbl...	1,320

Yields of products:

	Percent of feed		Percent of crude	
	Weight	Volume	Weight	Volume
C ₅ + liquid product.....	95.20	101.68	39.55	41.94
C ₅ - 175° F.....	1.92	2.52	.80	1.04
175° - 350° F.....	9.25	10.77	3.84	4.44
350° - 550° F.....	23.75	24.92	9.87	10.28
550° F+.....	60.28	63.47	25.04	26.18
Coke.....	.12		.05	
Hydrogen.....	-2.24		-.93	
Methane.....	.77		.32	
Ethane.....	.87		.36	
Propane.....	.88		.37	
Isobutane.....	.30	.47	.12	.19
Butane.....	.90	1.36	.37	.56
Ammonia.....	1.82		.76	
Hydrogen sulfide.....	.49		.20	
Water.....	.89		.37	

TABLE 7. - Hydrogenation of 350° to 550° F light oil

Operating conditions:

Temperature.....	° F...	750
Pressure.....	psig...	1,500
Space velocity.....	W ₀ /W _c /hr...	1.0
Hydrogen feed.....	scf/bbl...	5,000
Hydrogen consumed.....	scf/bbl...	1,050

Yields of products:

	Percent of feed		Percent of crude	
	Weight	Volume	Weight	Volume
C ₅ + liquid product.....	98.00	102.93	55.19	60.36
C ₅ - 175° F.....	1.22	1.54	.69	.90
175° - 350° F.....	15.66	17.10	8.82	10.03
350° - 550° F.....	81.12	84.29	45.68	49.45
Coke.....	.19		.11	
Hydrogen.....	-1.78		-1.00	
Methane.....	.17		.10	
Ethane.....	.24		.13	
Propane.....	.20		.11	
Isobutane.....	.19	.28	.11	.17
Butane.....	.56	.82	.32	.49
Ammonia.....	1.24		.70	
Hydrogen sulfide.....	.49		.28	
Water.....	.50		.28	

The 175° to 350° F naphthas from the two previous hydrogenation runs were combined with the total naphtha from the third distillation of in situ crude shale oil

and coker distillate. The combined naphthas were then hydrogenated in a continuous 48-hour run. Operating conditions and product yields are shown in table 8. Under the conditions used, only 4.3 weight-percent of the charge was converted to products boiling below 175° F.

TABLE 8. - Hydrogenation of 175° to 350° F naphtha

Operating conditions:

Temperature.....	° F...	700
Pressure.....	psig...	1,500
Space velocity.....	V_o/V_c /hr...	1.0
Hydrogen feed.....	scf/bbl...	5,000
Hydrogen consumed.....	scf/bbl...	720

Yields of products:

	Percent of feed		Percent of crude	
	Weight	Volume	Weight	Volume
C5+ liquid product.....	99.83	102.09	20.45	23.67
C ₅ - 175° F.....	4.14	4.40	.85	1.02
175° - 350° F.....	95.69	97.69	19.60	22.65
Coke.....	.01		.00	
Hydrogen.....	-1.39		-.28	
Methane.....	.00		.00	
Ethane.....	.13		.02	
Propane.....	.24		.05	
Isobutane.....	.01	.01	.00	-
Butane.....	.02	.03	.00	-
Ammonia.....	.59		.12	
Hydrogen sulfide.....	.32		.07	
Water.....	.24		.05	

Properties of the charge stocks and liquid products from the various hydrogenation runs are shown in table 9. Hydrogenation of the 550° to 850° F heavy oil under the conditions used reduced the nitrogen content from 16,100 ppm in the charge stock to 935 ppm in the 550° to 850° F fraction of the hydrogenated liquid product. Sulfur was reduced from 4,630 ppm to 9 ppm and the gravity increased from 27.2° API to 35.6° API.

Hydrogenation of the 350° to 550° F light oil under the conditions used reduced the nitrogen content from 10,850 ppm in the charge stock to 79 ppm in the 350° to 550° F fraction of the hydrogenated liquid product. Sulfur was reduced from 4,590 ppm to 1.2 ppm and the gravity increased from 35.0° API to 41.5° API.

Hydrogenation of the 175° to 350° F naphtha under the conditions used reduced the nitrogen content from 4,900 ppm in the charge stock to less than 1 ppm in the 175° to 350° F fraction of the hydrogenated liquid product. Sulfur was reduced from 3,010 ppm to 10 ppm and the gravity increased from 47.3° API to 52.6° API.

These results indicate that nitrogen removal is considerably more efficient when the naphtha, light oil, and heavy oil are hydrogenated separately. For example, the light oil produced during hydrogenation of the 550° to 850° F heavy oil contained 1,220 ppm nitrogen; the light oil produced by hydrogenation of the 350° to 550° F light oil contained only 79 ppm nitrogen. The 175° to 350° F naphtha produced during hydrogenation of the heavy oil contained 299 ppm nitrogen and that produced during hydrogenation of the light oil contained 53 ppm nitrogen, but the 175° to 350° F naphtha produced during hydrogenation of the naphtha fraction contained only 0.8 ppm of nitrogen.

TABLE 9. - Properties of charge stocks and liquid products from hydrogenation runs

Hydrogenation of--	550°-850° F heavy oil	350°-550° F light oil	175°-350° F naphtha
Charge stock			
Gravity..... ° API...	27.2	35.0	47.3
Nitrogen..... ppm...	16,100	10,850	4,900
Sulfur..... ppm...	4,630	4,590	3,010
Liquid product			
Gravity..... ° API...	37.6	43.9	53.1
Nitrogen..... ppm...	880	70	1.3
Sulfur..... ppm...	9	7	16
C ₅ - 175° F naphtha			
Gravity..... ° API...	77.2	77.6	60.8
Nitrogen..... ppm...	3.7	3.8	.5
Sulfur..... ppm...	22	7	3
175° - 350° F naphtha			
Gravity..... ° API...	53.3	49.6	52.6
Nitrogen..... ppm...	299	53	.8
Sulfur..... ppm...	9	3	10
350° - 550° F light oil			
Gravity..... ° API...	35.0	41.5	-
Nitrogen..... ppm...	1,220	79	-
Sulfur..... ppm...	8	1.2	-
550° - 850° F heavy oil			
Gravity..... ° API...	35.6	-	-
Nitrogen..... ppm...	935	-	-
Sulfur..... ppm...	9	-	-

In table 10 the properties of the syncrude prepared from in situ crude shale oil are compared with the properties of a syncrude listed by the NPC. Relative amounts and properties of the naphthas, light oils, and heavy oils are also compared. These data show that the nitrogen content, sulfur content, pour point, viscosity, and API gravity of syncrude prepared from in situ crude shale oil are lower than those suggested in the NPC report. The lower gravity of syncrude prepared from in situ crude shale oil may be attributable in part to the lower content of butanes and butenes and in part to the greater volumes of materials boiling above the naphtha range. The sulfur content of the naphtha is somewhat high, but the sulfur contents of the other fractions are much lower than those suggested by the NPC.

A summary of the yields from the various steps used in the preparation of syncrude from in situ crude shale oil is shown in table 11. The overall yield of syncrude was 103 volume-percent of the original crude.

SUMMARY AND CONCLUSIONS

Hydrogenation tests made on the 600° to 1,000° F heavy gas oil from in situ crude shale oil showed that a nickel-molybdenum-on-alumina catalyst was superior to either cobalt-molybdenum-on-alumina or nickel-tungsten-on-alumina catalysts for removing nitrogen from shale oil fractions. This nickel-molybdenum-on-alumina catalyst was used in the preparation of a synthetic crude oil by hydrogenation of various distillate fractions of an in situ crude shale oil. A high yield of premium refinery feedstock whose properties compared favorably to those of a "syncrude" described by the NPC was attained.

TABLE 10. - Comparison of NPC and in situ syncrudes and distillate fractions

	NPC	In situ
Syncrude:		
Gravity..... ° API...	46.2	43.9
Pour point..... ° F...	50	<32
Viscosity..... SUS at 100° F...	40	32
Nitrogen..... ppm...	350	250
Sulfur..... ppm...	50	5
Butanes and butenes..... vol-pct...	9.0	1.7
C ₅ - 350° F naphtha..... vol-pct...	27.5	24.8
Gravity..... ° API...	54.5	54.7
Nitrogen..... ppm...	1	1
Sulfur..... ppm...	<1	8
Aromatics..... vol-pct...	18	14
Naphthenes..... vol-pct...	37	44
Paraffins..... vol-pct...	45	42
350° - 550° F distillate..... vol-pct...	41.0	48.1
Gravity..... ° API...	38.3	41.5
Nitrogen..... ppm...	75	79
Sulfur..... ppm...	8	1.2
Aromatics..... vol-pct...	34	24
Freezing point..... ° F...	-35	-29
550° - 850° F distillate..... vol-pct...	22.5	25.4
Gravity..... ° API...	33.1	35.6
Nitrogen..... ppm...	1,200	935
Sulfur..... ppm...	<100	9
Pour point..... ° F...	80	55

TABLE 11. - Summary of yields from preparation of syncrude

Process ^{1/} wt-pct...	A	B	C	D	Totals
C ₅ - 175° F naphtha.....	-	0.80	0.69	0.85	2.34
175° - 350° F naphtha.....	-	-	-	19.60	19.60
350° - 550° F light oil....	-	-	45.68	-	45.68
550° - 850° F heavy oil....	-	25.04	-	-	25.04
Coke.....	3.08	.05	.11	-	3.24
Hydrogen.....	.02	-.93	-1.00	-.28	-2.19
Methane.....	.27	.32	.10	-	.69
Ethane.....	.16	.36	.13	.03	.68
Ethylene.....	.03	-	-	-	.03
Propane.....	.20	.37	.11	.04	.72
Propylene.....	.09	-	-	-	.09
Isobutane.....	.03	.12	.11	-	.26
Butane.....	.10	.37	.32	-	.79
Butenes.....	.10	-	-	-	.10
Carbon monoxide.....	.03	-	-	-	.03
Carbon dioxide.....	.02	-	-	-	.02
Ammonia.....	-	.76	.70	.11	1.57
Hydrogen sulfide.....	.07	.20	.28	.07	.62
Water.....	-	.37	.28	.04	.69

^{1/} A. Distillation and coking. B. Hydrogenation of 550° - 850° F heavy oil.
C. Hydrogenation of 350° - 550° F light oil. D. Hydrogenation of 175° - 350° F naphtha.

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LITERATURE CITED

1. Burwell, E. L., H. C. Carpenter, and H. W. Sohns. Experimental In Situ Retorting of Oil Shale at Rock Springs, Wyo. BuMines TPR 16, June 1969, 8 pp.
2. Burwell, E. L., T. E. Sterner, and H. C. Carpenter. Shale Oil Recovery by In Situ Retorting--A Pilot Study. J. Petrol. Technol., 1970, pp. 1520-1524.
3. Carpenter, H. C., E. L. Burwell, and H. W. Sohns. Evaluation of an In Situ Retorting Experiment in Green River Oil Shale. J. Petrol. Technol., 1972, pp. 21-26.
4. Harak, A. E., L. Dockter, and H. C. Carpenter. Some Results from the Operation of a 150-Ton Oil Shale Retort. BuMines TPR 30, 1971, 14 pp.
5. Carpenter, H. C., S. S. Tihen, and H. W. Sohns. Retorting Ungraded Oil Shale as Related to In Situ Processing. Preprints, Div. Petrol. Chem., ACS, v. 13, No. 2, April 1968, pp. F50-F57.
6. Dockter, L., A. Long, Jr., and A. E. Harak. Retorting Ungraded Oil Shale as Related to In Situ Processing. Preprints, Div. Fuel Chem., ACS, v. 15, No. 1, 1971, pp. 2-11.
7. Jensen, H. B., R. E. Poulson, and G. L. Cook. Characterization of a Shale Oil Produced by In Situ Retorting. Preprints, Div. Fuel Chem., ACS, v. 15, No. 1, 1971, pp. 113-121.
8. Harak, A. E., A. Long, Jr., and H. C. Carpenter. Preliminary Design and Operation of a 150-Ton Oil Shale Retort. Quarterly of Colo. School of Mines, v. 65, No. 4, October 1970, pp. 41-56.
9. U. S. Energy Outlook, An Interim Report. National Petroleum Council, v. 2, 1972, pp. 80-90.
10. Carpenter, H. C., and P. L. Cottingham. Evaluation of Catalysts for Hydrogenating Shale Oil. BuMines RI 5533, 1959, 27 pp.
11. Benson, D. B., and L. Berg. Catalytic Hydrotreating of Shale Oil. Chem. Eng. Prog., v. 62, No. 8, August 1966, pp. 61-67.
12. Montgomery, D. P. Refining of Pyrolytic Shale Oil. Ind. Eng. Chem. Prod. Res. Develop., v. 7, No. 4, December 1968, pp. 274-282.

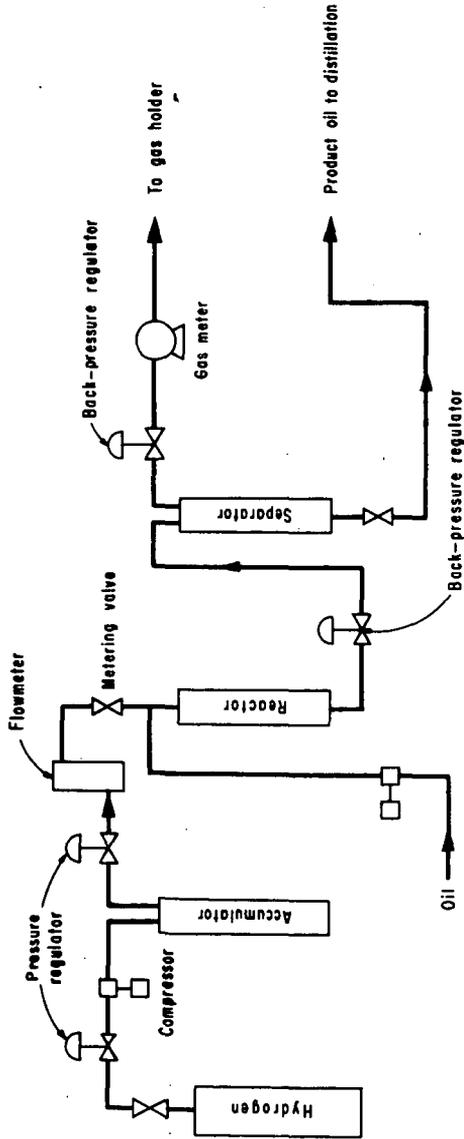


FIGURE 1. — Simplified Flow Diagram of Hydrogenation Unit.

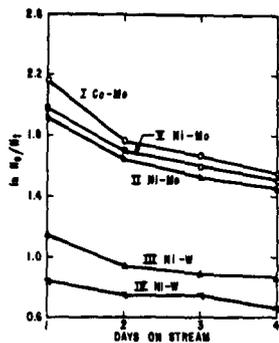


FIGURE 2.-Effect of Operating Time on Denitrification Rate Constants at 1,000 PSIG.

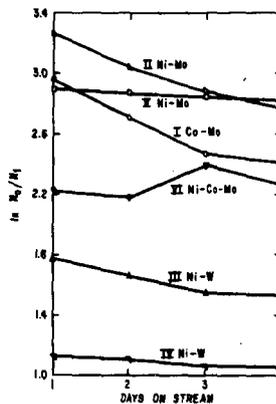


FIGURE 3.-Effect of Operating Time on Denitrification Rate Constants at 1,500 PSIG.

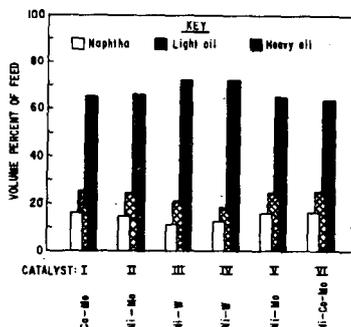


FIGURE 4.-Effect of Catalyst on Distillate Yields at 1,500 PSIG.

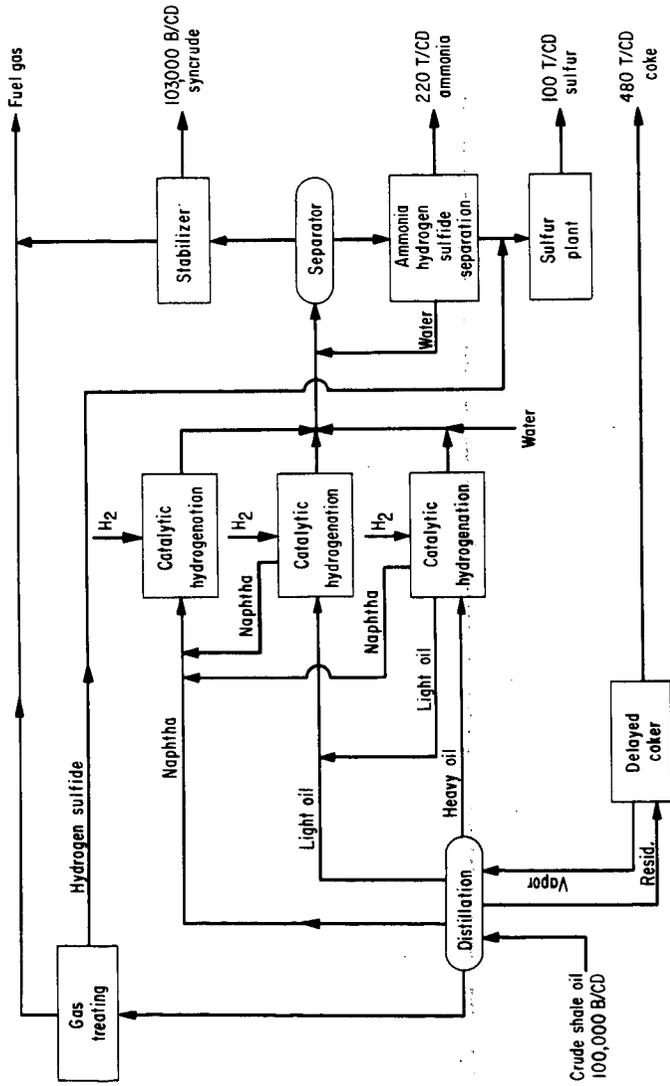


FIGURE 5.-Flow Diagram For Upgrading In Situ Crude Shale Oil.