The invention relates to a method of conversion of heavy oil feedstock with 5 wt. % boiling less than 343°C and at least 40 wt. % of molecules boiling above 540°C, comprising:

a first deasphalting with a heavy solvent constituted essentially of a saturated hydrocarbon having at least 5 carbon atoms,

a second deasphalting on the unprecipitated fraction obtained from the first deasphalting (called first unprecipitated fraction), with a light solvent constituted essentially of a saturated hydrocarbon having 3 or 4 carbon atoms,

the second unprecipitated fraction obtained from the 2nd deasphalting is converted by catalytic cracking to products boiling below 343°C,

the precipitated fractions are mixed together and treated by hydroconversion to products boiling above 540°C, the hydroconversion being carried out in a fluidized bed or in a slurry

at least one portion of the aromatic cuts boiling above 220°C obtained in the catalytic cracking is added to at least one of the precipitated fractions before the hydroconversion.
Figure 1:
Figure 2:
Figure 3:

**Chemical Reaction Process Diagram**

- **DAT** (1)
- **DSV** (2)
- **SDA C3** (18)
- **FCC** (22)
- **HDC** (5)

Reactions and Products:
- **H2S, NH3, C1-C2** (25)
- **C3-C4** (24)
- **C5-220°C** (23)
- **Coke** (22)
- **H2S, NH3, C1-C2** (29)
- **C3-C4** (30)
- **H2** (28)
- **C5-220°C** (31)
- **220-343°C** (32)
- **343-540°C** (33)
- **540°C+** (34)

Temperature Ranges:
- **22°C** (19)
- **220°C** (16)

Flow Paths:
- (1) DAT to DSV
- (2) DSV to SDA C3
- (4) SDA C3 to FCC (220°C)
- (5) FCC to C3-C4 (24)
- (11) DAT to SDA C3
- (12) DSV to SDA C3
- (14) SDA C3 to HDC
- (15) HDC to SDA C3
- (16) FCC to Coke
- (17) SDA C3 to HDC
- (18) FCC to C3-C4
- (19) SDA C3 to 220°C
- (20) C3-C4 to HDC
- (21) H2S, NH3, C1-C2 to HDC
- (22) Coke from FCC
- (23) C5-220°C from FCC
- (24) C3-C4 from FCC
- (25) H2S, NH3, C1-C2 from HDC
- (26) DSV to DAT
- (27) HDC to SDA C3
- (28) H2 to HDC
- (29) H2S, NH3, C1-C2 from HDC
- (30) C3-C4 from HDC
- (31) C5-220°C from HDC
- (32) 220-343°C from HDC
- (33) 343-540°C from HDC
- (34) 540°C+ from HDC
Figure 4:
METHOD OF CONVERSION OF RESIDUES COMPRISING 2 DEASPHALTINGS IN SERIES

[0001] The invention relates to the treatment of petroleum residues, resulting for example from the atmospheric distillation of a petroleum fraction. More precisely, it relates to hydrocarbon feedstock obtained from petroleum and having a boiling curve such that less than 10 wt. % of the fraction is distilled at a temperature of 343° C. in ambient conditions.

[0002] Petroleum residues are characterized by a molecular continuum that is difficult to characterize in detail. For characterization of the residues, usually the molecules are placed in groups defined by their affinity for solvents of increasing polarity (Jewell D. M., Albaugh E. W., Davis B. E., and Ruberto R G, "Integration of chromatographic and spectroscopic techniques for the characterization of residual oils", Ind. Eng. Chem. Fundam., 13, 3, 1974). Thus, the "Saturates" fraction, the "Aromatics" fraction, the "Resins" fraction and the "Asphaltenes" fraction are defined. These fractions can be measured using techniques of liquid chromatography.

[0003] The various fractions contained in the residues have widely varying properties associated with their chemical structure:

[0004] The "Saturates" fraction is characterized by structures with a high hydrogen content owing to the absence of aromatic rings.

[0005] The "Aromatics" fraction

[0006] The "Resins" fraction

[0007] The "Asphaltenes" fraction is characterized by molecules containing a large number of aromatic rings, most often combined in poly cyclic structures.

[0008] The petroleum residues contain heteroatoms. Thus, large amounts of sulphur-containing compounds are found to be present (the S content is typically from 0.5 to 5%), nitrogen-containing compounds (typically, the nitrogen content varies from 0.05 to 1%), metals (Ni, V, possibly Fe etc.). These heteroatoms are not distributed uniformly in all the fractions. Thus, metals are found essentially in the "Asphaltenes" fraction and a small amount in the "Resins" fraction. However, they are absent from the "Saturates" and "Aromatics" fractions. The nitrogen concentration is higher in the "Asphaltenes" and "Resins" fractions than in the "Saturates" and "Aromatics" fractions. Finally, sulphur is distributed fairly uniformly in all the fractions.

[0009] Upgrading of the petroleum residues is relatively difficult. In fact, there is a particular demand for fuel oils, distilling at atmospheric pressure at a temperature below 320-360° C. Crudes are characterized by variable contents of atmospheric residues depending on the origin of the crudes being processed. Said content varies in the range 20-50% typically for conventional crudes, but can reach 50 to 80% for heavy and extra heavy crudes such as those produced in Venezuela or in the Athabaska region in the north of Canada. It is therefore necessary to convert these residues, by breaking the heavy molecules in the residues to produce smaller molecules by cracking.

[0010] The invention relates to a method of conversion of residues comprising at least four stages: a deasphalting of the residue in the presence of a heavy solvent (C5-C7), a second deasphalting in the presence of a light solvent (C3-C4), catalytic cracking of the fractions of the residue dissolved by the solvents in the two successive stages of deasphalting, and hydroconversion of the fractions of the residue that were not dissolved in the two successive stages of deasphalting.

[0011] Methods of conversion of residues comprising a single deasphalting, fluidized-bed hydroconversion of the asphaltenes, and hydrotreating of the deasphalted oil are known, for example from application WO-04/74408.

[0012] The use of 2 successive deasphaltings is described in application EP-246,956 relating to a method for producing an oil phase suitable for use as feed for catalytic cracking.

[0013] In this method, the heavy feedstock undergoes 2 successive deasphaltings, with mixtures of solvents that are preferably identical, one being a C3 hydrocarbon and the other a hydrocarbon with at least 5 carbon atoms. Preferably the solvents used are identical for the 2 deasphaltings, with variable proportions. The 1st deasphalting is carried out with a heavy mixture of solvents to precipitate the asphaltenes and the 2nd with a light mixture of solvents to precipitate the resins. The deasphalted and deresined fraction is sent to catalytic cracking, the asphaltenes are not upgraded (used as solid fuel).

[0014] In application FR-2,007,587 relating to a method of hydrodesulphurization, the aim is physical separation of the asphaltenes with high sulphur content and the complete extraction of the resins from the feed that is to be desulfurized, as these resins are considered to be troublesome compounds for the hydrodesulphurization reaction. To this end, successive deasphaltings are performed, the first with a C5-C10 heavy solvent, followed by a second with a light solvent with less than 5 carbon atoms, which is preferably gaseous ethane. The asphaltenes are separated in the first deasphalting, and the resins in the second. The resins that are separated are mixed back in the desulfurized feedstock.

[0015] The aim of the present invention is to maximize the conversion of the residues in their entirety, i.e. also including the asphaltenes, the resins, the aromatics, and the saturated hydrocarbons, to produce light fractions and to upgrade the heavy fraction boiling above 540° C.

[0016] In general, the crude undergoes atmospheric distillation, the residue is submitted to vacuum distillation and the vacuum residue constitutes the feed for the first deasphalting. No treatment, for example hydrogenation, is carried out before the deasphalting.

[0017] More precisely, the present invention relates to a method of conversion of heavy oil feedstock with 5 wt. % boiling at least 343° C. and at least 40 wt. % of molecules boiling above 540° C., comprising:

[0018] a first deasphalting with a heavy solvent constituted essentially of a saturated hydrocarbon having at least 5 carbon atoms,

[0019] a second deasphalting on the unprecipitated fraction obtained from the first deasphalting (called first unprecipitated fraction), with a light solvent constituted essentially of a saturated hydrocarbon having 3 or 4 carbon atoms,

[0020] the second unprecipitated fraction obtained from the 2nd deasphalting is converted by catalytic cracking to products boiling above 343° C.,

[0021] the precipitated fractions are mixed together and treated by hydroconversion to products boiling above 540° C., the hydroconversion being carried out in a fluidized bed or in a slurry.
at least one portion of the aromatic cuts boiling above 220° C. obtained in the catalytic cracking is added to at least one of the precipitated fractions before the hydroconversion.

With catalytic cracking (FCC), fractions boiling below 360° C., or below 340° C., are obtained (gasoline, LCO) at advantageous operating costs. In the method according to the invention, only the portions of the feed that are more difficult to treat are to be converted in the hydroconversion process (in a fluidized bed of slurry) to fractions boiling below 540° C. (distillates), the hydroconversion process being more expensive than FCC.

With the combination of double deasphalting, FCC and fluidized-bed or slurry hydroconversion with recycling of the aromatic cuts from FCC, a method was obtained for overall upgrading of the residues at lower cost than previously while maintaining good product characteristics, and increasing the yields of converted products.

Relative to the prior art, the costs of hydroconversion have thus been reduced considerably, and the stages of deasphalting have been greatly simplified.

The aim of the invention is therefore to propose a flow sheet in which the conversion is optimized by separating the residue beforehand into different fractions, said different fractions then being converted by the methods that are the most suitable. This results in a substantial gain in performance, the conversion being maximized and the yields and qualities of products in light fractions being improved.

By carrying out two successive stages of deasphalting, by liquid-liquid extraction in the presence of a solvent, it is possible to separate the various fractions of the residue so as to obtain on the one hand a fraction DARO, containing most of the “Saturates” and “Aromatics” fractions, rich in hydrogen, with low metal content, less nitrogen and low content of coke precursors (asphaltenes), and the polyaromatic structures contained in the molecules are essentially constituted of 2 and 3 aromatic rings, and on the other hand a fraction ASRES, containing most of the “Resins and Asphaltenes” fractions, with high content of metals, nitrogen and coke precursors (asphaltenes) and low hydrogen content, and containing polyaromatic structures often containing more than 3 or 4 polyaromatic rings. The fraction DARO is a fraction that can be converted advantageously by catalytic cracking (FCC). The fraction ASRES is a fraction that can only be converted in harsh conditions, and only hydroconversion can perform this operation efficiently.

Successive deasphalting in two stages, the first being carried out by contacting with a heavy solvent (preferably C5-C7) and the second with a light solvent (preferably C3-C4), makes it possible to maximize the yield of fraction DARO rich in hydrogen (greater than or equal to 11 wt. %, preferably 11.5 wt. %), and with low content of metals (<40 ppm and preferably ~5 ppm) and of coke precursors (asphaltenes less than or equal to 1 wt. %, preferably <0.5 wt. %).

Initial removal of the “Asphaltenes” by contacting with the heavy solvent (C5-C7) then permits much more effective and selective separation between the “Resins” and the “Saturates” and “Aromatics” fractions. This results in a much higher yield of fraction DARO, with content of metals and asphaltenes similar to that obtained in a single stage of deasphalting with a light solvent.

Preferably, the solvent in the first deasphalting is an n-paraffin having from 5 to 7 carbon atoms and the solvent in the second deasphalting is an n-paraffin having at least 3 or 4 carbon atoms.

Preferably the solvent in the first deasphalting is n-pentane and the solvent in the second deasphalting is propane or n-butane.

The deasphaltinings are carried out in the range 30-40 bar (3-4 MPa). The temperatures are generally between 45 and 130° C. for C3 and C4 solvents, more precisely preferably between 45 and 90° C. for a C5 solvent and between 80 and 130° C. for a C4 solvent, and generally the temperatures are between 140 and 250° C. for C5 to C7 solvents and more precisely preferably between 140 and 210° C. for a C5 solvent and between 150 and 250° C. for a C6 or C7 solvent. The ratio of solvent to deasphalting feedstock is generally between 5 and 10 for the C3 and C4 solvents, and more precisely preferably between 6 and 10 for a C3 solvent and between 5 and 8 for a C4 solvent, and generally the ratio is between 3 and 6 for C5 to C7 solvents. The number of theoretical stages is generally at least 2 for the C3 and C4 solvents, and more precisely preferably at least 3 for a C3 solvent and between 2 and 3 for a C4 solvent, and generally between 1 and 2 for C5 to C7 solvents.

Different methods of cracking of heavy fractions can be envisaged depending on the operator’s needs:

Visbreaking permits thermal cracking of the residues. The conversion of the residue to lighter fractions is however limited by the problem of the stability of the residual fuel oils associated with the problem of the stability of the unconverted asphaltenes.

Coking permits thermal cracking of the residues at high conversion, but generates a high coke yield, directly proportional to the amount of asphaltenes present in the residues, which are coke precursors. This results in limited upgrading, since the coke yield can reach 20-30 wt. % on feeds containing 10 to 20% of asphaltenes.

Fluidized-bed catalytic cracking (FCC) enables the residues to be converted by acid catalysis at high temperature (typically 500-600° C). The feeds supplied to FCC must contain sufficient hydrogen to produce high yields of light fractions. The aromatics are not hydrogenated in this process. The feed must have a limited nitrogen content in view of the acidity of the catalyst. The metals content must also be limited (typically Ni and V less than 20 ppm) as the metals are deposited on the catalyst, which is added continuously. Finally, the content of coke precursor asphaltenes must be low, in order to restrict the yield of coke produced, on which the technologies for catalyst regeneration will depend.

Fixed-bed hydrocracking employs acid catalysis in the presence of hydrogen. This permits conversion of distillates containing little if any asphaltenes (typically ~1000 ppm) and little if any metals, as the catalyst is not added continuously. The presence of nitrogen necessitates a pretreatment before acid catalysis to prevent deactivation of the catalyst.

Fluidized-bed or slurry hydroconversion of the residues permits cracking at high temperature (400-480° C) and at high hydrogen partial pressure (typically 50-150 bar) of residues in the presence of a metallic catalyst promoting hydrogenation of the cracked molecules. Continuous addition of catalyst makes it possible to maintain catalyst activity...
despite the presence of metals. This method is suitable for the conversion of very heavy feedstock with high metal contents (typically 100-800 ppm), low hydrogen content and high contents of asphaltenes, the latter being converted by cracking and hydrogenation. This method requires long residence times. The capital expenditure associated with such a method is therefore high.

[0039] It can thus be seen that the performance of the various methods of conversion is closely linked to the nature of the feed being processed.

[0040] According to the invention, FCC and fluidized-bed or slurry hydroconversion are employed so as to optimize the economics of the method.

[0041] FCC produces a gasoline with a good octane number (Research Octane Number between 85 and 95 and Motor Octane Number between 75 and 85). In contrast, the gas oil and the unconverted fractions are very aromatic (typically containing polycyclic aromatic structures with 2, 3 or 4 aromatic rings). The cetane number of the gas oil is not very good, generally between 15 and 30. These fractions additionally contain large amounts of sulphur. The fractions heavier than gasoline can therefore be used advantageously as fluxes of the ASRES feedstock obtained from the two stages of desphalting. In fact, the aromatic cuts will make it possible to stabilize the asphaltenes and the resins in the reaction mixture, preventing flocculation of the latter before conversion and in the process effluents. These fractions will in addition be desulphurized and partially converted to gas oil and to gasoline. The gas oil from hydroconversion has a better cetane number than that from FCC, generally between 35 and 45. The octane number of the gasoline is not so good, however. Thus, the research octane number or motor octane number is generally close to 50. The invention makes it possible to maximize the gasoline fractions produced by FCC and the gas oil fractions produced by hydroconversion. Therefore not only the conversion of the residue, but also the quality of the products formed, are maximized.

BRIEF DESCRIPTION OF DRAWINGS
Figures

[0042] FIG. 1: method according to the invention
[0043] FIG. 2: method of the prior art in Example 2 route 1
[0044] FIG. 3: method with single desphalting in Example 2 route 2
[0045] FIG. 4: method according to the invention, Example 2 route 3
[0046] FIG. 1 describes an example of application of the method of conversion of residues according to the present invention.

[0047] A petroleum feedstock (crude) (10) is distilled in atmospheric conditions and produces a substantial amount of a fraction (26) of atmospheric residue or ATR. Fraction (26) is defined as the feed of the process according to the present invention. Generally it contains less than 10% of molecules distilling at 343°C in these conditions and at least 40 wt. % boils above 540°C.

[0048] According to a preferred embodiment of the invention, this feedstock is distilled under vacuum in a column (2), collecting a vacuum distillate (11), called VAD and a vacuum residue (12) called VAR. Fractions VAD and VAR are separated at a temperature varying, depending on the crudes, in a temperature range generally from 480 to 565°C. The VAD fraction contains little or no metals Ni and V (<2 ppm) and the asphaltenes content of the feedstock is less than or equal to 1% and most often 0.5 wt. %. Its hydrogen content is greater than or equal to 11 wt. %, and most often 11.5%. The VAR fraction contains most of the asphaltenes and metals contained in the feedstock (10). Generally, the metals content (Ni+V) generally varies from 100 to 800 ppm, and the asphaltenes content varies from 2 to 25 wt. % depending on the feed being processed. This fraction is of high viscosity (between 50 and 2000 cSt at 150°C, typically 400 cSt).

[0049] The VAR (12) is then sent to the first stage of desphalting (3), in which the residue is contacted with a heavy solvent essentially constituted of saturated hydrocarbon molecules containing from 5 to 7 carbon atoms, preferably of n-pentane, n-hexane or n-heptane. After contact, two phases form: one constituted of the portions of the residual insoluble in the solvent is called the ASPHALT fraction (14); the other is constituted of the solvent and the soluble portions of the residue. The solvent is separated by distillation of the soluble portions and recycled within the desphalting process (3). A soluble fraction (13) is obtained, called DAO fraction phase for “Desphalted Oil” fraction. This fraction (13) is then sent to the second stage of desphalting (4), in which the residue is contacted with a light solvent, essentially constituted of saturated hydrocarbon molecules containing from 3 to 4 carbon atoms, preferably of n-propane or n-butane. After contact, two phases form: one constituted of the portions of the residue that are insoluble in the light solvent is called the RESIN fraction (17); the other is constituted of the solvent and of the soluble portions of the residue. The solvent is separated by distillation of the soluble portions and recycled within the desphalting process (4). The solvent-free soluble fraction (16) is called the DARO fraction phase for “DeAsphaltedResinsOil” cut.

[0050] The DARO fraction (16) contains small amounts of metals (Ni+V<35 ppm) and of asphaltenes (<0.5 wt. %) which can vary depending on the solvent used. In a preferred embodiment of the invention and according to FIG. 1, it is mixed with all of fraction (11) obtained from vacuum distillation (2) to produce the feed (18) of the fluidized-bed catalytic cracking (FCC) process (5). In this mixture, the metals content is less than 20 ppm, preferably less than 5 ppm, the asphaltenes content is less than 0.4 wt. %, preferably 0.2 wt. % and the hydrogen content is greater than 11 wt. %, preferably 11.5 wt. %. The characteristics of this feed are favourable for catalytic cracking.

[0051] It would also be possible for only the DARO to be treated by FCC, with the VAD fraction being treated by another process; according to another variant, the VAD is treated partly by FCC mixed with the DARO, the other portions being treated in a similar way.

[0052] It is then possible to produce effluents containing a significant proportion of gasoline (23) C5 - C220°C C. (+20 wt. % of the feed, preferably from 30 to 60%, typically from 30 to 45%), a high proportion of gas oil 220-343°C (19) (generally between 10 and 30%), a fraction 343+-373°C (19) (often between 10 and 30% of the feed), gases (25) (mainly H2, H2S, NH3, C1, C2, typically representing from 2 to 5 wt. % of the feed), and C3-C4 (24) (typically representing from 5 to 15 wt. % of the feed). The cut points of the different effluents given here are purely indicative, they are selected by the operator in the distillation ranges known by a person skilled in the art for the type of fraction.

[0053] The catalytic cracking is carried out in a reaction zone containing a reaction chamber and a catalyst regenera-
tion chamber, between which the catalyst circulates continuously. The feed (18) is vaporized on contact with the hot regenerated catalyst and reacts with the catalyst in the reactor. The temperature at the end of reaction is typically between 500 and 600°C, preferably 520-540°C, the ratio of the flow rate of catalyst to the flow rate of feed being between 4 and 15, preferably between 5 and 8. The reaction products are then separated by distillation downstream from the reactor. The catalyst is regenerated by combustion with air to remove the coke deposited during the reaction and reheat the catalyst. All the coke produced by cracking (22) is therefore consumed by combustion during regeneration. The catalyst used for carrying out the cracking reaction is a catalyst based on silica alumina containing for example crystals of ultra-stable zeolite Y (USY) at a level of 10-40 wt. %. The catalyst is finely divided to facilitate its circulation. Typically, the average diameter of the particles is between 50 and 100 microns. The metals accumulate on the catalyst over time, and catalyst is added continuously in the process to keep the metals content limited to about 2000-15000 ppm on the catalyst, preferably 5000-10000 ppm. The pressure at which cracking is carried out is generally less than 5 bar.

[0054] The liquid fractions heavier than gasoline (19) (for example the fraction 220° C.+, this cut point being given purely indicatively), can be used partially or entirely, for fluxing (line 20 in FIG. 1) the fractions ASPHALT (14) and RESIN (17) produced in the two successive stages of deasphalting (3) and (4).

[0055] At least 50 wt. %, and preferably the whole, of the aromatic cuts boiling above 220° C. obtained in catalytic cracking is added to at least one of the precipitated fractions prior to hydroconversion. In this way desulfurization is maximized and the quality of these aromatic cuts is improved.

[0056] The feed (15) thus constituted is treated in a process of hydroconversion of the residues (6), permitting the production of a fraction (29) rich in gases (H2S, NH3, C1, C2), a fraction C3-C4 (30), a gasoline fraction C5-220 (31), a gas oil fraction (32) (220-343° C.), a distillate fraction (33) (343-540° C.), and a residue fraction (34) 540° C. + (the distribution between the fractions and the different cut points of the various effluents are given here purely indicatively).

[0057] Depending on the feedstock and the operating conditions, the yield of gasoline can vary between 5 and 20 wt. % of the feed, the yield of gas oil can vary between 15 and 25 wt. % of the feed, the yield of distillates between 30 and 50 wt. % of the feed and the yield of residue from 5 to 50 wt. % of the feed.

[0058] Hydroconversion of the residues (6) is carried out in an assembly of one or more successive reactors, in conditions of high pressure (100 to 500 bar, preferably 150 to 250 bar), with a hydrogen partial pressure greater than 50 bar, preferably between 100 and 200 bar. Therefore hydrogen (28) is added continuously in the process, with the hydrogen consumption representing from 1 to 4 wt. % of the feed depending on the operating conditions. This hydrogen can be obtained for example from natural gas reforming or from the gasification of coke or of residue. The feed is introduced as a liquid into the reactors and is submitted to cracking at a temperature generally between 400 and 500° C., for a time between 1 and 10 h. Several types of application of hydroconversion are possible. If the catalyst is dispersed, the catalyst can then be injected continuously in the feed upstream of the reactor and can be recovered from the effluents. In this case, the catalyst can be a liquid containing at least molybdenum (for example molybdenum naphthenate or octoate, phosphomolybdic acid) precipitating as sulfides in the reactor, or a finely-divided solid (molybdenum deposition on alumina for example) the average particle size being less than 500 microns. The catalyst is then injected in such a way that the molybdenum concentration is greater than 50 ppm in the feed.

[0059] If the catalyst is supported, it is generally formed by extrusion, the diameter of the extrudates generally being greater than 0.75 mm. In these conditions, the catalyst forms a fluidized bed in the reactors and is not entrained in the effluents. It generally contains at least 5 wt. % of molybdenum supported on alumina of very low acidity. In these conditions, the catalyst is progressively laden with metals Ni, V originating from the feed. It is then necessary to add fresh catalyst continuously and withdraw used catalyst from the fluidized bed to compensate for the deactivation and maintain catalytic activity. The content of metals derived from the feed (15) deposited on the catalyst can then reach between 10 and 150 wt. % of the catalyst depending on the conditions, the feedstock and the catalysts used.

[0060] The invention described in FIG. 1 includes a vacuum distillation column (2). It is also possible not to use vacuum distillation. In these conditions, the residue (26) supplies the first stage of deasphalting (3) directly and FCC (5) is supplied with a fraction originating essentially from the second stage of deasphalting.

[0061] It is also possible for the distillate (11) produced in vacuum distillation (2) and the DARO fraction (16) obtained from the second stage of deasphalting to be treated separately, in two different catalytic cracking processes, or only treat fraction (16) in the FCC catalytic cracking process (5), the distillate then being upgraded differently, for example in a hydrocracking process.

**EXAMPLE 1**

[0062] The first example intended to illustrate the advantage of using two successive stages of deasphalting first with a heavy solvent (C5-C7) and then a light solvent (C3-C4).

[0063] The feed chosen for illustrating this example is a vacuum residue obtained from a bitumen produced in the Athabaska region in the north of Canada.

[0064] This vacuum residue was submitted to a first deasphalting with n-heptane at a temperature of 220/230° C., the solvent/residue ratio being 8/1; the operating conditions of deasphalting are well known by a person skilled in the art.

[0065] The fraction DAO underwent a second deasphalting. In the course of this second deasphalting, the role of the solvent was investigated.

[0066] Deasphalting of the DAO with n-butane was carried out with a solvent/feed ratio of 12/1 at a temperature of 100° C./80° C./60° C.

[0067] Deasphalting with n-propane was carried out with a solvent/feed ratio of 12/1 at a temperature of 70° C./55° C./45° C.

[0068] Table 1 summarizes the results obtained. The properties of the feed, of the DAO C7 obtained, of the DARO C4 and of the DARO C3 are shown, as well as the yields of the various fractions.
The results in Table 1 clearly show that single deasphalting with C7 does not provide a DAO fraction of sufficient quality for it to be converted in FCC; the hydrogen content is too low, and the metals content and nitrogen content are too high.

If a second deasphalting is performed on the DAO, however, we see a notable improvement of the DARO fractions obtained from this second deasphalting: the metals content and nitrogen content decrease considerably, whereas the hydrogen content of the DARO fraction increases.

It can be seen that there is a notable drop in yield, since DARO C4 represents 45% of the starting residue, and DARO C3 only represents 34%. DARO C3 and C4 are therefore a priori potentially interesting feedstocks for FCC and are an important fraction of the residue. Double deasphalting, by selectively extracting the “Saturates” and “Aromatics” fractions, permits physical separation of the fractions, which can be converted by catalytic cracking.

We compared the results obtained by double deasphalting with those obtained by single deasphalting using the data of S. Ng et al. (Energy Fuels, Vol. 11, 1997), who present a study of deasphalting on a vacuum residue obtained from a similar bitumen, also produced in the Athabaska region in northern Canada. These data are presented in Table 2.

If we compare the results obtained by double deasphalting (Table 1) with those that would be obtained by a single deasphalting with propane (Table 2), it can be seen that the characteristics of the DAO C3 are very similar to those obtained in DARO C3, but the yield of DAO C3 is far lower (11% against 34% by double deasphalting).

A double deasphalting, coupling extraction with a heavy solvent with extraction with a light solvent, therefore makes it possible to obtain a fraction of similar quality to that obtained by single deasphalting with the same light solvent, but at a far higher yield.

EXAMPLE 2

We evaluated the performance of different conversion flowsheets described respectively in FIGS. 2, 3 and 4 for upgrading an atmospheric residue obtained from a bitumen produced in the Athabaska region of northern Canada, the properties of which are shown in Table 3 below. This atmospheric residue has an initial boiling point at 343°C, and contains 59 wt. % of molecules whose boiling point is above 540°C.

| TABLE 3 | Analysis and composition of the atmospheric residue |
|-----------------------------------------------|
| d4, 15 (—) | 0.99 |
| S (ppm) | 4.9 |
| Ni (ppm) | 81 |
| V (ppm) | 224 |
| N (ppm) | 0.51 |
| CCR (ppm) | 15.0 |
| Asphaltics C7 (% pds) | 10.0 |
| coupe 343-540° | 41% |
| coupe 540°+ | 59% |

We investigated the performance that would be obtained by three routes, the first two being known by a person skilled in the art, and the third being a characteristic feature of the invention claimed in this patent application:

route 1 (FIG. 2): fractionation of the residue to a VAD and a VAR. The VAD is sent to FCC. The VAR is sent to hydroconversion.

route 2 (FIG. 3): fractionation of the residue to a VAD and a VAR. The VAR undergoes a single deasphalting with n-propane, the DAO C3 is sent to FCC with the VAD, the asphalt and the liquid fraction 220°C produced in FCC are sent to hydroconversion of the residues.

route 3 (FIG. 4 invention): fractionation of the residue to a VAD and a VAR. The VAR undergoes a single deasphalting with n-heptane, then the DAO C7 undergoes a deasphalting with n-propane. The DARO C3 is sent to FCC with the VAD, the asphalt produced in deasphalting C7 and the resins produced in deasphalting C3 are mixed with the liquid fraction 220°C produced in FCC and are sent to hydroconversion of the residues.

In all cases, the vacuum distillation column operates in the same conditions. The composition of the VAD and that of the VAR remain unchanged, the cut point being approx. 480°C.

So as to be able to compare the different flowsheets, we operated the FCC and hydroconversion processes in similar conditions of severity:

The FCC operates in similar reaction conditions, with the same catalyst. The flow rate of catalyst relative to the flow rate of feed is approx. 7.5, and the temperature at outlet from the FCC riser is maintained at 538°C. FCC comprises a single regenerator operating by total combustion. The required regeneration temperature and preheat temperature vary from one case to another, with the result that the coke yields are different from one
route to another. These differences do not have a significant effect on the overall results of the study. [0083] Fluidized-bed hydroconversion operates in the following conditions: 2 identical reactors in series, flow rate of feed/reaction volume = 0.3 hr⁻¹, \( T = 426^\circ C \), PPH2 = 128 bar, \( P = 160 \) bar. The catalyst is an alumina-based supported catalyst, containing nickel and molybdenum. The type of catalyst, the mass of catalyst relative to reactor volume, and the additions of catalyst are identical in the three routes investigated. [0084] Table 4 shows the composition of the feed of the FCC process in the 3 routes investigated. It can be seen that the feed is heavier when DAO C3 is integrated with VAD (route 2), or DARO C3 with VAD (route 3), as shown by the CCR (Carbon ConRadson; ConRadson carbon value) of the fraction, which varies from 0.4 to 1.3. This will be reflected in an increase in production of coke, which is limited, however, and will mainly affect the thermal balance (temperature of regeneration and preheating in FCC). It can also be seen that the feed treated in FCC increases considerably on passing from route 1, to route 2 and then to route 3. The feed treated by FCC varies from 29.3% to 53.3% of the initial amount of atmospheric residue. However, the quality of the feed decreases somewhat, as shown by the densities, which change from 0.89 to 0.93, indicating that the feed becomes heavier.

<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of the FCC feed depending on the route selected</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>ndt (% RAT)</td>
</tr>
<tr>
<td>d4, 15 (ppm)</td>
</tr>
<tr>
<td>S (% pds)</td>
</tr>
<tr>
<td>Ni (ppm)</td>
</tr>
<tr>
<td>V (ppm)</td>
</tr>
<tr>
<td>N (% pds)</td>
</tr>
<tr>
<td>CCR (% pds)</td>
</tr>
<tr>
<td>Asphaltene C7 (% pds)</td>
</tr>
</tbody>
</table>

(voe = route)

[0085] Table 5 shows the composition of the feed of the hydroconversion process in the 3 routes investigated. The amount of feed to be treated is least with double deasphalting. The overall properties of the feed to be treated are very similar in the 3 routes, owing to introduction of the 220°C + fraction from FCC which fluxes the Asphalts or the Asphalts and the Resins, in increasing amounts as we pass from route 1 to route 2 and then to route 3.

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of the feed of the hydroconversion process depending on the route selected</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>ndt (% RAT)</td>
</tr>
<tr>
<td>d4, 15 (ppm)</td>
</tr>
<tr>
<td>S (% pds)</td>
</tr>
<tr>
<td>Ni (ppm)</td>
</tr>
<tr>
<td>V (ppm)</td>
</tr>
<tr>
<td>N (% pds)</td>
</tr>
<tr>
<td>CCR (% pds)</td>
</tr>
<tr>
<td>Asphaltene C7 (% pds)</td>
</tr>
</tbody>
</table>

(voe = route)

[0086] Table 6 describes the yields obtained in the 3 routes, relative to the amount of atmospheric residue treated. It shows the yields of H2S+NH3, of dry gases mainly containing H2, methane, ethane and ethylene, the C3-C4 fraction, the gasoline fraction C5-220°C, the gas oil fraction 220-343°C, the VAD fraction produced at 343-540°C, and the Residue fraction 540°C +. It also shows the coke yield (consumed in the FCC unit) relative to the amount of atmospheric residue treated and the consumption of hydrogen in the hydroconversion unit, once again relative to the amount of atmospheric residue. The sum of the yields (the hydrogen consumption obviously being counted as negative) is very close to 100%.

[0087] It can be seen that route 1 and route 2 give quite similar overall conversion performance. In fact, if we compare the amount of bases that can be upgraded (C3-C4+C5-220+220-343), route 1 produces 48% of these bases whereas route 2 produces 49%. Route 1 produces less C3-C4 fraction, less gasoline but more gas oil. The overall conversion can be estimated from the amount of residual fractions 343°C +. These values are close to 43%-45%. Note that the 540°C + fraction is greatly reduced as it now only represents 14%, against 59% in the starting feed.

[0088] Route 3, according to the present invention, makes it possible to increase the conversion of the residue. Thus, the production of C3-C4 fraction and of gasoline is increased, whereas the production of gas oil fraction remains similar to that obtained by route 2.

[0089] The quantity of bases that can be upgraded (fraction C3-C4+C5-220°C + fraction C5-220°C + fraction C3-343°C +) now represents 53%, or 4%-5% more than routes 1 or 2. The residual fraction 343°C + represents 37%, or 6%-8% less than routes 1 or 2 and the residual fraction of 540°C + drops to 11%, or 3% less than routes 1 or 2.

[0090] Route 3 therefore offers better conversion of the atmospheric residue than routes 1 and 2, producing larger amounts of gasoline. The gasolines produced are of higher quality, since the proportion of gasoline from FCC in route 3 is 63%, against 53-55% for routes 1 and 2, and the gasoline from FCC has a RON of 90 and a MON of 80 whereas that from hydroconversion is limited to 50 for RON and MON.

[0091] The same comment applies to fractions C3-C4, which are more olefinic when they are obtained from FCC and therefore more upgradeable.

[0092] The quality of the gas oil fraction produced by route 3 will be better than the quality of the gas oil fraction produced by route 1, with the whole of the gas oil fraction resulting from hydroconversion ending the gas oil with a higher cetane number than FCC (40 against 25).

[0093] Finally, it will be noted that the hydroconversion feed is lower in route 3, in similar operating conditions (Table 5). This means that the capital cost will be lower, as the unit can be dimensioned to be smaller. Conversely, FCC will be greater in route 3 (Table 4), but the capital expenditure associated with an FCC unit is far lower than the capital expenditure associated with a hydroconversion unit, and the overall capital cost associated with the three routes will therefore be at best similar or generally lower with route 3 than with the other two routes studied in this example.
<table>
<thead>
<tr>
<th>TABLE 6</th>
<th>Yield of products depending on the route selected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>voie 1</td>
</tr>
<tr>
<td>H₂S + NH₃ (% pds)</td>
<td>3.8</td>
</tr>
<tr>
<td>H₂, C₁, C₂ (% pds)</td>
<td>2.6</td>
</tr>
<tr>
<td>C₃-C₄ (% pds)</td>
<td>5.3</td>
</tr>
<tr>
<td>C₅-220 (% pds)</td>
<td>22.5</td>
</tr>
<tr>
<td>220-343 (% pds)</td>
<td>20.4</td>
</tr>
<tr>
<td>343-540 (% pds)</td>
<td>31.0</td>
</tr>
<tr>
<td>540°C+ (% pds)</td>
<td>14.3</td>
</tr>
<tr>
<td>coke FCC (% pda)</td>
<td>1.6</td>
</tr>
<tr>
<td>cenco H₂ (% pds)</td>
<td>-1.5</td>
</tr>
<tr>
<td>total (% pds)</td>
<td>100.0</td>
</tr>
</tbody>
</table>

*ex FCC* denotes obtained from FCC
(qualité des produits = product quality)
(voie = route)

**[0094]** Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting of the remainder of the disclosure in any way whatsoever.

**[0095]** In the foregoing and in the examples, all temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

**[0096]** The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

**[0097]** The entire disclosures of all applications, patents and publications, cited herein and of corresponding French application No. 06/11,401, filed Dec. 21, 2006 are incorporated by reference herein.

**[0098]** From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

1. Method of conversion of heavy oil feedstock with 5 wt. % boiling at least 343°C. and at least 40 wt. % of molecules boiling above 540°C., comprising:
   a first deasphalting with a heavy solvent constituted essentially of a saturated hydrocarbon having at least 5 carbon atoms,
   a second deasphalting on the unprecipitated fraction obtained from the first deasphalting (called first unprecipitated fraction), with a light solvent constituted essentially of a saturated hydrocarbon having 3 or 4 carbon atoms,
   the second unprecipitated fraction obtained from the 2nd deasphalting is converted by catalytic cracking to products boiling above 343°C.,
   the precipitated fractions are mixed together and treated by hydroconversion to products boiling above 540°C., the hydroconversion being carried out in a fluidized bed or in slurry
   at least one portion of the aromatic cuts boiling above 220°C. obtained in the catalytic cracking is added to at least one of the precipitated fractions before the hydroconversion.

2. Method according to claim 1 wherein the solvent in the first deasphalting is an n-paraffin having from 5 to 7 carbon atoms and the solvent in the second deasphalting is an n-paraffin having at least 3 or 4 carbon atoms.

3. Method according to claim 1 wherein the solvent in the first deasphalting is n-pentane and the solvent in the second deasphalting is propane or n-butane.

4. Method according to claim 1 wherein all of the aromatic cuts heavier than gasoline obtained in the catalytic cracking are added to at least one of the precipitated fractions before hydroconversion.

5. Method according to claim 1 wherein the feed is a vacuum residue obtained from atmospheric distillation of a petroleum crude, and a vacuum distillate is sent to catalytic cracking mixed with said second unprecipitated fraction.

6. Method according to claim 1 wherein the feed is a vacuum residue obtained from atmospheric distillation of a petroleum crude, and a vacuum distillate is sent to a catalytic cracking different from the catalytic cracking in which said second unprecipitated fraction is treated.

7. Method according to claim 1 wherein the feed is a vacuum residue obtained from atmospheric distillation of a petroleum crude, and a vacuum distillate is treated by hydrocracking.

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