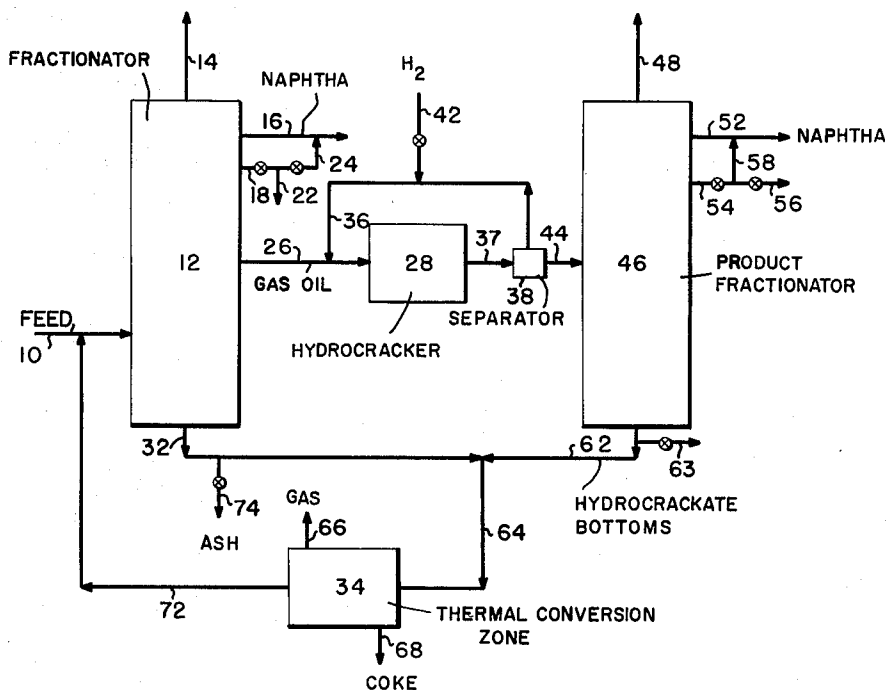


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HYDROGENATED DONOR DILUENT
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1

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CONVERSION OF HYDROCARBONS IN THE PRESENCE OF A HYDROGENATED DONOR DILUENT

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This invention relates to the conversion of high boiling hydrocarbon oils to lower boiling hydrocarbons. More particularly, the invention relates to the conversion of crude petroleum oil or residual fractions thereof to naphtha in an integrated process involving hydrocracking of a gas oil fraction and conversion of the high boiling residue to suitable hydrocracking feed in a non-catalytic thermal step using the hydrocrackate bottoms as a solvent and hydrogen donor.

Hydrocarbon conversion processes are known where a relatively high boiling aromatic compound is partially hydrogenated to form a hydrogen donor which is then used in a hydrogen exchange step. Following the hydrogen exchange step the spent donor is rehydrogenated partially and reused in another hydrogen exchange step. Crude oil contains ash and if the crude oil as such is catalytically hydrocracked, the catalyst becomes deactivated by the ash components. The present invention discloses an integrated process for treating whole petroleum crude oil or residual fractions thereof to produce ash-free gas oil for hydrocracking. The crude oil is fractionated and the separated gas oil fraction is hydrocracked. Hydrocracked products are fractionated and the hydrocrackate bottoms are mixed with the crude residue and treated in a thermal non-catalytic conversion step to upgrade the residue and also produce a better gas oil feed for hydrocracking.

The present invention is especially adapted for the treatment and conversion of crude petroleum oils in which a gas oil fraction separated from the crude oil is hydrocracked, and the hydrocrackate bottoms separated from the hydrocracked products are used as a hydrogen donor in the HDDC thermal conversion of the residual oil fraction separated from the crude oil in a non-catalytic thermal conversion. The thermally converted products may be separately fractionated but are preferably combined with the whole petroleum crude oil feed and fractionated. The crude oil is preferably a naphthenic crude.

More specifically, the crude petroleum oil and thermally cracked or converted products are fractionated or separated into a naphtha fraction, a gas oil fraction for hydrocracking, and a bottoms fraction. Hydrocrackate bottoms containing hydrogen donor diluent formed during hydrocracking are mixed with the crude oil bottoms fraction and passed to the thermal non-catalytic HDDC conversion zone or reactor. The products from the thermal reactor are combined with the original crude oil feed and fractionated as just described. This provides a recycle of the unconverted crude oil bottoms to the thermal reactor to convert the bottoms to lower boiling hydrocarbons.

The thermal conversion step is conducted at a temperature in the range between about 700 and 1000° F. and at a pressure in the range between about 200 and 2000 p.s.i.g. The flow rate of total oil feed in the thermal converter is between about 0.25 and 10 v./v./hr. Internal recycle of the higher boiling components can be achieved by control of the temperature and pressure so that some of the product is withdrawn as a vapor phase from the thermal converter. The solvent action of the hy-

2

drogen donor in the thermal conversion zone prevents or minimizes deposition of poly condensed aromatic hydrocarbons in the thermal conversion zone or hydrogen exchange zone and hence a minimum amount of coke is made in the thermal conversion zone.

Normally an ash concentration builds up in the thermal conversion zone resulting from a concentration of ash in the residual or bottoms fraction from the crude oil fractionator. The quantity of ash is maintained within bounds and at a low level by a purge or by withdrawing a portion of the bottoms fraction, filtering or separating the ash, and returning the treated bottoms to the thermal conversion zone.

The drawing represents a diagrammatic showing of apparatus adapted for carrying out the process of the present invention.

Referring now to the drawing, the reference character 10 designates a line for feeding whole crude petroleum oil to a crude fractionator 12. The crude is preheated to a temperature between about 600° F. and 800° F. before introduction into tower 12, and in the tower is fractionated or segregated into a plurality of fractions. Hydrocarbon gases and low boiling hydrocarbons boiling up to about 180° F. pass overhead through line 14. This overhead fraction may be treated to separate low boiling hydrocarbons from gases, if desired.

A naphtha fraction is withdrawn as a top side stream through line 16. This naphtha fraction forms an excellent hydroforming feed. A higher and narrow boiling naphtha boiling between about 375 and 430° F. can be withdrawn as a side stream lower down the tower 12 through line 18, and provision is made for separate withdrawal of this stream from the process through line 22 or for combining it with the naphtha side stream in line 16 by passing it through line 24.

Further down the crude fractionating tower 12 a gas oil fraction boiling between about 430 and 650° F. or up to about 1000° F. is withdrawn through line 26 and hydrocracked in hydrocracking zone 28 presently to be described in greater detail. Crude oil bottoms boiling above about the end point of the gas oil fraction are withdrawn from the bottom of crude tower 12 through line 32 for further treatment in a thermal non-catalytic HDDC conversion zone 34 to be later described in greater detail. The products from this thermal conversion step are combined with the feed in line 10 as will be hereinafter described.

Returning now to the hydrocracking step, the gas oil fraction withdrawn through line 26 is heated to a temperature between about 550° F. and 850° F., and under a pressure between about 500 and 2500 p.s.i.g., and passed through the hydrocracking zone 28 at a feed rate between about 0.4 and 4 v./v./hr. The gas oil fraction contains virgin and recycled constituents and condensed ring naphthenes or aromatic-naphthenic molecules having a few aromatic nuclei with attached naphthenic or partially hydrogenated ring structures. The gas oil fraction itself contains hydrogen donor diluent precursors which have the ability to readily take up hydrogen in the hydrocracking zone, and to release it in the thermal non-catalytic thermal HDDC zone 34. Hence, it is not necessary to add a hydrogen donor diluent from an extraneous source to the gas oil feed going to the hydrocracking zone 28. The catalyst may be any suitable hydrocracking catalyst, such as nickel sulfide on silica-alumina, a noble metal such as platinum or palladium on a molecular sieve base having uniform pore openings between about 6 and 15 angstrom units, noble metal on silica-alumina, and various catalysts comprising Group VI and VIII metals, oxides and sulfides on suitable supports such as silica-alumina, clays, etc.

3

Hydrogen is introduced into hydrocracking zone 28 through line 36 and is introduced in an amount between about 500 and 20,000 s.c.f./b. of gas oil feed introduced into the hydrocracking reactor 28. The hydrogen should be at least 70% by volume pure.

It is generally preferred to operate the hydrocracking reactor 28 in the range between about 20 and 70% conversion to 430° F. and lighter, but this is governed by the amount of gas oil feed available and the amount of hydrocrackate bottoms required for recycle. The hydrocrackate products are withdrawn from the hydrocracking zone 28 through line 37, are cooled and passed to a gas-liquid separator 38 to separate hydrogen-containing gas from liquid. The gas is passed overhead and recycled to the hydrocracking zone 28 through line 36. Preferably the gas is treated in a conventional manner (not shown) to concentrate the hydrogen in the gas to be recycled to at least 70% by volume of hydrogen, and also to remove any impurities such as sulfur or nitrogen compounds. Make-up hydrogen is introduced into line 36 as desired through line 42.

The separated liquid from separator 38 is passed through line 44 to product fractionator 46 wherein it is fractionated into several fractions including a light fraction boiling up to about 180° F. and including C₃ minus gas which passes overhead through line 48. This overhead fraction may be further treated to separate low boiling hydrocarbons, if desired. A light naphtha fraction boiling between about 180° F. and 375° F. may be withdrawn as a top side stream through line 52 and may be combined with the light naphtha fraction withdrawn from the crude tower 12 through line 16 to form a hydroforming feed.

Further down in second or product tower 46, a higher boiling narrow cut naphtha boiling between about 375° F. and 430° F. is withdrawn through line 54 as a side stream which may be withdrawn as such through 56 or passed through line 58 and combined with the side stream withdrawn through line 52.

The hydrocracking in the zone 28 is carried out under conditions and at a selected conversion to produce a hydrocrackate bottoms boiling above about 430° F. and having more than about 20 vol. percent of condensed ring naphthenes.

Hydrocracking conditions for accomplishing this purpose will depend upon the nature of the feed and the catalyst employed. In general, pressures greater than 800 p.s.i.g. and temperatures less than 800° F. are employed. As the naphthene content of the hydrocrackate bottoms varies with conversion, the feed rate is chosen to limit the conversion to less than 70% and preferably to less than 60% so that the volume percent of condensed ring naphthenes is more than about 20. The effect of conversion on condensed ring naphthene content is shown in the following Table I.

TABLE I

Feed boiling range, ° F.-----	430-650				430-850		
Hydrocracking conversion, vol. percent.-----	0 (Feed)	25	45	74	20	47	72
Hydrocracking conditions:							
Temperature, ° F.-----		575	710	713	766	775	775
Pressure, p.s.i.g.-----		1,500	1,500	1,510	1,500	1,500	1,500
Feed rate, v./v./hr.-----		3.0	4.0	2.7	0.54	0.5	0.4
Gas rate, s.c.f./b.-----		6,700	6,000	7,700	6,000	6,000	6,000
Vol. percent condensed ring naphthenes.-----	20	30	27	20	31	27	20

The above Table I shows that the conversion should be kept below 70% so as to maintain a desired amount of condensed ring naphthenes or partially hydrogenated condensed ring naphthenes.

The hydrocrackate bottoms are withdrawn through line 62, combined with the residual or crude oil bottoms in line 32 from crude tower 12, and the mixture passed

4

through line 64, heated and passed to the thermal non-catalytic conversion zone 34. A portion of the hydrocrackate bottoms may be withdrawn from the process through line 63, if desired or if necessary, to adjust the ratio of hydrocrackate bottoms to crude residual oil. The hydrocrackate bottoms have a boiling range above about 430° F. The hydrocrackate bottoms and crude residual oil are mixed in a weight ratio between about 0.3/1 to 4/1 of bottoms to residual oil.

In the thermal conversion zone 34, the temperature is maintained between about 700° F. and 1000° F. to crack higher boiling hydrocarbons in the crude residual oil to naphtha hydrocarbons, gas, and to upgrade the crude residual oil with the production of a small amount of coke. Also, hydrogen exchange occurs between the residual oil and the hydrocrackate bottoms by the release of hydrogen from the hydrogen donor diluent to produce from the residual oil lower boiling hydrocarbons including additional gas oil feed for the hydrocracking zone 28. The hydrocrackate bottoms act as a hydrogen donor and as a diluent and solvent to reduce the production of coke during the non-catalytic thermal conversion in zone 34.

Gases including C₃ minus hydrocarbons are withdrawn overhead through line 66 from zone 34, and if desired, the small amount of coke made may be withdrawn through bottom line 68. The normally liquid fraction boiling above about C₄ hydrocarbons is withdrawn through line 72 which discharges into feed line 10 to the crude fractionator 12. In the fractionator 12 the thermally converted products are fractionated into the separate fractions above described in connection with tower 12, and so additional naphtha and gas oil are produced for further processing as desired and essentially all of the crude oil is converted to naphtha, and gas, with only a small coke make.

Accumulation of ash in the crude residue bottoms in line 32 is minimized by withdrawal or purging at intervals from line 32 through withdrawal line 74. Instead of withdrawing coke through line 68, the small quantities of coke made may be removed with the liquid purge through line 74.

In a specific example for converting West Texas crude oil, about 10,000 barrels of whole petroleum crude oil feed per day plus 10,885 barrels per day of recycle from line 72 are passed through line 10 at a temperature of about 750° F. and introduced into crude tower 12 where the mixture is fractionated into gas, naphtha, gas oil, and crude oil bottoms. About 860 barrels (liquid) per day of butane and higher hydrocarbons boiling up to about 180° F. pass overhead through line 14. About 2900 barrels per day of naphtha boiling between about 180° F. and 430° F. are withdrawn as a side stream through line 16. This naphtha is preferably hydroformed to produce high octane gasoline. About 12,050 barrels per day of gas oil boiling between about 430° F. and 1000° F.

are withdrawn through line 26 as a side stream as feed to the hydrocracking zone 28. About 5075 barrels per day of crude residue and recycle are withdrawn from the bottom of crude tower 12 through line 32.

In the hydrocracking zone 28 the temperature is maintained at about 650° F. and the pressure at about 1500 p.s.i.g. About 8000 s.c.f./b. of feed of hydrogen-contain-

ing gas are introduced into hydrocracking zone 28. The catalyst is a hydrocracking catalyst containing about 0.5% palladium on a zeolitic molecular sieve base having pore openings of uniform size between about 6 and 15 angstrom units as described in Gladrow et al. Patent No. 2,971,904, granted Feb. 14, 1961. The conversion to 430° F. minus is about 58%.

About 13,275 barrels per day of hydrocrackate product leave hydrocracking zone 28 (after hydrogen removal in separator 38) and pass through line 44 into product fractionator 46 where the hydrocrackate products are fractionated into C₃ minus hydrocarbon gas, hydrocrackate naphtha and hydrocrackate bottoms. About 730,000 cubic feet per day of C₃ minus hydrocarbons are taken overhead through line 48. About 8200 barrels per day of hydrocrackate naphtha consisting of butane and liquid hydrocarbons, boiling up to 430° F., are withdrawn through line 52 as a side stream and none withdrawn through line 54. This stream may be further fractionated into components that may be blended directly into motor gasoline. The heavier portion, i.e., 200–375° F. boiling material, is preferably hydroformed.

Hydrocrackate bottoms in the amount of about 5,075 barrels per day are withdrawn through line 62. These bottoms have a boiling point range of between about 430° F. and 1000 F. and contain about 25% by volume of aromatic hydrocarbons, about 35% by volume by naphthenes, and about 40% by volume of acyclic paraffins. These hydrocrackate bottoms are mixed with the crude residual and recycle from line 32, and the mixture passed through thermal non-catalytic conversion zone 34 where it is maintained at a temperature of about 770° F. and a pressure of about 400 p.s.i.g. The v./v./hr. flow rate of oil feed is about 1, consequently the time of heating is one hour in zone 34.

The converted products leaving the conversion zone 34 comprise about 670,000 cubic feet per day of C₃ minus gas, about 25 tons per day of coke (or 1.5 weight percent on crude feed), and about 10,885 barrels per day of converted hydrocarbons containing mostly naphtha and gas oil with some components boiling above about 1000° F. which are recycled to thermal conversion zone 34.

From the actual numbers given it will be seen that more volumes of liquid hydrocarbons leave zone 34 through line 72 than enter zone 34 through 64. The gas oil hydrocrackate feed is substantially free of ash and therefore hydrocracking catalyst in hydrocracking zone 28 is not deactivated by ash components.

Based on 10,000 barrels per day of whole West Texas crude, the yields from the present process are as follows:

Virgin and thermal naphtha	b./d.	3,760
Hydrocrackate naphtha	b./d.	8,200
Total naphtha	b./d.	11,960
C ₃ minus gas	s.c.f./d.	1,300,000
Coke	tons	25

Data are also included showing the hydrocracking conversion of virgin gas oil from South Louisiana crude oil with 0.5% palladium on a zeolitic molecular sieve having uniform pore sizes between 6 and 15 angstrom units. The pressure was about 1000 p.s.i.g.

Temperature, ° F.	567	633	665
Feed rate, v./v./hr.	1.0	1.96	1.99
Hydrogen rate, s.c.f./b.	13,413	9,473	9,384
Produced yields:			
C ₃ minus, wt. percent on feed	1.4	1.8	1.8
C ₄ -430, vol. percent on feed	53.4	75.7	85.0
430+ bottoms	55.4	38.2	27.2
Vol. percent conversion to 430° F. minus	45.5	62.1	72.6

These data show good conversion and also show that a variation in conversion can be achieved by adjusting the operating conditions (temperature, feed rate, etc.). It is generally preferred to operate the process in the range of 40–60% conversion to 430° F. minus, but this

is governed by the amount of gas oil feed available and the amount of hydrocrackate bottoms required for recycle.

Additional data are included to show results obtained in treating an mixture of a vacuum residuum having a gravity of 7° API and boiling above about 1000° F., and a hydrocrackate bottoms having an API gravity of 35° and obtained from hydrocracking a South Louisiana virgin gas oil boiling between about 430° F. and 850° F. The mixture was in a 50/50 volume ratio. The mixture was heated for about 1 hour in a stirred autoclave at 755° F. and at autogenic pressure.

Product yields are as follows:

Yields on charge	Wt. percent	Vol. percent
C ₃ minus gas	1.5	
C ₄ -430° F. naphtha	11.1	14.4
430–850° F. gas oil	56.6	
850–1,000° F. gas oil	10.7	74.3
1,000° F. plus residuum	18.5	18.5
Coke	1.6	
Conv. of 1,000° F. + residuum to 1,000° F.	65	

The feed for the above data consisted of a 1/1 volume ratio, thus the coke make shown amounts to 2.9 wt. percent of the residuum portion of the feed. This is considerably lower than the 7% obtained by thermally converting the residuum to the same extent in the absence of the hydrocrackate bottoms as diluent and hydrogen donor.

The conversion of residuum may vary between about 40 and 80%.

In the example of the large unit of 10,000 barrels of fresh crude feed per day, the conversion of residuum to material boiling below 1000° F. in the thermal conversion zone 34 is maintained to give 65% conversion of 1000° F. + residuum and this requires a 58% conversion of 430° F. + to 430° F. in the hydrocracking zone 28 to maintain a 1 to 1 ratio of hydrocrackate bottoms to residual feed for the thermal zone 34. The quantities of the various products vary with the different feeds. The hydrocracking zone 82 may be operated at a lower conversion by withdrawing some of the hydrocrackate bottoms for specialty uses such as diesel and jet fuel or heating oil. Also, the hydrocrackate bottoms-residuum ratio can be increased so as to further reduce the coke made in the thermal conversion zone 34.

By integration of the hydrocracking of distillate and the thermal hydrogen transfer conversion of the residual to distillate, essentially all of the whose crude petroleum oil can be converted to naphtha.

Catalyst contamination is avoided by employing a non-catalytic conversion of the residuum to distillate of low ash content. Carrying out this conversion in the presence of the hydrocrackate bottoms as a hydrogen donor allows high conversion of the residuum with only a slight coke make.

The integration of the thermal conversion and the hydrocracking step provides utilization of the available hydrogen in the donor diluent which would be a debit to the hydrocracking step alone.

The quantity of ash material in line 32 is maintained within bounds by purging through line 74 as needed or by withdrawing a portion of the stream through line 74 or line 68 from thermal conversion zone 34, filtering or centrifuging or the like to remove solids containing vanadium and nickel compounds, etc., and returning the oil filtrate to the thermal conversion zone 34 or to tower 12. The amount of ash filtered or centrifuged may be kept at a minimum by providing a settling zone ahead of the filter to settle out most of the solids from the oil. The efficiency of the settler may be enhanced by incorporating the hydrogen donor diluent with the material purged or removed through line 74 or line 68. The recovered solids

may be reworked to recover various metals such as vanadium, nickel etc.

What is claimed is:

1. A method of treating whole petroleum crude oils to recover lower boiling hydrocarbons which comprises fractionating a whole petroleum crude oil into a gas oil fraction and a bottoms residue, catalytically hydrocracking the gas oil fraction to produce lower boiling hydrocarbons and higher boiling hydrogenated donor diluents, fractionating the hydrocrackate product into naphtha and hydrocrackate bottoms containing hydrogenated donor diluents, mixing the hydrocrackate bottoms with the bottoms residue and maintaining the mixture under superatmospheric pressure at an elevated temperature in a thermal non-catalytic HDDC conversion zone to effect hydrogen transfer and upgrading of said bottoms residue to naphtha and gas oil and fractionating the products from said thermal conversion zone to recover additional gas oil distillate and naphtha.

2. A method of treating whole petroleum crude oil which comprises fractionating a whole crude oil combined with thermally converted products as hereinafter produced into a gas oil fraction containing virgin and treated components and a bottoms crude residue, catalytically hydrocracking said gas oil fraction at a temperature between about 550° F. and 850° F. in the range of below about 70% conversion to 430° F. minus to produce hydrocrackate bottoms having more than about 20 volume percent of condensed ring naphthenes, separating naphtha and hydrocrackate bottoms from the hydrocrackate product, mixing at least part of the hydrocrackate bottoms with the bottoms crude residue and subjecting the mixture to an elevated temperature in a thermal non-catalytic HDDC conversion zone to effect conversion of about 40 to 80% of the bottoms crude residue to naphtha and gas oil, recycling the products from said thermal conversion zone to said whole crude fractionation step as the thermally converted products above referred to and recovering additional gas oil feed for said hydrocracking step.

3. A method of treating whole petroleum crude oils to recover lower boiling hydrocarbons which comprises fractionating a whole petroleum crude oil into a gas oil fraction containing condensed ring aromatics and a bottoms residue, catalytically hydrocracking the gas oil fraction to produce lower boiling hydrocarbons and to partially hydrogenate the condensed ring aromatics to hydrogen donor diluents, fractionating the hydrocrackate product into naphtha and hydrocrackate bottoms containing the hydrogen donor diluents, mixing the hydrocrackate bottoms with the bottoms residue and maintaining the mixture under superatmospheric pressure at an elevated temperature in a thermal non-catalytic HDDC conversion zone to effect hydrogen transfer and upgrading of bottoms residue to naphtha and gas oil and recycling the products from said thermal conversion zone to said whole crude oil fractionation step to recover additional naphtha and gas oil feed.

4. A method of treating whole petroleum crude oil which comprises fractionating a whole crude oil combined with thermally converted products as hereinafter produced into a gas oil fraction containing virgin and treated components and a bottoms crude residue, catalytically

hydrocracking said gas oil fraction at a temperature between about 550° F. and 850° F. in the range of below about 60% conversion to 430° F. minus to produce lower boiling hydrocarbons and hydrogen donor diluent compounds boiling above about 430° F., separating naphtha and hydrocrackate bottoms boiling above about 430° F. and containing hydrogen donor diluent compounds from the hydrocrackate product, mixing at least part of the hydrocrackate bottoms with the bottoms crude residue and subjecting the mixture to an elevated temperature in a thermal non-catalytic HDDC conversion zone to effect conversion of the bottoms crude residue to naphtha and gas oil, recycling the products from said thermal conversion zone to said whole crude fractionation step as the thermally converted products above referred to and recovering additional gas oil feed for said hydrocracking step.

5. A method according to claim 3 wherein the weight ratio of hydrocrackate bottoms to the bottoms residue is between about 0.3/1 to 4/1.

6. A method according to claim 4 wherein a portion of the converted liquid products from the thermal conversion zone is treated to remove ash solids from liquid products and the liquid products are recycled to the process.

7. A method according to claim 6 wherein the recovered liquid products are recycled to the thermal conversion zone.

8. A method according to claim 1 wherein said whole crude oil contains condensed ring aromatic hydrocarbons, the gas oil fractionated therefrom and fed to said hydrocracking step contains condensed ring aromatic hydrocarbons and the hydrocrackate bottoms contain at least 20 volume percent condensed ring naphthene hydrocarbons.

9. A method according to claim 2 wherein said whole crude oil contains condensed ring aromatic hydrocarbons, the gas oil fractionated therefrom and fed to said hydrocracking step contains condensed ring aromatic hydrocarbons and the hydrocrackate bottoms contain at least 20 volume percent condensed ring naphthene hydrocarbons.

10. A method according to claim 6 wherein the removal of ash solids is accomplished by filtering.

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