

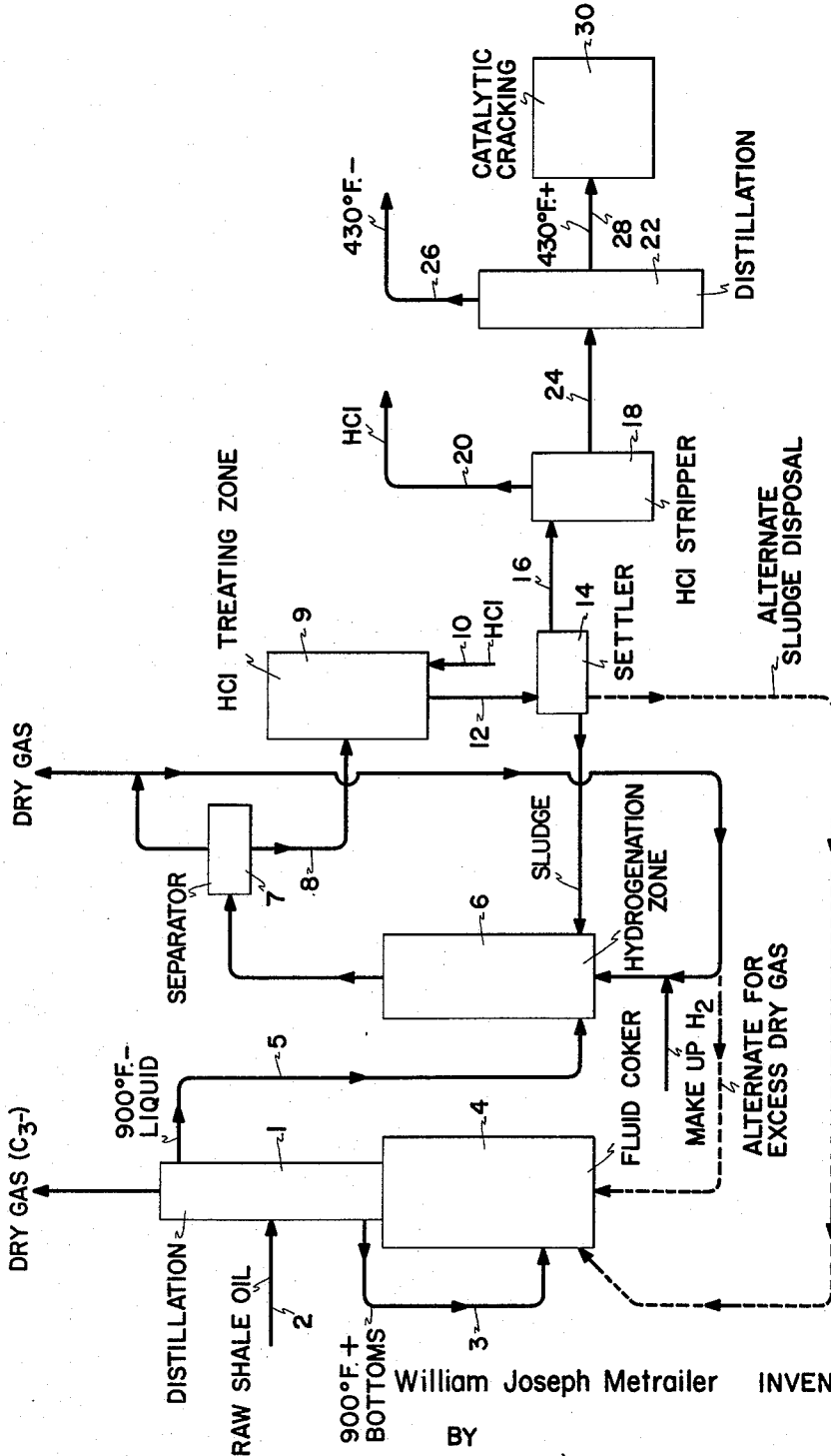
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W. J. METRAILER

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SHALE OIL REFINING PROCESS

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William Joseph Metrailer INVENTOR

BY

Richard W. Nagel

PATENT ATTORNEY

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SHALE OIL REFINING PROCESS

William Joseph Mettraler, Baton Rouge, La., assignor to Esso Research and Engineering Company, a corporation of Delaware

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The present invention relates to the refining of shale oil. More particularly, the present invention relates to a method for improving the characteristics of charging stocks from shale oil for use in catalytic cracking processes while minimizing the loss of suitable cracking feed stocks.

Shale oil as produced by retorting of oil shale contains only a minor proportion of materials suitable for use directly in motor fuels without processing and chemical conversion. An important problem in the use of shale oil for the customary conversions to which petroleum oils are normally subjected is the excessive coke formed when the oil is subjected to catalytic cracking.

Shale oil cannot be satisfactorily refined by standard petroleum processing techniques chiefly because of its high nitrogen content, amounting to about 2%, and high sulfur content. Only about 20 to 25% of the oil is aliphatic; possibly over 50% is composed of compounds containing nitrogen, oxygen and sulfur.

Considerable work has been done in attempting to separate undesirable from desirable components of shale oil by a variety of treatments, from thermal soaking, hydrogenation, visbreaking, to extraction with liquid solvents. However, those solvents which removed undesirable nitrogenous material were unselective and removed desirable cracking constituents as well.

It is an important object of the present invention to provide an improved method for the upgrading of shale oil. It is a further object of the present invention to produce from shale oil feed stocks of improved quality for catalytic conversion thereof into motor fuel and other valuable hydrocarbons while minimizing the loss of suitable cracking material and the consumption of expensive hydrogen.

The foregoing and other objects and advantages of the present invention will be more clearly understood from the detailed description of the invention, made with reference to the accompanying drawing, which represents diagrammatically a preferred method for carrying out the invention.

In accordance with the present invention it has been found that shale oil is effectively upgraded in a two-step operation. In the first stage, raw shale oil is subjected to a mild hydrotreatment which does not result in significant formation of naphtha, preferably less than 20 volume percent, but serves to remove most of the sulfur. In this first stage the nitrogen content is only reduced slightly, from 5 to 50% of its original value, and hydrogen consumption is small, about 500 s.c.f./b., which gives less than 10% change in the hydrogen to carbon ratio of the oil. Thereafter, the hydrotreated liquid product is further treated with anhydrous hydrogen chloride to form a sludge containing substantially all the nitrogen. There is further obtained a large yield of high quality cracking stock substantially free of nitrogen impurities. The raw shale oil preferably is fractionated prior to the hydrotreating step to remove the high boiling portion (above about 900° F.) of the raw shale oil and this high boiling material converted to lower boiling products by fluid coking. These low boiling products may be treated in the hydrotreating step along with the raw shale oil to obtain a hydrotreated product. The sludge from the acid treating step may also be fed to the fluid coking step.

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Turning now to the drawing, raw shale oil obtained by retorting oil shale at a temperature of about 800° to 1200° F. for a period of about 0.1 to 2 hours is fed to a distillation section 1 which also serves to distill the fluid coker 4 products. The bottoms fraction from this distillation section, 800° F.+ to 1050° F.+, is fed to the fluid coker via line 3. Operating conditions for the fluid coker are 900° to 1000° F., preferably 950° F., 0.5 to 6 atmospheres pressure, preferably 2 atmospheres and 10 to 30 seconds vapor holding time, preferably 15 seconds. The lower boiling liquid fraction from the distillation section is fed by means of line 5 to hydrogenation zone 6. A suitable hydrotreating catalyst that may be employed is cobalt molybdate supported on alumina, or MoO₃ supported on alumina. The hydrogenation conditions prevailing in reactor 6 includes temperatures of 650° to 900° F., preferably about 700° to 800° F., pressures of 50 to 175 p.s.i.g., preferably 70 to 100 p.s.i.g., a liquid feed rate of 0.25 to 5.0 v./v./hr., preferably 0.5 to 2.5 v./v./hr., and a hydrogen recycle rate of 2,000 to 10,000 s.c.f./b. with sufficient hydrogen addition to maintain 50 to 90 mole percent hydrogen in the recycle gas.

The hydrotreated product from this mild hydrogenation process, having essentially the same hydrogen to carbon ratio as the feed to said hydrogenation zone, which still contains about 5 to 50% of the originally combined nitrogen, is freed from gaseous reagents and reaction products in separation zone 7, and passed via line 8 to precipitation zone 9. Although a hydrocarbon solvent, such as light naphtha produced in the process, or extraneous pentane, hexane or naphtha may be added to the precipitation zone, it is one of the advantages of this combination process that no solvent need be added to assist in the precipitation of the nitrogen-containing impurities.

Zone 9 may be a mixer-settler of conventional design, provided, if desired, with agitation and heating means. The mildly hydrogenated shale oil is treated in vessel 9 with anhydrous hydrogen chloride in amounts sufficient to saturate the oil. The HCl is admitted through line 10, and 0.5 to 4.0, but preferably 0.9 to 1.5 equivalents of hydrogen chloride per equivalent of nitrogen in the oil may be used.

The temperature prevailing within reactor 9 must be carefully controlled. If too low, wax will likewise precipitate, while if too high, and in excess of about 130° to 150° F., sludge will redissolve in the oil. In general, it is desired to maintain the temperature of precipitation within the rather narrow limits of about 90° to 130° F., particularly if a total shale oil product is fed to the hydrogenation stage.

The oil-HCl mixture is maintained in a state of agitation, preferably for a contact period of about 1 to 60 minutes, and then passed to settling zone 14 via line 12. The upper oil layer is passed by line 16 to stripping zone 18 where HCl is stripped off and withdrawn via line 20 for further use in the system. Shale oil product free of HCl is then passed to distillation zone 22 via line 24, wherein low boiling hydrocarbons, such as the fraction boiling in the naphtha range up to 430° F. is withdrawn overhead through line 26 and recovered as product; a portion of this may be recycled to the precipitation zone 9 to provide solvent medium for this zone. The shale oil fraction, the bulk of which boils in the range of 400° to 1015° F., is now passed to catalytic cracking zone 30 via line 28.

Returning now to settler 14, the lower layer is a sludge-like material comprising in part high molecular weight hydrogen-deficient material known as Conradson carbon and also the salt-like reaction product of the HCl and the nitrogen compounds. About 7 to 15 lbs. of HCl per barrel of oil are required in this process.

This low quality sludge, amounting to some 3 to 20% of the total shale oil, may also be utilized to increase the over-all yield of motor fuel and lubricants. In one embodiment of the invention, it is withdrawn as a lower layer from vessel 14 and passed to the hydrogenation zone 6 where it undergoes further hydrogenation. In an alternate scheme this low quality sludge is sent to the fluid coker.

The process of the present invention may be subject to many variations without departing from its spirit. Thus, the shale oil, after the retorting step, may be given a preliminary thermal treatment or subjected to a visbreaking operation. Similarly, it may be desirable, instead of treating the total crude shale oil, to separate the latter into appropriate fractions by distillation, and separately hydrogenate and precipitate the respective cuts.

The process of the present invention may be further illustrated by the following specific example:

Example

A total crude shale oil was distilled to remove a bottoms fraction boiling above about 900° F. The 900° F. distillate containing 1.5% N₂ and 0.5% sulfur, having a specific gravity of 23.3° API and a distillation inspection of:

IBP -----	358
10% -----	501
20% -----	563
50% -----	711
95% -----	876

was hydrogenated in the presence of a cobalt molybdate catalyst supported on alumina at the very mild conditions of 785° F. temperature, 80 p.s.i.g. pressure, a feed rate of 0.69 v./v./hr., and a hydrogen rate of 3,420 s.c.f./b. By this process the nitrogen 430° F.+ product was reduced to 1.25% at a gas oil yield of 87.9% by volume, based on shale oil passed to the process. In addition, the 430° F.— liquid product amounting to 12.2% by volume was obtained. The total liquid product from the mild hydrotreating was thereafter treated by saturating it with anhydrous HCl at 100° to 120° F. A final product was recovered representing 77.5 vol. percent yield of liquid product based on original shale oil distillate. The gas oil portion of this HCl treated product contained only 0.07% by weight of nitrogen. In the absence of the hydrotreating step, but with solution in 3 volumes of hexane per volume of shale oil distillate and saturating with hydrogen chloride, an oil yield of only 72% by volume is recovered, and this oil has a nitrogen content of 0.4%. On the other hand, hydrogenating alone to this low N₂ value (0.07%) would require much more severe conditions of about 3,000 p.s.i.g. or low space velocity of 0.2 v./v./hr. at lower pressures.

The very mild hydrogenation conditions employed in this operation consist merely of a hydrotreat. This is evidenced by the fact that the hydrogen to carbon atomic ratio in the 430° F.+ hydrogenated product was 1.67 which was exactly the same as the shale oil distillate feed to the process. Also, the calculated hydrogen consumption was only about 200 standard cubic feet per barrel. Under more conventional hydrogenation conditions, there is a definite increase in hydrogen to carbon ratio and the hydrogen consumption is three to ten times as great. Thus, the proposed hydrotreating step merely converts the objectionable nitrogen compounds to a form where they can be more readily removed, without excessive consumption of hydrogen.

The gas oil prepared in the above example of the process was subjected to catalytic cracking in direct comparison to a known suitable catalytic cracking feed stock,

West Texas heavy atmospheric gas oil. Correlated results of this comparison are tabulated below:

Gas Oil Feed Stock	Hydro-+HCl-Treated Shale Oil Distillate		West Texas Heavy Atmospheric	
430° F. Conversion, Vol. Percent.....	45	51	45	56
Carbon Yield, Wt. Percent..	2.6	3.5	2.1	3.5
Dry Gas, Wt. Percent.....	7.3	8.5	7.2	10.3
C ₈ -430° F. Naphtha, Vol. Percent.....	32.7	35.3	34.3	37.7
Octane Numbers:				
Research + 3 cc. of TEL..	96.8	97.2	97.4	98.0
Motor + 3cc. of TEL.....	84.4	85.2	85.0	86.0

It is seen that the above gas oil produced from shale oil distillate is essentially equivalent to the gas oil prepared from an acceptable crude oil.

What is claimed is:

1. In a process for recovering from raw shale oil an oil suitable for catalytic conversion, the improvement which comprises segregating a raw shale oil into a low boiling fraction and a high boiling fraction, said high boiling fraction containing constituents boiling above about 900° F., coking said high boiling fraction in a coking zone and recovering therefrom hydrocarbonaceous product boiling below about 900° F., passing said recovered hydrocarbonaceous product and at least a portion of said low boiling fraction to a hydrotreating zone, maintaining mild hydrotreating conditions including a temperature in the range of about 650° to 900° F. and a pressure in the range of about 50 to 175 p.s.i.g. in said zone, to obtain a hydrotreated product passing the hydrotreated product to a precipitation zone, said hydrotreated product having essentially the same hydrogen to carbon ratio as the feed to said hydrotreating zone, contacting said hydrotreated product with anhydrous HCl in said precipitation zone, and recovering a hydrocarbon product of superior cracking characteristics.

2. The process of claim 1 wherein said hydrotreated product is contacted with anhydrous HCl at a temperature within the range of about 90° to 130° F.

3. The process of claim 1 wherein said hydrotreated product is contacted with about 0.5 to 4.0 equivalents of anhydrous HCl per equivalent of nitrogen in said hydrotreated product.

4. The process of claim 1 wherein a sludge fraction formed in said precipitation zone is recycled to said coking zone.

5. The process of claim 1 wherein a sludge fraction formed in said precipitation zone is recycled to said hydrotreating zone.

6. The process of claim 1 wherein the hydrotreating conditions include temperatures in the range of about 700° to 800° F., pressures in the range of about 70 to 100 p.s.i.g., a liquid feed rate of about 0.5 to 2.5 v./v./hr., and a hydrogen recycle rate of about 2,000 to 10,000 s.c.f./b.

7. The process of claim 6 wherein the hydrotreating catalyst comprises molybdenum.

8. The process of claim 1 wherein a light hydrocarbon solvent is added to said precipitation zone.

9. An improved process for producing oil from oil shale which comprises passing a raw shale oil fraction boiling below about 900° F. to a hydrotreating zone, containing a hydrotreating catalyst, maintaining mild hydrotreating conditions including a feed rate of about 0.25 to 5.0 v./v./hr., temperatures of 650° to 900° F. and pressures of 50 to 175 p.s.i.g. in said zone to obtain a hydrotreated product passing the hydrotreated product having essentially the same hydrogen to carbon ratio as the feed to said hydrotreating zone to a precipitation zone contacting said hydrotreated product with anhydrous HCl in said zone, to precipitate a sludge fraction containing nitrogen compounds and recovering a product of superior cracking characteristics.

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10. The process of claim 9 wherein said hydrotreating conditions include temperatures in the range of about 700° to 800° F., pressures in the range of about 70 to 100 p.s.i.g., a liquid feed rate of about 0.5 to 2.5 v./v./hr., and a hydrogen recycle rate of about 2000 to 10,000 s.c.f./b. wherein the recycle gas contains 50 to 90 mole percent hydrogen concentration.

11. The process of claim 9 wherein a sludge fraction formed in said precipitation zone is recycled to said hydrotreating zone.

12. The process of claim 9 wherein said hydrotreated product is contacted with anhydrous HCl at a temperature less than about 150° F.

13. The process of claim 12 wherein said temperature is within the range of from about 90° to about 130° F.

14. The process of claim 9 wherein said hydrotreated product is contacted with about 0.5 to 4.0 equivalents of anhydrous HCl per equivalent of nitrogen in said hydrotreated product.

15. In a process for recovering from raw shale oil an oil suitable for catalytic conversion including segregating a raw shale oil into a slow boiling fraction and a high boiling fraction, said high boiling fraction containing constituents boiling above about 900° F. coking said high boiling fraction in a coking zone and recovering therefrom a hydrocarbonaceous product boiling below about 900° F., the improvement which comprises passing said recovered hydrocarbonaceous product and at least a portion of said low boiling fraction to a hydrotreating zone at a rate of 0.5 to 2.5 v./v./hr., maintaining mild hydrotreating conditions including a temperature in the range of 650-900° F. and a pressure in a range of 50-175 p.s.i.g. in said zone to obtain a hydrotreated product, passing the hydrotreated product to a precipitation zone, contacting said hydrotreated product in said precipitation zone with 0.5 to 4.0 equivalents of anhydrous HCl per

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equivalent of nitrogen in said product, at a temperature of 90-130° F. precipitating a sludge fraction containing nitrogen compounds and recovering hydrocarbon product of superior cracking characteristics.

16. A process for producing oil from oil shale consisting essentially of passing a raw shale oil fraction boiling below about 900° F. to a hydrotreating zone containing a hydrotreating catalyst, maintaining mild hydrotreating conditions including a feed rate of about 0.25 to 5.0 v./v./hr., temperatures of 650-900° F. and pressures of 50-175 p.s.i.g. in said zone to obtain a hydrotreated product, passing the hydrotreated product having essentially the same hydrogen to carbon ratio as the feed to said hydrotreating zone to a precipitation zone, contacting said hydrotreated product with 0.5 to 4.0 equivalents of anhydrous HCl per equivalent of nitrogen in said hydrotreated product at a temperature of 90°-130° F. to precipitate the nitrogen compounds in a sludge fraction and recovering a product of superior cracking characteristics.

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