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(54) PROCESS FOR THE CONVERSION OF HEAVY CHARGE STOCKS SUCH AS HEAVY CRUDE OILS AND DISTILLATION RESIDUES

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(57) ABSTRACT

Process for the conversion of heavy charge stocks selected from heavy and extra-heavy crude oils, distillation residues, heavy oils from catalytic treatment, thermal tars, bitumens from oil sands, carbons of different origins and other high boiling charges of a hydrocarbon origin known as "black oils", using at least the following process units: solvent deasphalting (SDA), hydroconversion with slurry phase catalysts (HT), distillation or flash (D), which process includes:

solvent deasphalting, thereby forming a deasphthalted oil (DAO), as described;

hydrotreating the DAO in the presence of a hydrogenation catalyst precursor and hydrogen or hydrogen and H_2S, as described;

sending the product therefrom to distillation or flash (D) step(s), and separating the most volatile fractions from the distillation residue (tar) or from the liquid coming from the flash unit, as described;

recycling at least a portion of the tar or the liquid, to the hydrotreating section, as described.

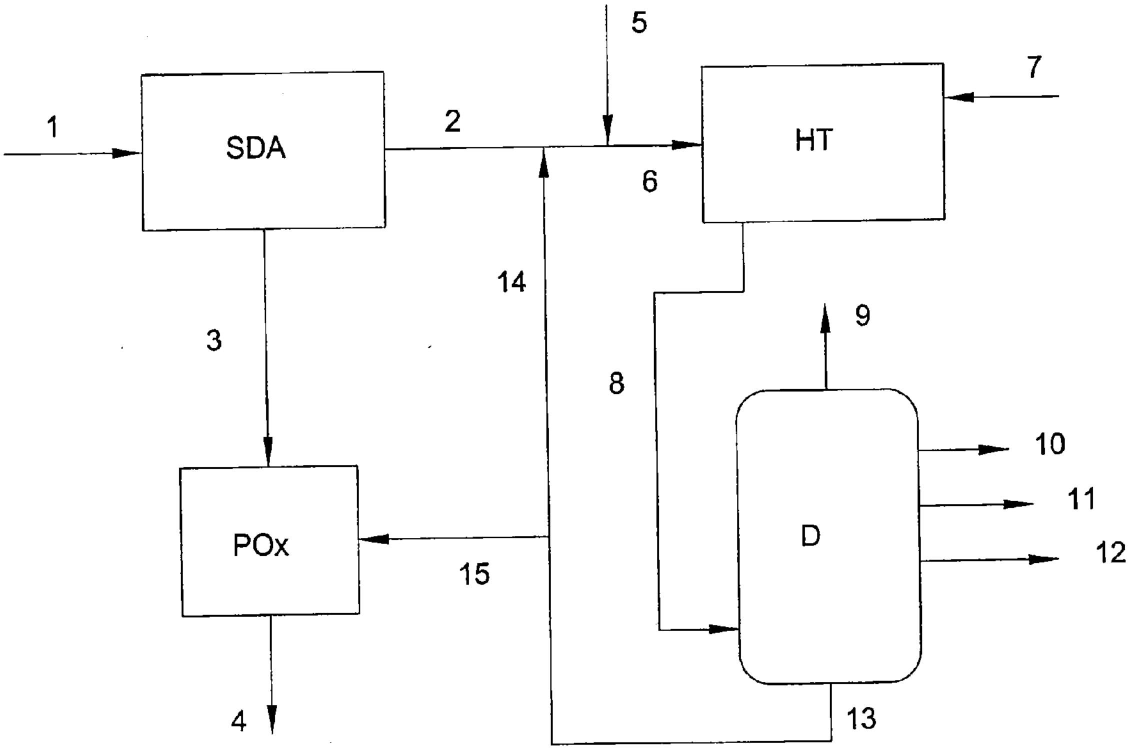
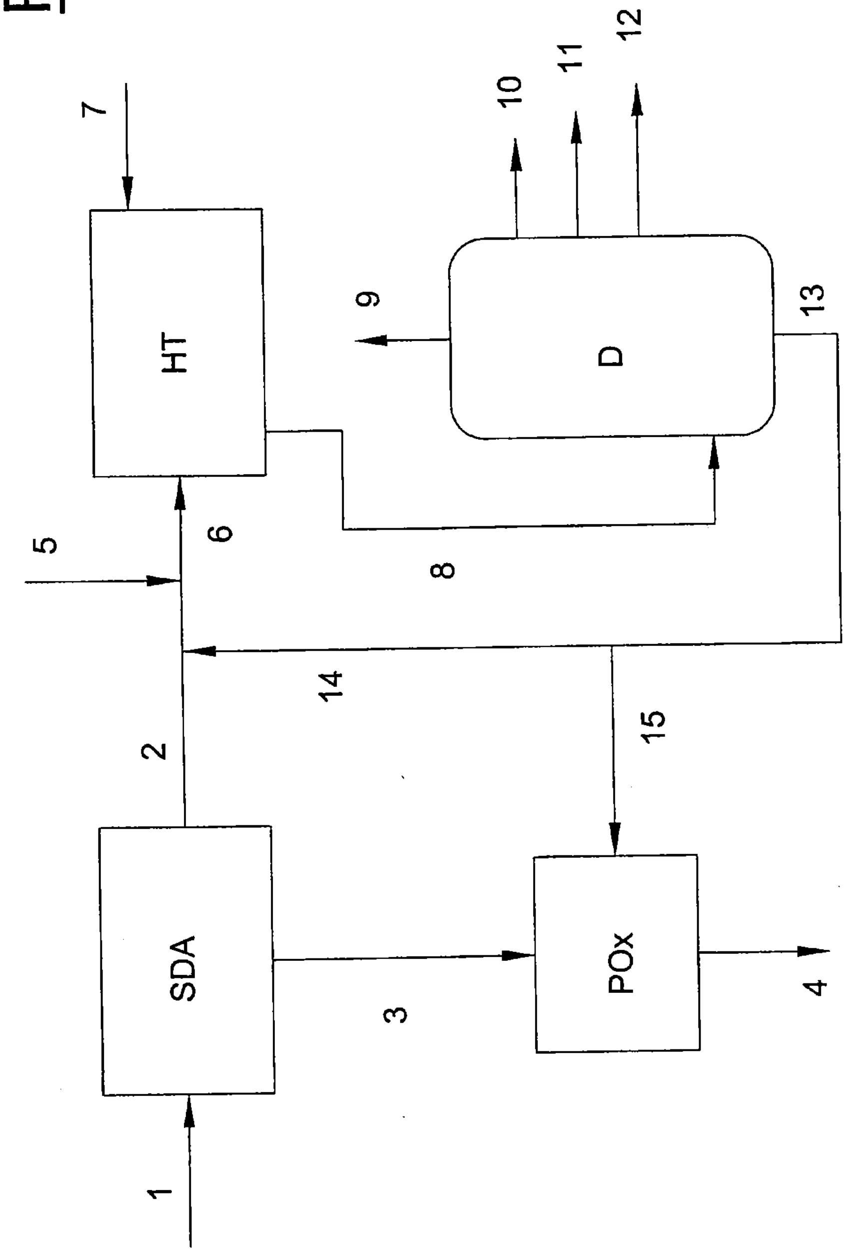


Fig. 1



PROCESS FOR THE CONVERSION OF HEAVY CHARGE STOCKS SUCH AS HEAVY CRUDE OILS AND DISTILLATION RESIDUES

[0001] This is a continuation application of U.S. application Ser. No. 13/278,244, filed Oct. 21, 2011, which is a continuation application of U.S. application Ser. No. 11/311,134, filed Dec. 20, 2005.

[0002] The present invention relates to a process for the conversion of heavy charge stocks, among which heavy crude oils, bitumens from oil sands and distillation residues, by means of at least three process units: deasphalting, hydroconversion of the charge stock using phase-dispersed catalysts and distillation.

[0003] The conversion of heavy crude oils, bitumens from oil sands and petroleum residues into liquid products can be substantially effected in two ways: an exclusively thermal one and the other by means of hydrogenating treatment.

[0004] Current studies are mainly directed towards hydrogenating treatment, as thermal processes create problems relating to the disposal of the by-products, such as, in particular, coke (obtained in amounts even higher than 30% by weight with respect to the charge stock) and to the poor quality of the conversion products.

[0005] Hydrogenating processes consist of treating the charge stock in the presence of hydrogen and suitable catalysts.

[0006] The hydroconversion technologies which are at present on the market, use fixed or ebullated bed reactors and make use of catalysts generally consisting of one or more transition metals (Mo, W, Ni, Co, etc. . . .) supported on silica/alumina (or equivalent material).

[0007] Fixed bed technologies have several problems in treating particularly heavy charge stocks, containing high percentages of hetero-atoms, metals and asphaltenes, as these contaminants lead to a fast deactivation of the catalyst.

[0008] Ebullated bed technologies have been developed and commercialized for treating these charge stocks, which give interesting performances but are complex and costly.

[0009] Hydrotreating technologies using dispersed phase catalysts can represent an interesting solution to the drawbacks of the fixed and ebullated bed technologies. Slurry processes, in fact, combine the advantage of a high flexibility on the charge stock with high performances in terms of conversion and upgrading, proving, at least in principle, to be simpler from a technological point of view.

[0010] Slurry technologies are characterized by the presence of catalyst particles having very small average dimensions and suitably dispersed in the medium: for this reason the hydrogenation processes are easier and immediate in all parts of the reactor. The formation of coke is considerably reduced and the upgrading of the charge stock is high.

[0011] The catalyst can be introduced as powder with sufficiently reduced dimensions (U.S. Pat. No. 4,303,634) or as an oil-soluble precursor (U.S. Pat. No. 5,288,681). In this latter case, the active form of the catalyst (generally the metal sulphide) is formed in situ by thermal decomposition of the compound used, during the reaction itself or after suitable pre-treatment (U.S. Pat. No. 4,470,295).

[0012] The metal components of the dispersed catalysts are normally one or more transition metals (preferably Mo, W, Ni, Co or Ru). Molybdenum and tungsten have much more satisfactory performances with respect to nickel, cobalt or ruthenium, and even more with respect to vanadium and iron (N. Panariti et al., Appl. Ctal. A: Gen. 2000, 204, 203).

[0013] Even if the use of dispersed catalysts solves most of the problems of the technologies described above, it has drawbacks mainly due to the catalyst life and to the quality of the products obtained.

[0014] The way these catalysts are used (type of precursors, concentrations, etc . . .) are extremely important both from an economical and environmental point of view.

[0015] The catalyst can be used at a low concentration (a few hundred ppm) in the "once-through" mode, but in this case the upgrading of the reaction products is generally unsatisfactory (N. Pnariti et al., Appl. Ctal. A: Gen., 2000, 204, 203 and 215). If very active catalysts are used (for example, molybdenum) and with higher catalyst concentrations (thousands of ppm of metal), the quality of the product obtained is certainly higher, but it is necessary to effect the recycling of the catalyst.

[0016] The catalyst at the reactor outlet can be recovered by separation of the product obtained from the hydrotreating (preferably from the bottom of the distillation column downstream of the reactor) through conventional methods such as, for example, decanting, centrifugation or filtration (U.S. Pat. No. 3,240,718; U.S. Pat. No. 4,762,812) which are, however, extremely complex if applied to heavy charge stocks rich in poisoning substances.

[0017] As far as the chemical description of the conversion processes is concerned, it is very useful to introduce the stability concept which, for a crude oil or an oil residue, expresses its tendency to precipitate the asphaltene component due to a change in the operative conditions or in the chemical composition of oil and/or asphaltenes (incompatibility) following dilution with hydrocarbon cuts or chemical transformation induced by cracking processes, hydrogenation, etc . . . .

[0018] Conventionally, asphaltenes are hydrocarbons which can be precipitated from a crude oil or an oil residue, by treatment with a paraffinic hydrocarbon with a number of carbon atoms ranging from 3 to 7, for example n-heptane under the standard conditions provided for by the regulation IP-143.

[0019] From a quality point of view, it can be asserted that incompatibility phenomena occur when products having very different characteristics with respect to the nature of the malthene component, i.e. the non-asphaltene component, are mixed, as in the case of the mixing of paraffinic crude oils with aromatic oils, or the dilution of oil residues with cutter stocks of a paraffinic nature (a typical case is the fluxing of tars from visbreaking with low aromatic gas oils).

[0020] In conversion processes of oil residues, bitumens from oil sands and heavy crude oils to distillates, the maximum conversion level is limited by the stability of the residue produced. These processes, in fact, modify the chemical nature of oils and asphaltenes causing a progressive decrease in stability with an increase in the severity level. Over a certain limit, the asphaltenes present in the charge can give rise to a phase separation (i.e. precipitate) and therefore trigger coke formation processes.

[0021] From a physico-chemical point of view, the phase separation phenomenon can be explained by the fact that the asphaltene phase becomes more and more aromatic with the advancing of the conversion reactions, due to the effect of the dealkylation and condensation reactions.

[0022] Consequently, beyond a certain level, the asphaltenes are no longer soluble in the malthene phase, also because, in the meantime, the latter has become more "paraffinic".

[0023] The control of the loss of stability of a heavy charge stock during a thermal and/or catalytic conversion, is therefore fundamental for obtaining the maximum conversion degree without creating problems due to the formation of coke or fouling.

[0024] In "once-through" processes, the optimum operative conditions (mainly reaction temperature and residence time) are simply determined on the basis of the stability of the reactor effluent through direct measurements on the non-converted residue (P value, Hot Filtration Test, Spot Test, etc . . .).

[0025] All these processes allow more or less high conversion levels to be reached, according to the charge stock and the technology used, in any case generating a non-converted residue at the stability limit, which we will call tar, which, from case to case, can vary from 30 to 85% of the initial charge stock. This product is used for producing combustible oil, bitumens or it can be used as charge stock in gasification processes.

[0026] Schemes have been proposed for increasing the overall conversion level of cracking processes, which include the recycling of more or less significant amounts of tar in the cracking unit.

[0027] In the case of hydroconversion processes with dispersed catalysts in slurry phase, the recycling of tar also allows the recovery of the catalyst, to the extent that the same Applicants have described, in patent application IT-95A001095, a process which allows the recycling of the catalyst recovered to the hydrotreatment reactor, without the necessity of a further regeneration step, obtaining, at the same time, a good-quality product without the production of residue ("zero residue refinery").

[0028] This process comprises the following steps:

- **[0029]** mixing of the heavy crude oil or distillation residue with a suitable hydrogenation catalyst and sending the mixture obtained to a hydrotreatment reactor, introducing into the latter hydrogen or a mix of hydrogen and H_2S;
- **[0030]** sending the stream containing the hydrotreatment reaction product and the catalyst in dispersed phase to a distillation zone in which the most volatile fractions are separated;
- **[0031]** sending the high-boiling fraction obtained in the distillation step to a deasphalting step and the consequent formation of two streams, one consisting of deasphalted oil (DAO) and the other consisting of asphalt, catalyst in dispersed phase and possibly coke, and enriched with the metals coming from the initial charge stock;
- **[0032]** recycling of at least 60%, preferably at least 80%, of the stream consisting of asphalt, catalyst in dispersed phase and possibly coke, rich in metals, to the hydrotreating zone.

[0033] The same Applicants describe in the subsequent patent application IT-MI2001A001438 different process configurations with respect to that described above.

[0034] The process claimed therein by the combined use of the following three process units: hydroconversion with catalysts in slurry phase (HT), distillation or flash (D), deasphalting (SDA), is characterized in that the three units operate on mixed streams consisting of fresh charge stock and recycled streams, using the following steps:

- **[0035]** sending at least one fraction of the heavy charge stock to a deasphalting section (SDA) in the presence of solvents, obtaining two streams, one consisting of deasphalted oil (DAO), the other of asphalts;
- **[0036]** mixing the asphalt with a suitable hydrogenation catalyst and possibly with the remaining fraction of the heavy charge stock not sent to the deasphalting section and sending the mix obtained to a hydrotreating reactor (HT), introducing into the same reactor hydrogen or a mix of hydrogen and H_2S;
- **[0037]** sending the stream containing the product of the hydrotreating reaction and the catalyst in dispersed phase to one or more distillation or flash (D) steps, whereby the most volatile fractions are separated, among which the gases produced in the hydrotreating reaction;
- **[0038]** recycling of at least 60% by weight of the distillation residue (tar) or of the liquid coming from the flash unit, containing catalyst in dispersed phase, rich in metal sulphides produced by de-metallation of the charge stock and possibly coke, to the deasphalting zone.

[0039] With said configurations, the following advantages can be obtained:

- **[0040]** maximation of the conversion yields into distillable products (derivatives from both atmospheric and vacuum distillation), and deasphalted oil (DAO), which, in most cases, can be over 95% with respect to the charge;
- **[0041]** maximation of the upgrading degree of the charge stock, i.e. of the removal of the poisoning products present (metals, sulphur, nitrogen, coal residue), minimizing the production of coke;
- **[0042]** maximum flexibility in treating charges different by nature from the hydrocarbon component (density) and level of the pollutants present;
- **[0043]** possibility of completely recycling the hydrogenation catalyst without the necessity of regeneration.

[0044] The treatment of a heavy hydrocarbon charge stock by means of Solvent Deasphalting allows the separation of two pseudo-components conventionally defined DeAsphalted Oil (DAO) and asphaltenes Cn (wherein n represents the number of carbon atoms of the paraffin used in the deasphalting operation (normally from 3 to 6).

[0045] We have surprisingly found that if the DAO is subjected to a hydrotreatment section and the asphaltenes to a gasification section, the catalyst make-up is reduced, following the significant decrease in the purging quantity necessary for removing the heavy metals (Ni, V, Fe, ect . . .) present in the feeding stream to the hydrotreatment itself.

[0046] The process, object of the present invention, for the conversion of heavy and extra-heavy charge stocks by the combined use of at least the three following process units: solvent deasphalting (SDA), hydroconversion with catalysts in slurry phase (HT), distillation or flash (D), is characterized in that it comprises the following steps:

- **[0047]** sending the heavy charge stock to a deasphalting section (SDA) in the presence of solvents, obtaining two streams, one consisting of deasphalted oil (DAO), the other containing asphaltenes;
- **[0048]** mixing the stream consisting of deasphalted oil (DAO) with a suitable hydrogenation catalyst precursor and sending the mix obtained to a hydrotreatment reac-

tor (HT), introducing into the same, hydrogen or a mix containing hydrogen and H_2S;

[0049] sending the stream containing the product of the hydrotreatment reaction and the catalyst in dispersed phase to one or more distillation or flash (D) steps, whereby the most volatile fractions are separated, among which the gases produced in the hydrotreatment reaction, from the distillation residue (tar) or from the liquid coming from the flash unit, containing catalyst in dispersed phase, rich in metal sulphides produced by de-metallation of the charge and possibly coke;

[0050] recycling of at least a portion of the distillation residue (tar) or of the liquid coming from the flash unit, containing catalyst in dispersed phase, rich in metal sulphides produced by de-metallization of the charge and possibly coke, to the hydrotreating section (HT).

[0051] The heavy charge stocks treated can be of a varying nature: they can be selected from heavy crude oils, distillation residues, heavy oils coming from catalytic treatments, for example "unconverted oils" from fixed or ebullated bed hydrotreatment, "heavy cycle oils" from catalytic cracking treatment, "thermal tars" (coming, for example from visbreaking or similar thermal processes), bitumens from "oil sands", different kinds of coals and any other high boiling charge stock of a hydrocarbon origin, normally known in the art as "black oils".

[0052] The stream containing asphaltenes obtained in the deasphalting section (SDA) can be optionally mixed with the remaining part of the distillation residue (tar), or the liquid coming from the flash unit, not recycled to the hydrotreatment section (HT).

[0053] Said stream containing asphaltenes, mixed or not mixed with part of the distillation residue (tar) or of the liquid coming from the flash unit, can be:

[0054] sent to a gasification section (PO_x) so as to obtain a mix of H_2 and CO;

[0055] sent to a coking or visbreaking section;

[0056] used for the formulation of fuels or as fuel for the production of power

[0057] used in cement works.

[0058] It is advisable for at least part of the distillation residue (tar) or liquid coming from the flash unit, preferably at least 80% by weight, more preferably at least 90% by weight, even more preferably at least 99% by weight, to be recycled to the hydrotreatment section (HT), whereas the possible remaining part is sent to the gasification section PO_x). The gasification can be effected by feeding to the gasification unit, in addition to the charge stock, oxygen and vapour which react under exothermic conditions at a temperature of over 1300° C. and a pressure ranging from 30 to 80 bar, to produce mainly H_2 and CO.

[0059] A stream of syngas, or a mix of H_2 and CO, can be obtained from the gasification section, which can be further used as fuel by means of combustion with combined cycles (IGCC) or transformed into paraffinic hydrocarbons by means of Fisher-Tropsch synthesis or converted into methanol, di-methyl ether, formaldehyde and, more generally, into the whole series of products deriving from Cl chemistry.

[0060] The same paraffinic hydrocarbons obtained via Fisher-Tropsch can be mixed with the various cuts obtained from the distillation or flash step, improving their composition characteristics.

[0061] The catalyst precursors used can be selected from those obtained from easily decomposable oil-soluble precursors (metal naphthenates, metal derivatives of phosphonic acids, metal-carbonyls, etc . . .) or from preformed compounds based on one or more transition metals such as Ni, Co, Ru, W and Mo: the latter is preferred thanks to its higher catalytic activity.

[0062] The catalyst concentration, defined on the basis of the concentration of the metal or metals present in the hydroconversion reactor, ranges from 350 to 30,000 ppm, preferably from 3,000 to 20,000 ppm, more preferably from 5,000 to 15,000 ppm.

[0063] The hydrotreatment step (HT) is preferably carried out at a temperature ranging from 360 to 450° C., more preferably from 380 to 440° C., and at a pressure ranging from 3 to 30 MPa, preferably from 10 to 20 MPa.

[0064] Hydrogen is fed to the reactor, which can operate in both a down-flow mode and, preferably, up-flow. Said gas can be fed to several sections of the reactor.

[0065] The distillation steps are preferably effected under reduced pressure, ranging from 0.001 to 0.5 MPa, preferably from 0.1 to 0.3 MPa.

[0066] The hydrotreatment step (HT) can consist of one or more reactors operating within the condition range mentioned above. Part of the distillates produced in the first reactor can be recycled to the subsequent reactors of the same step.

[0067] The deasphalting step (SDA), effected by means of an extraction with solvent, either a hydrocarbon solvent or not, is normally carried out at temperatures ranging from 40 to 200° C. and a pressure of 0.1 to 7 MPa.

[0068] It can also consist of one or more sections operating with the same solvent or different solvents; the solvent recovery can be effected under sub-critical or super-critical multistep conditions, thus allowing a further fractionation between the deasphalted oil and resins.

[0069] It is advisable for the solvent of this deasphalting step to be selected from light paraffins having from 3 to 6 carbon atoms, preferably from 4 to 5 carbon atoms, more preferably having 5 carbon atoms.

[0070] With the use of the gasification step (PD_x), in addition to obtaining a significant reduction in the purging quantity of the entire complex, there is the production of hydrogen, of which a portion can be adopted for the hydrotreatment reaction (HT).

[0071] In the process according to the invention a further secondary section can be optionally present for the hydrogenation post-treatment of the C_2-500° C. fraction, preferably the C_5-350° C. fraction, coming from the section of high pressure separators envisaged upstream of the distillation.

[0072] In this case, before being sent to one or more distillation or flash steps, the stream containing the hydrotreatment reaction product and the catalyst in dispersed phase, is subjected to a separation pre-step, effected at high pressure, so as to obtain a light fraction and a heavy fraction, this heavy fraction alone being sent to said distillation (D) step(s).

[0073] The light fraction obtained from the high pressure separation step, can be sent to a hydrotreatment section, producing a lighter fraction containing C_1-C_4 and H_2S gas and a less light fraction containing hydrotreated naphtha and gas oil.

[0074] The possible insertion of the secondary post-treatment hydrogenation section of the C_2-500° C. fraction, preferably of the C_5-350° C. fraction, exploits the availability of this fraction together with hydrogen at a relatively high pressure, which is that of the hydrotreatment reactor, allowing the following advantages to be obtained:

- **[0075]** fuels can be obtained, starting from oil charge stocks which are extremely rich in sulphur, in line with the strictest specifications on the sulphur content (<10-50 ppm of sulphur) and improved as far as other characteristics of diesel gas oil are concerned, such as density, poly-aromatic hydrocarbon content and the cetane number;
- **[0076]** the distillates produced do not suffer from stability problems.

[0077] The post-treatment hydrogenation on a fixed bed consists of the preliminary separation of the reaction effluent of the hydrotreatment reactor (HT) by means of one or more separators operating at high pressure and high temperature.

[0078] Whereas the heavy part, extracted from the bottom, is sent to the main distillation unit, the aliquot which is extracted from the head, a C_5-350° C. fraction, is sent to a secondary treatment section in the presence of hydrogen, available at high pressure, where the reactor is of the fixed bed type and contains a typical desulphurisation/dearomatisation catalyst, in order to obtain a product which having a considerably lowered sulphur content and also lower nitrogen contents, a lower total density and, at the same time, increased cetane numbers as far as the gas oil fraction is concerned.

[0079] The hydrotreatment section normally consists of one or more reactors in series;, the product of this system can be subsequently further fractionated by distillation to obtain a thoroughly desulphurated naphtha and a diesel gas oil within specification as fuel.

[0080] The fixed-bed hydrodesulphurisation step, normally uses typical fixed-bed catalysts for gas oil hydrodesulphurisation; said catalyst, or possibly a mix of catalysts or a series of reactors with various catalysts having different properties, causes a deep refining of the light fraction, significantly reducing the sulphur and nitrogen content, increasing the hydrogenation degree of the charge stock, thus diminishing the density and increasing the cetane number of the gas oil fraction, at the same time reducing the formation of coke.

[0081] The catalyst normally consists of an amorphous part based on alumina, silica, silico-alumina and blends of different mineral oxides, on which a hydrodesulphurizing component in association with a hydrogenating product, is deposited (with several methods). Catalysts based on molybdenum or tungsten with the addition of nickel and/or cobalt, deposited on a mineral amorphous carrier, are typical catalysts for this type of operation.

[0082] The post-treatment hydrogenation reaction is effected at an absolute pressure slightly lower than that of the primary hydrotreatment step, normally ranging from 7 to 14 MPa, preferably from 9 to 12 MPa; the hydrodesulphurizing temperature ranges from 250 to 500° C., preferably from 280 to 420° C.; the temperature normally depends on the desulphuration level required. The space velocity is another important variable in controlling the quality of the product obtained: it can range from 0.1 to 5 h^{-1}, preferably from 0.2 to 2 h^{-1}.

[0083] The quantity of hydrogen mixed with the charge stock is fed at a flow-rate ranging from 100 to 5,000 Nm^3/m^3, preferably from 300 to 1,000 Nm^3/m^3.

[0084] An embodiment of the present invention is now provided with the help of the enclosed FIG. **1**, which should not be considered as limiting the scope of the invention.

[0085] In FIG. **1** the heavy charge stock (**1**) is sent to the deasphalting unit (SDA): this operation is carried out by means of a solvent extraction operation.

[0086] Two streams are obtained from the deasphalting unit (SDA): one stream (**2**) consisting of deasphalted oil (DAO), the other stream containing asphaltenes (**3**).

[0087] The stream containing asphaltenes (**3**) is sent to a gasification section (PO_x) in order to obtain syngas, i.e. a gaseous mix of H_2 and CO (**4**).

[0088] The stream consisting of deasphalted oil (**2**) is mixed with the fresh make-up catalyst (**5**) (necessary for reintegrating that lost with the stream (**15**) described hereunder) and with the stream (**14**) (described hereunder) coming from the bottom of the distillation or flash column (D) to form the stream (**6**) which is fed to the hydrotreatment reactor (HT) into which hydrogen (or a mix containing hydrogen and H_2S) (**7**) is fed.

[0089] The hydrogen fed can be part of the hydrogen coming from the gasification step (PO_x)(not schematised in the figure). A stream (**8**) leaves the reactor (HT), containing the hydrogenation product and the catalyst in dispersed phase, which is fractionated in a distillation or flash column (D) from which the lighter fraction (**9**) separates together with the distillable products (**10**), (**11**) and (**12**) from the distillation residue (**13**) containing the dispersed catalyst and coke.

[0090] This stream (**13**) (called tar) is mostly recycled (**14**) to the hydrotreatment unit (HT), the remaining part (**15**) being sent to the gasification section (PD_x).

[0091] An example is provided for a better understanding of the invention, it being understood that the invention should not be considered as being limited thereto or thereby.

EXAMPLEe 1

[0092] Following the scheme represented in FIG. **1**, the following experimentation was carried out.

Deasphalting Step (SDA)

[0093] Charge stock: 250 g vacuum residue from Ural crude oil (Table 1)

[0094] Deasphalting agent: about 2.5 1 of n-pentane

[0095] Temperature: 180° C.

[0096] Pressure: 16 atm.

The vacuum residue is charged into an autoclave together with a volume of n-pentane equal to 8-10 times the volume of residue. The mixture of charge stock and solvent is heated to a temperature of 180° C., with stirring (800 rpm) by means of a mechanical impeller for a period of minutes. At the end of the operation, decantation takes place and also separation between the two phases, the asphaltene phase which is deposited at the bottom of the autoclave and that of the deasphalted oil diluted in the solvent. The decantation lasts for about two hours. The DAO-solvent phase is transferred, by means of a suitable recovery system, to a second tank. The DAO-pentane phase is then recovered, and the solvent is sub-sequently eliminated by evaporation.

[0097] The yield obtained by the procedure described is equal to 82% by weight of deasphalted oil with respect to the starting vacuum residue.

[0098] The properties of the RV Ural and deasphalted oil (DAO C5) are shown in table 1.

TABLE 1

Characteristics of the vacuum residue Ural 500° C. and DAO n-C5 extracted.

Charge	C (w %)	H (w %)	N (w %)	S (w %)	CCR (w %)	d^{20} (g/cm^3)	V (ppm)	Ni (ppm)
RV Ural	84.82	10.56	0.69	2.60	18.9	1.0043	262	80
DAO C5	85.40	11.40	0.43	2.33	9.78	0.9760	71	23

DAO Hydrotreatment Step

[0099] Catalytic tests were carried out using a stirred micro-autoclave of 30 cm^3, in accordance with the following general operative procedure:

[0100] about 10 g of the charge stock are introduced into the reactor and the catalyst precursor is added;

[0101] the system is then pressurized with hydrogen and brought to temperature by means of an electrically heated oven;

[0102] the system is maintained under stirring during the reaction by a swinging capillary system operating at a rotational rate of 900 rpm; moreover, the total pressure is kept constant by means of an automatic reintegration system of the hydrogen consumed;

[0103] quenching of the reaction is carried out once the test has been completed; the autoclave is then de-pressurised and the gas collected in a sampling bag; the gaseous samples are then sent for gas-chromatographic analysis;

[0104] the products present in the reactor are recovered without the addition of any solvent, and analyzed in terms of distribution of the distillates, sulphur content, nitrogen content, coal residue and metal content.

[0105] Hydrotreatment tests were effected using the DAO produced in the deasphalting step, according to the following procedure. The reactor was charged with DAO and the molybdenum compound and pressurized with hydrogen. The reaction was carried out under the operative conditions shown in table 2, which indicates the data relating to the distribution of products and quality.

TABLE 2

characteristics of the reaction product from the test according to Example 1

w %	420° C.; 3 hrs	420° C.; 5 hrs	430° C.; 3 hrs
Naphtha C5-170° C.	2.5	6.7	7.6
AGO 170-350° C.	22.2	29.5	32.8
VGO 350-500° C.	32.9	31.9	32.8
500° C.+	39.4	27.6	22.2
Gas (HC + H_2S)	3.0	4.3	4.6
S	0.79	0.44	0.48
N	0.35	0.30	0.33
Ni (ppm)	0.9	<0.5	<0.5
V (ppm)	1.1	<0.5	<0.5

EXAMPLE 2

[0106] The following experimentation was carried out following the scheme represented in FIG. **1**.

Deasphalting Step (SDA)

[0107] Effected according to what is described in example 1.

Hydrotreatment Step

[0108] Reactor: 3,500 cc steel reactor equipped with magnetic stirring

[0109] Catalyst: 3,000 ppm of Mo/charge added using an organometallic, oil-soluble precursor containing 15% w/w of metal

[0110] Temperature: 430° C.

[0111] Pressure: 16 MPa of hydrogen

[0112] Residence time: 3 hrs.

[0113] Using the DAO produced in the deasphalting step, hydrotreatment tests were performed according to the procedure described below. The reactor was charged with DAO and the molybdenum compound and pressurized with hydrogen. The reaction was carried out under the operative conditions described. Quenching was effected once the test had been completed; the autoclave was depressurised and the gas collected in a sampling bag for gas-chromatographic analysis. The liquid product present in the reactor was recovered and subjected to distillation in order to separate the 500° C.+residue from the other distillation cuts. The distillation residue (500° C.+) containing the catalyst, was charged again into the reactor and mixed with a suitable amount of DAO C5 previously prepared, in order to keep the quantity of the total charge stock constant. This procedure was repeated until stabilization of the quantity of the residue obtained, i.e. until stationary conditions were reached.

Distillation Step

[0114] Effected by means of laboratory equipment for the distillation of oil charge stocks.

Results of the Experimentation

[0115] 6 consecutive hydrotreatment tests of DAO C5 were carried out, following the above-mentioned procedure. The ratio between the quantity of recycled residue and the quantity of fresh charge stock reached under these operative conditions was 0.47.

[0116] The data relating the outlet streams after the last recycling (% weight with respect to the charge) are provided hereunder:

[0117] Gas: 4%

[0118] Naphtha (C_5-170° C.): 8%

[0119] Atmospheric gas oil (AGO, 170-350° C.): 27%

[0120] Vacuum gas oil (VGO, 350-500° C.): 31%

[0121] Vacuum residue (500° C+): 30%

TABLE 3

characteristics of the reaction products according to Example 2.

	Sulphur (w %)	Nitrogen (ppm)	Sp. Gr. (g/cm^3)
Naphtha C5-170° C.	0.03	300	0.7403
AGO 170-350° C.	0.11	1800	0.8451
VGO 350-500° C.	0.41	4400	0.9256

1. A process for the conversion of a heavy charge stock selected from heavy and extra-heavy crude oils, distillation residues, heavy oils from catalytic treatment, thermal tars, bitumens from oil sands, carbons of different origins and other high boiling charges of a hydrocarbon origin known as “black oils”, by the combined use of at least the three following process units: solvent deasphalting (SDA), hydroconversion with slurry phase catalysts (HT), distillation or flash (D),

which process comprises the following:

(1) sending a composition consisting of the heavy charge stock directly to a deasphalting section (SDA) in the presence of a solvent, obtaining two streams, one consisting of deasphalted oil (DAO), the other comprising asphaltenes;

(2) mixing the stream consisting of deasphalted oil (DAO) with a suitable hydrogenation catalyst precursor and sending the mix obtained to a hydrotreatment reactor (HT), introducing into the same reactor, hydrogen or a mix comprising hydrogen and H_2S;

(3) sending the stream comprising the product of the hydrotreatment reaction and the catalyst in dispersed phase to one or more distillation or flash (D) steps, whereby the most volatile fractions are separated, among which the gases produced in the hydrotreatment reaction, from the distillation residue (tar) or from the liquid coming from the flash unit;

(4) recycling of a portion of the distillation residue (tar) or of the liquid coming from the flash unit, comprising catalyst in dispersed phase, rich in metal sul phides produced by de-metallization of the charge and possibly coke, to the hydrotreatment section (HT),

wherein the stream comprising asphaltenes obtained in the de-asphalting section (SDA) and the remaining part of the distillation residue (tar) or the liquid coming from the flash unit which was not recycled to the hydrotreatment section (HT) are sent to a gasification section (PD_x) in order to obtain a mix of H_2 and CO.

2. The process according to claim **1**, wherein the gasification is effected by feeding to the gasification unit, in addition to the charge stock, oxygen and vapour which react under exothermic conditions at a temperature of over 1300° C. and a pressure ranging from 30 to 80 bar, to produce mainly H_2 and CO.

3. The process according to claim **1**, wherein at least 80% by weight of the distillation residue (tar) or the liquid coming from the flash unit is recycled to the hydrotreatment section (HT).

4. The process according to claim **3**, wherein at least 90% by weight of the distillation residue or the liquid coming from the flash unit is recycled to the hydrotreatment section (HT).

5. The process according to claim **4**, wherein at least 99% by weight of the distillation residue or the liquid coming from the flash unit is recycled to the hydrotreatment section (HT).

6. The process according to claim **1**, wherein part of the hydrogen obtained from the gasification section (PO_x) is sent to the hydrotreatment (HT) step.

7. The process according to claim **1**, wherein the distillation steps are carried out at reduced pressure, ranging from 0.001 to 0.5 MPa.

8. The process according to claim **7**, wherein the distillation steps are carried out at reduced pressure, ranging from 0.01 to 0.3 MPa.

9. The process according to claim **1**, wherein the hydrotreatment (HT) step is carried out at a temperature ranging from 360 to 450° C. and at a pressure ranging from 3 to 30 MPa.

10. The process according to claim **9**, wherein the hydrotreatment (HT) step is carried out at a temperature ranging from 380 to 440° C. and at a pressure ranging from 10 to 20 MPa.

11. The process according to claim **1**, wherein the deasphalting (SDA) step is carried out at temperatures ranging from 40 to 200° C. and a pressure ranging from 0.1 to 7 MPa.

12. The process according to claim **1**, wherein the solvent of the deasphalting step (SDA) is a light paraffin with a number of carbon atoms ranging from 3 to 6.

13. The process according to claim **12**, wherein the deasphalting solvent is a light paraffin with a number of carbon atoms ranging from 4 to 5.

14. The process according to claim **1**, wherein the deasphalting (SDA) step is effected with recovery of the solvent in supercritical phase.

15. The process according to claim **1**, wherein, before being sent to one or more distillation or flash steps, the stream comprising the hydrotreatment reaction product and the catalyst in dispersed phase, is sent to a separation pre-step carried out at high pressure so as to obtain a light fraction and a heavy fraction, said heavy fraction alone being sent to said distillation (D) step(s).

16. The process according to claim **15**, wherein the light fraction obtained by the high pressure separation step, is sent to a secondary post-treatment hydrogenation step, thus producing a lighter fraction comprising C_1-C_4 gas and H_2S and a heavier fraction comprising hydrotreated naphtha and gas oil.

17. The process according to claim **16**, wherein the post-treatment hydrogenation reaction is effected at a pressure ranging from 7 to 14 MPa.

18. The process according to claim **1**, wherein the hydrogenation catalyst is an easily decomposable precursor or a preformed compound based on one or more transition metals.

19. The process according to claim **18**, wherein the transition metal is molybdenum.

20. The process according to claim **1**, wherein the catalyst concentration in the hydroconversion reactor, defined on the basis of the concentration of the metal(s) present, ranges from 350 to 30,000 ppm.

21. The process according to claim **20**, wherein the catalyst concentration in the hydroconversion reactor ranges from 3,000 to 20,000 ppm.

22. The process according to claim **21**, wherein the catalyst concentration in the hydroconversion reactor ranges from 5,000 to 15,000 ppm.

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