Oct. 14, 1969 N. J. PATERSON 3,472,760

PROCESS FOR CONVERTING ASPHALTENIC OILS AND OLEFINIC GASOLINES TO HIGH-VALUE PETROLEUM PRODUCTS

Filed Dec. 4, 1967 2 Sheets-Sheet 1

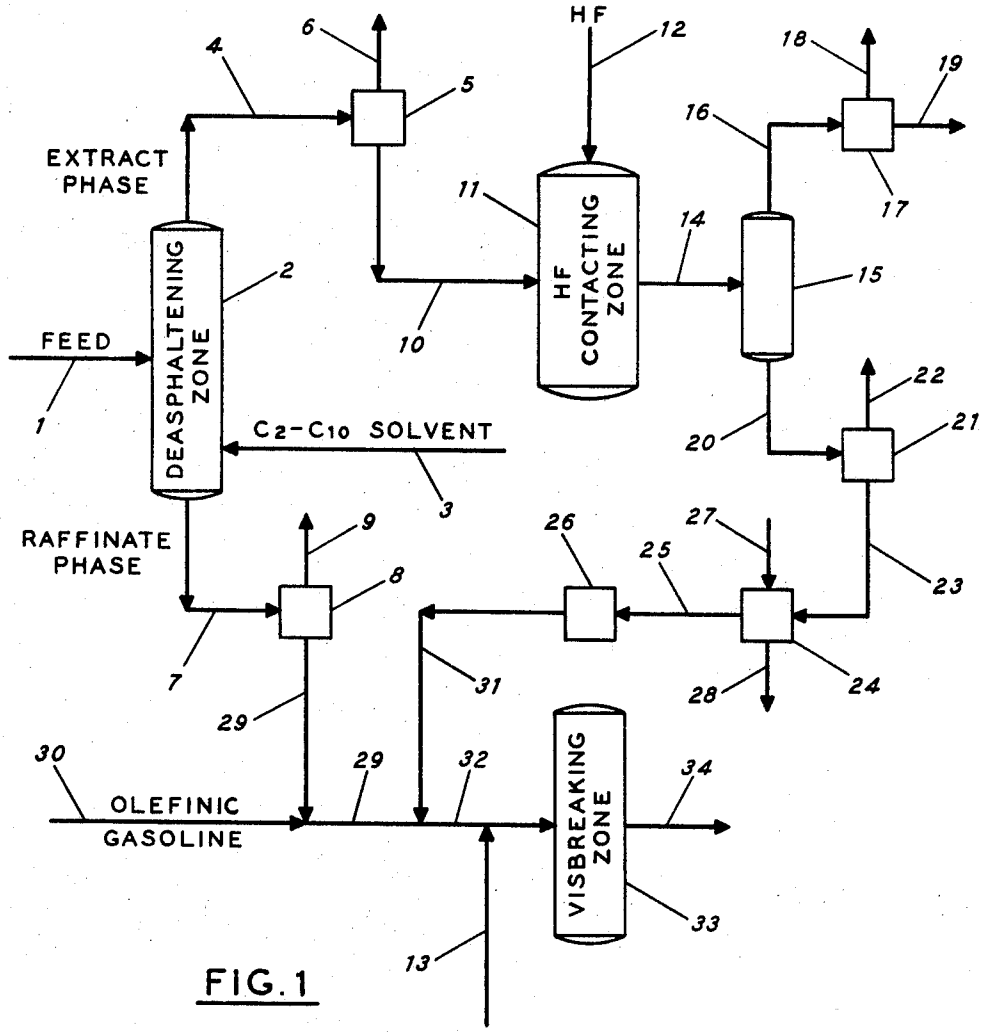


FIG. 1

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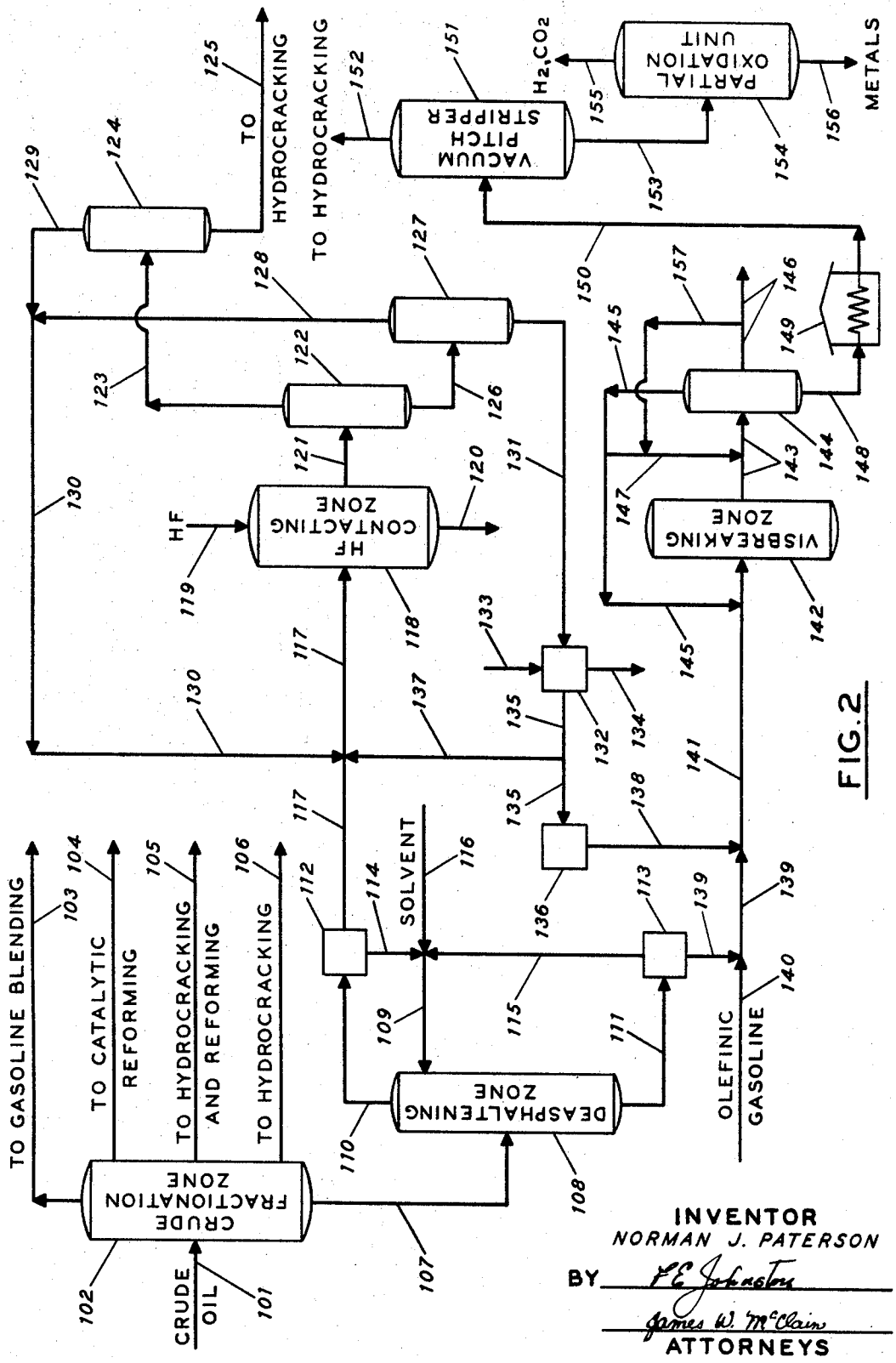


FIG. 2

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PROCESS FOR CONVERTING ASPHALTENIC OILS AND OLEFINIC GASOLINES TO HIGH-VALUE PETROLEUM PRODUCTS

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U.S. Cl. 208—86 8 Claims

ABSTRACT OF THE DISCLOSURE

A process for the conversion of an asphaltene- and metals-containing hydrocarbon oil to products boiling above 250° F. which comprises separating the oil by solvent deasphaltening into a paraffinic-naphthenic extract phase and an aromatic raffinate phase so that the bulk of the metals are concentrated in the raffinate phase; contacting the extract phase with HF to remove polynuclear aromatics and other heavy maltenes as well as metals from the extract phase; combining the HF-removed materials with the raffinate phase and olefinic gasoline; and visbreaking the combined material to produce high-value end products and fuels for other conversion processes. Sulfur may be present in the feed, and H_2S may be added to the visbreaker. A portion of the visbroken product may be vacuum pitch stripped and subjected to partial oxidation.

BACKGROUND OF THE INVENTION

The present invention relates to the conversion of hydrocarbons and, more particularly, to a highly integrated process in which solvent deasphaltening, hydrogen fluoride demetalation, and visbreaking are utilized to minimize production of low-quality gasoline and enhance production of higher-boiling materials suitable for use as hydrocracker feed.

It has long been recognized that hydrocarbon fractions, such as crude petroleum oil, atmospheric residuum or vacuum bottoms, normally contain iron, nickel, vanadium and other metallic contaminants which have an adverse effect upon various catalysts employed in petroleum process and conversion operations, such as hydrofining and hydrocracking, and upon combustion equipment in which such petroleum fractions are burned as fuels. In the high boiling fraction or residual type fuels, such contaminants attack the refractories used to line boilers and combustion chambers, cause slagging and the buildup of deposits upon boiler tubes, and severely corrode metallic surfaces with which they come into contact.

Further, well-known difficulties have been encountered in attempts to convert asphaltenes containing refractory types of sulfur compounds into gasoline. Gasoline blend stocks must be relatively free of sulfur in order to have good susceptibility to lead alkyls for octane improvement. Sulfur is particularly objectionable in fuel oils since it burns mainly to sulfur dioxide which is highly corrosive under certain temperature conditions and contributes to air pollution.

Further, it is known that some of the products ordinarily produced by standard refinery processes are of too low quality for use as motor fuels or jet fuels because of their particular chemicals structure, despite the fact that they normally boil in the fuel boiling range. A typical example is olefinic gasoline, such as that produced by a fluid catalytic cracker. Another example is the low octane gasoline produced in relatively small amounts by visbreaking of heavy viscous residual materials. It is desirable to upgrade such products to higher value materials which

either may have values as finished products in their own right or may be used as feed to processes, such as hydrocracking, which have the ability to produce high-quality finished products.

SUMMARY OF THE INVENTION

The present invention is a process whereby an asphaltene- and metals-containing hydrocarbon oil is converted into high-quality products and feed for processes capable of producing high-quality products, while at the same time minimizing production of some low-quality products.

This process involves, in its broadest form, contacting an asphaltene- and metals-containing hydrocarbon oil with a light paraffinic solvent in a deasphaltening zone, forming an asphalt- and metals-rich reaffinate phase and an asphalt- and metals-lean extract phase, withdrawing these phases separately from the deasphaltening zone, contacting the extract phase with HF in a contacting zone, separating the effluent of the contacting zone into a lighter portion and a heavier portion, said heavier portion comprising polynuclear aromatics, metals, and the bulk of the HF, combining at least a portion of said heavier portion with the raffinate phase, and then visbreaking the combined phases in the presence of added olefinic gasoline to produce products boiling above 250° F.

In a narrower embodiment of the invention, a portion of the visbroken products is passed to a vacuum pitch stripper wherein it is converted into a light stripped phase and a heavy stripped phase containing metals.

In a still narrower embodiment, at least a portion of the heavy stripped phase from the vacuum pitch stripping zone is converted to hydrogen in a partial oxidation zone and the metals are recovered.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates schematically a typical arrangement of the process units and flow streams which constitute the basic steps in the process of this invention. Auxiliary equipment often commonly associated with these basic steps is also shown.

FIG. 2 illustrates schematically the preferred embodiments of the process and shows in a typical example how the process of this invention might be integrated into a refinary complex.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention can best be understood after reference to the drawings. In FIG. 1, an oil, such as a crude oil, shale oil, residual oil, or other heavy oil, which contains asphaltenes, metals, and in many cases sulfur, is passed through line 1 into deasphaltening zone 2 wherein it is contacted with a deasphaltening solvent which enters zone 2 through line 3. Typical solvents suitable for use in this process are the C_2–C_{10} paraffins, particularly propane. In the deasphaltening zone 2, the feed is separated into two phases. The lighter extract phase contains the bulk of the solvent, the light paraffinic and naphthenic components of the feed (which are commonly referred to collectively as the maltenes), a small portion of the feed metals, and a portion of the sulfur that may have been present in the feed. The heavier raffinate contains a small amount of solvent, the heavier asphaltene components of the feed, and the bulk of the metals and sulfur. The extract phase is removed from deasphaltening zone 2 through line 4 and passed to solvent recovery zone 5 wherein the solvent is separated and removed through line 6. The raffinate phase is removed from deasphaltening zone 2 through line 7 and passed to solvent recovery zone 8 wherein the solvent is separated and removed through line 9. The solvent in lines 6 and 9 may be separately recovered or may be recycled back to deasphaltening zone 2 through line 3.

The solvent-free maltenes are passed from solvent recovery zone **5** through line **10** to HF contacting zone **11** wherein they are contacted with hydrogen fluoride which enters HF contacting zone **11** through line **12**. The hydrogen fluoride may be in the form of gaseous HF or may be anhydrous hydrogen fluoride or may be in an aqueous solution of concentrated hydrofluoric acid. A minor amount of other materials, such as BF_3, may also be present with the HF, if they do not impair the effectiveness of the HF. The preferred form will depend on the temperature at which HF contacting is to be done and the type of equipment which is to be used. Generally, the HF converts the small amount of metals in the extract phase to insoluble metal fluorides and at the same time extracts some of the polynuclear aromatics which are removed as a liquid phase carrying the insoluble metallic fluoride contaminants in suspension. The effluent of zone **11** is removed through line **14** and passed into separator **15** wherein a demetallized desulfurized oil containing the lighter portions of the maltenes is removed overhead through line **16** and passed to HF removal zone **17**. HF removal zone **17** is commonly a stripper although other conventional means of separating HF from an oil stream may be used. The HF separated is removed from zone **17** through line **18** while the demetallized oil is removed through line **19** and passed to whatever further processing is desired. As will be illustrated below, this further processing may include hydrocracking, reforming, or other well-known refining processes.

The HF layer, which comprises the heavier portion of the maltenes, including the heavy polynuclear aromatics containing the suspended metallic fluorides and any sulfur, along with the remainder of the HF, is removed from zone **15** through line **20** and passed to HF separation zone **21**. HF separation zone **21** is similar to HF separation zone **17**. The separated HF is removed through line **22**. The recovered HF in lines **18** and **22** is commonly recycled to HF contacting zone **11** and line **12** by means not shown, although the material in either or both lines **18** and **22** may be separately recovered or withdrawn from the process for other uses. The HF-free heavier portion of the maltenes which comprises highly aromatic materials is removed from separator **21** through line **23**. In the event some traces of HF or fluorine still remain in the oil, the oil may be water washed in water washing zone **24** and then passed through line **25** to defluorination zone **26**. Water enters water washing zone **24** through line **27**, and the waste water and extracted fluorine are withdrawn through line **28**. Defluorination zone **26** contains bauxite, alumina, or any other conventional fluorine absorbent.

The solvent-free raffinate phase containing the heavy asphaltenes and the bulk of the metals is withdrawn from solvent recovery zone **8** through line **29**. A quantity of olefinic gasoline enters through line **30** and is combined with the raffinate phase. Defluorinated aromatic maltenes are withdrawn from zone **26** and passed through line **31** to be combined with the raffinate phase and olefinic gasoline. In the event that aromatic maltenes are sufficiently fluorine-free when they leave zone **21**, they may be passed directly to line **31** for combination with the raffinate phase and olefinic gasoline without being water washed and defluorinated in zones **24** and **26**. The combined materials are passed through line **32** to visbreaking zone **33**. Zone **33** generally comprises a conventional visbreaker and performs mild thermal cracking of the asphaltenes in the presence of the aromatics, olefinic gasoline, and suspended metallic fluoride contaminants. During the bisbreaking operation, usually conducted at low temperatures and over extended time periods to favor polymerization, some of the olefinic materials and gasoline constituents are alkylated and polymerized to create higher boiling gas oils. The ultimate result is a consumption of low-value olefins and production of valuable higher boiling aromatic gas oils, middle distillates and heavier oils.

These gas oils by virtue of their aromatic composition are valuable feed stocks to conversion processes, such as hydrocracking, wherein high octane gasoline products are produced. Under certain operating conditions, a high heating value jet fuel of excellent thermal stability and freeze point may be produced from this type of feed stock. The visbroken materials are withdrawn from bisbreaking zone **33** through line **34** and passed to separation and whatever further processes may be desired. Although visbreaking zone **33** is generally operated as a thermal cracking zone, it may also be operated as a hydrovisbreaking zone, with hydrogen introduced at the coil inlet from an outside source through line **13**. Under preferred conditions, the metallic constituents may be converted to the sulfides by the introduction of hydrogen sulfide along with the added hydrogen, whereby the asphaltene content of the charge is rapidly converted into liquid gas oils by hydrogenation and mild hydrocracking, thus increasing the yield of the desired heavier gas oil product. Under these circumstances the conversion of the added olefinic gasoline and other gasoline constituents proceeds as before but at an accelerated rate due to the catalytic effect of the heavy metal sulfides which promote splitting and hydrocracking of the paraffinic and cyclic compounds in the added and/or recycled gasoline.

In FIGURE 2, the process of this invention is described in more detail schematically and an illustration is given indicating how the process of this invention might be integrated into an overall refinery scheme. Examples are given below showing typical stream compositions and reaction conditions based on this illustration. Crude oil in line **101** is introduced into crude fractionation unit **102** wherein it is fractionated into several streams of differing boiling ranges. In a typical example, a C_5 to 200° F. gasoline cut would be taken off overhead through line **103** and sent to gasoline blending. Near the top of the column, a 200°–375° F. cut would be taken and passed through line **104** to catalytic reforming to produce additional gasoline. A 375°–650° F. cut would be taken at a middle point in the column and passed through line **105** to hydrocracking and reforming to produce additional gasoline. Near the bottom of the column, a 650°–1,000° F. cut of gas oil would be taken and passed through line **106** to hydrocracking to produce gasoline and jet fuel. The heavy residual material from the crude oil which would typically be a 1,000° F.+ residuum is taken from the bottom of the column through line **107** to deasphaltening zone **108** wherein it is contacted with a light solvent which enters zone **108** through line **109**. The solvent separates the residuum into an extract phase containing maltenes which is withdrawn from deasphaltening zone **108** through line **110** and the raffinate phase containing the asphaltic material which is withdrawn from zone **108** through line **111**. Solvent is separated from the two phases in zones **112** and **113**, respectively; and the solvent is recycled through lines **114** and **115**, mixed with any needed fresh solvent brought in through line **116**, and all solvent is returned through line **109** to deasphaltening zone **108**. In some cases where the maltenes are particularly viscous, it may be desirable not to make a complete separation of solvent from the maltenes in zone **112** but rather to let some solvent act as a cutter stock and pass with the maltenes through line **117** to HF contacting zone **118**.

In HF contacting zone **118**, the maltenes and whatever metals and sulfur they contain are contacted with HF which enters through line **119**. The HF converts the metals to insoluble metal fluorides which may be removed through line **120**, although preferably they may be passed along with the maltenes and HF out of HF contacting zone **118** and separated at some later point. The treated maltenes pass through line **121** to separation zone **122** wherein the maltenes are fractionated and the lighter, less aromatic maltenes are removed through line **123** to HF separation unit **124** wherein any remaining

HF and solvent are separated and the lighter maltenes are passed on through line **125** to hydrocracking for the production of gasoline and jet fuels.

The heavier, more aromatic compounds in the HF extract containing the insoluble metallic constituents in suspension are removed from zone **122** through line **126** and passed into HF separation zone **127**. The HF and solvent are separated and removed through line **128**. They are mixed with HF and solvent coming from zone **124** through line **129**, and the combined streams are recycled to zone **118** through line **130**. The solvent-free, heavier aromatic maltenes, containing suspended metals and in some cases sulfur, are removed from zone **127** through line **131** and may, if necessary to remove remaining fluorine, be water washed in zone **132**, into which water enters through line **133**, and water and fluorine are removed through line **134**. The maltenes are then passed through line **135** to defluorination zone **136** for a final bauxite, alumina, or similar treating to remove any residual fluorine. In some cases, it may be desirable to recycle some portion of the maltenes to the HF treating zone through line **137**. Preferably, however, all the heavier maltenes pass through zone **136** and are withdrawn through line **138**.

The raffinate phase from the deasphaltening zone **108** which comprises the bulk of the asphaltenes and the heaviest aromatics and most of the metallic contaminants that were originally in the crude oil is passed from solvent separation zone **113** through line **139** and is combined with a quantity of olefinic gasoline which enters the system through line **140**. The raffinate and the olefinic gasoline are in turn combined with the heavier HF-treated maltenes, containing metals and sulfur in line **138**, and the combined material is passed through line **141** into visbreaking zone **142**. After visbreaking, under conditions which will be described below, the visbroken material is withdrawn through line **143** and passed into separation zone **144**. The visbroken material is fractionated in zone **144** into a plurality of streams. In a typical operation, three streams would be produced: a naphtha stream, rich in olefins, withdrawn overhead from zone **144** and recycled at least in part to zone **142**; a light gas oil stream, withdrawn through line **146** and preferably passed to further processing, such as hydrocracking; and a heavy fraction containing the metals and sulfur. Generally, the pressure of the visbroken material is reduced and its temperature is lowered by means of a combination pressure-reducing/quenching valve, placed in line **143** upstream of zone **144**, in order to arrest the cracking reactions and to permit additional flashing of the products of reaction in the visbreaker coil. The quenching material is preferably a portion of the recycled naphtha, passed from line **145** through line **147** to the quenching valve in line **143**. Alternatively, a portion of the gas oil in line **146** can be recycled through line **157** to serve, either alone or in combination with a portion of the naphtha, as the quenching material The heaviest portion of the visbroken material, containing the metals and sulfur, is withdrawn from the bottom of zone **144** through line **148**, is heated in furnace **149** in admixture with added steam and usually a light diluent oil, such as a portion of the light gas oil stream in line **146**, and the heated material is passed through line **150** into vacuum pitch stripping zone **151**. Here light materials are separated from the visbroken residuum and are passed through line **152** to hydrocracking or other processing. The remaining heavy material is passed through line **153** into partial oxidation zone **154** wherein it is heated in the presence of a controlled amount of oxygen to produce hydrogen and carbon dioxide and allow recovery of the material. The hydrogen and carbon dioxide along with the hydrogen sulfide produced in the reducing atmosphere of the partial oxidation step are removed through line **155** and separated by conventional means. The hydrogen sulfide may, if desired, be oxidized by well known means to elemental sulfur and the carbon dioxide dehydrated and separated as a solid or liquid product. The hydrogen is used in various hydrogen-consuming processes within the refinery, such as hydrocracking. The metals are removed through line **156** and may, if there is sufficient economic incentive, be recovered or may be discarded as ash.

In the process of this invention, the inclusion of the HF-treated maltenes, which are highly aromatic, in the feed to the visbreaker permits visbreaking of the aramatic asphaltenes from the solvent deasphaltening process under more severe conditions than would be possible if the asphaltenes alone were to be visbroken. This is because the inclusion of the aromatic maltenes tends to solubilize the unstable fragments and asphaltenes formed during the thermal visbreaking operation as well as keeping the unstable compounds formed by any thermal cracking during visbreaking in solution and thus preventing their deposition in the visbreaker coil which would result in rapid coke formation necessitating premature shutdown of the visbreaker. The inclusion of the aromatic maltenes also appears to prevent the deposition of the metallic complexes that are present in the asphaltenes and the HF-treated maltenes when the metals have not previously been removed from the latter. Although some amount of water will be present in the visbreaker feed following the water washing of the maltenes, a small amount is preferentially injected into the visbreaker feed, thus increasing the velocity of the charge to the visbreaker. The shorter contact time thus resulting may be compensated for by the higher outlet temperatures which are permitted in the visbreaker since the formation of coke is inhibited by the inclusion of the HF-treated aromatic maltenes in the visbreaker feed. In contrast, visbreaking of asphaltenes alone would result in rapid coking at the severity conditions desirable in this process while, if less severe conditions were used to prevent coking, little or no conversion would result. Consequently, this process provides a method whereby the severity required in the visbreaker to convert a reasonable proportion of the asphaltenes can be obtained without unnecessarily rapid coke formation.

The inclusion of the olefinic gasoline, which may be obtained from a fluid catalytic cracking unit, a thermal reformer or cracker, or any other process which produces olefins boiling in the gasoline range, results in conversion of the olefinic gasoline in the visbreaker to give increased production of high boiling distillates due to polymerization and alkylation reactions occurring under the conditions of severe heat and pressure and in the presence of whatever fluorine or metal fluorides may still be present after the HF treating of the maltenes. This process includes a self-moderating feature, however; for the presence of aromatic maltenes reduces the tendency of the polymerization reactions to go to extremes and retains any high boiling polymers in solution. Many olefinic gasolines also are highly sulfurous or nitrogenous and tend to be highly poisonous to catalysts. Consequently, by visbreaking of the olefinic gasolines to polymerize and alkylate them to higher boiling materials, they are made more readily handled by downstream catalytic processes, such as hydrocracking. In such downstream processes, the sulfur and nitrogen may be more readily removed from the nonolefinic compounds, and more stable and valuable nonolefinic gasoline components may be produced. Recycling of the material boiling in and below the gasoline range permits either zero net gasoline production from the visbreaker or a net negative production of olefinic gasoline, since any olefinic gasoline which might have passed through the visbreaker unconverted is recycled to extinction. Thus, while olefinic gasoline passes into the visbreaker, there is no net production of gasoline following separation of the products from the visbreaker.

The middle cuts from the visbreaker may be passed

on to hydrocracking or other conventional refinery processes to process gasoline, jet fuel and other high value products. The visbreaker tar or residuum is preferably passed to a pitch stripping zone to remove whatever light materials may still be included in the residuum, and these light materials serve as additional hydrocracker feed. Thus, the maximum amount of material suitable for processing to gasoline, jet fuel, and other high value products is obtained from the original crude oil. The remaining residual stripped tar, which contains suspended metals, is preferably passed to a partial oxidation zone wherein it is converted to hydrogen and carbon dioxide and the metals removed and, if desired, recovered. This hydrogen is used in hydrogen-consuming processes throughout the refinery to aid in conversion of the other portions of the crude oil to higher value products.

The solvent deasphaltening zone used in this process is a conventional deasphalter using a light paraffinic solvent, preferably in the C_2–C_{10} range. Propane and pentane are particularly preferred. The solvent to oil ratio may range from 3:1 to 12:1. The deasphaltening zone is conventionally a tower with the temperature at the top of the tower on the order of 20–80° lower than that at the bottom of the tower. Average tower temperatures are in the range of 100–400° F., and pressures are sufficient to maintain all components in a liquid phase. The primary purpose of the solvent deasphaltening zone is to separate asphaltenes. Consequently, it is desired to take as high a yield of maltenes from the zone as possible. In a typical operation, the extract phase would contain a maximum of 0.5 weight percent asphaltenes (measured as n-pentane insoluble asphaltenes) and would constitute 50–85 volume percent of the feed to the zone. The metals content of the extract would be 1–250 p.p.m. or higher of metals measured as metallic vanadium, iron, nickel, and copper.

The HF treating zone, as well as the HF stripping zone, the water washing zone, and the bauxite defluorination zone, are also conventional units. The HF treating zone is generally a tower designed for liquid-liquid contacting, and the internal portion is constructed of materials which are not readily susceptible to HF corrosion. The tower is operated at a temperature and pressure sufficient to maintain the maltenes and the HF in a liquid phase. In the event a minor portion of other components, such as BF_3, is present with the HF, the temperature and pressure in the HF treating zone should be adjusted accordingly so that all components are maintained in the liquid phase. The exact temperature and pressure used will depend on the concentration of the HF, the presence or absence of any minor components with the HF, the boiling point and viscosity of the maltene fraction taken from the deasphaltening zone, and the presence or absence of any solvent remaining with the maltenes. Thus temperature and pressure may vary over a wide range and are not critical as long as all components are kept in the liquid phase.

The visbreaking zone is conventionally a furnace followed by one or more reaction chambers. Preferably there are a plurality of reaction chambers with alternating upflow and downflow operation. In some instances, however, the use of reaction chambers involves the tendency of the oil to overcrack in the vapor phase, thus producing a larger amount of gasoline which must be separated and recycled. In order to maximize production of the desired gas oil hydrocracker feed, it is preferred to use a soaking coil either in the main furnace or in a secondary furnace so that polymerization reactions in the liquid phase predominate rather than the cracking reactions in the vapor phase which would occur in reaction chambers. A more preferred operation is the use of a visbreaker coil supplemented by a soaking coil, either in the same or a separate furnace, to provide a longer residence time in the visbreaking zone during which increased alkylation and polymerization may take place. When a soaking coil is used, it is generally necessary to quench the outlet of the furnace to a temperature below 775° F. to arrest any cracking reactions that might be occurring and to prevent deposition of the coke in the bottom of the fractionator in which the visbroken materials are separated. The quenching material may be naphtha produced during visbreaking, a visbroken gas oil, or cooled stripped or unstripped tar. Other materials which might be used will readily be suggested to one skilled in the art; and all these equivalents are meant to be included within the scope and spirit of this invention, for the actual nature of the quenching material is not critical to the process of this invention.

Several examples will serve to illustrate the process of this invention:

Example 1

A feed of 100,000 b.p.o.d. of 21.5° API California crude oil is distilled in a conventional fractionation unit into 5,000 b.p.o.d. C_5–200° F. straight-run gasoline which is sent to gasoline blending; 10,700 b.p.o.d. of 200°–375° F. heavy naphtha which is sent to catalytic reforming; 22,300 b.p.o.d. of 375°–650° F. light gas oil which is sent to hydrocracking; 31,500 b.p.o.d. of 650°–1,000° F. heavy gas oil which is sent to separate hydrocracking; and 30,500 b.p.o.d. of 1,000° F.+5.2° API residuum which contains 455 p.p.m. of iron, nickel and vanadium. This residuum is contacted in a deasphaltening zone with normal pentane to produce 24,400 b.p.o.d. of an 8.7° API maltene fraction and 6,100 b.p.o.d. of a −7.2° API asphaltene fraction. The maltene fraction contains 188 p.p.m. metals, and the asphaltene fraction contains 1,402 p.p.m. metals. The maltene fraction is HF treated and separated into 19,520 b.p.o.d. of a 10.5° API light maltene stream containing 0.75 weight percent sulfur, 0.6 weight percent nitrogen and 8 p.p.m. metals, and 4,880 b.p.o.d. of a 1.9° API heavy maltene fraction containing 9.2 weight percent sulfur, 2.76 weight percent nitrogen and 871 p.p.m. metals. The 6,100 b.p.o.d. of deasphaltener asphalt and the 4,880 of HF treated heavy maltenes are combined with 500 b.p.o.d. of C_5–225° F. catalytically cracked light olefinic naphtha obtained from the catalytic cracking of California crude oil and 550 b.p.o.d. of recycled visbroken olefinic naphtha and are passed into the visbreaker along with one weight percent water. The visbreaker outlet temperature is 878° F., and the outlet pressure is 270 p.s.i.g. The product distribution from the visbreaker is 6.7 weight percent C_4— material, no net production of C_5–350° F. material, 45 volume percent of 350°–1,000° F. gas oil and the remainder 1,000° F.+ material. Overall conversion to 1,000° F.— material is 55 volume percent.

Example 2

In this examle, the feeds and products to crude fractionation, deasphaltening, and HF treating are the same as in Example 1. In this example, however, the asphaltenes and heavy HF-treated maltenes are not combined with any external olefinic gasoline but are combined only with 545 b.p.o.d. of recycled visbroken olefinic naphtha and one weight percent water. The visbreaker outlet temperature is 875° F. and the outlet pressure is 250 p.s.i.g. Product distribution is 5.2 weight percent C_4— material, 0.5 volume percent C_5–350° F. naphtha, 41.8 volume percent of 350–1,000° F. gas oil, and the remainder 1,000° F.+ material. Total conversion to 1,000° F.— material is 50 volume percent.

Example 3

Here again, the feed and products of the crude fractionation unit, deasphaltening zone, and HF treating zone are the same as in Example 1. The asphaltenes and HF-treated heavy maltenes are combined with 550 b.p.o.d. of recycled visbroken olefinic naphtha and 500 b.p.o.d. of C_5–400° F. olefinic naphtha from the thermal reforming of an SO_2 extracted material obtained from treated 320°–500° F. kerosene distillates from a California crude oil. Aromatic content of the reformed naphtha is 45 per-

cent, and the sulfur content of the naphtha is 2 weight percent. Visbreaker outlet temperature is 870° F., and outlet pressure is 285 p.s.i.g. Water in the amount of one weight percent of feed is again injected. Product distribution is 8 weight percent C_4— material, 5 volume percent C_5–350° F. material, 48.8 volume percent 350°–1,000° F. gas oil and the remainder 1,000° F. residuum. Total conversion to 1,000° F.— material is 54 volume percent.

The above examples and specific operating conditions and flow systems are given for illustrative purposes only. It is apparent that many widely different embodiments of this invention may be made without departing from the scope and spirit thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A process for the conversion of an asphaltene- and metals-containing hydrocarbon oil to products boiling above 250° F., which comprises:

(a) contacting said oil in a deasphaltening zone with a light paraffinic solvent and forming a raffinate phase rich in metals and asphaltenes, and an extract phase lean in asphaltenes and metals;

(b) withdrawing said phase separately from said deasphaltening zone;

(c) contacting said extract phase with HF in a contacting zone, and thereafter separating the effluent of said contacting zone into a lighter portion and a heavier portion, said heavier portion comprising metals, polynuclear aromatics, and the bulk of said HF;

(d) combining at least a portion of said heavier portion with said raffinate phase; and

(e) visbreaking in a visbreaking zone the combined materials of (d) in the presence of added olefinic gasoline to produce products boiling above 250° F.

2. The process of claim 1 wherein at least a portion of the effluent of said visbreaking zone is passed into a vacuum pitch stripping zone wherein it is converted into a light stripped phase and a heavy stripped phase, the latter containing metals.

3. The process of claim 2 wherein at least a portion of said heavy stripped phase is converted to hydrogen in a partial oxidation zone and said metals are recovered.

4. The process of claim 1 wherein sulfur is present in said hydrocarbon oil and is recovered as a reaction product of the process.

5. The process of claim 1 wherein there is a net negative production of olefinic gasoline.

6. The process of claim 1 wherein in said contacting zone said extract phase is contacted with HF in the form of anhydrous hydrogen fluoride.

7. The process of claim 1 wherein said visbreaking zone comprises a visbreaking coil and a soaking coil.

8. The process of claim 7 wherein the effluent of said visbreaking zone is quenched to a temperature below 775° F.

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