Sept. 30, 1958 W. T. KNOX, JR 2,854,398

PREPARATION OF CATALYTIC CRACKING FEED STOCKS

Filed Feb. 24, 1955 2 Sheets-Sheet 1

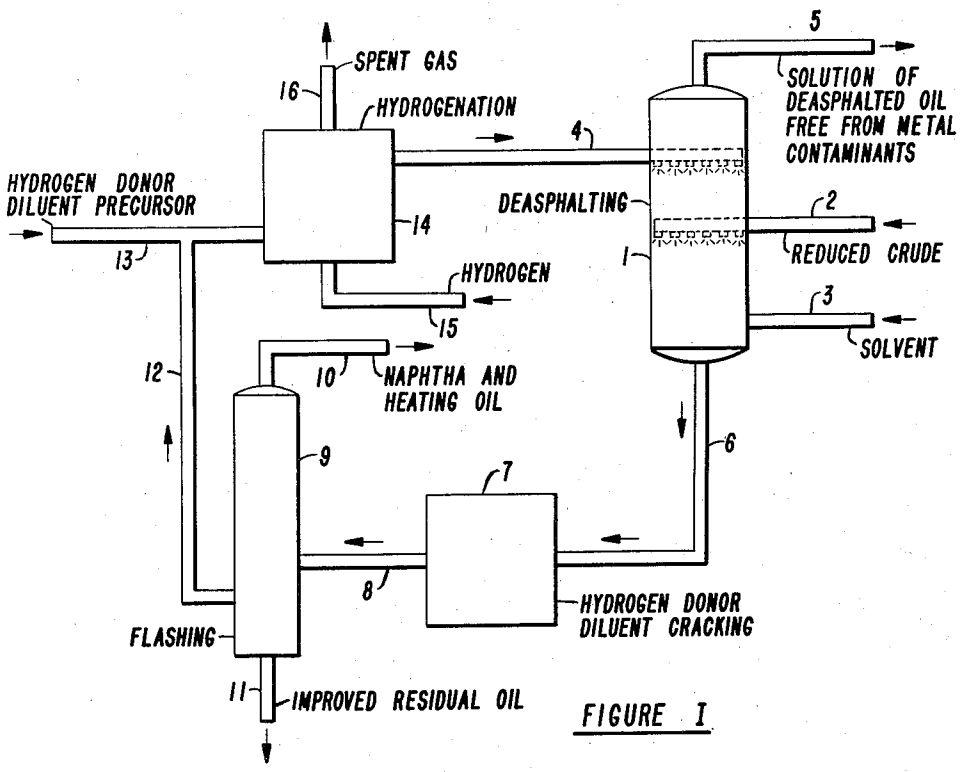


FIGURE I

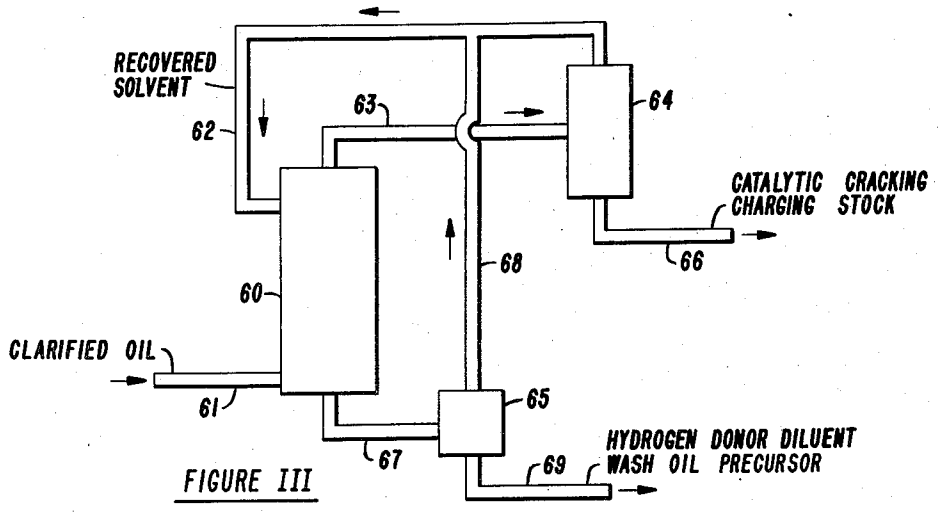


FIGURE III

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PREPARATION OF CATALYTIC CRACKING FEED STOCKS

Filed Feb. 24, 1955 2 Sheets-Sheet 2

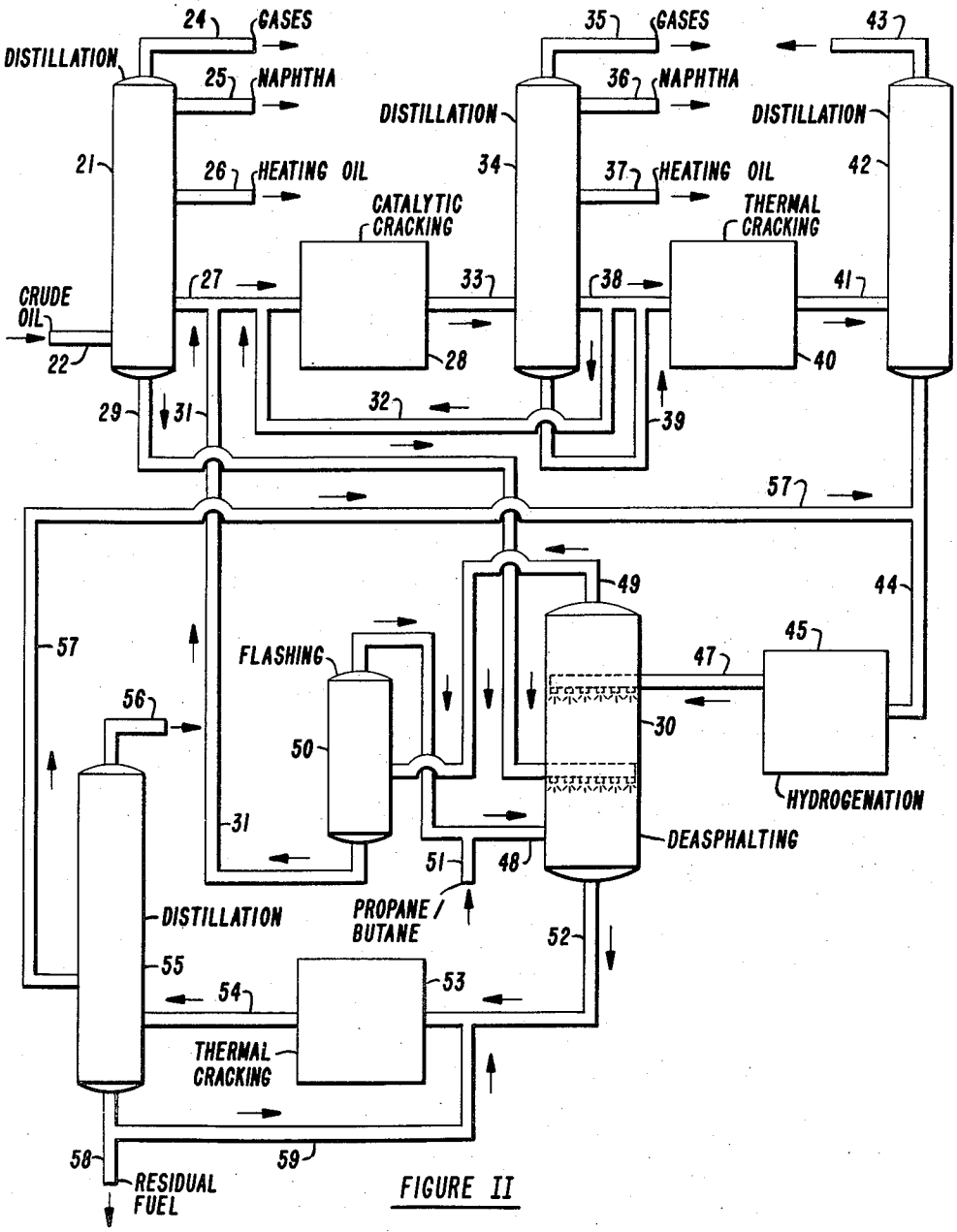


FIGURE II

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Patented Sept. 30, 1958

2,854,398

PREPARATION OF CATALYTIC CRACKING FEED STOCKS

William T. Knox, Jr., Cranford, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application February 24, 1955, Serial No. 490,186

3 Claims. (Cl. 208—80)

This invention relates to the upgrading of heavy oils, particularly high boiling petroleum residual oils. More specifically, this invention proposes an integrated process for deasphalting residual oils to obtain catalytic feed stocks, and for further converting the asphalt remaining from the deasphalting step to obtain further amounts of lighter distillate products.

According to this invention, a high boiling petroleum oil is treated by deasphalting the oil, using as a solvent liquefied normally gaseous hydrocarbons, while washing the solution with a relatively high boiling hydrogen donor diluent to obtain a deasphalted oil phase substantially free from catalyst contaminants and an asphaltic phase containing a major portion of the hydrogen donor diluent. The asphaltic phase is then thermally treated under hydrogen donor transfer conditions to obtain lighter distillate fractions and an asphaltic residue or residual fuel.

It has been previously proposed to obtain deasphalted oils of catalytic cracking quality from residual petroleum fractions contaminated with a substantial amount of catalyst poisoning metal contaminants by treating the residual fraction in a deasphalting zone with a liquefied normal gaseous hydrocarbon such as propane, using a wash oil that is selective to metal contaminants. In this process, a deasphalted oil phase is obtained from the deasphalting zone which, upon removal of the solvent, yields an oil amenable to catalytic cracking. The asphaltic phase contains the contaminants and heavy asphaltene constituents of the residual petroleum fraction, and a major amount of the wash oil which is normally separated and recovered. Through the use of wash oils, as much as 95% of the original catalyst contaminants in the residual petroleum fraction may be removed with the asphaltic phase. Previously proposed wash oils have comprised the heavy bottoms cycle stock from a catalytic cracking unit and/or synthetic asphalt. The synthetic asphalt may be prepared, for example, by thermally cracking the bottoms cycle stock from a catalytic cracking unit.

Another process, termed hydrogen donor diluent cracking (HDDC) has also recently been introduced into the art of residuum upgrading. In this HDDC process, a heavy, low value residual oil is upgraded by admixing it with a hydrogen donor diluent material, aromatic-naphthenic in nature, and thermally cracking the mixture as in a thermal cracking coil. The hydrogen donor diluent comprises selected polycyclic condensed ring aromatics having attached naphthenic rings. The hydrogen donors are especially prepared by partial hydrogenation from selected normally surplusage refinery streams, such as catalytic stocks and thermal tars. The hydrogen donor diluent used has the ability to take up hydrogen in the hydrogenation zone and readily release it in a thermal cracking zone.

In this manner of hydrocracking oils, the oil being upgraded, usually a residual oil, is not contacted directly with the hydrogenation catalyst and does not, therefore, impair the activity of the catalyst by contamination. The amount of concomitant light gases and coke produced by this process is relatively small, usually being in the order of about 5 to 10%. The use of a hydrogen donor diluent cracking process is preferred in many applications over the use of direct catalytic hydrogenation because the product yields and selectivities are superior. This technique of HDDC is more fully presented by co-pending application entitled, "Upgrading of Heavy Hydrocarbon Oils," Serial No. 365,335, filed July 1, 1953, and now abandoned, by Langer.

The present invention proposes to integrate the two above-described processes whereby even further quantities of distillates may be rescued from low value residual oil fractions or asphalts. In the present process, the above deasphalting process for preparing catalytic cracking feed stocks is modified in that the customary wash oil is replaced with a selected relatively high boiling hydrogen donor diluent which, after the deasphalting step, appears in the asphaltic phase. The asphaltic phase is then thermally treated to cause cracking of the heavy molecules or asphaltenes precipitated in the deasphalting step, and to cause transfer of hydrogen from the hydrogen donor molecules to the products of the cracking.

Through this integration, certain advantages are obtained. Besides the increased conversion of the asphaltic material normally discarded from the deasphalter, two other principal advantages are secured. In normal deasphalting operation, part of the wash oil is soluble in the solvent and as a result ends up in the catalytic cracking feed prepared by the process. Because the wash oil used in the present invention is hydrogenated, it is more amenable to catalytic cracking. The catalytic cracking feed prepared according to this invention is of higher quality to the extent that portions of the wash oil appear in deasphalted oil. Secondly, the passage of the hydrogen donor diluent through the deasphalting step increases the concentration of the desirable aromatic-naphthenic molecules in the diluent, thereby greatly improving its quality and action. This latter advantage particularly inures to recycle operations wherein spent hydrogen donor diluent is recovered from the thermally cracked mixture and returned to the process.

It is to be appreciated, aside from the advantages described above, that this invention results in obtaining, in reduced amounts, an improved residual oil fuel because of the hydrogenation of the fuel. In certain applications, however, it may be desired to substantially eliminate any residual fuel produced by this process and in this case the high boiling material can be recycled substantially to extinction.

In light of the above, it is an object of this invention to present to the art an improved method for upgrading contaminant containing residual oils. Another object of this invention is to integrate a deasphalting process for preparing catalytic cracking feed stocks with a hydrogen donor diluent cracking process for converting residual oils.

These and other objectives and advantages will become readily apparent as this description proceeds during which the attached drawings, forming a part of this specification, are described in detail.

Figure I schematically presents the process of this invention reduced to its simplest form.

Figure II illustrates a particularly preferred process sequence wherein this invention is integrated with a catalytic cracking process.

Figure III depicts an alternative processing scheme for preparing the hydrogen donor diluent wash oil used in the present invention.

A particularly preferred modification of this invention comprises the use of a hydrogen donor diluent wash oil obtained from catalytic cracking cycle oils. A preferred processing sequence using this wash oil comprises the

steps of contacting the residual oil in a deasphalting zone with a liquefied solvent comprising normally gaseous hydrocarbons and with a wash oil comprising major proportions of aromatic molecules displaying hydrogen donor properties, to obtain a deasphalted oil phase substantially free from metal contaminants and an asphaltic phase containing major proportions of the wash oil. A catalytic cracking charging stock is separated from the deasphalted oil phase and subjected to catalytic cracking in a catalytic cracking zone. The catalytically cracked material is then separated to obtain heavy cycle oils and the cycle oils are partially hydrogenated to obtain the hydrogen donor diluent wash oil. The asphaltic phase containing the hydrogen donor molecules of the wash oil is then cracked under hydrogen donor diluent cracking conditions to obtain lighter distillate fractions.

The heavy cycle oils recovered from the catalytically cracked materials, including the bottoms fraction, can be subjected to a separation step using suitable solvents to obtain an aromatic concentrate which, upon partial hydrogenation results in a superior hydrogen donor diluent wash oil.

Alternatively the aromatic content of the wash oil may be increased by other methods. For example, the heavy cycle oils obtained from the catalytically cracking zone may be subjected to thermal cracking to obtain a thermal tar which, upon partial hydrogenation, results in a wash oil having superior hydrogen donor properties.

Spent hydrogen donor diluent wash oil can be recovered from the thermally treated asphaltic phase and can then be partially hydrogenated and returned to serve as the wash oil. Also, the heavy asphalt remaining after the separation of the material from the thermal treating zone may be recycled, at least in part, to the thermal treating zone to be further converted therein.

The heavy oil that comprises the principal charging stock of the present invention is preferably a hydrogen deficient petroleum derived residual oil characterized by an API gravity of −5° to 20°, a Conradson carbon of 5 to 50 wt. percent and an initial boiling point above 850° F. This invention is, however, capable of enjoying broader applications in that in some cases, crude oils, distillate fractions therefrom, coal tars, shale oils, tars, asphalts, etc. may be also processed. Inspections of typical feed stocks used in the present invention are given in Table I presented hereinafter.

The hydrogen donor diluent wash oil used in the present invention is especially selected to meet the specific processing demands of this process. Besides having hydrogen donor qualities and susceptibility to partial hydrogenation, the hydrogen donor diluent of this invention is also readily amenable to being precipitated during the deasphalting step so as to appear in the asphaltic phase. More specifically, it has been found that catalytic cycle oils and bottoms alone, or extracts, precipitates, or thermal tars therefrom, boiling above about 900° F. make excellent hydrogen donor diluent wash oils. It has also been found that certain lube oil extracts, and thermal tars from thermal cracking operations will yield suitable hydrogen donor diluent precursors.

The prime consideration for the selection of the hydrogen donor diluent wash oil is that the material is composed of predominate proportions of aromatic-naphthenic molecules or condensed ring structures having the ability to take up hydrogen in a hydrogenation zone and to readily release it in a thermal cracking zone. Such condensed ring structures are relatively refractory and will pass through a thermal cracking zone substantially unaltered except for the loss of hydrogen. The condensed ring structures are, therefore, susceptible to being recovered from a reaction mixture and being regenerated by partial hydrogenation. In many cases, feed streams to the process will supply a sufficient amount of aromatic-naphthenic molecules, or material that will reduce to aromatic-naphthenic molecules, to meet the loss of diluent encountered in the process. Inspections of typical hydrogen donor diluent wash oils are listed in Table II.

The operating conditions applicable to the following description of Figure I are conveniently summarized in Table III presented hereinafter. Referring specifically to Figure I, a heavy oil, e. g. a reduced crude, is introduced into a deasphalting zone **1**, via line **2**, in an intermediate portion thereof. A liquefied normally gaseous hydrocarbon solvent is admitted by line **3** to the lower portion of the deasphalting zone and passed upwardly through the zone countercurrently to the reduced crude. A hydrogen donor diluent wash oil is admitted to the upper portion of the zone by line **4**. A solution of deasphalted oil substantially free from metallic contaminants is withdrawn from the top of the deasphalting zone through outlet line **5**. An asphaltic fraction containing substantially all of the metal contaminants introduced into the tower with the reduced crude is withdrawn through outlet line **6**. This asphaltic phase also contains a major proportion of the hydrogen donor molecules in the wash oil.

The use of a liquefied, normally gaseous hydrocarbon in this manner is well known in the art. As specific examples of solvent materials which can be used, there may be mentioned: ethane, propane, propylene, butylene, butane and mixtures thereof.

The hydrogen donor diluent wash oil functions as a scrubbing agent to further remove metallic contaminants from the deasphalted oil in the solvent. The wash oil is also precipitated by the action of the solvent, although a minor amount of it may appear in the solvent. In a typical case, it has been found that without the use of a wash oil, the deasphalting step may remove only about 75% of the metallic contaminants present in the reduced crude, whereas through the use of a wash oil as much as 95% of the metal contaminants are removed and carried out in the asphaltic phase. The metal contaminants that are particularly objectionable are those of nickel, iron and vanadium, principally nickel, existing as organic complexes. It is customary to express the contamination level of catalytic cracking charging stocks in nickel equivalents per 1000 bbls. of oil.

The contents of line **5**, i. e., the solution of deasphalted oil, is separated to recover the solvent and a heavy residual oil of catalytic cracking quality which normally contains less than 5 lbs./1000 bbls. of nickel equivalent contaminants.

The asphaltic phase in line **6** may be processed to remove any entrapped solvent (not shown) and then is transferred to a thermal treating zone **7**. The thermal treating zone comprises preferably a coil and/or drum arrangement. The asphaltic phase is subjected in the thermal treating zone to conditions of hydrogen donor diluent cracking. Because of the presence of the donor diluent molecules, little, if any, coke deposition occurs in this step, although there will be substantial cracking of the heavy asphaltene-like molecules precipitated in the deasphalting zone **1** from the reduced crude. After this thermal treatment, the mixture is transferred via line **8** to a flashing zone **9** or equivalent separation means.

The hydrogen donor diluent cracking process is preferred in many cases over straight catalytic hydrogenation of heavy residua or asphalts. This is true not only because this circuitous method of hydrogenation substantially avoids the problem of contamination of the hydrogenation catalyst, but also because this method of cracking is extremely selective in producing distillate products in the naphtha and heating oil ranges, and results in surprisingly high conversions. It is to be understood, then, that direct catalytic hydrogenation or hydrocracking of the asphaltic phase will not secure conversions and selectivities equivalent to that of the HDDC step used in this present process.

The variation of the invention here illustrated is di-

rected to obtaining besides a catalytic cracking feed stock reduced amounts of residual fuel of improved quality. Accordingly, the thermally cracked mixture is separated in unit **9** to recover overhead through line **10** lighter distillate fractions. The gas oil so obtained may be subjected to catalytic cracking or other conversion processes if desired. The remainder of the material is withdrawn via line **11** as a residual fuel product. In many operations, however, it may be desired at this point to recover, at least in part, the spent hydrogen donor diluent wash oil in order that they may be recycled. Thus as illustrated, a fraction boiling in the range within the limits of about 700° to 1150° F. can be recovered via line **12**.

To form the wash oil used in the deasphalting zone, a hydrogen donor diluent precursor is supplied to the process by line **13** and may be admixed with the recovered and recycled spent hydrogen donor diluent in line **12**. The precursor material is partially hydrogenated in hydrogenation zone **14** by conventional methods using preferably sulfur insensitive catalysts such as cobalt molybdate, and nickel-tungsten sulfide. It is important at this point that the hydrogen donor diluent wash oil precursor be only partially hydrogenated. Complete or substantially complete conversion of the aromatic-naphthenes to naphthenes will substantially reduce or eradicate to effectiveness of the materials to serve as hydrogen donors, and will also increase loss of this material to the solvent. A sufficient amount of hydrogen should be introduced into the diluent wash oil to have it serve as an effective hydrogen donor in the thermal cracking zone **7**. Hydrogen is supplied to the hydrogenation zone by line **15** and the spent gas is removed by line **16**. A portion of this spent gas may be recycled as is conventional. The hydrogenated material is then transferred to the deasphalting zone by line **4** as previously described.

Table I lists the inspections of heavy oil feed stocks that can be processed according to this invention. Table II lists the inspections of hydrogen donor diluent wash oils that can be used in the practice of this invention. Table III summarizes the ranges of operating conditions pertinent to the present invention and presents a specific example thereof.

TABLE I

Typical heavy oil feed inspections

	1	2	3	4	5
Percent on crude	9	30	25	10	14
Gravity, ° API	8.7	21.6	19.2	9.3	16.0
Viscosity, SSU @ 210° F.	10,000	65.4	202	4,050	950
Conradson carbon, Wt. Percent	17.3	2.9	4.5	17.6	8.9
Sulfur, Wt. Percent	3.7	3.0	0.7	3.0	2.5
Contaminant, Ni PTB	13.3	3.6	3.1	7.9	5.0
Initial boiling point, ° F.	1,050	950	950	1,050	1,050

Names: 1. West Texas. 2. Tomball. 3. Mixed Sweet. 4. West Texas Salt Flat. 5. Heavy Coastal.

TABLE II

Typical hydrogen donor diluent wash oil inspections

	1	2
Elemental Analysis, Wt. Percent:		
Carbon	88.8	88.4
Hydrogen	7.2	8.6
Sulfur	3.0	1.9
Nitrogen	0.5	0.7
Oxygen	0.5	0.4
C/H atomic ratio	12.5	10.3
Gravity, ° API	−5	15.9
Conradson carbon, Wt. Percent	19.1	2.2
Ash @ 800° C., Wt. Percent	0.003	0.05
Aniline point, ° F.	700	
Refractive Index @ 68° F.	575	725
Initial boiling point, ° F.	82.5% @ 1,020°	60% @ 940°

1. Thermal tar from cycle oil from fluid catalytic unit.
2. Lube oil extract.

TABLE III

Operating conditions

	Range	Example
Deasphalting Unit:		
Pressures, p. s. i.	100 to 600	400.
Hydrogen donor diluent feed rate, vol./vol. of heavy oil feed.	0.1 to 2	0.5.
Solvent feed rate, vol./vol. of heavy oil feed.	2 to 10	4.
Temperature, ° F. avg	110 to 180	150.
Hydrogen Donor Diluent Cracking Unit:		
Temperature, ° F	750 to 1,000	850.
Total feed rate, v./v./hr.	0.25 to 15	4.5.
Pressure, p. s. i.	15 to 800	400.
1,000° F. conversion,[1] Vol. Percent	40 to 80	55.
Hydrogenation Unit:		
Pressure, p. s. i.	400 to 3,000	500.
Temperature, ° F.	600 to 700	675.
Feed rate, v./v./hr.	0.5 to 10	1.
Hydrogen consumption, SCF/bbl. diluent.	50 to 1,000	350.
Catalyst		Nickel Tungsten Sulfide.

[1] 1,000° F. conversion is defined 100 vol. percent fresh feed from deasphalter minus vol. percent of products boiling above 1,000° F.

With specific reference to Figure II, a particularly preferred processing sequence will be described wherein the hydrogen donor wash oil is especially selected from catalytic cracking cycle oil. The process initiates with the separation of a whole crude. The initial separation zone **21** comprises an atmospheric fractionation tower followed by a vacuum distillation unit as is customary. The crude oil is injected into the separation zone **21** via line **22** and has removed therefrom light fractions. For example, gases may be removed by line **24**, naphthas by line **25** and heating oils by line **26**. Materials in the catalytic cracking gas oil boiling range are removed by line **27** and transferred to catalytic cracking unit **28**. The remaining bottoms, which may boil above about 850° to 1050° F., are removed by line **29** and transferred to a deasphalting zone **30**. The gas oils in line **27** may be further augmented by catalytic cracking feed stocks obtained in the process, as will appear, supplied by lines **31** and **32**.

Any conventional catalytic cracking process may be used in the practice of the invention. It is preferred, however, to use a fluid catalytic unit with a separate fluid regenerating system. Such a process is depicted in U. S. Patent 2,587,554, issued February 26, 1952, in the name of John Weikart. The catalytically cracked material is transferred by line **33** through separation unit **34** which may again include atmospheric and vacuum units. Lighter materials such as gases, naphthas and heating oils are separated and removed via lines **35**, **36** and **37** respectively. If desired, cycle oils boiling within the limits of 700° to 950° F. may be separated and removed by line **38**, a portion of which can be recycled via line **32** as is customary in "heart-cut recycle" operations. The remaining cycle oil and the bottoms removed from the tower by line **39** are designated as the hydrogen donor diluent wash oil precursor.

This precursor material may be suitably prepared in several alternative manners, one of which is shown in Figure III. In some cases, it may be desired without further preparation to subject this material to partial hydrogenation to prepare the donor diluent wash oil. As shown, however, the cycle oil and bottoms are subjected to thermal cracking in zone **40** to concentrate the desirable aromatic-naphthenic molecules therein. The cracked materials are then transferred by line **41** to a separation zone **42** wherein materials boiling below about 600° to 700° F. are removed and taken off overhead by line 43 as product. If desired, a portion of these materials can be transferred to the catalytic cracking zone. The remaining material is passed to a hydrogenation zone **45** via line **44**. Alternatively, the bottoms fraction in line

44 can be subjected to solvent extraction prior to being hydrogenated.

The material transferred to zone 45 is partially hydrogenated as previously described and then is passed via line 47 to the deasphalting zone to serve as a wash oil.

The deasphalting zone operates as previously described. A solvent is admitted to the base of the deasphalting zone by line 48 and flows countercurrent to the residual oil introduced into the zone via line 29 and to the wash oil. The solution of deasphalted oil is removed overhead by line 49 and transferred to a flashing zone 50 wherein the solvent is recovered. The recovered solvent is returned to the deasphalting zone via line 48 and may be augmented by makeup solvent supplied by line 51. The contaminant free improved residual oil is transferred to the catalytic cracking zone via line 31.

The asphaltic material in line 52 is transferred to a thermal cracking zone 53, subjected to conditions of hydrogen donor diluent cracking therein and then is transferred by line 54 to a separation zone 55. In this zone, materials boiling above the hydrogen donor diluent wash oil boiling range are taken off overhead via line 56. The gas oil portions of these materials may be subjected to catalytic cracking, if desired. In this processing scheme, the spend hydrogen donor diluent wash oil is recovered and recycled via line 57 to the hydrogenation zone 45.

The heavy material remaining from this separation in zone 55 may be removed as a residual fuel product by line 58. Preferably, however, a major portion of this material is recycled via line 59 to the thermal cracking zone, whereby increased conversions can be obtained and the residual fuel product can be substantially eliminated.

With reference to Figure III, an alternative method of preparing the hydrogen donor diluent precursor will be described. A bottoms fraction, such as clarified oil from catalytic cracking unit, including materials boiling above about 700° F. is introduced into a solvent extraction zone 60 via line 61. A solvent such as phenol, furfural, nitrobenzine or ethylene glycol is admitted to the zone via line 62. This solvent has an affinity for the heavy aromatic molecules that form the hydrogen donor wash oils. A solution is removed overhead by line 63 and transferred to a separation zone 64. In separation zone 64 the solvent is recovered by conventional methods and recycled by line 62 to the extraction zone. A non-aromatic fraction is removed from separation 64 by line 66 and may be charged to the catalytic cracking unit. The heavy aromatic material not taken off by the solvent is removed from the extraction zone via line 67 and is transferred to a separation zone 65. Solvent is recovered from the heavy material by conventional means and is returned to the solvent extraction zone by line 68. The remaining highly aromatic material is removed by line 69 and upon partial hydrogenation will serve as an excellent hydrogen donor diluent wash oil.

Having described the invention, various modifications will occur to those skilled in the art of residuum upgrading. What is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. A method for upgrading heavy petroleum oils which comprises partially hydrogenating a hydrogen donor diluent wash oil precursor comprising a material selected from the group consisting of catalytic cycle oils and bottoms, extracts, precipitates and thermal tars therefrom, and mixtures thereof to form a hydrogen donor diluent wash oil boiling above about 900° F., passing said hydrogenated hydrogen donor diluent wash oil downwardly through a heavy petroleum oil deasphalting zone employing a light hydrocarbon solvent whereby major portions of said hydrogen donor diluent wash oil are removed with the asphaltic phase from said deasphalting zone, and thermally treating said asphaltic phase under hydrogen donor diluent cracking conditions to convert substantial proportions of said asphaltic phase to lighter fractions.

2. The method of claim 1 wherein spent hydrogen donor diluent is recovered from the thermally treated asphaltic phase and recycled to form said hydrogen donor diluent precursor.

3. An improved method for treating petroleum oils comprising the steps of contacting a residual oil in a deasphalting zone with a liquefied solvent comprising normally gaseous hydrocarbons and with a hydrogenated wash oil comprising major proportions of aromatic molecules boiling above 900° F. displaying hydrogen donor properties to obtain a deasphalted oil phase substantially free from metal contaminants and an asphaltic phase contining a major portion of said wash oil, recovering a catalytic cracking charging stock from said deasphalted oil phase, thermally treating said asphaltic phase under hydrogen donor diluent cracking conditions to obtain lighter distillate fractions, catalytically cracking said catalytic cracking charging stock, separating the catalytically cracked materials to obtain heavy cycle oils, and partially hydrogenating said heavy cycle oils to obtain said wash oil.

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