

JOINT SYMPOSIUM ON OIL SHALE, TAR SANDS, AND RELATED MATERIAL  
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.  
AND THE DIVISION OF WATER, AIR, AND WASTE CHEMISTRY  
AMERICAN CHEMICAL SOCIETY  
SAN FRANCISCO MEETING, April 2-5, 1968

REFINING OF PYROLYTIC SHALE OIL

By

D. P. Montgomery

Phillips Petroleum Company, Development Division, Bartlesville, Oklahoma

I. INTRODUCTION

Because of revived interest by both industry and government in the production of petroleum products from oil shale, a pilot-scale study of the refining of pyrolytic shale oil was made by Phillips Petroleum Company. This study used current refining technology and incorporated no novel or unproved refining steps. Only commercially available catalysts were employed.

The question to be answered was not whether shale oil can be refined to a synthetic crude and then to finished products, but what refining severity is required to reduce the nitrogen to a satisfactory level for continuous processing in a conventional refinery and what yields and qualities of the products would result.

Domestic oil shale locations and a thorough statement of the problems associated with recovering oil from these shales were presented in 1964 (7). A set of papers citing recent refining developments was published in 1966 (1). Pyrolytic shale oils are characteristically high in concentrations of nitrogen, sulfur, and oxygen; concentrations are typically two, one, and one per cent, respectively. Because nitrogen is a potent poison for modern acidic type refining catalysts, its removal is of paramount importance. The oils are black, waxy, and foul smelling, with high pour points and viscosities and high concentrations of olefins and diolefins make them unstable. A detailed description of shale oil is given by Hellwig, et al (4). Facilities for refining may be non-existent at shale retort locations, since known oil shales are located in remote areas that are mountainous, arid, and cold.

For this study the most economic sequence of refining steps was postulated to be recycle coking and hydrostabilization at the retort, followed by pipeline delivery to a refinery near a marketing area. There the oil would be hydrodenitrogenated (HDN) in one or more passes, fractionated, and those distillates requiring further nitrogen reduction would be separately processed. Naphtha would be reformed and heavier distillates would be catalytically cracked. In pilot-plant operations we found that one-pass HDN of the hydrostabilized coker distillate was sufficient for distillates heavier than naphtha. In fact, the 400-650°F distillate was a satisfactory diesel fuel without additional processing. Both 400+°F and 650+°F distillates were catalytically cracked. A second-pass HDN of the hydrostabilized coker distillate was carried out, but the fractions were not further processed.

The following sections present in sequential order the experimental details, product properties, and yields for each refining step. Figure 1 is a block diagram of the processing scheme; in this figure areas separated by dotted lines represent the process steps.

II. FEEDSTOCK (RAW, PYROLYTIC SHALE OIL)

The shale oil used as raw feed was obtained by pyrolysis of a Colorado oil shale. Properties of this oil are given in Table I.

Determination of the consumption of hydrogen in many of the refining steps is important. Since this determination was based upon a balance of the hydrogen contained in feeds and products, unusual accuracy was required in analyses of the liquids processed. The requisite accuracy was attained by comparing the nuclear magnetic resonance spectra of protons in feedstocks and products and relating these spectra to those of pure hydrocarbons of approximately the same hydrogen content. A statistical study of this procedure by R. S. Silas of Phillips Petroleum Company has shown that hydrogen content can be determined to  $\pm 0.05$  per cent, at a 95 per cent confidence level (8).

TABLE I

COKING

Conditions: 14 psig, 810 F, 0.208 vol<sup>a</sup>/coker vol-hr.

Yields, % R.S.O.			Properties			
	Wt.	Vol.		RSO <sup>b</sup>	Coker <sup>c</sup> Dist.	Coke
Hydrogen	0.09					
Hydrogen Sulfide	0.11	-	API Gravity	19.5	26.9	
Methane	1.39	-	Pour Point	+75	+40	
Ethylene	0.42	-	Vis., CS@100	-	5.05	
Ethane	1.16	-	" " @210	-	1.55	
Propylene	0.67	-	Aniline Point	-	83.6	
Propane	0.87	-	Mol. Wt.	-	252	
Butylenes	0.67	1.0	Br. No.	-	45.3 <sup>d</sup>	
i-Butane	0.14	0.2	Carbon Res, wt %	3.08	0.4 <sup>d</sup>	
			Composition, wt %			
n-Butane	0.44	0.7	C	84.6	84.3	89.5
Pentane and Heavier	81.43	85.5	H	10.84	11.30	3.4
Coke	12.61	-	S	0.61	0.54	0.32
	100.00	87.4	O	1.5	1.2	2.34
			N	2.2	2.0	4.5
			Ash			0.55

<sup>a</sup>Coke drum filled in 32 hours.

<sup>b</sup>No free water was observed in the raw shale oil.

<sup>c</sup>Not stabilized.

<sup>d</sup>From another run.

TABLE II

HYDROSTABILIZATION

Conditions: 470 F (455 inlet, 485 outlet, exothermic Δ T), 500 psig, 0.89 LHSV, 1150 SCF hydrogen/bbl coker distillate, Filtrol 475-8 catalyst (pre-sulfided cobalt-molybdenum on alumina).

	Yields				Properties of C <sub>5</sub> + Liquid	
	% Coker Distillate		% R S O		API Grav.	
	Wt	Vol	Wt	Vol	29.0	
Hydrogen	-0.71 <sup>a</sup>		-0.58		Pour Point, F	+40
Water	0.07	0.1	0.06		Vis 100 F, CS	4.51
Hydrogen sulfide	0.02		0.02		" 210 F, "	1.46
Methane	0.03		0.02		Aniline Point, F	94.7
Ethane	0.01		0.01		Bromine No.	37.2
Propylene	0.01		0.01		Composition	
Propane	0.02		0.02		C	84.3
Butylenes	0.01		0.01		H	11.93
i-Butane	0.01		0.01		S	0.49
n-Butane	0.01		0.01		O	0.83
Pentanes and heavies	100.52	101.7	81.8	86.8	N	2.0
Total	100.71	101.8				

<sup>a</sup>Hydrogen Consumption 414 SCF/bbl feed

Distillation (Corr. to 1 atm)

IBP	120F
10%	330
20%	412
30%	476
40%	516
50%	561
60%	608
70%	655
80%	708
90%	769
EP	900

**TABLE III**  
**HYDRODENITROGENATION & FRACTIONATION OF**  
**HYDROSTABILIZED COKER DISTILLATE**

Conditions: 1500 psig, 812 F, 1.002 LHSV, 5200 SCF hydrogen/bbl feed, Harshaw 4303-E catalyst (nickel-tungsten on alumina, pre-sulfided)

	Yields			
	% of Feed		% of Raw Shale Oil	
	Wt.	Vol.	Wt.	Vol.
Hydrogen <sup>a</sup>	-3.41		-2.79	
Water	0.92		0.84	
Hydrogen sulfide	0.31		0.25	
Ammonia	2.42		1.99	
Methane	1.21		0.99	
Ethane	1.21		0.99	
Propane	1.16		0.96	
i-Butane	1.96	3.1	1.61	2.7
n-Butane	0.91	1.4	0.77	1.2
C <sub>5</sub> -180 F	3.29	4.3	2.71	3.7
180-400 F	30.78	34.9	24.96	30.1
400-650 F	44.96	47.3	36.86	41.3
650+ F	4.28	14.8	11.66	12.9
Total	103.41	105.8	84.59	91.9

<sup>a</sup>Hydrogen Consumption 1970 SCF/bbl

**TABLE IV**  
**PROPERTIES OF HYDRODENITROGENATED LIQUID PRODUCTS**

	Total Liquid Product <sup>a</sup>	C <sub>5</sub> -180F				Chicago Area Diesel Fuel Spec.		650+ F
		180-400F	400+ F	400-650F				
API Gravity	42.7	76.8	51.3	36.1	37.5		34.9	
C, wt %	86.06	-	85.79	-	-		-	
H, wt %	13.84	-	14.19	-	-		-	
N, total ppm wt.	917	10	240	710	695		-	
N, basic, ppm wt.	-	-	-	415	-		100	
S, ppm wt.	60	110	10	11	30	4000 max.	-	
RON, Clear	-	61.4	32.8	-	-		-	
RON, +3 ml TEL	-	82.2	61.4	-	-		-	
Cetane No.	-	-	-	-	50.2	50 min.	-	
Pour Point, F	-	-	-	+45	-15	-15 max.	+95	
Saturates <sup>b</sup>	69.8	-	-	67.8	-		-	
Aromatics <sup>b</sup>	27.5	-	-	26.2	-		-	
Olefins <sup>b</sup>	2.7	-	-	6.0	-		-	
Paraffins	-	-	47.7	-	-		-	
Monocyclicnaphthenes	-	-	34.5	-	-		-	
Dicyclicnaphthenes	-	-	2.4	-	-		-	
Benzenes	-	-	13.2	-	-		-	
Heavy Aromatics	-	-	2.2	-	-		-	
ASTM Color	-	-	-	-	<1.0	2 max.	-	
Vis, 100F, SUS	-	-	-	-	36.1	33 min.	-	
" 210F, CS	-	-	-	1.46	-	45 max.	-	
Mol. Wt.	-	-	-	234	-		3.21	
Carbon Res., Ram., Full range	-	-	-	0.03	0.01	0.02 max	0.1	
Carbon Res. Rams., 10% Bms.	-	-	-	-	0.18	0.15 max	-	
Copper Corrosion	-	-	-	-	Sl. tarnish	3 max.	-	
Flash Point, F, P. M.	-	-	-	-	210	150 min.	-	
Storage Stability, Dupont (Nalco) pad rating	-	-	-	-	7	7 max.	-	

<sup>a</sup>Snap sample taken after 100 hrs continuous operation - contains 0.4 wt % C<sub>3</sub>+C<sub>4</sub>'s.

<sup>b</sup>By FIA Analysis - olefins not reliable.

TABLE V

## HYDRODENITROGENATION OF NAPHTHA

Conditions: 1500 psig, 698F, 0.988 LHSV, 4730 SCF hydrogen/bbl feed  
Harshaw 4303-B catalyst (nickel-tungsten on alumina, pre-sulfided)

	Yields, Percent			
	Feed		Raw Shale Oil	
	Wt	Vol	Wt	Vol
H <sub>2</sub> <sup>a</sup>	-1.23		-0.31	
C <sub>1</sub>	0.33		0.08	
C <sub>2</sub>	1.25		0.31	
C <sub>3</sub>	1.35		0.34	
iC <sub>4</sub>	1.44	2.1	0.36	0.7
nC <sub>4</sub>	1.18	1.6	0.29	0.5
C <sub>5</sub> <sup>b</sup>	95.68	97.3	23.92	29.3
	101.23	101.0	25.30	30.5

<sup>a</sup>Hydrogen Consumption - 627 SCF/bbl

<sup>b</sup>Separator liquid product, not stabilized

TABLE VI

## PROPERTIES OF NAPHTHA AFTER HDN

API Gravity	54.0	ASTM Distillation
RON, Clear	20.0	IBP
RON, +3ml TEL	52.8	5
Paraffins	46.9	10
Monocyclicnaphthenes	46.6	20
Dicyclicnaphthenes	5.5	30
Benzenes	1.0	40
Bromine No.	<0.1	50
C wt%	84.93	60
H wt%	15.07	70
N ppm wt	1.5	80
S " "	8	90
As ppb wt	10	95
Pb " "	13	EP
		402

TABLE VII

REFORMING OF NAPHTHA-CONDITIONS AND YIELDS  
OF NAPHTHA FEEDSTOCK

Conditions: (All runs with same portion of initially new U.O.P. R-5 Catalyst)

Test	1		2		3		4		5		6	
Temp., °F	806		829		853		878		908		954	
LHSV	2.96		2.89		2.96		2.96		2.95		2.96	
Moles H <sub>2</sub> /naphtha	8.35		8.52		8.21		8.59		8.72		8.59	
Press., psig.	500		500		500		500		500		500	
Yields:	wt	vol										
H <sub>2</sub>	1.81		1.84		1.89		2.05		1.86		1.01	
C <sub>1</sub>	0.30		0.48		0.82		1.26		2.13		3.49	
C <sub>2</sub>	0.89		0.96		1.22		2.24		4.03		6.98	
C <sub>3</sub>	1.48		1.78		2.52		4.32		6.70		11.50	
iC <sub>4</sub>			0.06	0.1	0.98	1.3	1.12	1.5	1.97	2.7	2.67	3.6
nC <sub>4</sub>	0.98	1.3	2.43	3.2	2.41	3.1	3.03	4.0	4.26	5.6	7.71	10.1
C <sub>5</sub> <sup>a</sup>	94.54	91.5	92.45	89.6	90.16	87.1	85.98	82.8	79.05	75.5	66.64	62.8
Total	100.00	92.8	100.00	92.9	100.00	91.5	100.00	88.3	100.00	83.8	100.00	76.5

Hydrogen Prod., SCF/bbl	905	920	946	1028	931	507
Yield-Oct. No. (Liq. vol% × RON, +3) × 10 <sup>-2</sup>	59.0	76.7	78.1	77.3	74.0	64.1

<sup>a</sup> Mean reading of nine evenly spaced TC's in catalyst bed

### III. PILOT PLANT AND PROCEDURE

#### Coking and Hydrostabilization

Raw shale oil was pumped through a preheater into the bottom of the coking vessel, made from a 20-in. length of 8-in. diameter pipe and closed with weld caps. The coker was vertically mounted in a two-section furnace, with each section separately controlled. Within the coker was a concentric thermowell for determining the temperature at any height. Heaters were set so that incoming feed and outgoing distillate were in the range 800-850°F.

Coker distillate passed through a heated line to the flash still; temperature in the flash zone was 665°F. Product gases were cooled in an external condenser and the condensate was metered, sampled, and collected. A regulator ahead of the gas meter held the still pressure at 10-12 psig and also determined coker pressure. Distillate was condensed and flowed into a water knockout, from where it was pumped to the hydrostabilizer. Bottoms were continuously recycled to the coker.

Coker distillate was mixed with metered hydrogen, preheated to 450°F, and fed to the hydrostabilizer. Reactants passed down-flow through a one-gallon reactor filled with pre-sulfided catalyst, Filtrol 475-8. A temperature increase of 30°F was noted as reactants passed through the bed. Effluent was cooled and the gas and liquid phases separated in the chamber of a liquid-level controller. Pressure was maintained at 500 psig by action of a regulator on tail gas from the separator (75°F). This gas was sampled and metered, as was the gas evolved from the liquid discharged from the separator. The liquid product was sampled and held for HDN operations.

#### Hydrodenitrogenation

The composited, hydrostabilized liquid was mixed with 5200 SCF hydrogen per barrel, preheated to 750°F, and passed downflow over the bed of pre-sulfided Harshaw 4303-E catalyst, heated by a five-zone furnace. A sharp increase in temperature of 50°F occurred at the bed top. The remainder of the reactor was virtually isothermal at 812°F and 1500 psig. The space velocity was 1.0 liquid volume per hour. To prevent effluent lines from plugging with deposits of ammonium sulfides, water was injected into the effluent at a rate of 50 ml/hr. A high pressure tail gas from the liquid-gas separator (ambient temperature) was sampled and metered. Similar measurements were made on the gas desorbed when pressure on the liquid was reduced to atmospheric.

As 10-gallon portions of liquid product accumulated, each portion was fractionated into gas (butanes and lighter), C<sub>5</sub> to 180°F and 180 to 400°F distillates, and 400+°F bottoms. The 180 to 400°F distillate was feed for naphtha HDN and reforming, and the 400+°F bottoms were catalytically cracked. Corresponding distillates and bottoms from each distillation were composited and analyzed. A 10-gallon portion of the 400+°F bottoms was further fractionated at 20 mm pressure to yield a 400 to 650°F diesel fuel and 650+°F bottoms for catalytic cracking.

#### Hydrodenitrogenation of Naphtha

The 180 to 400°F distillate obtained by fractionation of the initially hydrodenitrogenated oil comprised the feedstock naphtha. Other than the use of a fresh portion of catalyst (pre-sulfided), and a bed temperature of 700°F, the apparatus and procedure were the same as in the initial HDN operation. Since little nitrogen and sulfur remained in the naphtha feedstock, water was not injected into the reactor effluent.

#### Reforming of Nitrogen-Free Naphtha

The total liquid product from naphtha hydrodenitrogenation was used as feedstock without stabilization. A 300 ml bed of fresh U. O. P. R-5 catalyst was used, and the reactants were preheated in a tube furnace to reaction temperature. All tests were carried out at 500 psig, with nominal values of 8/1 for hydrogen/naphtha (molar) and 3.0 for liquid hourly space velocity. Reactor effluent was cooled by exchange with tap water and charged to a gas-liquid separator at 75°F. Samples of reformates were caught at 500 psig and stabilized to yield butane-free reformates and gases composed of butanes and lighter components. Tests were performed in the chronological sequence 2, 3, 4, 5, 6, and 1 of Table VII.

#### Cracking of Gas Oils

Both 400+°F and 650+°F oil from the first-pass HDN were catalytically cracked. Properties of these oils are given in Table IV. The catalyst was an equilibrium catalyst withdrawn from a refinery FCC reactor and was composed of 75 per cent Filtrol-800 and 25 per cent of a mixture of other catalysts.

The confined bed cracking apparatus was described by Johnson and Stark (6). Measured



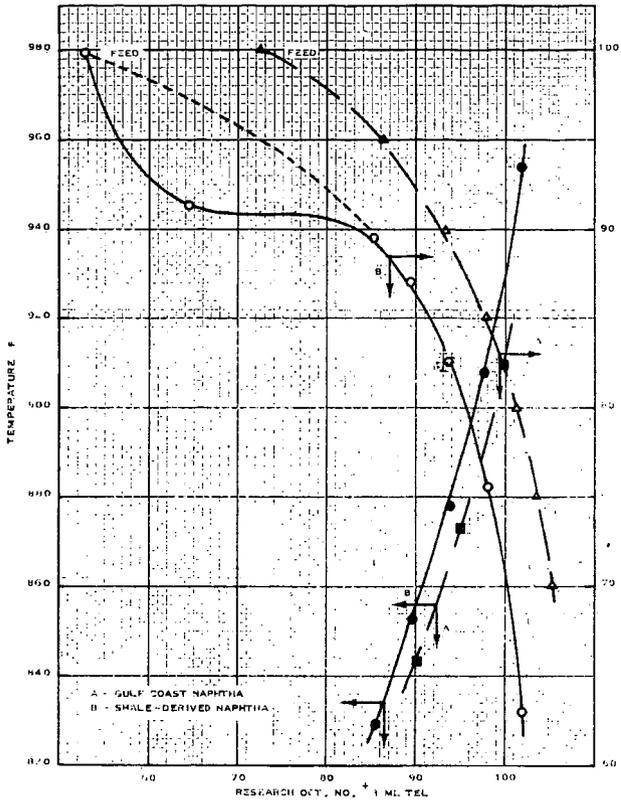


FIGURE 3  
REFORMATE OCTANE VS.  
TEMPERATURE AND YIELD

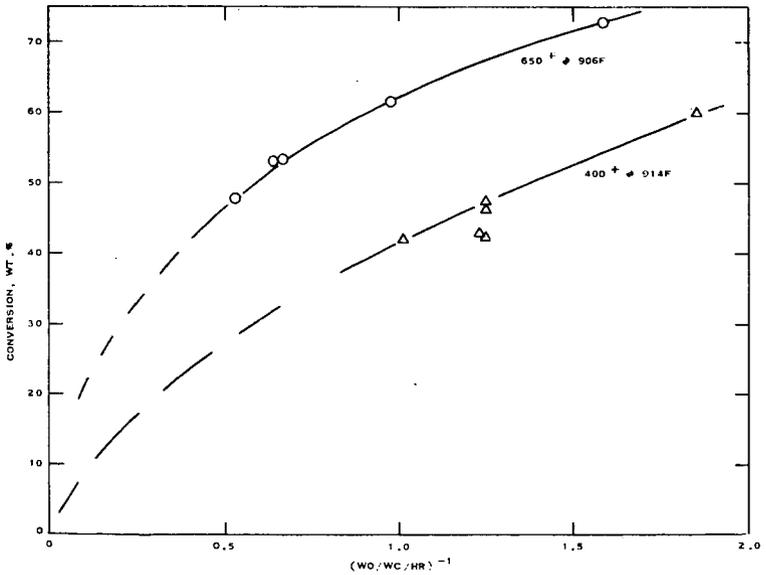


FIGURE 4  
FCC CONVERSION VS.  
RECIPROCAL SPACE VELOCITY

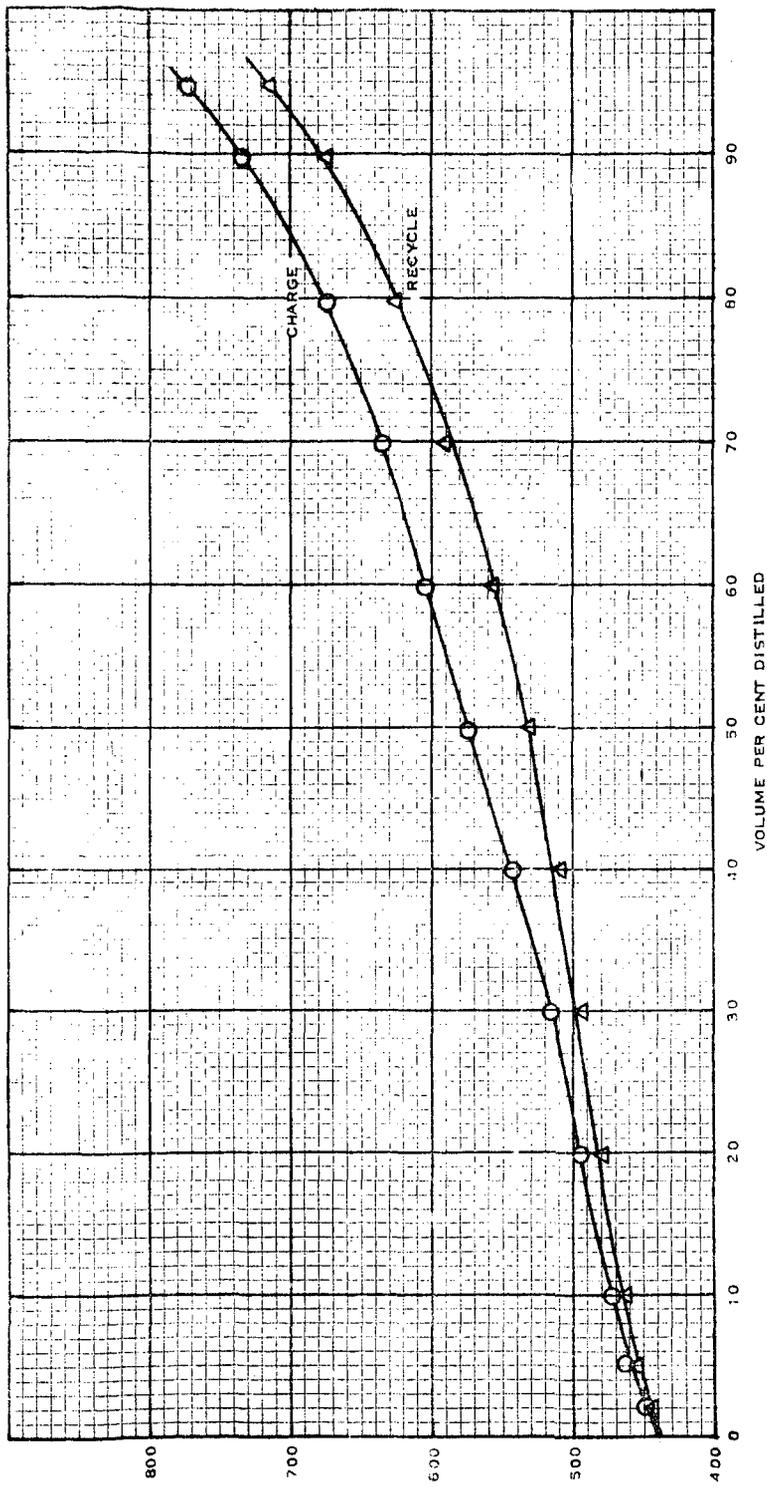


FIGURE 5  
 DISTILLATIONS OF FCC  
 CHARGE (400° F) AND  
 RECYCLE

TABLE IX

## Catalytic Cracking of 400+ HDN Product

Conditions: 914F, 10 psig, 0.8 Wc/Wc-hr., 16.2 lbs H<sub>2</sub>O/bbl, 33 min. cycle, 0.93 Cc, K. C. equil. cat. (75% F-800)

Yields, Percent	Feed		Raw Shale Oil		Properties of Liq. Prod.	
	Wt.	Vol.	Wt.	Vol.	Gas <sup>a</sup>	400 <sup>b</sup>
H <sub>2</sub>	0.11	63.8 SCF/bbl	0.05		API	58.5 32.8
C <sub>1</sub>	0.99	191 " "	0.48		RON,0	92.2 ----
C <sub>2</sub> <sup>=</sup>	0.57		0.28		RON,+3	98.9 ----
C <sub>2</sub>	0.96		0.47		MON,0	----
C <sub>3</sub> <sup>=</sup>	2.24		1.11		MON,+3	87.8 ----
C <sub>3</sub>	1.14		0.55		ASTM Dist	
C <sub>4</sub> <sup>=</sup> s	2.98	4.11	1.45		BP	119 ----
iC <sub>4</sub>	2.80	4.19	1.36	2.26		444
nC <sub>4</sub>	2.11	3.05	1.05	1.69	5	137 455
C <sub>5</sub> -400F Gaso.	28.43	31.8	13.82	17.2	10	151 461
400+ C.O.	54.20	53.1	26.3	28.6	20	168 478
Coke	2.42	---	1.66		30	185 492
Total	100.00				40	205 509
Total Gasoline <sup>a</sup>		45.1		24.2	50	327 530
					60	354 560
Conversion	45.8	46.9			70	382 590
					80	307 626
					90	138 674
					95	158 716
					EP	405 ----
					BMCI	---- 40.1

<sup>a</sup>(C<sub>5</sub>-400 F Gasoline) + 1.7 (Vol C<sub>3</sub> + Vol C<sub>4</sub>)

<sup>b</sup> Contains no alkylate

TABLE VIII

## REFORMING OF NAPHTHA-PROPERTIES OF REFORMATES

Test	1	2	3	4	5	6
IBP	224	192	161	136	129	120
5	251	226	212	188	167	176
10	265	251	239	216	189	191
20	279	274	262	246	220	214
30	291	282	276	264	245	235
40	304	296	292	280	265	253
50	318	304	307	296	282	271
60	333	326	322	314	299	289
70	346	342	338	328	318	308
80	358	358	354	346	338	328
90	374	378	375	371	366	358
95	388	401	399	402	401	385
EP	416	430	437	449	452	422
API Gravity	48.1	48.3	47.7	47.1	45.5	43.5
Octane Nos.						
RON, Clear	51.6	69.0	74.9	83.1	90.9	97.6
RON, +3	64.4	85.6	89.7	94.0	98.0	102.1
MON, Clear	52.0	65.0	68.8	75.2	82.4	86.7
MON, +3	64.4	78.2	82.2	85.2	87.6	91.4

TABLE X

## Catalytic Cracking of 650+ HDN Product

Conditions: 906F, 10 psig, 1.89 Wc/Wc-hr., 15.9 lbs H<sub>2</sub>O/bbl, 16.5 min. cycle, 0.93 Cc, K. C. equil. cat (75% F-800)

Yields, Percent	Feed		Raw Shale Oil		Properties of Liq. Prod.	
	Wt.	Vol.	Wt.	Vol.	Gas <sup>a</sup>	400 <sup>b</sup>
H <sub>2</sub>	0.06	34.2SCF/bbl	0.01		API	64.4 31.4
C <sub>1</sub>	0.47	101.2	0.06		RON,0	90.3 ----
C <sub>2</sub> <sup>=</sup>	0.36		0.04		RON,+3	97.7 ----
C <sub>2</sub>	0.51		0.06		MON,0	----
C <sub>3</sub> <sup>=</sup>	2.76		4.96	0.32		MON,+3
C <sub>3</sub>	0.90		0.11		ASTM Dist	
C <sub>4</sub> <sup>=</sup> s	3.42	4.64	0.40		BP	104 ----
					2	459
iC <sub>4</sub>	3.39	5.13	0.40	0.66	5	115 492
					10	128 551
nC <sub>4</sub>	1.02	1.50	0.12	0.19	20	143 672
					30	158 699
C <sub>5</sub> -400F Gaso.	32.40	38.5	3.80	4.93	40	177 ----
					50	201 723
400+ C.O.	52.11	51.1	6.10	6.59	60	229 746
					70	263 747
Coke	2.60	---	0.30	---	80	294 763
					90	331 793
Total	100.00				95	354 816
Total Gaso. <sup>a</sup>		54.8		7.0	EP	391 ----
					BMCI	--- 28.6
Conversion	47.8	48.6				

<sup>a</sup>(C<sub>5</sub>-400 F Gasoline) + 1.7 (Vol C<sub>3</sub> + Vol C<sub>4</sub>)

<sup>b</sup> Contains no alkylate

quantities of steam and oil were pumped into the catalyst bed, and non-condensed products were metered and analyzed by gas-liquid chromatography (GLC). Coke deposits were determined by analysis of the regeneration gases. After fractionation of condensed products, fractionation gases were analyzed by GLC.

Cracking was carried out at 10 psig, a nominal steam-oil ratio of 15 pounds/barrel, and cycle times to accomplish a value of 1.0 wt per cent for the mean carbon content of the catalyst ( $\bar{C}$ ). Space velocities were varied to determine the WHSV conversion relationship, as shown in Figure 4. The 650°F oil was cracked at 906°F; the more refractory 400°F oil was cracked at 914°F.

#### IV. RESULTS AND DISCUSSION

##### Coking and Hydrostabilization

Table I contains data characterizing the raw shale oil, conditions of coking, and yields and properties for products of the coker. The porous, friable coke was easily removed from the coker. Hydrostabilizer yields and product properties are given in Table II. The reported data are for 32 hours of operation. Recovered gases plus hydrostabilized liquid equalled 100.8 weight per cent of the 214.5 pounds of raw shale oil fed. Catalyst coke was not determined.

Charging raw shale oil to the flash still rather than to the coker would reduce the volume of coker feed. Also, shale oil components of coker distillate boiling range would not undergo degradation in the coker. However, this mode of operation could not be practiced because an insoluble, organic material separated from the flash-still bottoms and plugged transfer lines. The nature of this insoluble matter was not determined.

Coker distillate with a higher end-point would be possible, but this might make hydrodenitrogenation more difficult. Over all yields would probably be little affected by increasing coker distillate end-point. The coker distillate was immediately hydrostabilized in the pilot plant to insure against its properties changing radically while awaiting further processing. Commercially, this step may not be required because retained samples of coker distillate did not show any obvious changes, such as precipitates or increased viscosity, after 6 months storage in glass. Elimination of hydrostabilization, however, may require a higher severity operation in the subsequent hydrodenitrogenation step and would certainly increase hydrogen consumption during HDN.

If coking and hydrostabilization take place at the retort site, three economies may be possible. First, unsold coke could be mixed with raw shale charged to the retort so that coke combustion could provide heat otherwise derived by burning, and thus prevent loss of oil precursors in the shale. Second, steam reforming of coker (flash) gas could provide hydrogen in excess of that needed for hydrostabilization. Third, additional heat could be obtained by adding air to the retort gases, followed by burning of carbon monoxide and hydrocarbons in the retort gas.

##### Hydrodenitrogenation of Liquid Product from Hydrostabilization

Yields and properties of the various fractions from HDN are given in Tables III and IV. A material balance was calculated for a 6.75-hour period, during which products exceeded hydrocarbon feed by 4.1 wt per cent. Hydrogen consumption and yields of hydrogen sulfide, ammonia, and water were calculated from feed and product contents of hydrogen, sulfur, nitrogen, and oxygen, respectively.

Carbon on the catalyst was not determined until the second pass of HDN operation was completed (not reported in detail because of its ineffectiveness). At that time carbon content of the catalyst was 2.2 per cent. No decline in catalyst activity was observed.

The value of this HDN process can be seen in the high qualities of the product fractions, particularly the diesel fuel (400-650°F). No further processing would be required to market the diesel fuel, and its volume was 41 per cent of the raw shale oil. Either the 400°F or 650°F bottoms could be charged to a catalytic cracker although it may prove desirable to market the 400-650°F as diesel fuel. The light gasoline (C<sub>5</sub>-180°F) from coker distillate HDN was of a modest octane number (82.2 RON + 3), but the small volume of this fraction would not upset pooled octane number of a refinery.

The conditions for this hydrodenitrogenation process were suggested from unpublished results of N. J. Kertamus. However, catalyst studies by Falk and Berg (2) indicated that nickel-tungsten promoters were best for HDN. Our results validated and extended these studies to show that high concentrations of these promoters gave best HDN. Since plant costs would be reduced if only one HDN catalyst were utilized, such a single catalyst should have maximum HDN activity, and for this reason Harshaw 4303-E was chosen. After 100 hours of operation, a snap sample of total liquid product contained 917 ppm nitrogen; this was comparable to the combined,

total product and indicates no catalyst aging took place.

Although the results obtained were satisfactory for the purposes of our study, better yields and properties might be realized after further exploratory study. For instance, most of the hydrogen consumed (1970 SCF/bbl) was taken up by saturation reactions, not by direct reactions of nitrogen elimination. The hydrogen contents of feed and products bear this out; it was also evidenced by the heat released. Had the feed nitrogen been present as pyridine, for instance, only 830 SCF of hydrogen would have been required to convert the pyridine to pentane and ammonia.

#### Naphtha Hydrogenitrogenation

Table V cites the conditions and yields of products from the naphtha hydrogenitrogenation. The properties of the liquid product from the gas separator were similar to the naphtha charge except for the nitrogen content which was reduced from 240 ppm to 1.5 ppm (see Tables IV and VI). The liquid product was not stabilized, because unstabilized liquid from first-pass HDN contained only 0.4 per cent propane plus butanes, and tail gas from the present operation contained even less hydrocarbons than that from HDN of the total coker distillate. At the end of the naphtha HDN, coke-on-catalyst was 0.7 per cent.

The goal of naphtha HDN was to reduce the nitrogen content of the product naphtha to a level permissible for long-term reforming. This goal was achieved, since the naphtha product contained 1.5 ppm nitrogen. An alternate route to nitrogen-free naphtha by two-stage HDN of total coker liquid reduced the naphtha only to 7 ppm, too high a level to sustain long life of a platinum reforming catalyst.

This HDN was run at 700°F and 1500 psig. These conditions had been found to be near optimum for cycle oils and may not be optimum for this feedstock. However, since most of the hydrogen consumed in naphtha HDN is recoverable in subsequent reforming, the effects of pressure and temperature upon hydrogen consumption probably have little economic significance.

Catalyst aging was not studied. The low level of catalyst coke (0.7 per cent) at the end of the operation indicated a long period of satisfactory use. The catalyst can be regenerated.

#### Reforming of Nitrogen-Free Naphtha

Material balances were calculated for separator products from each test and were in the range 96.5 to 100.7 wt per cent. Fractionation balances were virtually 100 per cent. For yield calculations, separator gases were allotted the same isobutane to normal butane ratio as was found for the fractionation gases.

Table VII contains detailed test conditions, yields of products based on feeds, and yield-octane values. Properties of the reformates are given in Table VIII. Figure 2 shows that both hydrogen production and yield-octane are nearly optimum at 910°F. Octane numbers of reformates are plotted against yields and temperatures in Figure 3.

Because the reformer feedstock contained virtually no aromatics and was about 50 per cent naphthenic, volumetric yields of reformate were low at high octane levels. At the high temperatures required for maximum octane reformate, cracking reactions caused a loss of reformate and a lowered hydrogen yield. Although less severe treating of naphtha during HDN would have increased the aromatic content of the reformer feed and would have resulted in less loss upon reforming, the yield based on raw shale oil would have been about the same since the severe HDN increased naphtha volume.

In Figure 3, data from reforming of a Gulf Coast naphtha, which was slightly lower in overall boiling range, are shown together with that from the shale-derived naphtha. Relations of octane number to reformer temperature and yield were found to be similar for the two naphthas. The yield-octane number (RON + 3) curve for the shale oil reformates exhibits an inflection at low octane. This is not observed in corresponding plots for reformates of straight run naphtha. Research clear octanes of the shale reformates (not shown) also show the inflection. In addition, plots of specific gravities vs octanes for these reformates are similarly S-shaped. A possible explanation for this abnormality is that the naphthenes of the shale-derived naphtha were virtually all cyclohexanes, with little cyclopentanes. This seems reasonable since the naphtha was obtained from hydrotreating reactions accompanied by much saturation of aromatic rings and the HDN catalyst was low in isomerization activity. In contrast, the cyclopentanes of straight run naphthas usually equal or exceed the quantities of cyclohexanes (3). With platinum reforming catalysts, Hettinger and co-workers showed that cyclopentanes isomerize to cyclohexanes much more slowly than the latter dehydrogenate to benzenes (5). Also, the rates for paraffin isomerizations are comparable to the rates for conversion of cyclopentanes to cyclohexanes. Consequently the initial reforming reaction of the shale oil naphtha may have been the rapid and almost complete dehydrogenation of cyclohexanes to benzenes, with abrupt volume decrease. In support of this,

results in Figure 2 show that hydrogen yield at the mildest condition was almost equal to the maximum yield of hydrogen. As temperature was increased, no cyclopentanes were present to isomerize and dehydrogenate at accelerated rates. Instead, paraffin isomerization (and dehydrocyclization) took place with increase of octane number but with little increase in product density or hydrogen yield. At severe conditions, hydrocracking eliminated alkyl groups with accompanying hydrogen consumption and resultant increase in aromaticity, density, and octane number.

#### Catalytic Cracking of Gas Oils

Tables IX and X contain yields and properties of products from both feedstocks cracked at about 50 per cent conversion. Total volumetric yields of gasoline were calculated as the sum of observed gasoline volumes plus additional volumes potentially available by alkylation and polymerization of propylenes and butylenes. Since the synthesis gasolines were not actually produced and blended with FCC gasolines, the yields based on raw shale oil were calculated from densities of FCC gasoline, and gasoline properties were determined for FCC gasolines alone.

At the 50 per cent conversion level, gasolines from both cracking stocks were of high octane number, 99 RON + 3 from the 400°F and 98 RON + 3 from the 650°F stock. Yields were greater for the 650°F feed. On the other hand, gasoline from the 650°F stock represented only 4.9 vol. per cent of the raw shale oil vs 17.2 vol. per cent for the lighter stock, because the quantity of 650°F stock was smaller. Potential gasoline from alkylation of C<sub>3</sub> and C<sub>4</sub> olefins was 2.1 vol. per cent of shale oil for the 650°F and 7.0 vol. per cent for 400°F.

Both feedstocks were sufficiently free of nitrogen, sulfur, and carbon residue as to be desirable cracking stocks. Both were paraffinic; the 400°F had a Bureau of Mines Correlation Index of 27 and the 650°F a value of 19. A real difference was found in the more refractory nature of the 400°F stock as shown by the longer cycle times and higher temperature required for cracking. Figure 5 shows that the higher boiling components of the 400°F feed were preferentially cracked, since the recycle is lower boiling than the feed. Probably a better alternate to the cracking of this stock would be the sale of the 400-650°F portion as diesel fuel, or hydrocracking of the entire 400°F stock.

#### CONCLUSIONS AND SUMMARY

1. The steps for converting Colorado pyrolytic shale oil into saleable products were:
  - a. recycle coking combined with hydrostabilization;
  - b. hydrodenitrogenation and fractionation;
  - c. hydrodenitrogenation of naphtha from (b);
  - d. reforming of product naphtha from (c);
  - e. catalytic cracking of gas oil from (b).

These steps were perhaps not performed at optimum conditions, since for most operations conditions were pre-selected and effects of process variations were not determined. The maximum temperatures and pressures of 914°F and 1500 psig were well within the limits of conventional refining processes.

2. The hydrostabilization step may not be required commercially.
3. Nitrogen content of reformer feed and cat cracker feed (650°F+) were reduced to satisfactory levels, 1.5 ppm total N and 100 ppm basic N respectively. These stocks could be processed in conventional refinery units.
4. The 400 to 650°F material from the denitrogenated coker distillate was suitable for diesel fuel.
5. Yields of hydrogen, coke, hydrocarbons, and non-hydrocarbons, for one set of operating conditions and based on raw shale oil were:

Process (see below) (wt %)	A	B	C	D	E	Total
Hydrogen	-0.49	-2.79	-0.31	0.44	0.01	-3.14
Hydrogen sulfide	0.13	0.25				0.38
Water	0.06	0.84				0.90
Ammonia		1.99				1.99
Methane	1.41	0.99	0.08	0.51	0.06	3.05
Ethylene	0.42				0.04	0.46
Ethane	1.17	0.99	0.31	0.96	0.06	3.49
Propylene	0.68				0.32	1.00
Propane	0.89	0.96	0.34	1.61	0.11	3.91
Butenes	0.68				0.40	1.08
i-Butane	0.15	1.61	0.36	0.47	0.40	2.99
n-Butane	0.45	0.77	0.29	1.02	0.12	2.65
Coke	12.61				0.30	12.91
C5-180°F Gasoline		2.71				2.71
Reformate				18.91		18.91
FCC Gasoline					3.80	3.80
400-650°F Distillate		36.86				36.86
FCC Cycle Oil					6.10	6.10
						103.19

- A. Recycle coking to 850°F end point followed by hydrostabilization at 470°F, 500 psig, and 0.9 LHSV.
- B. Hydrodenitrogenation of hydrostabilized coker distillate at 812°F, 1500 psig, and 1.0 LHSV.
- C. Hydrodenitrogenation of 180-400°F naphtha from B at 700°F, 1500 psig, and 1.0 LHSV.
- D. Reforming of naphtha from C at 500 psig, 3 LHSV, and 945°F to yield 75.5 vol % of 98.0 RON + 3 reformate.
- E. Cat cracking of 650+ gas oil from B.

#### LITERATURE CITED

1. Chem. Eng. Prog. 62 No. 8, 49 (1966).
2. Falk, A. Y., and Berg, L., "Tungsten as a Hydrodenitrogenation Catalyst", Fifty-eighth Annual Meeting AIChE, December 5-9, 1965.
3. Haensel, V., "The Chemistry of Petroleum Hydrocarbons" 2, 189-219, New York, N. Y. 1953.
4. Hellwig, K. C., Feigelman, S., and Alpert, S. B., Chem. Eng. Prog. 62, No. 8, 71 (1962).
5. Hettinger, W. P., Keith, C. D., Gring, J. L., and Teter, J. W., Ind. Eng. Chem. 47, 719 (1955).
6. Johnson, P. H., and Stark, C. P., Ind. Eng. Chem. 45, 849 (1953).
7. Oil and Gas Journal, 62, No. 10, 65-81 (1964).
8. Silas, R. S., private communication.