

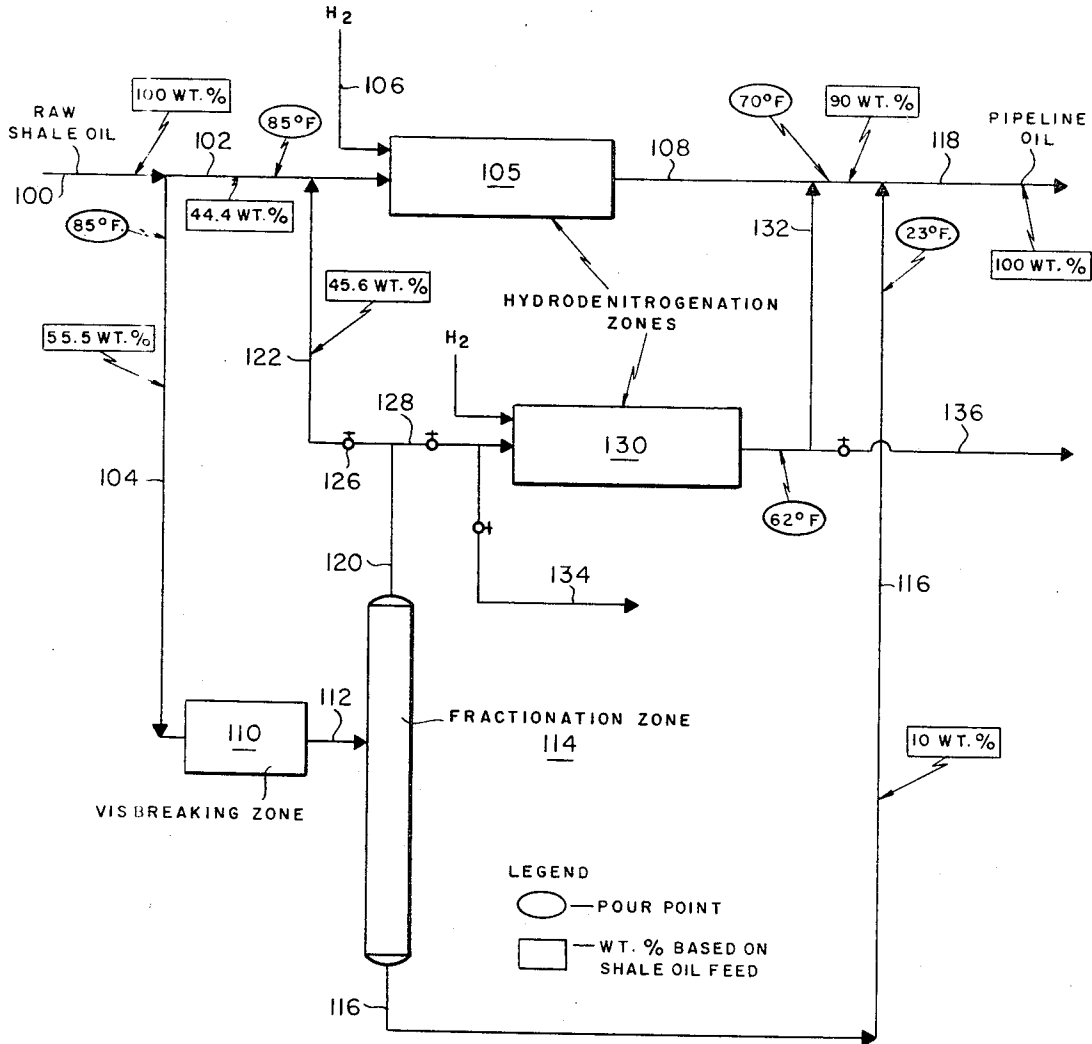
Aug. 4, 1970

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3,523,071

PROCESS FOR REDUCING THE POUR POINT OF SHALE OIL

Filed Aug. 1, 1968



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PROCESS FOR REDUCING THE POUR POINT OF SHALE OIL

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Filed Aug. 1, 1968, Ser. No. 749,550

Int. Cl. C10g 1/00, 23/00

U.S. Cl. 208—14

10 Claims

ABSTRACT OF THE DISCLOSURE

A raw shale oil is pretreated to lower the pour point and reduce the nitrogen content by separating the shale oil into two portions, hydrodenitrogenating the first portion and visbreaking the second portion. The heavy portion of the visbroken shale oil (1000° F.+) is an effective pour point reducer when blended with the hydrodenitrogenated shale oil or with hydrodenitrogenated light (1000° F.—) visbroken shale oil. The light visbroken shale oil may be hydrodenitrogenated (separately or along with the total shale oil) and made a part of the hydrodenitrogenated shale oil to which is added the heavy visbroken shale oil pour point reducing agent. The heavy visbroken oil should be used in quantities of from about 2 weight percent to about 30 weight percent of the final product.

Preferably, the hydrodenitrogenated first portion of the shale oil will comprise about 45 weight percent, the hydrodenitrogenated light visbroken shale oil will comprise about 45 weight percent, and the heavy visbroken shale oil will comprise about 10 weight percent of the final product.

Both the process and the blended final product are claimed.

The present invention is directed to the pretreatment of raw shale oil before it is introduced into a pipeline for transmission to a refinery. Raw shale oil, as obtained from oil shale, has a pour point which is too high for transmission by pipeline. This pour point (about 85° F.) is higher than ambient temperature during most of the year, and thus the shale oil would tend to solidify within and plug the pipeline through which it is being transported. Further, the shale oil has a nitrogen content of about 2 weight percent, which is too high for handling by most refineries, and is preferably pretreated to reduce the nitrogen content before it is placed in a pipeline in order to have a saleable product. Further, it is highly desirable that a process for reducing the pour point and the nitrogen content be of such a character that, if necessary, all of the shale oil being processed can be recombined and introduced into the pipeline, without removing substantial quantities as constituents unsuitable for transportation and sale.

The present invention meets all of the requirements providing a balanced process whereby all of the raw shale oil can be processed and introduced into the pipeline if desired. Alternatively, a lighter portion of the visbroken shale oil can be removed and sold as a separate product if a market exists for such a product. The present invention utilizes as a pour depressant the heavier product from visbreaking of raw shale oil, which is effective in reducing the pour point of hydrodenitrogenated shale oil. Although the pour depressant of the present invention does contain nitrogen (about 2.5 weight percent), due to its high boiling

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range it may be easily removed from the hydrodenitrogenated oil by distillation at the refinery without excessive loss of hydrodenitrogenated shale oil.

By the present invention, a raw shale oil feedstock to the treating unit is split into two portions. The first portion is hydrodenitrogenated, while the second portion is visbroken and fractionated. The first portion may comprise from about 40 to about 50 weight percent of the total shale oil feed to the treating unit, while the second portion will correspondingly concentrate about 50 to about 60 weight percent. In the balanced process later described, 45 weight percent of the total shale oil feed is hydrodenitrogenated and about 55 weight percent is visbroken.

The heavy visbroken shale oil (e.g., 1000° F.+), obtained by distillation of the visbreaker product, is added to the hydrodenitrogenated shale oil in amounts effective to reduce the pour point to 60° F. or less (preferably less than 40° F.). A concentration of heavy visbroken shale oil from about 2 weight percent to about 30 weight percent should be used. It has been found that, in a concentration of about 10 weight percent, the pour point of hydrodenitrogenated shale oil can be reduced to 0° F. The light visbroken shale oil (e.g., 1000° F.—) may be sold as a separate product or may be hydrodenitrogenated (separately or along with the first portion of shale oil) so as to constitute a part of the pipeline oil. At a concentration of heavy visbroken oil of about 10 weight percent, the pour point of a 50/50 mixture of the hydrodenitrogenated oils will be about 23° F.

FEEDSTOCK

In order to understand the present invention, it is first necessary to describe the shale oil feedstock which is subjected to the treating process of the present invention. Shale oil is obtained by retorting the oil shale which is obtained as a mineral product in many of the Northwestern States of the United States, such as Colorado. Widespread deposits of kerogen-bearing oil shale of differing degrees of richness are available in Colorado and have been made the subject of many experimental retorting processes. For example, the Bureau of Mines has operated a retort similar to that described in U.S. Pat. 2,757,129 whereby a partial combustion of the oil shale provides the heat for decomposing kerogen and producing a hydrocarbon product. Other processes are shown in U.S. Pat. 3,117,072, assigned to Texaco, Inc., and U.S. Pat. 3,162,583, assigned to Esso Research and Engineering Company.

While the above patents refer to the production of shale oil by retorting the mined oil shale, other patents have suggested that the retorting can be accomplished while the oil shale remains in situ. Exemplary of this second type of production scheme is U.S. Pat. 3,001,776.

The physical characteristics of oil shale obtained by the various processes may vary over a substantial range. By reference to Table II of the Bureau of Mines patent, U.S. 2,757,129, it is seen that the shale oil has a gravity of 18.6 to 22.4° API, a viscosity of 42.2 through 56.0 Saybolt Universal seconds measured at 210° F. The pour point of all product oils, however, appears to be about 85° F.

The Texaco patent, U.S. 3,117,072, discloses that the product oil has a pour point of about 90° F. and a nitrogen content of 2.6 weight percent. The Esso Research patent, U.S. 3,162,583, discloses a pour point of 82° F. and a nitrogen content of 1.97 weight percent.

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Regardless of the method of producing the shale oil, however, the present invention can be applied to reduce the pour point and to reduce nitrogen content of the shale oil product.

The shale oil used in the examples later given was produced in a vertical retort similar to that disclosed in the Bureau of Mines patent, U.S. 2,757,129. The shale oil had the inspection data described below in Table I.

TABLE I

Inspection data on shale oil

Gravity, API	19.8±0.2
Pour point, ° F.	83.5
Nitrogen (Dohrmann), wt. percent	2.14±0.15
Sulfur (X-ray F), wt. percent	0.699±0.025
Oxygen (neutron act.), wt. percent	1.67
Carbon, wt. percent	83.92
Hydrogen, wt. percent	11.36
Conradson carbon, wt. percent	4.71
Bromine No.	33.2
SBA wax, wt. percent	8.1
Viscosity, SUS:	
100° F.	270
212° F.	47.6
Sediment, wt. percent	0.042
Ni, p.p.m.	6.4
V, p.p.m.	6.0
Fe, p.p.m.	108.0
Flash (O.C.), ° F.	240
Molecular weight	328

Distillation	D-1160 1 mm. (GC) avg. of 3
450° F. at volume percent	11.1
650° F. at volume percent	36.1
5 volume percent at ° F.	378
10	465
20	570
30	650
40	715
50	775
60	830
70	875
80	940
90	1,040
95	1,145

The shale oil shown in Table I was employed in all of the examples later given.

STREAM PROPORTIONS

The shale oil feedstock is separated into a first portion (comprising about 40 to 50 weight percent thereof) and a second portion (comprising about 60 to 50 weight percent thereof). The second portion is visbroken, and a heavy visbroken shale oil recovered which comprises about 20 weight percent of the second portion. The light visbroken shale oil may be recombined with the first portion prior to hydrodenitrogenation thereof, or separately hydrodenitrogenated and recombined with the hydrodenitrogenated first portion in a ratio of 0 to 55 parts by weight of the light visbroken shale oil to (correspondingly) 100 to 45 parts by weight of said hydrodenitrogenated first portion (the total being 100 parts by weight). To the blend thus obtained, heavy visbroken shale oil is added in amounts sufficient to produce a concentration thereof in said blend from about 2 weight percent to about 30 weight percent. For a balanced operation, the hydrodenitrogenated first portion and hydrodenitrogenated light visbroken shale oil will be used in equal proportions (50/50) and the heavy visbroken shale oil will constitute about 10 weight percent of the final product.

HYDRODENITROGENATION STEP

The first portion of the shale oil feed is subjected to hydrodenitrogenation. The light visbroken shale oil (e.g., boiling lower than 1000° F.) may also be hydrodenitrogenated, either separately or in admixture with the first portion of the shale oil feed. Hydrodenitrogenation is

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accomplished, as well known to those skilled in the art, in the liquid phase in contact with a catalyst such as a combination of a Group VI metal (such as chromium, molybdenum and tungsten) with an iron group metal (such as iron, nickel and cobalt). Cobalt molybdate is preferred. The operating conditions for hydrodenitrogenation include a temperature from 650° F. to 900° F. (preferably 740° F.), a pressure from 1000 p.s.i.g. to 3000 p.s.i.g. (preferably 1500 p.s.i.g.), a liquid hourly space velocity from 0.1 to 1.0 volume per hour per volume (preferably 0.3 v./v.hr.), and a hydrogen treat rate (based on molecular hydrogen) from 2000 s.c.f./b. to 10,000 s.c.f./b. (preferably 5000 s.c.f./b.).

In the hydrodenitrogenation step, the nitrogen content of the feed oils is reduced from about 2 weight percent to a level below about 0.3 weight percent. In this step there is consumed about 1000 to 3000 s.c.f. of hydrogen per barrel of oil being treated (usually about 1700 s.c.f./b.).

VISBREAKING

The second portion of the shale oil feed is subjected to a liquid phase visbreaking operation. Visbreaking is in essence a thermal cracking step, carried out under a temperature from about 800° F. to about 1100° F. (preferably 900° F.), a pressure from about 100 p.s.i.g. to about 1000 p.s.i.g. (preferably about 400 p.s.i.g.), and for an oil residence time from about 1 minute to about 15 minutes (preferably about 3.5 minutes). The products from the visbreaking step are passed into a fractionator for gross separation into a heavy bottoms fraction boiling above a cut point of 900° F. to 1100° F. (preferably above 1000° F.) and comprising about 20 weight percent of the fractionator feed, and a lighter overhead stream boiling lower than the cut point and constituting about 80 weight percent of the fractionator feed. The oil preferably is fractionated batchwise, initially in a column filled with protruded stainless steel packing having 15 theoretical plates. In this column about 60% is distilled off, finishing with an overhead pressure of 10 mm. of Hg and a vapor temperature of 760° F. The oil not taken overhead is then fractionated batchwise in a column with no packing or plates under a pressure of 200 microns of Hg to take off an additional 20 weight percent.

PROCESS FLOW SCHEME

The process of the present invention can best be understood by reference to the drawing, wherein the single figure schematically sets forth the preferred flow scheme of the present invention. A preferred mode is discussed below in connection with this preferred flow scheme.

In the drawing, a total shale oil feedstock is introduced by way of line 100 and separated into a first portion (45 weight percent) in line 102 and a second portion (55 weight percent) in line 104. The first portion is admixed with light visbroken shale oil (obtained as hereinafter described) and introduced into a hydrodenitrogenation zone 105 wherein it is contacted with a cobalt molybdate catalyst at a temperature of about 740° F., a pressure of about 1500 p.s.i.g., and at a space velocity of about 0.3 volume of oil per volume of catalyst per hour. Hydrogen is introduced by way of line 106 at a rate of about 5000 s.c.f./b. of oil being treated. The product is removed from the hydrodenitrogenation zone by way of line 108.

The second portion of the total shale oil feed is introduced by way of line 104 into a visbreaking zone 110 wherein the oil is contacted for about 13.6 minutes at a temperature of about 850° F. and a pressure of about 400 p.s.i.g., whereby the effects of thermal breaking can be carried out. A visbroken total product is removed by way of line 112 and introduced into a fractionator system 114 operating at a cut point of about 1000° F., from which a heavy visbroken oil bottoms product (20 weight percent of fractionator feed) is removed by way of line 116 and is admixed with the hydrodenitrogenation product in line

108 to obtain a pipeline oil which is carried by way of line 118 into the pumps for the pipeline transmission.

An overhead product (80 weight percent of fractionator feed) is obtained from the fractionator 114 by way of line 120. This overheads product, boiling lower than 1000° F., is hydrodenitrogenated in admixture with the first portion of the total shale oil feed. This admixture may be obtained by passing the overhead product by way of line 122 into line 102 upstream of the hydrodenitrogenation zone 104. (Alternatively, block valve 126 may be closed and the light visbroken oil may be passed by way of line 128 into hydrodenitrogenation zone 130, for separate hydrodenitrogenation prior to blending with the hydrodenitrogenated first portion of the total shale oil, accomplished by way of line 132 or, if desired, untreated light visbroken oil may be removed by way of line 134, or hydrodenitrogenated light visbroken oil may be removed by way of line 136.)

As is seen by advertence to the figure, the concentration of heavy visbroken oil is about 10 weight percent of the total blend when the light visbroken oil is admixed with total shale oil upstream of the hydrodenitrogenation zone 104. As will be seen by advertence to the examples, this will reduce the pour point of the total shale oil for pipeline transmission to about 23° F. Further, it should be seen by advertence to the flow scheme that substantially all of the total shale oil introduced by way of line 100 can, if desired, be removed by way of line 118 for transmission to the refinery.

PRODUCTS

By the process of the present invention, a shale oil product can be obtained which is suitable for pipeline transportation which comprises a blend of (1) a base stock consisting essentially of from about 45 to 100 parts by weight of a hydrogenated shale oil and from about 50 to about 0 parts by weight of a hydrodenitrogenated light visbroken shale oil having a boiling range under 1100° F., the total being 100 parts by weight, and (2) a heavy visbroken shale oil having a boiling range over 900° F., said heavy visbroken shale oil comprising from about 2 weight percent to about 30 weight percent of said blend. In the preferred embodiment, the base stock will contain 50 parts by weight of each of the two constituent oils and the blend will contain about 10 weight percent of the heavy visbroken shale oil.

EXAMPLES

In order to illustrate the present invention, several runs comparing the effect of various processing schemes were made and the results are presented below. In reviewing the examples given below, it will become apparent that the pour point of raw (i.e., not hydrodenitrogenated) shale oil cannot be significantly reduced by

blending with the heavy visbroken oil. Further, it will be seen that the pour point of hydrodenitrogenated low-boiling fraction from raw shale oil cannot be significantly reduced by blending with the heavy visbroken oil. The hydrodenitrogenated shale oil can, however, be successfully blended with the heavy visbroken oil to obtain a pipeline oil of acceptably low pour point, and a blend of hydrodenitrogenated shale oil and hydrodenitrogenated light visbroken oil can also be successfully combined with heavy visbroken shale oil.

Example 1

A shale oil having the characteristics shown in Table I was blended with heavy visbroken shale oil, at a ratio of 90 parts by weight of shale oil to 10 parts of weight of heavy visbroken oil. The pour point of the resulting blend was 80° F. as compared to 85° F. for the raw shale oil. At concentrations of 2 weight percent and 5 weight percent, the pour point was unaffected (still 85° F.).

Example 2

The unhydrotreated low-boiling, visbroken shale oil from the fractionator was blended with the heavy visbroken shale oil from the fractionator in a 90-10 ratio. The pour point of the light visbroken oil was 68.5° F.; the pour point of the blend was 58° F.

Example 3

Hydrodenitrogenated shale oil having a pour point of 77° F. was blended with heavy visbroken shale oil at a ratio of 90 to 10. The pour point of the resulting blend was 0° F. At 2 weight percent and 5 weight percent concentrations, the pour points were 50° F. and 25° F., respectively.

Example 4

A 50-50 blend of hydrodenitrogenated light visbroken shale oil having a pour point of 62° F. and hydrodenitrogenated shale oil having a pour point of 77° F. are mixed with heavy visbroken shale oil at a 90 to 10 weight ratio. The resulting blend has a pour point of 23° F. At 2 weight percent and 5 weight percent concentrations, the blend has pour points of 54° F. and 38° F., respectively.

Example 5

A hydrodenitrogenated light, raw shale oil fraction having a boiling range up to 1050° F. was blended with heavy visbroken oil at a weight ratio of 90 to 10. The raw hydrodenitrogenated shale oil had a pour point of 75° F. The blend had the same pour point, 75° F. At concentrations of 2 weight percent and 5 weight percent, the blend still had the same pour point, 75° F.

In Table II, below, data from the examples is compared (along with other data) to show the effectiveness of heavy visbroken shale oil as a pour point depressant.

TABLE II.—EFFECTIVENESS OF HEAVY VISBROKEN SHALE OIL (HVSD) AS POUR POINT DEPRESSANT

Weight percent HVSD ¹	Pour point, ° F.				
	Raw ² shale oil	HDN ³ shale oil	HDN ⁴ shale oil, IBP-1050° F. fraction	HDN ⁵ light visbroken shale oil	50% HDN ³ shale oil, 50% HDN ⁴ light visbroken oil ⁶
0.....	85	77	75	62	70
2.....	85	50	75	58	54
5.....	85	25	75	50	38
10.....	80	0	75	45	23

¹ 1,000° F.+ fractionator bottoms obtained after visbreaking at 850° F., 400 p.s.i.g. for about 10-15 min. The fractionator overhead (IBP-1,000° F.) was recovered and hydrodenitrogenated to obtain the HDN light visbroken shale oil.

² Obtained by Bureau of Mines vertical retorting at Rifle, Colorado.

³ Hydrodenitrogenated in contact with cobalt molybdate catalyst at 740-747° F., 1,500 p.s.i.g., 0.3 vol./hr./vol. of catalyst, 5,000 s.c.f. of hydrogen per barrel of shale oil.

⁴ Hydrodenitrogenated in contact with cobalt molybdate catalyst at 745-785° F., 1,500 p.s.i.g., 0.6 vol./hr./vol. of catalyst, 5,000 s.c.f. of hydrogen per barrel of light visbroken shale oil. Boiling range IBP-1,000° F.

⁵ Visbroken at 850° F., 400 p.s.i.g. and 4.4 LHSV (on basis of volumes at 60° F.). Hydrodenitrogenated at 720° F., 1,500 p.s.i.g., 0.3 vol./hr./vol., 5,000 s.c.f. of hydrogen per barrel of visbroken shale oil having a boiling range of IBP-1,000° F.

⁶ Calculated on basis of 50-50 (weight) blend of components. Other data indicate that the calculated values are reasonable.

From Table II it is seen that the heavy visbroken shale oil is very effective in reducing the pour point of hydrodenitrogenated shale oil and to a lesser extent is effective in reducing the pour point of hydrodenitrogenated light visbroken shale oil. It was not effective in reducing the pour point of raw shale oil or of a hydrodenitrogenated light cut (IBP—1050° F.) from the total shale oil. From these data, it is concluded that the heavy visbroken shale oil can be used to reduce the pour point of hydrodenitrogenated shale oil or hydrodenitrogenated light visbroken shale oil, or a mixture thereof.

Having disclosed our invention and a specific example of the way in which it is carried out, what we desire to protect by Letters Patent should be limited not by the examples herein given, but rather by the appended claims. We claim:

1. A shale oil product suitable for pipeline transportation which comprises a blend of:

(1) a base stock consisting essentially of from about 45 to about 100 parts by weight of a hydrodenitrogenated shale oil, and

from about 55 to about 0 parts by weight of a hydrodenitrogenated light visbroken shale oil having a boiling range under 1100° F., the total being 100 parts by weight, and

(2) a heavy visbroken shale oil having a boiling range over 900° F.,

said heavy visbroken shale oil comprising from about 2 weight percent to about 30 weight percent of said blend.

2. A shale oil product as set forth in claim 1 wherein the base stock contains about 50 parts by weight of hydrodenitrogenated shale oil and about 50 parts by weight of said hydrodenitrogenated light visbroken shale oil,

and the blend contains about 10 weight percent of said heavy visbroken shale oil.

3. A process for reducing pour point of a shale oil which comprises:

(1) separating said shale oil into a first portion and a second portion;

(2) visbreaking said second portion to obtain a visbroken shale oil;

(3) fractionating said visbroken shale oil to obtain a light visbroken shale oil boiling above a cut point of from about 900° F. to about 1100° F. and a heavy visbroken shale oil boiling above said cut point;

(4) mixing from 0 to 100% of said light visbroken shale oil with said first portion;

(5) hydrodenitrogenating said mixture to obtain a hydrodenitrogenated shale oil; and

(6) blending said heavy visbroken shale oil with said hydrodenitrogenated shale oil in amounts sufficient to produce a concentration of said heavy visbroken shale oil in said blend within the range from 2 weight percent to 30 weight percent.

4. A method in accordance with claim 3 wherein the visbreaking step is carried out under conditions including a temperature from about 800° F. to about 1100° F., a pressure from about 100 p.s.i.g. to about 1000 p.s.i.g., and

an oil residence time from about 1 minute to about 15 minutes.

5. A method in accordance with claim 4 wherein the hydrodenitrogenation step is carried out in the presence of a cobalt molybdate catalyst under conditions including a temperature from about 650° F. to about 900° F., a pressure from about 1000 p.s.i.g. to about 3000 p.s.i.g.,

a liquid hourly space velocity from about 0.1 to about 1.0 v./v./hr., and

a hydrogen treat rate from about 2000 s.c.f./b. to about 10,000 s.c.f./b.

6. A method in accordance with claim 5 wherein 100% of said light visbroken shale oil is mixed with said first portion before hydrodenitrogenation in a ratio of about one part by weight of said light visbroken shale oil per part by weight of said first portion.

7. A method in accordance with claim 6 wherein the visbreaking conditions include

a temperature of about 900° F.,

a pressure of about 400 p.s.i.g., and

an oil residence time of about 3.5 minutes,

and the fractionation is carried out to separate the visbroken shale oil into two products:

(1) a light visbroken shale oil boiling below about 1000° F., and

(2) a heavy visbroken shale oil boiling above about 1000° F.

8. A method in accordance with claim 7 wherein the hydrodenitrogenation conditions include

a temperature of about 740° F.,

a pressure of about 1500 p.s.i.g.,

a liquid hourly space velocity of about 0.3 v./v./hr., and

a hydrogen treat rate of about 5000 s.c.f./b.

9. A method in accordance with claim 8 wherein said heavy visbroken shale oil comprises about 20 weight percent of the visbroken shale oil and about 10 weight percent of the blend.

10. A method in accordance with claim 9 wherein said first portion comprises about 45 weight percent of the shale oil and said second portion comprises about 55 weight percent thereof.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

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