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PETROLEUM REFINING PROCESS

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This invention relates to the treatment of crude oils for the production of motor fuels or motor fuel components therefrom. More particularly, this invention relates to the treatment of a petroleum crude oil, particularly a heavy asphaltic fraction therefrom such as an asphaltic short residuum, by a combination of operations wherein there is produced a feed stock particularly suitable for use in a catalytic cracking operation for the production of gasoline, motor fuels and the like. In accordance with one embodiment this invention relates to a petroleum refining process or petroleum refinery operation wherein crude oil or a heavy residual fraction thereof is supplied as feed thereto and wherein after suitable treatment in accordance with the teachings of this invention there is produced a treated finished naphtha fraction particularly suitable as a motor fuel for an internal combustion engine or a fuel component thereof. In accordance with yet another embodiment of the practice of this invention there is disclosed herein a petroleum treating process suitable for the treatment of heavy asphaltic petroleum fractions, particularly asphaltic fractions which contain a substantial amount of metal-containing contaminants therein, such as nickel-containing, iron-containing and vanadium-containing contaminants, for the removal of these metal-containing contaminants therefrom and the production of a feed stock for a catalytic cracking operation.

It is an object of this invention to provide an improved process for the treatment of a petroleum crude oil.

It is another object of this invention to provide a process for the treatment of a residual asphaltic petroleum fraction by a combination of operations for the production of a deasphalted oil fraction particularly suitable as a catalytic cracking feed stock.

Still another object of this invention is to provide a process for the treatment of a residual asphaltic hydrocarbon oil wherein there is recovered a deasphalted oil fraction having a relatively reduced metals content and which is particularly suitable for use as a catalytic cracking charge stock.

Finally, still another object of this invention is to provide a petroleum refining process wherein there is produced a relatively high quality motor fuel.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure and drawing wherein there is schematically illustrated one embodiment of the practice of this invention.

Referring now in detail to the drawing a crude oil, such as an asphaltic California crude, is introduced via line **11** into crude still or fractionator **12** wherein the crude oil is fractionated into its various components, such as a gaseous fraction recovered overhead from fractionator **12** via line **14**, a naphtha fraction such as a straight run naphtha fraction recovered via line **15**, a kerosene, diesel oil and/or jet fuel fraction recovered via line **16**, a lube oil and/or gas oil fraction recovered via line **18** and a residual (long residuum) or bottoms fraction recovered via line **19**. As indicated in the drawing, there may be separated from the straight run naphtha fraction (by means not shown) via line **20** a heavy straight run naphtha, such as a naphtha fraction having a boiling range in the range 225°–450° F. Similarly, a gas oil fraction may be recovered from fractionator **12** via lines **18** and **21**.

The long residuum recovered as a bottoms fraction from fractionator **12** via line **19**, such as a residuum having an initial boiling point greater than about 550° F., usually having an initial boiling point greater than about 650° F. or a boiling point higher than about 800° F. and amounting to about 10–60% by volume of the original crude, is supplied via line **19** to vacuum pipe still and fractionator **22**. Vacuum pipe still and fractionator **22** serves as a combination vis-breaker and fractionator and is operated under reduced pressure to effect a fractionation of the relatively high boiling, high molecular weight components of the long residuum introduced thereinto via line **19**. Under the high temperature operating conditions employed unit **22** also serves as a viscosity reducing zone. Within vacuum pipe still and fractionator **22** the long residuum introduced thereinto is subjected to elevated conditions of temperature and pressure and other throughput conditions so as to mildly lower the viscosity of the long residuum charged thereto. Vis-breaking conditions at a temperature in the range 800–1000° F. and under suitable pressure, in the range 50–500° p.s.i.g., are usually sufficient to effect mild vis-breaking of the long residuum.

Vis-breaking of the long residuum serves to reform or otherwise alter the high molecular weight of high boiling constituents of the reduced crude into relatively low molecular weight or low boiling constituents. The vis-breaking operation tends to produce lower boiling, more aromatic constituents which are generally more refractory in the subsequent catalytic cracking operation than low boiling, more paraffinic hydrocarbons which are also produced. The vis-breaking operation complements and otherwise cooperates with a subsequent combination of fractionation, deasphalting, catalytic cracking, catalytic reforming and solvent extraction operations in accordance with this invention and described hereinafter for the production of a superior motor fuel or motor fuel component. The vis-breaking operation increases the yield of naphtha recoverable from the reduced crude or long residuum in that the relatively more aromatic hydrocarbons produced during the vis-breaking operation are separated in the subsequent combination of fractionation and deasphalting hydrogenation operations with the resultant production of a more paraffinic catalytic cracking stock particularly suitable for the production of a catalytic cracked naphtha.

The mildly vis-broken reduced crude is fractionated within vacuum pipe still and fractionator **22** into an overhead distillate naphtha fraction recovered via line **24**, a vacuum gas oil fraction recovered therefrom via line **25** and a bottoms asphaltic fraction or short residuum recovered therefrom via line **26**.

The short residuum recovered from vacuum pipe still and fractionator **22** via line **26** usually has a gravity in the range 3–12° API and a Conradson carbon residue in the range 10–40%, more or less. As disclosed herein and in accordance with this invention the short residuum

in line 26 is subjected to solvent deasphalting upon introduction into solvent deasphalting zone 28. The solvent deasphalting operation may be a batch operation, a multiple vessel operation or a substantially continuous liquid-liquid countercurrent treating operation wherein the short residuum to be deasphalted is introduced into the top of a deasphalting tower and flowed therein in liquid-liquid direct countercurrent contact with a suitable liquid deasphalting solvent, such as a liquefied normally gaseous hydrocarbon, e.g., propane, n-butane, isobutane or mixtures thereof.

A suitable deasphalting solvent in accordance with the practice of this invention is a liquefied normally gaseous hydrocarbon, such as ethane, ethylene, propane, propylene, n-butane, isobutane, n-butylene, isobutylene, pentane, isopentane and mixtures thereof, either alone or in the presence of a minor amount of additive materials effective to improve the deasphalting operation or otherwise to increase the yield and quality of the deasphalted oil and the recovered asphalt. The deasphalting operation is carried out at any suitable combination of deasphalting temperature and pressure, the temperature and pressure being adjusted so as to maintain the deasphalting solvent in the liquid phase during the deasphalting operation. A deasphalting temperature in the range 150–325° F., usually not more than 50 degrees Fahrenheit lower than the critical temperature of the deasphalting solvent and a pressure in the range 300–800 p.s.i.g. usually are suitably employed depending upon the composition of the deasphalting solvent and, to a minor extent, depending upon the composition of the short residuum undergoing solvent deasphalting. Generally a deasphalting solvent to short residuum volume ratio in the range 2–12 is employed within solvent deasphalter 28. Solvent deasphalter or the solvent deasphalting zone 28 may be operated isothermally or under a temperature gradient, e.g., top tower temperature greater than the bottom tower temperature by more than about 40 degrees Fahrenheit. Also deasphalter 28 may be operated so that the vacuum bottoms fraction or short residuum is introduced into the actual deasphalting zone at a number of points along the treating section thereof and/or the deasphalting solvent similarly introduced into the deasphalting treating section.

Following the deasphalting operation there is recovered from solvent deasphalter 28 a solvent deasphalted oil via line 29 and an asphalt fraction via line 30. The asphalt fraction may be withdrawn at this point as asphalt product or after dilution with a suitable cutter stock, such as a heavy catalytic cycle gas oil introduced via line 31 into contact with the asphalt in line 32, to form a blend which is separately recovered as a heavy fuel oil. The solvent deasphalted oil recovered from solvent deasphalting zone 28 via line 29 may have a gravity in the range 10–25° API and a Conradson carbon residue in the range 1–10% and a viscosity in the range 200–600 SUS at 210° F., more or less. The deasphalted oil is then introduced into oil hydrotreater or hydrogenation zone 34 wherein it is contacted with a gaseous hydrogen at a relatively elevated temperature and pressure, such as a temperature in the range 600–850° F. and a pressure in the range 500–1200 p.s.i.g. under suitable space velocity conditions, preferably in the presence of a hydrogenation catalyst such as a cobalt molybdate hydrogenation catalyst or a nickel tungsten sulfide hydrogenation catalyst. If desired, as indicated in the accompanying drawing, the vacuum gas oil fraction recovered from vacuum pipe still and fractionator 22 via line 25 may be admixed via line 35 with the deasphalted oil supplied to oil hydrotreater 34 via line 29. Generally it is desirable when the vacuum gas oil recovered from vacuum pipe still and fractionator 22 via line 25 contains asphaltic constituents and the like, such as resins and bitumens, to separate these materials from the vacuum gas oil by passing the vacuum gas oil via line 36 into solvent deasphalting zone 29 for the removal of these constituents therefrom. Further, as indicated in the drawing, the gas oil fraction recovered from crude still 12 via line 21 may also be admixed with the deasphalted oil recovered from solvent deasphalter 28 via line 29.

There issues from hydrogenation zone or oil hydrotreater 34 a hydrogenated oil characterized by a reduced metals content and particularly suitable as a charge stock to a catalytic cracking operation. The oil or oil blend charged to hydrotreater 34 comprising deasphalted oil from solvent deasphalter 29 together with the solvent deasphalted or untreated vacuum gas oil from vacuum pipe still and fractionator 22 and/or the gas oil recovered via line 21 from crude still 12 usually has a metals content, such as vanadium, nickel, copper and iron, in the range 5–15 p.p.m., more or less. The resulting hydrogenated oil recovered from hydrotreater 34 via line 38 will, however, have a relatively reduced metals content, e.g., metals content in the range 0.02–5 p.p.m., thus making the hydrogenated oil particularly useful and desirable as charge stock for treatment in fluid catalytic cracker 40. Within fluid catalytic cracker 40 the hydrogenated oil is contacted with a finely divided fluidized catalytic cracking catalyst. A suitable cracking catalyst generally comprises an oxide of metals of groups II, III, IV and V of the periodic table.

A suitable cracking catalyst comprises a silica-alumina catalyst containing about 5–30% by weight alumina. The average particle size of the cracking catalyst particles is below about 200 microns, a size sufficient to produce a dense fluidized bed of cracking catalyst. The resulting catalytic cracked effluent from fluid catalytic cracker 40 recovered via line 41 is introduced into fractionator 42 wherein it is fractionated into a catalytic cracked naphtha which is recovered via line 44 and a relatively heavy cycle gas oil which is recovered via line 45. The heavy catalytic cycle gas oil may be reintroduced into the fluid catalytic cracking zone via lines 45, 46 and 38 or advantageously blended with the heavy asphalt recovered from solvent deasphalter 29, as indicated, via lines 45, 31 and 32.

The catalytic cracked naphtha recovered from fractionator 42 via line 44 is introduced admixed with the heavy naphtha recovered from vacuum pipe still and fractionator 22 via line 24 together with, if desired, a heavy straight run naphtha fraction recovered from crude still 12 via lines 15, 21 and 48 into hydrogenation zone or naphtha hydrotreater 49 wherein the olefinic constituents of the aforementioned stream introduced thereinto are converted into the corresponding hydrocarbons. Advantageously, metals removal also occurs within hydrotreater 49 as well as desulfurization. Substantially the same catalyst as employed within oil hydrotreater 34 may be employed within hydrotreater 49 through the temperature and pressure conditions required to effect dehydrogenation within naphtha hydrotreater 49 need not be as severe as those employed with respect to the operation of hydrotreater 34. More specifically, a temperature in the range 400–800° F. and a pressure in the range 100–800 p.s.i.g. is usually suitable in the operation of hydrotreater 49.

The resulting hydrogenated naphtha is recovered from naphtha hydrotreater 49 via line 50 and introduced into Rexformer 51. Rexformer 51 is a combination of units comprising a catalytic reforming unit and a solvent extraction unit. The catalytic reforming unit or portion of Rexformer 51 usually comprises a regenerable or non-regenerable platinum-containing catalyst suitable to effect dehydrogenation of naphthene hydrocarbons to aromatic hydrocarbons, dehydrocyclization of saturated aliphatic hydrocarbons into aromatic hydrocarbons and isomerization of straight chain hydrocarbons into non-straight chain hydrocarbons. The aforesaid operations of dehydrogenation, dehydrocyclization and isomerization are

carried out substantially simultaneously with the catalytic reforming portion of Rexformer **51**. The resulting catalytic reformate now having an increased proportion of aromatic hydrocarbons with respect to the naphtha charged thereto is then contacted with an immiscible selective solvent for aromatic hydrocarbons, such as aqueous ethylene glycol, so as to preferentially extract the aromatic hydrocarbons from the reformate to yield a relatively more aromatic extract and a relatively more paraffinic raffinate. The extract removed by the selective solvent in the solvent extraction process, or portion of Rexformer **51** might also comprise the relatively low molecular weight n-paraffins such as n-pentane and n-hexane and the like, the higher molecular weight paraffinic hydrocarbons, e.g., n-octane, n-nonane, n-decane and the like, being present in the more paraffinic raffinate. The more aromatic extract is separately recovered from Rexformer **51** via line **52** and employed as indicated as a motor fuel or a motor fuel component. The more paraffinic raffinate comprising the relatively heavy n-paraffins are separately recovered via line **54** and may be recycled via lines **55** and **50** to Rexformer **51** so as to effect isomerization or dehydrocyclization of the recycled n-paraffins therein or, if desired, the relatively more paraffinic raffinate from Rexformer **51** may be separately recovered via lines **54** and **56** employed as a diesel and/or jet fuel component.

As indicated in the drawing, the catalytic reforming portion of Rexformer **51** wherein dehydrogenation of naphthenes to aromatics and dehydrocyclization of aliphatic hydrocarbons to aromatic hydrocarbons occur results in the production of gaseous hydrogen which is recovered from the catalytic reforming portion of Rexformer **51** via line **58**. This gaseous hydrogen may be employed as hydrogen feed via line **59** to naphtha hydrotreater **49** in order to effect hydrogenation of the naphtha charged thereto. Further, at least a portion of the gaseous hydrogen may be supplied via lines **58**, **59** and **60** to oil hydrotreater **39** wherein it supplies at least a portion of the hydrogen to effect hydrogenation of the deasphalted oil supplied thereto. Further, if desired, at least a portion of the gaseous hydrogen recovered from Rexformer **51** via line **58** may be admixed with the gaseous hydrocarbons recovered from crude still **12** via line **14** and the resulting blend in line **61** employed as fuel gas.

The following is illustrative of a practice of this invention. A mixture comprising California crudes was atmospherically distilled to about 50–55% volume reduced crude basis the original crude mixture and charged through a vacuum pipe still operated under mild viscosity-breaking conditions at an outlet temperature of 850° F. The resulting mildly viscosity-broken reduced crude was then introduced into an atmospheric flasher from which there was recovered overhead approximately a 46% volume yield of gas, naphtha and atmospheric viscosity-broken gas oil, all basis reduced crude in the following amounts: gas 1% volume; 430° F. end point naphtha 3.5% volume; gas oil 41.5% volume the atmospheric flasher being operated at a maximum temperature of 790–800° F. The flasher bottoms having a gravity of about 12° API and a Conradson carbon residue of about 15 was introduced into a vacuum still operated at about 25 mm. Hg and a temperature of 665° F. There was recovered overhead from the vacuum still gas oil fractions amounting to about 42% by volume of the charge to the vacuum still. There was also recovered from the vacuum still a heavy bottoms fraction amounting to about 16% by volume basis original crude or about 33.8% by volume basis reduced crude. The vacuum still bottoms had a gravity about 3.6° API, a penetration (100 gm./5 sec./77° F. cm.$\times 10^{-2}$) about 27–29 and a Conradson carbon residue in the range 26–33%.

The short residuum or vacuum still bottoms was solvent deasphalted employing liquid isobutane as the deasphalting solvent and a solvent:oil volume ratio of 5:1 at a temperature in the range 235–245° F., more particularly about 243° F., and a pressure in the range 350–385 p.s.i.g. There was recovered from the above deasphalting operation a deasphalted oil at a yield of about 42% by volume basis deasphalting charge stock. The resulting deasphalted oil had a gravity in the range 15.3–16.8° API, a viscosity SUS 210° F. in the range 238–281, a Conradson carbon residue in the range 4.1–5.0 and a K factor of about 11.70. A vacuum pipe still gas oil comparable to the vacuum gas oil fraction recovered from vacuum pipe still and fractionator **22** and having a metals content of about 5.2 p.p.m. (nickel, vanadium and iron), a gravity 22.8° API, a boiling range in the range 490–760 and a carbon residue of 0.31% by weight was contacted with hydrogen at a pressure of 1000 p.s.i.g., a temperature 650° F., space velocity v./hr./v. 3.54 and at a hydrogen recycle rate of 600 cubic feet of hydrogen per barrel of charge stock to yield a hydrogenated oil having a boiling point in the range 475–760° F., a substantially reduced carbon residue of 0.08% by weight and a sharply reduced metals content of about 1.0 p.p.m. During the foregoing operations hydrogen was consumed in an amount equivalent to about 39 cubic feet of hydrogen per barrel of charge gas oil. The resulting hydrogenated oil, because of its low carbon residue and low metals content, was particularly suitable as a catalytic cracking charge stock.

As will be apparent to those skilled in the art in the light of the foregoing disclosure many alterations, substitutions and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A petroleum treating process which comprises fractionating an asphaltic crude oil to produce a first naphtha fraction and a long residuum, subjecting said long residuum to high temperature vacuum distillation to yield a second naphtha fraction and a short residuum, solvent deasphalting said short residuum to yield an asphalt fraction and a deasphalted oil, hydrogenating said deasphalted oil, catalytically cracking the resulting hydrogenated deasphalted oil to yield a catalytic cracked naphtha fraction, combining said catalytic cracked naphtha fraction and said second naphtha fraction, hydrogenating the resulting combined naphtha fractions, combining the resulting combined hydrogenated naphtha fractions and said first naphtha fraction and catalytically reforming the same with the production of hydrogen, subjecting the resulting reformate to contact with a liquid selective solvent to separate as extract the more aromatic hydrocarbons therefrom and to yield a paraffinic raffinate, returning said paraffinic raffinate to the aforesaid catalytic reforming operation, recovering the hydrogen produced during the aforesaid catalytic reforming operation and employing the hydrogen in the aforesaid hydrogenating operations.

2. A method of treating a petroleum crude oil which comprises subjecting said crude oil to fractional distillation to yield a first naphtha fraction having a boiling range in the range 225°–450° F. and a long residuum, subjecting said long residuum to vis-breaking and high temperature vacuum distillation to yield a second naphtha fraction having a boiling range in the range 225°–450° F., a gas oil fraction and a short residuum, solvent deasphalting said short residuum to yield a deasphalted oil, combining said deasphalted oil and said gas oil fraction and subjecting the same to hydrogenation, subjecting the resulting hydrogenated effluent to catalytic cracking to yield a cracked naphtha fraction, combining said cracked naphtha fraction with said second naphtha fraction, hydrogenating the resulting combined naphtha fractions to yield a hydrogenated naphtha, combining the resulting hydrogenated naphtha with said first naphtha

fraction and subjecting the same to catalytic reforming with the production of gaseous hydrogen, subjecting the resulting reformate to contact with a liquid selective solvent to separate as extract the more aromatic hydrocarbons therefrom and to yield a paraffinic raffinate, recovering said gaseous hydrogen, employing said recovered gaseous hydrogen in the aforesaid hydrogenation operations and returning said paraffinic raffinate to the aforesaid catalytic reforming operation.

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