

## THE EFFECT OF MILD OXIDATION ON THE QUALITY OF A SHALE-OIL NAPHTHA FRACTION

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### INTRODUCTION

Green River shale-oil naphthas have several properties that make them require extensive refining before they can be utilized. These properties include high levels of sulfur, nitrogen, and olefinic compounds. Although Green River shale-oil naphtha is similar in hydrocarbon composition to thermally cracked petroleum naphthas, a higher nitrogen content of the shale-oil naphtha [typically about 1 weight-percent (1)<sup>1</sup>] distinguishes it from cracked petroleum naphthas. Another distinguishing characteristic of shale-oil naphtha is its higher reactivity to oxygen compared to thermally cracked petroleum naphthas. In one case, this high reactivity to oxygen was reported to cause the formation of as much as 10 weight-percent of high-molecular-weight gum containing 7 to 8 weight-percent nitrogen (2). This facile reaction with oxygen, which concentrates nitrogen in easily removable heavy products, suggests that oxidation of shale-oil naphthas might be employed to improve the quality of the naphtha.

To explore this possibility, a fraction boiling at 140° to 150° C and selected for its high nitrogen content and instability was distilled from a heavy shale-oil naphtha and portions of this fraction, hereafter called the naphtha fraction, were allowed to react with measured amounts of oxygen under mild conditions. Samples taken during the reactions were separated into gum and volatile material by vacuum distillation and the volatile material, hereafter called oxidized naphtha, was analyzed. The effect of oxidation on nitrogen content and major hydrocarbon groups was assessed. Also the susceptibility of an oxidized naphtha to further oxidation was investigated, and an oxidation experiment was conducted on the naphtha fraction after its nitrogen content was reduced by silica-gel treatment. This paper describes the results of these experiments.

### EXPERIMENTAL PROCEDURE

#### Preparation of Naphtha Fraction

The source of the naphtha fraction was a heavy naphtha from Green River shale oil produced in an internally fired retort. Based on preliminary testing and analyses of narrow boiling fractions of the heavy naphtha, material boiling at 140° to 150° C (760 Torr) was selected for study. This material, which had a high nitrogen content and showed high reactivity toward oxygen, was distilled from the source naphtha in a simple glass distillation apparatus under nitrogen protection. About 1.5 liters of this fraction were redistilled in a jointless all-Pyrex glass bulb-to-bulb vacuum distillation apparatus at 10<sup>-6</sup> Torr. The water-white, gum-free distillate was divided into samples of convenient size by pouring into glass ampoules under vacuum. The flame-sealed ampoules were stored in the dark until used for analyses or oxidation experiments. This naphtha fraction had a nitrogen content of 1.26 weight-percent.

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<sup>1</sup> Underlined numbers in parentheses refer to items in the list of references at the end of this report.

### Oxidation Apparatus

The apparatus consisted of an oxidation vessel, electrolytic oxygen supply system, and associated valves and tubing. The oxidation vessel was a flat-bottomed, wide mouthed, cylindrical glass vessel equipped with a water jacket and fitted with a glass head with access ports for introduction of sample and gas. The head was sealed to the main body by an O-ring.

The electrolytic oxygen supply system consisted of an electrolysis cell, constant current DC supply, AC control circuit, drying tower, and check valve. The electrolysis cell, made of Pyrex glass and equipped with platinum electrodes, was essentially two concentric cylindrical chambers held vertical by a clamp. The outer chamber, containing the negative electrode, was a cylinder, 55 mm ID and 120 mm high, open at the top. Hydrogen released in this chamber was vented to the atmosphere. The inner chamber, 30 mm ID by 110 mm high, closed at the top and ring-sealed to the outer chamber at the bottom, vented to the oxidation system through an inner concentric tube, 10 mm in diameter, ring-sealed at the bottom of the chamber, and extending to near the top of the inner chamber. A hole in the wall of the inner chamber near the bottom allowed free flow of the 0.5N sulfuric acid electrolyte between the inner and outer chambers of the cell. Electrolyte level was maintained below the top of this inner concentric tube. Oxygen released at the positive electrode in the inner chamber rose to the surface of the electrolyte and passed out of the cell through the inner concentric tube. This tube extended from the bottom of the cell and ended in an O-ring joint by which the cell was attached to the system.

The electrolysis cell was powered by a Sorensen QRB 20-1.5 DC supply,<sup>2</sup> wired for constant current operation that was turned on and off by an AC control circuit. This circuit included a relay, a General Electric elapsed-time meter displaying minutes and tenths, and a platinum wire contact that functioned as a pressure switch. This contact was set to touch the electrolyte surface in the cell outer chamber at equilibrium pressure, completing a circuit that held the relay contacts open. A drop in system pressure, causing the electrolyte level to rise in the inner cell chamber and drop in the outer cell chamber, broke the contact, allowing the relay points to close the AC circuit to the timer and power supply. Oxygen generated in the cell inner chamber restored system pressure to equilibrium and remade the contact, thus shutting off the power supply and timer. This cell and control arrangement were adapted from a system used for measuring biological oxygen demand (3).

Oxygen from the cell was dried by passing through 2 A molecular sieves in a water-jacketed glass tower, 25 mm ID by 150 mm high. The drying-tower outlet was connected to a water-jacketed glass check valve that prevented back flow through the oxygen supply system. This valve was a low-form, flat-bottomed, closed chamber with a vertical capillary inlet dipping 1 mm into a pool of mercury, and an outlet side arm above the mercury level that connected to the manifold.

The system components were connected in series by 1/8 inch OD Teflon tubing and stainless steel pressure fittings to form a gas-tight manifold. Stainless steel valves in the system permitted isolation of major components, control of gas flow, and provided access for pressure adjustment and gas inlet.

Auxiliary equipment included two Brinkmann/Lauda K2R circulating water baths, a Cole-Parmer 9" x 9" magnetic stirrer, and a Teflon-covered stirring disk. One bath controlled the temperature of the oxidation vessel; the other bath controlled the temperature of the drying tower and check valve. The magnetic stirrer activated a stirring disk that agitated the naphtha sample during oxidation experiments.

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<sup>2</sup> Reference to specific brand names is made for identification purposes only and does not imply endorsement by the Bureau of Mines to the exclusion of others that may be suitable.

### Oxidation Experiment

In a typical experiment, the circulating baths were adjusted to the desired temperatures (20° or 25° C), and the apparatus was evacuated and refilled with dry oxygen three times. During this operation, the cell contained no electrolyte and was plugged with a rubber stopper. The apparatus was evacuated through a port on the reaction vessel, and cylinder oxygen was admitted through the drying tower. With the system filled with oxygen at slightly above atmospheric pressure, the cell was unstoppered and filled with electrolyte. After adjusting the liquid in the inner and outer chambers to the same level, the platinum wire contact of the control circuit was adjusted to touch the electrolyte surface. The oxidation vessel was then shut off from the manifold and flushed with air. A weighed sample of the naphtha fraction was poured into the vessel through the sample introduction port and stirred 5 minutes with the port open. During this period the electrical system was turned on, pressure was reduced slightly in the oxygen supply system, the cell current was adjusted to 700 mA, and the system was brought to atmospheric pressure by cell operation. When the cell shut off, the sample port was closed, the elapsed time meter was set to zero, the vessel was opened to the manifold, and the time was recorded. At intervals throughout the run, the time and the reading of the elapsed-time meter were recorded. The quantity of oxygen supplied was calculated from the value of the cell current and the reading of the elapsed time meter, using Faraday's law.

The reaction mixture was sampled by syringe and needle several times in the first 24 hours of reaction and thereafter at random intervals of 24 to 72 hours. Each sample was transferred to an ampoule that was then attached by means of a stainless steel O-ring fitting to a vacuum transfer manifold. The sample was freeze-thaw degassed, the oxidized naphtha was distilled at room temperature and  $10^{-6}$  Torr into another ampoule immersed in liquid nitrogen, and the ampoules were sealed off by flame.

At the end of the run the oxidation vessel was shut off from the manifold and the reaction mixture was allowed to stand 1 hour without agitation. The liquid was then decanted into an ampoule and was distilled in the same manner as earlier samples.

### Analytical Methods

Total nitrogen was determined by microcoulometry (4) or the Kjeldahl method (5). Basic nitrogen was determined by potentiometric titration with 0.1 N perchloric acid-dioxane solution using a solvent medium composed of equal volumes of benzene and acetic anhydride (6).

A silica-gel adsorption method (7) was employed to determine hydrocarbon groups. Samples were not treated to remove tar acids and bases before analysis (a modification of the published method).

## RESULTS AND DISCUSSION

The results of the study demonstrate that the shale-oil naphtha fraction is much more reactive toward oxygen than is an unstable petroleum distillate. Furthermore, quantitative assessment of chemical changes in the naphtha fraction indicates that oxidation may be exploited as a means of improving shale-oil naphtha. A silica-gel adsorption treatment provided evidence of the constituents that are responsible for the instability of the naphtha fraction.

Selected properties of the naphtha fraction of this study, the heavy shale-oil naphtha from which it was separated, an NTU shale-oil naphtha, and an unstable thermally cracked petroleum naphtha are shown in table 1. The table gives the sulfur and nitrogen contents and the hydrocarbon composition of the materials. The thermally-cracked petroleum distillate chosen for this comparison,

TABLE 1. - Selected properties of three shale-oil distillates and an unstable petroleum distillate

Distillate type	Boiling range, °C	Sulfur, wt pct	Total nitrogen, wt pct	Basic nitrogen, wt pct	Hydrocarbon composition, vol pct		
					Saturates	Olefins	Aromatics
S.O. naphtha fraction (this work)	140-150	0.66	1.26	1.08	28	42	30
S.O. heavy naphtha	139-227	.87	1.53	1.20	28	49	23
NTU S.O. naphtha	67-213	1.24	1.21	1.00	30	48	22
TC <sup>1</sup> California dist. No. 126	189-368	1.19	.37	.18	34	21	45

<sup>1</sup> Thermally cracked.

although not typical of all thermally cracked petroleum naphthas, had properties similar to those of the shale-oil naphthas. This distillate had the highest nitrogen content and oxygen susceptibility of the 34 distillate fuels that were investigated in another stability study (8). The properties shown for the shale-oil naphthas, and in particular the high nitrogen and olefin contents, are typical for Green River shale-oil naphthas. Although most of the nitrogen is in the basic form (6), the difference between total nitrogen content and basic nitrogen content is probably pyrrole nitrogen. In the case of the naphtha fraction of this study, some confirming evidence for the presence of pyrroles was shown by the presence of an N-H stretching vibration in the infrared spectrum.

The first part of the research was a quantitative comparison of the rates of oxygen consumption by the naphtha fraction to the rate of oxygen consumption of the petroleum distillate of table 1. Oxygen absorption curves for the petroleum distillate at 66° C (8) and for the naphtha fraction at 20° and 25° C are shown in figure 1. The curves for the naphtha fraction, representing three oxidation runs at 20° C and two runs at 25° C, are the best that could be drawn through all data points. It can be seen that in 40 hours the naphtha fraction at 20° C had absorbed as much oxygen as the petroleum distillate at 66° C. At 25° C, the naphtha fraction absorbed more than twice as much oxygen in 40 hours as the petroleum distillate. The difference is especially notable when one considers that the petroleum distillate selected for this comparison represents an extreme case found among petroleum distillates for which oxygen consumption data are reported.

The effect of oxygen absorption on both the total nitrogen content and the basic nitrogen content was examined. Figure 2 shows the quantitative effect on these concentrations as oxygen is absorbed. In this figure, oxygen and nitrogen are expressed in moles per liter of naphtha. Early in the reaction, absorption of 0.04 mole of oxygen per liter of naphtha results in a total decrease of 0.07 mole of nitrogen per liter, but basic nitrogen is reduced only 0.04 mole per liter; the difference represents a reduction of 0.03 mole of nonbasic nitrogen per liter. Because nonbasic nitrogen is attributed to pyrroles, these data give indirect evidence of the early participation of pyrroles in the oxidation process. As the reaction progresses, basic nitrogen concentration decreases linearly in the ratio 0.4 mole of basic nitrogen per mole of oxygen absorbed. Total nitrogen concentration decreases somewhat more slowly, approaching half of the original concentration of total nitrogen. The resulting divergence of the two curves near the end of the reaction period reflects a buildup of nonbasic nitrogen compounds during the oxidation and a gradual decrease in the efficiency of nitrogen removal. The results of these experiments show that the concentration of total nitrogen was reduced 45 percent and the concentration of basic nitrogen was reduced 48 percent upon absorption by the naphtha of 0.3 mole of oxygen per liter. The gum recovered at this oxidation

level amounted to about 8 weight-percent of the starting material. Thus nitrogen was concentrated in heavy products easily removed from the mixture by distillation. These data indicate the possible utility of the mild oxidation reaction for improving the quality of shale-oil naphthas through nitrogen removal.

Hydrocarbon analyses were made on the original naphtha fraction and on oxidized naphtha at two levels of oxidation. The results of these analyses are given in table 2. The analyses show that

TABLE 2. - Hydrocarbon analysis of a 140° to 150° C shale-oil naphtha fraction at different levels of oxidation

Oxygen absorbed, moles/liter x 10 <sup>3</sup>	Hydrocarbon analysis, vol pct			Olefins	Aromatics
	Saturates	Olefins	Aromatics	saturates ratio	saturates ratio
0	30	40	30	1.33	1.00
171	33	43	24	1.30	.73
247	39	37	24	.95	.62

the oxidation results in a loss of both olefinic and aromatic compounds relative to saturates, which are assumed not to react. The aromatic portion of the naphtha decreased faster initially than did the olefinic portion. This effect is partly due to the formation of heavy products from reactive substances such as pyridines, pyrroles, and sulfur compounds during the oxidation. These compounds are measured in the aromatic portion of the naphtha in the method of analysis used [silica-gel displacement (7)]. As the oxidation progresses, the olefin concentration declines more rapidly than the aromatic concentration, shown by the relatively sharp decrease in the olefin-saturate ratio. The nitrogen content at the highest level shown was 0.75 weight-percent, or about 60 percent of the original concentration.

A test of the stability of the oxidized shale-oil naphtha was made by subjecting an oxidized naphtha to a second oxidation. The oxidized naphtha, containing 0.82 weight-percent nitrogen, was reoxidized at 20° C. It exhibited a rate of oxidation about one-fourth that of the original fraction. Oxygen absorbed in the first 60 hours was about  $11 \times 10^{-3}$  moles per liter compared with  $42 \times 10^{-3}$  moles per liter by the original material in the same period. This test shows the improvement in quality over the original naphtha as measured by stability to further oxidation brought about by the first oxidation. This apparent stabilization of the naphtha by oxidation may be due to the removal of reactive components or to the formation of substances that inhibit oxidation, or both. The selective removal of nitrogen compounds in the form of heavy oxidation products suggests that nitrogen compounds are important reactive components. Consequently, removal of nitrogen compounds from the naphtha fraction should lower its reactivity toward oxygen.

To examine this possibility, part of the nitrogen was removed from the naphtha fraction by silica-gel adsorption. The method was essentially the same as that used for hydrocarbon group analysis (7), scaled up to accommodate a large (134-gram) sample. The first 91 percent of the naphtha fraction (122 grams) that emerged from the column was collected. This method reduced the nitrogen content from 1.26 to 0.67 percent. When this material was subjected to mild oxidation, the oxygen absorption curve was found to be nearly the same as that for the reoxidized shale-oil naphtha. A comparison of the two absorption curves is shown in figure 3. The slightly higher rate of the silica-gel-treated sample is probably due to the slightly higher temperature of this oxidation (25° C compared with 20° C for the oxidized shale-oil naphtha). This experiment showed that mild oxidation of the naphtha was as effective as the use of adsorbents for improving the

quality of the naphtha. The use of oxygen (air) in a commercial process would probably be more economical than the use of adsorbents. This experiment also indicates that nitrogen compounds are important reactive components, and demonstrates the beneficial effects of lowering the nitrogen concentration of the naphtha.

The possibility that oxidized naphtha contains oxidation products that inhibit further oxidation is being investigated. Efforts are being made to isolate and identify the volatile nonbasic-nitrogen-containing products whose formation is indicated by the divergence of the curves in figure 2. The role of individual nitrogen compounds in the oxidation process and the composition of the heavy oxidation products are also under investigation.

### CONCLUSION

The results of this preliminary study indicate that mild oxidation of shale-oil naphthas could be used to improve the quality of the naphthas. The mild oxidation results in a significant reduction in the quantity of undesirable nitrogen compounds, leading to a naphtha of improved stability towards further oxidation. The oxidation treatment may provide a better quality naphtha for further processing into usable fuels.

### ACKNOWLEDGMENT

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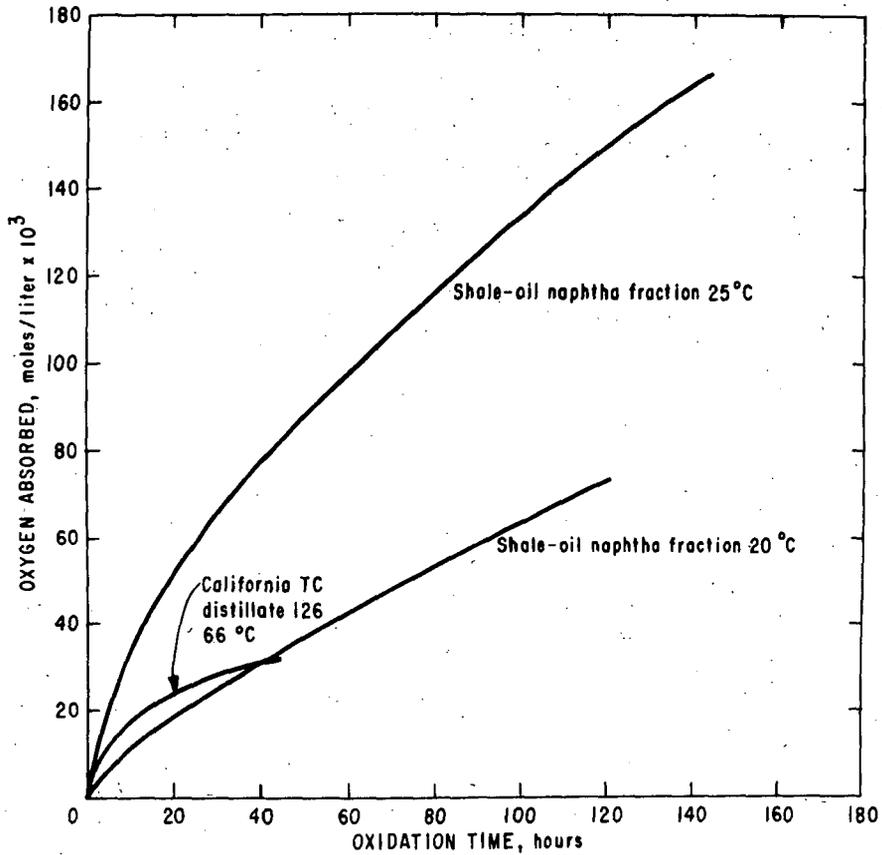


FIGURE 1.-Oxygen Absorption Curves for a Shale-Oil Naphtha Fraction And an Unstable Petroleum Distillate.

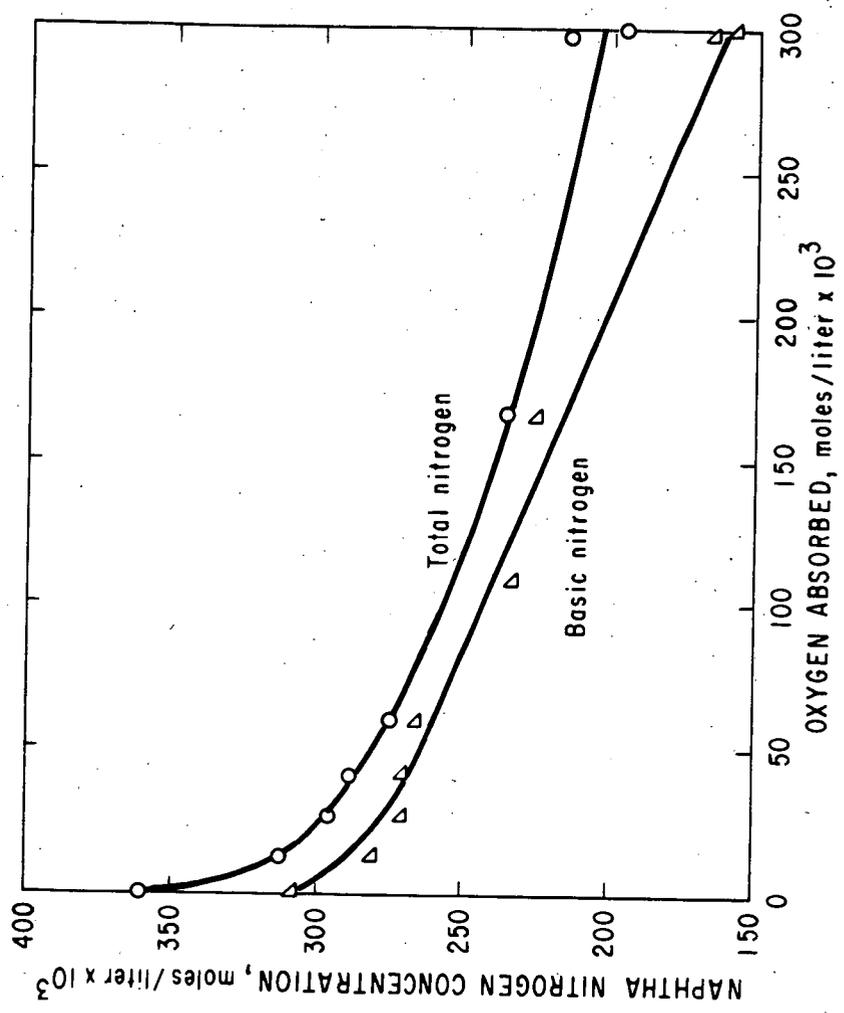


FIGURE 2.-Effect of Oxidation on Nitrogen Concentration in Shale-Oil Naphtha Fraction.

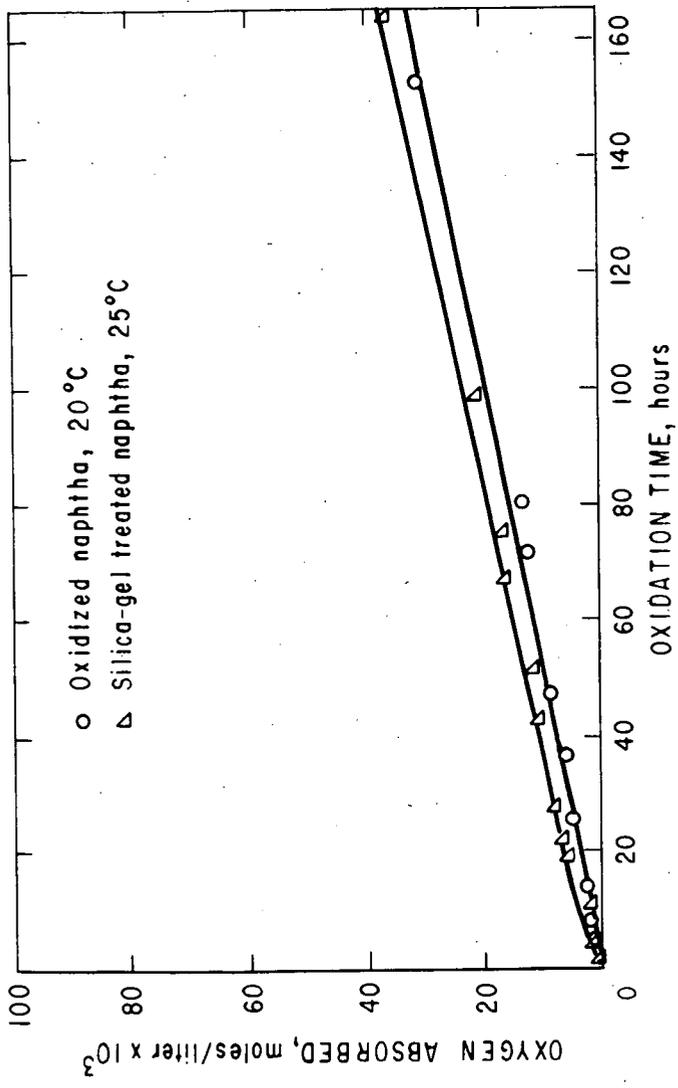


FIGURE 3.-Oxygen Absorption Curves for Oxidized Shale-Oil Naphtha Fraction, And by Shale-Oil Naphtha Fraction After Silica-Gel Treatment.