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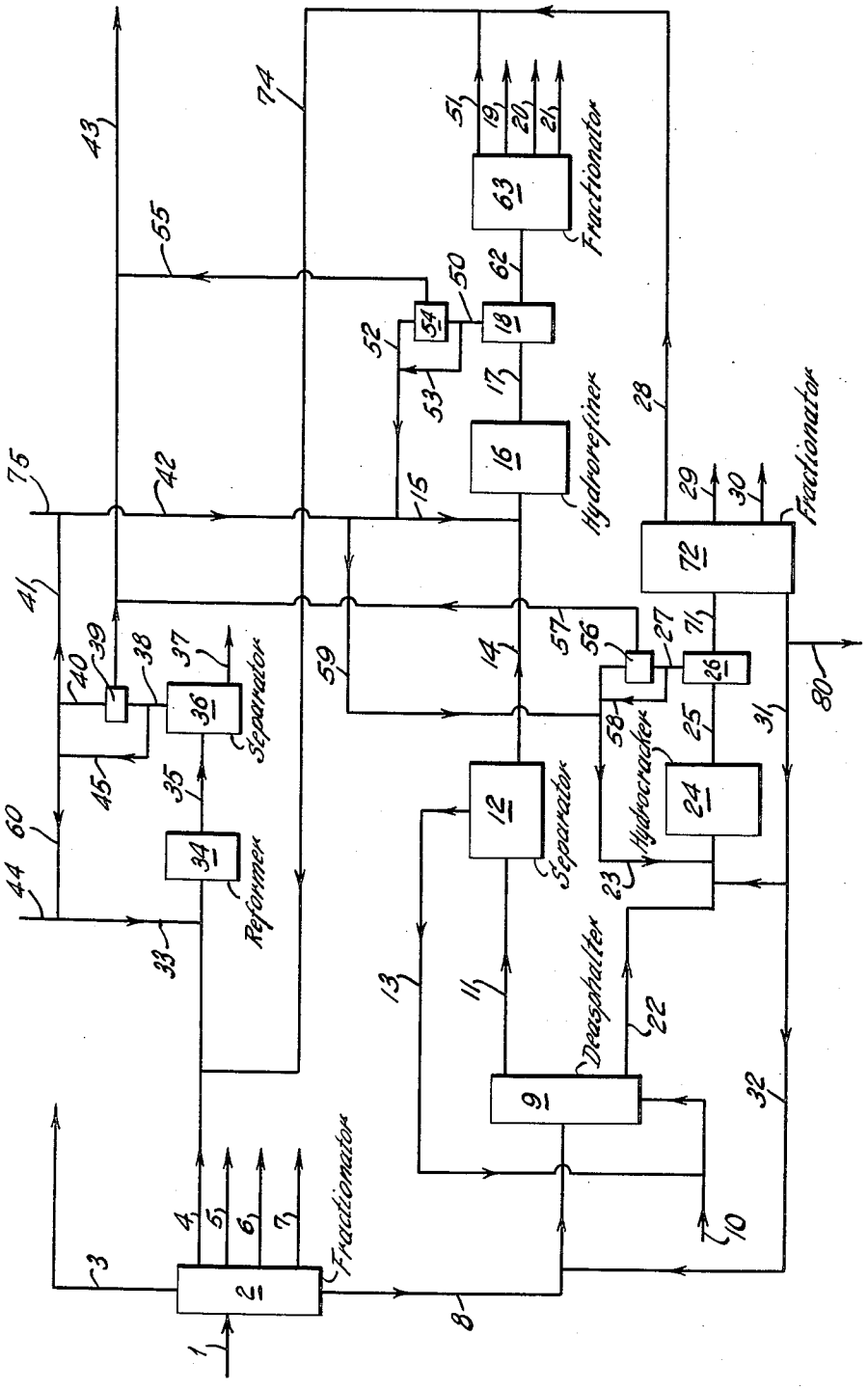

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TREATMENT OF DEASPHALTED OIL AND ASPHALT TO MAKE REFORMED GASOLINE

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This invention relates to the treatment of hydrocarbons. More particularly, it is concerned with the recovery of valuable products from an asphaltic petroleum residuum.

In the refining of petroleum, the crude oil is separated by fractional distillation into various fractions such as gasoline, naphtha, kerosine, fuel oil and lubricating oil fractions. When no further material can be distilled off under vacuum at a temperature below that at which cracking occurs, the remaining material, a pitch-like composition is termed the residuum. This residuum is a complicated mixture composed mainly of a great variety of paraffins and polynuclear aromatics and polynuclear naphthenes, some of these latter cyclic compounds having side chains of varying length.

The residuum is then further treated in a deasphalting step by the use of a solvent and from this procedure there are recovered a heavy product referred to as DA asphalt and a lighter product referred to as DA oil. The DA asphalt is a heavy residue and is customarily used in low value products such as road surfacing compositions and the like. The DA oil is generally used as a feed component to a catalytic cracking operation.

It is an object of this invention to provide a process for the conversion of low value residual products to high value products such as gasoline and lubricating oils.

Another object of the invention is to provide an integrated process for the production of gasoline and lubricating oils.

Various other objects will be obvious to those skilled in the art from the following disclosure.

In one specific embodiment of the invention a DA asphalt is subjected to hydrocracking conditions in the presence of a nickel tungsten sulfide catalyst to yield a product which can be fractionated into naphtha, kerosine, diesel distillate and heavy oil.

In another specific embodiment of the invention a residuum is subjected to a deasphalting, the DA oil is hydrorefined, the product is fractionated into at least a naphtha fraction and a lube oil fraction, the DA asphalt is hydrocracked in the presence of a nickel tungsten sulfide catalyst, the product is fractionated into naphtha, kerosine and diesel fuel fractions, the naphtha fractions are combined and subjected to reforming conditions in the presence of a reforming catalyst and the by-product hydrogen from the reforming process is returned to the hydrorefining and hydrocracking operations.

The invention will be further illustrated and explained in connection with the following description of the flow diagram shown in the accompanying drawing.

Crude oil is passed through line 1 into fractionator 2 wherein it is subjected to fractional distillation. Gas and light naphtha having an end boiling point of about 150° F. are removed through line 3. Straight run naphtha having a boiling range between about 150 and 400° F. is withdrawn through line 4. Light and heavy fuel oils are withdrawn through lines 5 and 6 respectively

and a lubricating oil fraction is withdrawn through line 7. The remaining heavy residuum is passed through line 8 to deasphalter 9.

In deasphalter 9 the residuum is contacted with a solvent introduced through line 10. The solvent is a lower hydrocarbon such as propane or butane or mixtures of low hydrocarbons such as ethane-propane or propane-butane mixtures. The oil in the residue is dissolved in the solvent and removed through line 11 to separator 12. In separator 12, the solvent is flashed off and the oil is withdrawn through line 14. The separated solvent is recycled through lines 13 and 10 to deasphalter 9.

From separator 12 the DA oil passes through line 14 and, with hydrogen from line 15, is introduced into hydrorefiner 16 which contains a hydrogenation catalyst. The temperature in hydrorefiner 16 is maintained between about 600 and 800° F. and the pressure between about 750 and 4000 p.s.i.g. The liquid hourly space velocity, that is liquid volumes of DA oil per hour per volume of catalyst may range from 0.1 to 1 v./v./hr. and hydrogen from line 15 is introduced at the rate of about 500 to 10,000 cubic feet per barrel of oil. The hydrorefining product is removed through line 17 to high pressure separator 18 from which a gas and light hydrocarbon fraction is removed through line 50. The balance of the hydrorefining product is passed through line 62 to fractionation tower 63 where it is separated into a naphtha fraction removed through line 51, a kerosine fraction removed through line 19, a diesel fraction removed through line 20 and a lube oil fraction removed through line 21. The gas and light hydrocarbon fraction may be recycled directly through by-pass 53 and lines 52, 15 and 14 to hydrorefiner 16 or may be separated into a hydrogen-rich gas and a light hydrocarbon fraction in separator 54. In the latter case, the light ends are removed through line 55 and the hydrogen-rich gas is recycled through lines 52, 15 and 14.

The DA asphalt is removed from deasphalter 9 through line 22 and, with hydrogen from line 23, is introduced into hydrocracking unit 24 wherein it is contacted with a nickel tungsten sulfide catalyst. The temperature in hydrocracking unit 24 is maintained at about 800 to 1000° F. and the pressure between 4000 and 6000 p.s.i.g. although higher pressures may be used. Hydrogen is introduced through line 23 at a rate of 8,000 to 50,000 cubic feet per barrel of DA asphalt and the liquid hourly space velocity of the DA asphalt is maintained at between 0.1 and 1.0 volume of asphalt per hour per volume of catalyst. The hydrocracked product is withdrawn from hydrocracking unit 24 through line 25 to high pressure separator 26 in which a gas and light hydrocarbon fraction is separated and withdrawn through line 27. The balance of the hydrocracked product passes through line 71 to fractionator 72 where it is separated into a naphtha fraction withdrawn through line 28, a kerosine fraction withdrawn through line 29 and a diesel fraction withdrawn through line 30. The gas and light hydrocarbon fraction which contains substantial amounts of hydrogen may be recycled from line 27 to hydrocracker 24 through by-pass 58 and lines 23 and 22 or may be separated into a hydrogen rich gas and a light hydrocarbon fraction in separator 56, the hydrogen rich gas being recycled through lines 23 and 22 and the light hydrocarbons being withdrawn through line 57. The heavy residual oil is withdrawn through line 31 and combined with the DA asphalt in line 22 and recycled through hydrocracking unit 24. Optionally, the heavy residual oil may be returned through line 32 and introduced with the residue from fractionator 2 into deasphalter 9, or may be withdrawn from the system through line 80.

The naphtha from lines 28 and 51 are combined in line 74 and together with the naphtha from line 4 and hydrogen from line 33 are introduced into reforming unit 34. In reforming unit 34 the naphtha is contacted with a reforming catalyst at a temperature between 850 and 1000° F. and a pressure between 200 and 1000 p.s.i.g. in the presence of hydrogen. The reformed products are withdrawn through line 35 and introduced into separator 36. Reformed gasoline is withdrawn through line 37. The light gaseous hydrocarbons and by-product hydrogen are introduced into separator 39 through line 38. From separator 39 the light hydrocarbon gases are removed through line 43 and a hydrogen rich gas is removed through line 40. A portion of this gas is recycled to reforming unit 34 through lines 60 and 33. Another portion of the gas is passed through line 42 and part of this portion is introduced into hydrorefining unit 16 through line 15 and part into hydrocracking unit 24 through lines 59 and 23. Makeup hydrogen if necessary is introduced into the system through line 44 or line 75. Optionally, the gases leaving separator 36 through line 38 may by-pass separator 39 through line 45. The gas and light naphtha obtained from line 3 and the light hydrocarbons from line 43 may be utilized as a source of the solvent used in the deasphalting step.

The location of various devices such as pumps, valves, etc. will be obvious to those skilled in the art and have been omitted from the drawing.

The deasphalting of the residuum is accomplished preferably by a continuous mode of operation, in which the residuum is introduced into a tower at approximately the mid point. Solvent such as propane, butane, isobutane or mixtures thereof is introduced near the bottom of the tower, the ratio of solvent to residuum being about 4 to 1. The solvent, flowing upwardly, countercurrently contacts the residuum as it descends through the tower and abstracts the oil therefrom. The oil-in-solvent phase is removed from the top of the tower and is passed to a separator where the solvent is flashed off and returned to the tower. The asphalt, substantially free of oil, is removed from the bottom of the tower.

In the reforming operation the naphtha and hydrogen are contacted with a reforming catalyst at a temperature between about 850 and 1000° F. and a pressure between 200 and 1000 p.s.i.g. The reforming catalyst may be of the platinum on alumina type and may also contain a combined halogen. Temperatures of 875 to 950° F. and pressures of 250 to 600 p.s.i.g. are preferred. Space velocities of 1.5–5.0 v./v./hr. are satisfactory and hydrogen is recycled at a rate between about 5 and 10 mols of hydrogen per mol of naphtha. If the reforming catalyst is of the non-regenerative type, it is advisable to pretreat the feed for the removal of catalyst poisons such as sulfur, nitrogen and the like.

The hydrorefining of the DA oil is conducted at temperatures between 600 and 800° F. although a range of 650 to 750° F. is preferred. Pressures of 700 p.s.i.g. and higher may be used. Satisfactory results are obtained at a pressure between about 750 and 1500 p.s.i.g. Hydrogen is fed at a rate between about 5000–10,000 cubic feet per barrel of oil and the space velocity of the oil is preferably maintained between 0.4 and 0.5 v./v./hr.

The catalyst used in the hydrorefining of the DA oil is preferably a nickel tungsten sulfide catalyst. Various mixtures of nickel sulfide and tungsten sulfide may be used. For example, the catalyst may contain from 5 to 95 mols of nickel sulfide and 95 to 5 mols of tungsten sulfide. Satisfactory results have been obtained using a catalyst containing one mol of nickel sulfide per 0.75 mol of tungsten sulfide. The catalyst may be supported on an inert base.

The hydrocracking conditions of the DA asphalt are somewhat more severe than the conditions to which the DA oil is subjected. Temperature ranges between 800 and 1000° F. may be used although a temperature of 850 to 900° F. is preferred. Pressures ranging from 4,000 to 10,000 lbs. p.s.i.g. or higher may be used. However, it is preferred to operate at a pressure in excess of about 5000 p.s.i.g. The catalyst used in the hydrocracking operation is a nickel tungsten sulfide catalyst. In both the hydrorefining and hydrocracking operations space velocities ranging from 0.1 to 1.0 v./v./hr. may be used. A preferred range is 0.4 to 0.5 v./v./hr.

Before starting the hydrocracking or hydrorefining operation, the unit containing the catalyst is flushed with hydrogen and then enough hydrogen is added to bring the unit approximately to operating pressure when the temperature reaches the operating level. This gives a hydrogen treatment to the catalyst during the heating up period. This treatment is further continued at the operating temperature until no further catalyst reduction is evident. The reactor is then ready to be placed on stream.

The following example is given to illustrate the invention.

EXAMPLE

A West Texas-New Mexico crude was subjected to fractional distillation. When no further material could be carried overhead under vacuum below cracking temperatures the remaining residuum was removed. It amounted to 14.67% by volume of the original charge. The residuum was then subjected to a propane deasphalting step. The results of the deasphalting are set forth below.

Table I

	DA Oil	DA Asphalt
Yield, volume percent	54.3	45.7
Kin. Vis.:		
At 150° F	243.0	----------
At 210° F	53.1	----------
Viscosity Index	76	----------
Carbon Residue, Weight percent	2.84	34
Sulfur, Weight percent	1.79	4.38–4.61
Melting Point, ° F	----------	189

The DA oil recovered from the deasphalting operation was hydrorefined in the presence of a nickel tungsten sulfide catalyst at 700° F. and 1500 lbs. pressure, a space velocity of 0.43 v./v./hr. and a hydrogen recycle rate of 6400 s.c.f. per barrel of oil. A weight percent yield of liquid products of 97.0 was obtained over a 38 hour run. Hydrogen consumption was 703 cubic feet per barrel of oil. The liquid product was fractionated to yield 1.8 volume percent naphtha, 6.7 volume percent kerosine, 4.2 volume percent diesel distillate and 87.3 volume percent oil. The oil had the following characteristics.

Table II

Kin. vis.:	
At 150° F	40
At 210° F	14.5
Vis. SUS at 210° F	75.8
Viscosity index	112
Carbon residue, percent	0.36
Sulfur, percent	0.22

The DA asphalt obtained from the propane deasphalting operation was hydrocracked over a nickel tungsten sulfide catalyst at 850° F., 5000 p.s.i.g., a liquid hourly space velocity of 0.4 and a hydrogen recycle rate of 43,000 s.c.f. per barrel. Hydrogen consumption amounted to 2993 cubic feet per barrel of asphalt. The volume percent yield of the liquid product was 112.8. The liquid product was fractionated to yield 41.7 volume percent naphtha, 32.8 volume percent kerosine, 9.1 volume percent diesel distillate and 16.4% residual oil. A hydrocarbon type analysis of the naphtha indicated that it contained 8% aromatics, 55% naphthenes

and 37% paraffins. The kerosine and diesel distillate had diesel indices of 74.3 and 69.4, respectively.

The naphtha obtained from the product of the DA asphalt hydrocracking, because of its high naphthene content, is a suitable reforming charge stock and is combined with the naphthas obtained from the fractional distillation of the crude and the hydrorefined DA oil. Hydrogen is added to the mixture which is then contacted with a platinum-alumina reforming catalyst at a temperature of 950° F. a pressure of about 500 p.s.i.g. a space velocity of 3.0 v./v./hr. and a hydrogen recycle rate of 6000 s.c.f. per barrel. The effluent is passed to a separator where the hydrogen containing gas is removed from the liquid products. The liquid products are then fractionated and a fraction boiling from 140° F. to 400° F. and having an ASTM research octane number clear of 90, leaded 98.2 is obtained in 87.2% yield. The net hydrogen production from the reforming operation is 750 cubic feet per barrel. The hydrogen containing gas may then be treated to remove the hydrocarbon gases and thus provide a gas rich in hydrogen. A portion of the hydrogen rich gas is then recycled to the reformer and the other portion is split, part being returned to the hydrorefining step and another part being returned to the hydrocracking step.

The foregoing example is for illustrative purposes only. Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for upgrading a residuum obtained from the fractional distillation of a crude petroleum oil which comprises separating said residuum into an oil portion and an asphaltic portion, contacting the asphaltic portion with a nickel tungsten sulfide catalyst at a temperature between about 800 and 1000° F., a pressure between about 5000 and 10,000 p.s.i.g. and a hydrogen feed rate within the range of from about 8000 to 50,000 cubic feet per barrel of said asphaltic portion, recovering at least a naphtha fraction from the hydrogenated asphaltic fraction, and contacting the oil portion with a nickel tungsten sulfide catalyst at a temperature between 600° and 800° F., a pressure between 750 and 4000 p.s.i.g. and a hydrogen feed rate between about 5000 and 10,000 cubic feet per barrel of oil, recovering at least a naphtha fraction from the hydrogenated oil portion, combining said recovered naphtha fractions and reforming the combined fractions to produce a reformed gasoline.

2. The process of claim 1 in which hydrogenation of the asphaltic portion is carried out at a liquid hourly space velocity between 0.4 to 0.5 volume of liquid per hour per volume of catalyst.

3. Process as claimed in claim 1 wherein the asphaltic residuum is hydrogenated at a temperature of about 850° F., a pressure of about 5000 p.s.i.g., a liquid space velocity of about 0.4 and a hydrogen feed rate of about 43,000 standard cubic feet per barrel of said residuum.

4. A process for upgrading a residuum obtained from the fractional distillation of a crude petroleum oil which comprises separating said residuum into an oil portion and an asphaltic portion, contacting the oil portion with a nickel tungsten sulfide catalyst at a temperature between about 650 and 750° F., a pressure between 750 and 4000 p.s.i.g., a space velocity between 0.4 and 0.5 v./v./hr. and a hydrogen feed rate between 5000 and 10,000 cubic feet per barrel of oil, recovering a naphtha fraction from the hydrogenated oil portion, contacting the asphaltic portion with a nickel tungsten sulfide catalyst at a temperature between about 850 and 900° F., a pressure between 5000 and 8000 p.s.i.g., a space velocity between 0.4 and 0.5 v./v./hr. and a hydrogen feed rate between 8000 and 50,000 cubic feet per barrel of said asphaltic portion, recovering a naphtha fraction from the hydrogenated asphalt fraction, combining the rceovered naphtha fractions; and subjecting the combined fractions to reforming under conditions to produce a reformed gasoline.

5. A process for the refining of a crude petroleum oil which comprises fractionating said oil into various fractions including a naphtha fraction, a fuel oil fraction and a lube oil fraction to leave a pitch-like residue, separating said residue into an oil portion and an asphaltic portion, hydrofining said oil portion by subjecting said oil portion to the action of a nickel tungsten sulfide catalyst at a temperature between about 600 and 800° F., a pressure between about 700 and 1500 p.s.i.g., and a hydrogen feed rate between about 5000 and 10,000 cubic feet per barrel of oil, hydrocracking said asphaltic portion by contacting said asphaltic portion with a nickel tungsten sulfide catalyst at a temperature between about 800 and 1000° F., a pressure between about 5000 and 10,000 p.s.i.g., and a hydrogen feed rate within the range of from about 8000 to 50,000 cubic feet per barrel of said asphaltic portion, recovering at least a naphtha fraction from the so-treated asphaltic portion; combining the naphtha fractions, reforming the combined naphtha fractions to produce a reformed gasoline, separating hydrogen from the products of reforming step, returning a portion of the separated hydrogen to the hydrocracking step, and returning another portion of the separated hydrogen to the hydrorefining step.

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