

## PREPARATION OF SHALE-OIL GASOLINE

Philip L. Cottingham  
Laramie Energy Research Center  
U.S. Energy Research & Development Administration  
Laramie, Wyoming 82071

### Abstract

Shale oil, produced from oil shale of the Rocky Mountain region by many of the usual retorting processes, consists mainly of high boiling compounds of nitrogen, sulfur, and oxygen; less than half is hydrocarbons. Gasoline boiling-range naphtha has been produced in a yield of 49.6 percent by volume by recycle thermal cracking of the crude. The raw naphtha, of poor quality, was upgraded by dilute acid and caustic treatment followed by concentrated sulfuric acid treatment. Hydrofining thermally cracked naphtha at 400 and 800 psig produced better yields of stable gasoline with slightly lower clear octane numbers but higher leaded octane numbers. Recycle hydrocracking of crude shale oil at 3,000 psig produced over 100 percent by volume of stable, low-sulfur, low-nitrogen gasoline with low octane numbers. Hydrotreating of a naphtha from hydrocracking crude shale oil, to reduce its nitrogen content to 7 ppm, followed by catalytic reforming raised its octane numbers to 89, clear, and 99 with 3 ml of TEL.

### Introduction

Oil shale of the Green River Formation in the Rocky Mountain region of the United States is one of the largest potential sources for alternate liquid fuels to supplement our supply of natural petroleum. In considering how shale oil can contribute to our liquid fuel supply, it is normal to consider its possible use in preparing motor gasoline. This paper reviews some of the

methods that have been investigated in former U.S. Bureau of Mines research and more recent Energy Research and Development Administration efforts in preparing motor gasolines from shale oil.

### Crude Shale Oils

Crude shale oils produced from Green River shale by several types of aboveground retorts have remarkably similar properties when the retorts are operated under conditions intended to maximize the yield of oil (Dineen and others 1952; Dineen 1954; Thorne and Ball 1954). Table 1 shows properties of shale oil produced by the N-T-U and gas-combustion retorts. The oil contains less than 5 percent by volume of naphtha distilling in the gasoline range; approximately half of the oil is nondistillable at a temperature of 807°F (corrected to 760 mm) by the Bureau of Mines analytical distillation method (Stevens and others 1952). Such oils have high specific gravities, high pour points, and high viscosities; they usually contain about 0.7 to 0.8 percent by weight of sulfur, about 2 percent nitrogen, and over 1 percent oxygen. The hydrogen/carbon atomic ratio is about 1.6. This ratio is considerably less than the ratio of 2.0 for monoolefins and the 2.0 or greater for saturated hydrocarbons.

In one extensive analysis (Cady and Seelig 1952), of a shale oil with properties similar to those shown in table 1, it was found that less than 40 percent by weight of the oil consisted of hydro-

Table 1. - Properties of crude shale oils

Type of retort	N-T-U	Gas-combustion
Gravity, °API	20.3	18.6
Specific gravity, 60/60°F	0.932	0.943
Pour point, °F	90	85
Viscosity at 100°F, cs	60.3	66.8
Viscosity at 100°F, SUS	280	310
Sulfur, wt%	0.79	0.69
Nitrogen, wt%	2.10	2.13
Oxygen (by difference), wt%	1.10	1.01
Carbon, wt%	84.61	84.87
Hydrogen, wt%	11.40	11.30
C/H wt ratio	7.42	7.50
H/C atom ratio	1.60	1.58
Distillation, BuMines Distillation Method (4), corrected to 760 mm, vol%:		
Naphtha, up to 392°F	2.7	4.4
Light distillate, 392° to 595°F	16.5	14.6
Heavy distillate, 595° to 807°F	31.2	31.3
Residuum, + 807°F	49.6	49.7

carbons: compounds containing only hydrogen and carbon; over 60 percent by weight was composed of nonhydrocarbons: compounds also containing sulfur, nitrogen, or oxygen. Nitrogen-containing compounds composed by far the largest group of nonhydrocarbons present, amounting to 36 percent by weight of the whole oil. The hydrocarbons were distributed as 18 percent by weight olefins, 11 percent paraffins plus naphthenes, and 10 percent aromatics. Most of the hydrocarbons were contained in the distillate portion of the oil. The distillate consisted of 58 percent by weight hydrocarbons and 42 percent by weight nonhydrocarbons. The residuum consisted of 20 percent by weight hydrocarbons and 80 percent by weight nonhydrocarbons.

### Recycle Thermal Cracking

The preparation of motor gasoline from shale oil requires a reduction of the boiling range by some method. The simplest method for accomplishing this is thermal processing. Between 1949 and 1954, thermal cracking, delayed coking, and various other thermal processes were studied with the 300-barrel per day unit operated by the U.S. Bureau of Mines near Rifle, Colorado. Of these methods, recycle thermal cracking produced the best yields of gasoline-range product within the limits of the operations studied (BuMines RI 4866-1952). Figure 1 is a flow diagram of the equipment used for recycle thermal cracking.

Table 2 shows operating conditions and yields for a recycle thermal cracking operation using this equipment, which produced 49.6 percent by volume of 405°F end-point naphtha. The naphtha had ASTM distillation temperatures of 89°F initial, 143°F at 10 percent, 295°F at 50 percent, and 396°F at 90 percent. It contained 0.72 percent by weight of sulfur and 1.10 percent by weight of nitrogen; the hydrocarbons consisted of 36 percent by volume of paraffins plus naphthenes, 46 percent olefins, and 18 percent aromatics. Motor-method octane numbers of the naphtha were 71.0 clear and 76.5 with 3 ml of tetraethyllead per gallon, while research octane numbers were 79.0 clear and 87.3 with 3 ml of tetraethyllead.

Acid Treating of Naphtha - Because of the poor stability of raw naphthas derived from thermal processing, they were treated at the small Rifle refinery with counter-current acid treating equipment. (Flow diagram, fig. 2, BuMines, RI 4943-1953). The tar acids were first removed with dilute sodium hydroxide solution, and then the tar bases were removed with dilute sulfuric acid. The naphtha was next treated with two stages of sulfuric acid sludge and then with fresh concentrated sulfuric acid. Finally, the naphtha was washed with water and treated with dilute sodium hydroxide solution to neutralize any acid left in it. The treated naphtha was distilled in a rerun distillation

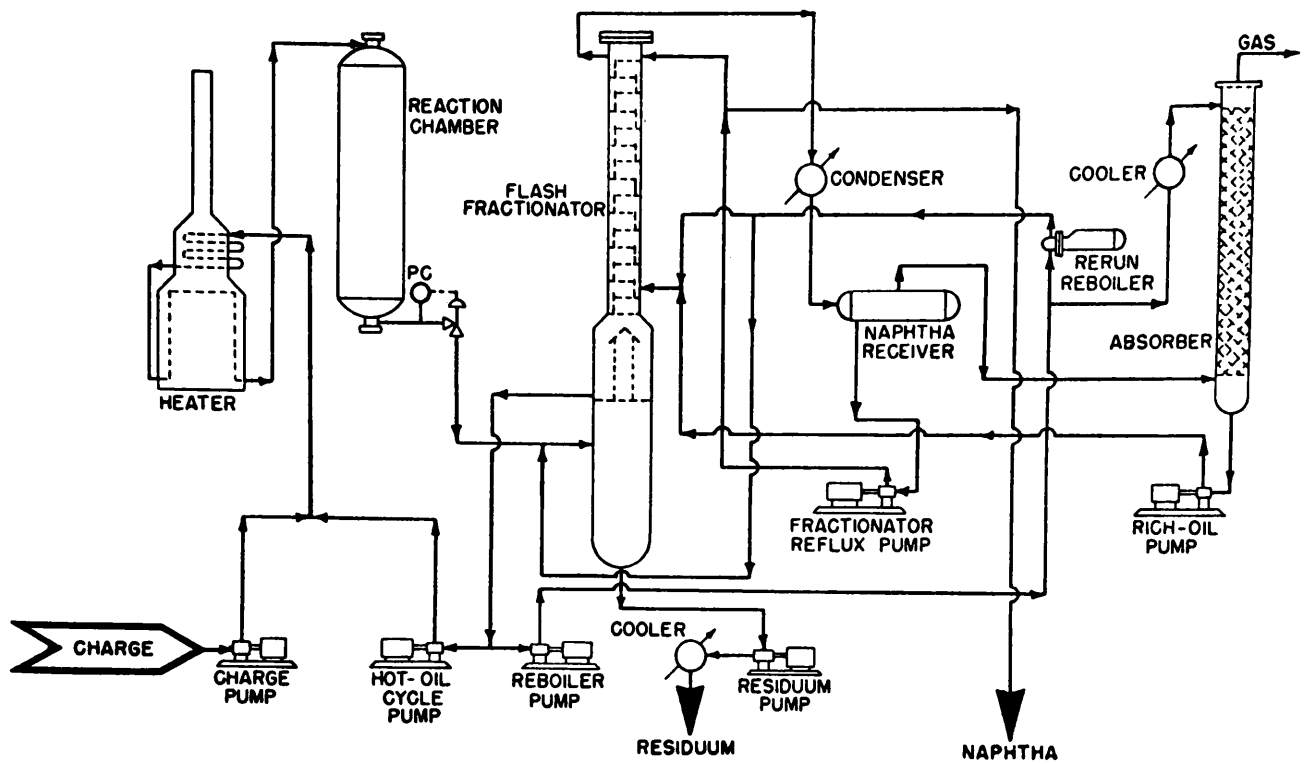


Figure 1. - Recycle cracking of crude shale oil.

Table 2. - Recycle cracking crude shale oil

	Heater outlet	Reaction chamber	Flash chamber	Fractionator	
				Top	Bottom
Temperature, °F	920	848	762	386	621
Pressure, psig	200	200	64		
		<u>Vol%</u>	<u>Wt%</u>		
		Naphtha	49.6	40.1	
		Residuum	45.9	51.9	
		Gas		7.7	
		Loss	—	0.3	
			95.5	100.0	

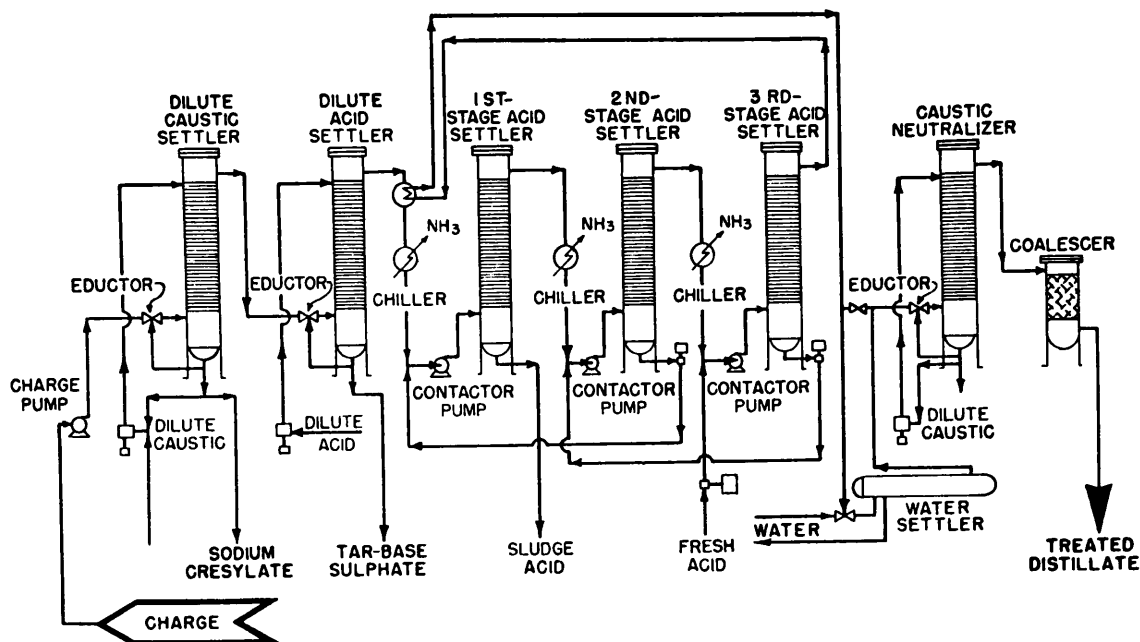


Figure 2. - Tar-acid and tar-base removal and acid treating of distillates.

unit to remove any polymer formed during the treatment.

Table 3 gives details for a typical acid treatment of naphtha from recycle thermal cracking, and table 4 shows yields and properties of the raw naphtha, treated naphtha, and redistilled polymer-free gasoline. The yield of stable, essentially nitrogen-free gasoline from this treatment was 80.7 percent by volume of the raw naphtha; the gasoline had research-method octane numbers of 73.0, clear, and 82.0 with 3 ml of tetraethyllead (BuMines RI 4866-1952). Some loss in octane numbers occurred during the treatment, but the rerun distillation usually restored most of the loss.

#### Catalytic Hydrofining of Naphtha -

Another method of stabilizing raw naphtha from thermal cracking of shale oil involves hydrofining the naphtha over a sulfur-resistant or sulfactive catalyst. The Laramie Energy Research Center laboratory

studied catalytic hydrofining of thermally cracked shale-oil naphthas, using the hydrogenation equipment whose simplified flow diagram is shown in figure 3.

The hydrogenation unit consisted of a downflow reactor containing 50 cc of catalyst in a stationary bed near the center of the reactor. Oil and hydrogen were mixed at the top of the reactor, passed downward through the catalyst, out of the reactor through an air-cooled section of tubing and a back-pressure regulator, and into a low-pressure separator vessel. Excess hydrogen and light hydrocarbons, including most of the butane and lighter gases, were separated from the liquid product at that point. Most of the water, ammonia, and hydrogen sulfide formed during the reaction were collected with the liquid product and later removed by a water wash.

Table 3. - Acid treating recycle cracked naphtha (at 45° to 55°F)

Tar acid removal	2.9 vol% of 15% NaOH
Tar base removal	16.2 vol% of 14.4% H <sub>2</sub> SO <sub>4</sub>
Fresh acid treatment	15.4 lb 66° acid per bbl
Neutralization	1.5 vol% of 15% NaOH

Table 4. - Acid treated recycle cracked gasoline

	Raw	Treated	Redistilled
Recovery, vol%	100.0	87.7	80.7
Gum, ASTM, mg/100 ml	351	ND	2.0
Sulfur, wt%	0.62	0.51	0.22
Nitrogen, wt%	0.93	0.01	0.00
Octanes:			
Motor, clear	68.8	64.7	65.4
+ 3 ml TEL	75.4	63.2	74.8
Research, clear	76.7	70.9	73.0
+ 3 ml TEL	84.3	70.0	82.0
Distillation, °F:			
IBP	94	107	111
50%	287	291	255
EP	403	494	393

Tables 5 and 6 show results obtained in hydrofining raw thermally-cracked naphtha over a commercial cobalt-molybdate-alumina catalyst (Cottingham and others 1956). Hydrofining temperatures in this work were kept high (961° to 979°F in the experiments shown) to prevent loss in octane numbers of the naphtha. Consequently, yields of hydrofined naphtha were lower than would have been obtained at lower operating temperatures. Nevertheless, yields were better

than those obtained by acid treating.

Clear octane numbers were lower, but leaded octane numbers were higher than those of gasolines produced by acid treating of cracked naphtha. This result was probably due to the highly paraffinic nature of the

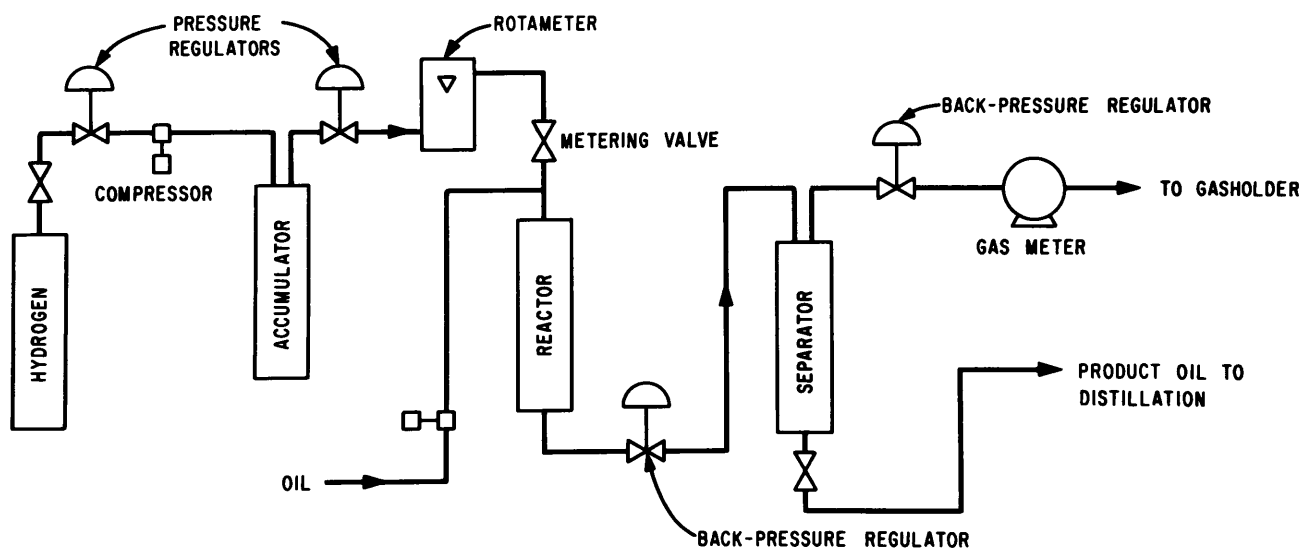


Figure 3. - Simplified flow diagram of hydrogenation unit.

Table 5. - Hydrofining recycle cracked naphtha over cobalt molybdate catalyst.

	Run 1	Run 2	Run 3
Temperature, °F	961	979	958
Pressure, psig	400	400	800
H <sub>2</sub> feed rate, scf/bbl	2,000	2,000	2,000
H <sub>2</sub> consumed, scf/bbl	760	780	910
Space velocity, V <sub>o</sub> /V <sub>c</sub> /hr	5.0	5.0	5.0
Throughput, V <sub>o</sub> /V <sub>c</sub>	120	120	120
400°F gasoline, vol%	89.7	86.7	87.0
+400°F polymer, vol%	2.6	1.9	4.1

Table 6. - Hydrofining recycle cracked naphtha.

Naphtha properties:	Feed	Run 1	Run 2	Run 3
Sulfur, wt%	0.71	0.02	0.01	0.01
Nitrogen, wt%	0.99	0.38	0.35	0.27
Gum, Cu dish, mg/100 ml	1,500	25.5	23.8	16.8
Induction period, hrs	0.3	24+	24	24+
Hydrocarbons, vol%:				
Paraffins	29	64	65	71
Naphthenes	6	3	0	2
Olefins	47	8	6	5
Aromatics	18	25	29	22
Octane numbers:				
Motor, clear	65	62	65	60
Motor, + 3 ml TEL	73	78	81	80
Research, clear	75	68	70	65
Research, + 3 ml TEL	81	84	86	83

hydrofined products. Nitrogen removal from the naphtha was not as good as was obtained with concentrated acid treatment, but sulfur removal was much better. The copper-dish gum values and the induction periods of over 24 hours in the oxidation-stability test showed the hydrofined naphthas to have acceptable stability.

#### Hydrogenation of Crude Shale Oil

Catalytic hydrogenation of crude shale oil offers a method for removing the sulfur

and nitrogen from the oil and, at the same time, eliminating the nondistillable heavy residuum fraction by converting it to lower-boiling distillate. This method has distinct advantages over thermal processing, which removes only part of the sulfur and nitrogen and converts part of the oil to residuum or coke.

Catalytic hydrogenation studies have been made in the laboratory with the apparatus whose flow diagram was shown in figure 3. Table 7 shows results from recycle hydrogenation of crude shale oil over cobalt molybdate catalyst at 3,000 psig and 889°F. Yield of C<sub>5+</sub> gasoline fraction was 99.3 percent by volume and yield of C<sub>4+</sub> gasoline, 106.8 percent by volume. The 1.7 percent by volume of recycle oil at the end of the experiment was accumulated as pump holdup material and samples removed for analysis during the run. Conversion of the recycle oil would have increased gasoline yields.

Table 8 shows properties of the gasoline fraction obtained during the recycle run. Sulfur in the gasoline was only 0.05 percent and nitrogen percentage was so low it

Table 7. - Recycle hydrogenation of gas combustion crude at 3,000 psig over cobalt molybdate catalyst.

Conditions:	
Average temp., °F	889
Pressure, psig	3,000
H <sub>2</sub> feed rate, scf/bbl	6,000
H <sub>2</sub> consumed, scf/bbl of fresh feed	2,040
Space velocity, V <sub>o</sub> /V <sub>c</sub> /hr	0.98
Throughput, V <sub>o</sub> /V <sub>c</sub>	82.2
Recycle/fresh feed vol ratio	1.03
Yields:	
Gasoline, vol%	99.3
C <sub>4+</sub> in gas, vol%	7.5
Gasoline, C <sub>4+</sub> , vol%	106.8
Recycle oil, vol%	1.7
Catalyst deposit, wt%	0.2

Table 8. - Gasoline from recycle hydrogenation of gas combustion crude at 3,000 psig.

Gravity, °API	57.7	Nitrogen, wt%	nil
Specific gravity, 60/60°F	0.748	Gum, ASTM, mg/100 ml	1.8
Hydrocarbons, vol%		Reid vapor pressure, psig	11.0
Paraffins + naphthenes	80	ASTM distillation, corrected	
Olefins	7	to 760 mm, °F:	
Aromatics	13	IBP	103
Octane numbers:		10% recovered	159
Motor, clear	48	50% recovered	272
Motor, + 3 ml TEL	73	90% recovered	374
Research, clear	51	EP	404
Research, + 3 ml TEL	76	Recovery, vol%	95.0
Sulfur, wt%	0.05	Loss, vol%	4.2

could not be detected by the Kjeldahl analytical procedure. Gum content of the gasoline was only 1.8 milligrams per 100 ml.

Catalytic Reforming Hydrogenated Naphtha-Gasoline fractions obtained from hydrogenating crude shale oil at any but extremely high temperatures usually have octane numbers too low to permit use of the fractions directly as automobile fuel. Catalytic reforming to increase octane numbers may require an additional hydrotreating step to reduce the nitrogen content even further before the naphthas are fed to a reforming unit. An investigation of such a process was made with a naphtha having properties very much like those shown in table 8, and produced by hydrogenation of gas combustion crude at 1,000 psig (Barker and Cottingham 1972, 1973). The naphtha was further hydrotreated over a commercial nickel tungsten catalyst

at 700°F, space velocity of 1.0  $V_0/V_C$ /hr, with hydrogen rate of 5,000 scf/bbl. This reduced its nitrogen content to 7 ppm and its sulfur content to below 10 ppm. Light naphtha was removed by distillation up to a cut temperature of 160°F, and the heavier portion was used as feed to a catalytic reforming unit. Table 9 shows operating conditions for three different reforming runs at 200 psig over a commercial platinum-containing catalyst. Table 10 shows properties of the hydrotreated feed and the reformates.

The highest octane product, obtained at the highest temperature investigated (917°F), was obtained in a yield of 79.9 percent by volume of the feed. The Research Method octane numbers were 89, clear, and 99 with 3 ml TEL. The unleaded octane number of 89 shows that the reformate could be used in a

Table 9. - Catalytic reforming hydrogenated naphtha (operating conditions).

	Run 1	Run 2	Run 3
Temperature, °F	860	886	917
Pressure, psig	200	200	200
$V_o/V_c/hr$	3	3	3
Throughput, $V_o/V_c$	68	71	70
$H_2$ feed, scf/bbl	3,000	3,000	3,000
Liquid yield, vol%	87.8	84.3	79.9
Liquid yield, wt%	91.0	87.9	84.4

refinery gasoline pool to produce lead-free gasoline.

#### Summary

Shale oil produced from oil shale of the Rocky Mountain region by many of the usual retorting processes consists mainly of high-boiling compounds of nitrogen, sulfur, and oxygen; less than half of the oil consists of hydrocarbons. Gasoline boiling range naphtha has been produced in a yield of 49.6 percent by volume by recycle thermal cracking of the crude. This poor quality naphtha was upgraded by hydrofining and by chemical extraction processes. A higher yield of better-quality naphtha was produced by hydrogenating the crude at 3,000 psig. Hydrogenated naphtha was catalytically reformed to a high-octane product.

#### References

- Barker, L. K., and Cottingham, P. L. Catalytic Reforming of Hydrogenated Shale-Oil Naphtha. I&EC Prod. Res. Dev., v. 11, 1972, pp. 399-404.
- \_\_\_\_\_. Refining Improvement of Shale-Oil Naphtha. BuMines RI 7740, 1973, 15 pp.
- Cady, W. E., and Seelig, H. S. Composition of Shale Oil. Ind. Eng. Chem., v. 44, 1952, pp. 2636-2641.
- Cottingham, P. L., Antweiler, J. C., Mayfield, L. G., Kelley, R. E., and Coker, W. P. Hydrofining Thermally Cracked Shale-Oil Naphtha. Ind. Eng. Chem., v. 48, 1956, pp. 1146-1151.

Table 10. - Catalytic reforming hydrogenated naphtha (properties).

	Feed	Run 1	Run 2	Run 3
IBP, °F	225	161	153	148
50%, °F	297	290	288	285
EP, °F	371	390	406	411
Paraffins, mole%	42	54	51	48
Napthenes, mole%	45	1	2	0
Alkylbenzenes, mole%	9	41	42	49
Other aromatics, mole%	4	4	5	3
Octane, research, clear	40	69	78	89
Octane, research, + 3 ml TEL	64	88	94	99

Dinneen, G. U., Ball, J. S., and Thorne, H. M. Composition of Crude Shale Oils. Ind. Eng. Chem., v. 44, 1952, pp. 2632-2635.

Dinneen, G. U. Shale Oil--What Is It? Petrol. Refiner (February) 1954, pp. 113-116.

Secretary of the Interior, Synthetic Liquid Fuels. Annual Report for 1952, Part II. BuMines RI 4866, 86 pp.

\_\_\_\_\_. Annual Report for 1953, Part II. BuMines RI 4943, 70 pp.

Stevens, R. F., Dinneen, G. U., and Ball, J. S. Analysis of Crude Shale Oil. BuMines RI 4898, 1952, 20 pp.

Thorne, H. M., and Ball, J. S. The Composition of Shale Oils. The Chemistry of Petroleum Hydrocarbons, v. 1. Brooks, Benjamin T., Ed., Reinhold, N.Y., 1954, pp. 63-82.