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(54) PROCESS FOR CONVERTING PETROLEUM FEEDSTOCKS COMPRISING A VISBREAKING STAGE, A MATURATION STAGE AND A STAGE OF SEPARATING THE SEDIMENTS FOR THE PRODUCTION OF FUEL OILS WITH A LOW SEDIMENT CONTENT

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(57) **ABSTRACT**

The invention relates to a process for converting a hydrocarbon-containing feedstock containing at least one hydrocarbon fraction having a sulphur content of at least 0.1% by weight, an initial boiling temperature of at least 340° C. and a final boiling temperature of at least 440° C., making it possible to obtain a heavy fraction having a sediment content after ageing of less than or equal to 0.1% by weight, said process comprising the following stages: a) a stage of visbreaking the feedstock in at least one maturation chamber (soaker), b) a stage of separating the effluent obtained at the end of stage a), c) a stage of maturation of the heavy fraction originating from stage b), d) a stage of separating the sediments from the heavy fraction originating from the maturation stage c) in order to obtain said heavy fraction.

PROCESS FOR CONVERTING PETROLEUM FEEDSTOCKS COMPRISING A VISBREAKING STAGE, A MATURATION STAGE AND A STAGE OF SEPARATING THE SEDIMENTS FOR THE PRODUCTION OF FUEL OILS WITH A LOW SEDIMENT CONTENT

[0001] The present invention relates to the refining and conversion of heavy hydrocarbon fractions containing, among other things, sulphur-containing impurities. It relates more particularly to a process for converting heavy petroleum feedstocks of the atmospheric residue and/or vacuum residue type for the production of heavy fractions that can be used as fuel-oil bases, in particular bunker oil bases, with a low sediment content. The process according to the invention also makes it possible to produce atmospheric distillates (naphtha, kerosene and diesel), vacuum distillates and light gases (C1 to C4).

[0002] The quality requirements for marine fuels are described in standard ISO 8217. From now on the specification concerning sulphur will relate to SO_x emissions (Annex VI of the MARPOL convention of the International Maritime Organization) and is expressed as a recommendation for the sulphur content to be less than or equal to 0.5% by weight outside the Sulphur Emissions Control Areas (SECAs) for the 2020-2025 time frame, and less than or equal to 0.1% by weight in the SECAs. Another very restrictive recommendation is the sediment content after ageing according to ISO 10307-2 (also known as IP390), which must be less than or equal to 0.1%.

[0003] The sediment content according to ISO 10307-1 (also known as IP375) is different from the sediment content after ageing according to ISO 10307-2 (also known as IP390). The sediment content after ageing according to ISO 10307-2 is a much more restrictive specification and corresponds to the specification that applies to bunker oils.

[0004] According to Annex VI of the MARPOL convention, a vessel will therefore be able to use a sulphur-containing fuel oil if the vessel is equipped with a system for treating fumes that makes it possible to reduce emissions of sulphur oxides.

[0005] The processes for visbreaking residues make it possible to convert low-value residues to distillates with a higher added value. Visbreaking consists of carrying out a partial cracking of the residue, therefore the conversion is always clearly lower (by at least 10 to 20%) than that obtained in a residue-hydrocracking process using an ebullating bed for example. However, the resulting heavy fraction corresponding to the unconverted residual cut is generally unstable. It contains sediments which are mainly precipitated asphaltenes. This unstable residual cut therefore cannot be upscaled as a fuel oil, in particular into a bunker oil, without a specific treatment when the visbreaking is carried out under severe conditions leading to a high conversion rate for this type of treatment. However, the implementation of a visbreaking process is much less expensive than a residue-hydrocracking process. Moreover, a large number of units have already been installed, it is therefore beneficial to use these units, while allowing them to improve the quality of the effluents and thus allowing them to function at greater severity.

[0006] The visbreaking process makes it possible to partially convert the heavy feedstocks in order to produce atmospheric distillates and/or vacuum distillates. Feedstocks of the residue type generally contain asphaltenes which can precipitate during visbreaking. In the feedstock, initially, the visbreaking conditions and in particular the temperature cause the asphaltenes to undergo reactions (dealkylation, polymerization, etc.) leading to their precipitation when the conditions are severe and the conversion rate is high for this type of process. Compared with a residue-hydrocracking process, the implementation of a visbreaking process in the absence of hydrogen and catalyst means that the reactions are exclusively thermal. Thus the conversion rate from which the sediments appear in the case of visbreaking is lower than in the case of residue hydrocracking. The sediments formed must be removed in order to satisfy a product quality such as bunker oil. Such a separation of the sediments in particular prevents the risks of clogging the boat engines and, in the case of any treatment stages implemented downstream of the visbreaking stage, preventing a clogging of the catalytic bed(s) used.

[0007] In his research, the applicant has developed a new process incorporating a stage of maturation and separation of the sediments downstream of a visbreaking stage. It was found that such a process made it possible to obtain heavy fractions having a low sediment content after ageing, said heavy fractions advantageously being able to be used completely or partially as a fuel oil or as a fuel-oil base complying with future specifications, namely a sediment content after ageing of less than or equal to 0.1% by weight.

[0008] More particularly, the invention relates to a process for converting a hydrocarbon-containing feedstock containing at least one hydrocarbon fraction having a sulphur content of at least 0.1% by weight, an initial boiling temperature of at least 340° C. and a final boiling temperature of at least 440° C., making it possible to obtain a heavy fraction having a sediment content after ageing of less than or equal to 0.1% by weight, said process comprising the following stages:

[0009] a) a stage of visbreaking the feedstock in at least one maturation chamber (soaker),

[0010] b) a stage of separating the effluent obtained at the end of stage a) into at least one light hydrocarbon fraction containing fuel bases and a heavy fraction containing compounds boiling at at least 350° C.,

[0011] c) a stage of maturation of the heavy fraction originating from the separation stage b) making it possible to convert a part of the potential sediments to existing sediments, carried out for a duration comprised between 1 and 1500 minutes, at a temperature comprised between 50 and 350° C., and at a pressure of less than 20 MPa,

[0012] d) a stage of separating the sediments from the heavy fraction originating from the maturation stage c) in order to obtain said heavy fraction.

[0013] In order to constitute the fuel oil complying with the viscosity recommendations, the heavy fractions obtained using the present process can be mixed with fluxing bases so as to achieve the target viscosity of the desired fuel oil grade.

[0014] Another beneficial point of the process is the partial conversion of the feedstock making it possible to produce, in particular by visbreaking, atmospheric distillates or vacuum distillates (naphtha, kerosene, diesel, vacuum distillate), that can be upscaled as bases in the fuel pools directly or after passing through another refining process such as hydrotreatment, reforming, isomerization-hydrocracking or catalytic cracking.

DETAILED DESCRIPTION

The Feedstock

[0015] The feedstocks treated in the process according to the invention are advantageously selected from atmospheric residues, vacuum residues originating from direct distillation, crude oils, topped crude oils, deasphalted oils, deasphalting resins, asphalts or deasphalting pitches, residues originating from conversion processes, aromatic extracts originating from lubricant base production chains, bituminous sands or derivatives thereof, oil shales or derivatives thereof, alone or in a mixture.

[0016] These feedstocks can advantageously be used as they are or also diluted with a hydrocarbon-containing fraction or a mixture of hydrocarbon-containing fractions which can be selected from the products originating from a fluid catalytic cracking (FCC) process, a light cut oil (or light cycle oil, LCO), a heavy cut oil (or heavy cycle oil, HCO), a decanted oil (DO), an FCC residue, or which can originate from distillation, gas-oil fractions, in particular those obtained by atmospheric or vacuum distillation, such as for example vacuum gas oil. The heavy feedstocks can also advantageously comprise cuts originating from the process for liquefaction of coal or biomass, aromatic extracts, or any other hydrocarbon-containing cuts or also non-petroleum feedstocks such as pyrolysis oil.

[0017] The feedstocks according to the invention generally have a sulphur content of at least 0.1% by weight, an initial boiling temperature of at least 340° C. and a final boiling temperature of at least 440° C., preferably a final boiling temperature of at least 540° C. Advantageously, the feedstock can contain at least 1% C7 asphaltenes and at least 5 ppm of metals, preferably at least 2% C7 asphaltenes and at least 25 ppm of metals.

[0018] The feedstocks according to the invention are preferably atmospheric residues or vacuum residues, or mixtures of these residues.

Stage a): Visbreaking

[0019] The feedstock according to the invention is subjected to a stage of visbreaking in at least one maturation chamber (soaker).

[0020] This stage consists of carrying out a partial cracking of the feedstock in order to reduce its viscosity.

[0021] The visbreaking stage is a mild cracking process in which heavy hydrocarbons are heated in a maturation chamber (soaker). The visbreaking stage is carried out at a temperature generally comprised between 370° C. and 500° C., preferably between 420 and 480° C., for a duration generally comprised between 1 and 60 minutes, preferably between 10 and 45 minutes, a total pressure generally of less than 10 MPa, preferably less than 5 MPa and more preferably less than 2 MPa. The crack per pass is controlled by regulating the residence time of the hydrocarbons in the maturation chamber (soaker). A quench of the effluent is then generally carried out and the cracked products are separated using flash distillation and optionally using vapour stripping. Such a process is described for example in the patents U.S. Pat. No. 7,220,887 B2 and U.S. Pat. No. 7,193,123 B2 or in the publication "Le raffinage du Pétrole" volume 3, chapter 11, Editions Technip. Such a process of visbreaking residues is for example the TERVAHL process marketed by the company Axens.

[0022] It is possible to carry out the hydrotreatment of the feedstock upstream of the visbreaking stage in order to obtain better-quality products, in particular with a low sulphur content. It is therefore preferable to add a hydrotreatment stage (for example a hydrodesulphurization and/or hydrodenitrogenation stage) just before the visbreaking stage a) in order to increase the saturation rate of the hydrocarbons, while partially eliminating the sulphur-containing or nitrogen-containing compounds. Such a process of hydrotreating residues is for example the HYVAHL process marketed by the company Axens.

[0023] In a variant of the process according to the invention, the visbreaking stage is carried out in the presence of hydrogen (hydrovisbreaking), which makes it possible simultaneously to saturate and to crack the hydrocarbons. In fact, the visbreaking of a hydroprocessed feedstock (i.e. in which the content of saturated hydrocarbons is greater) makes it possible to obtain higher conversion rates during the visbreaking stage. Such techniques of visbreaking in the presence of hydrogen are therefore preferred within the framework of the present process, to the extent that they avoid the addition of an additional hydrotreatment stage, while making it possible to obtain a very satisfactory quality of the effluents from this stage. It is also possible to carry out a process of visbreaking in the presence of hydrogen using a hydrogen donor is solvent, such as is described for example in the patent U.S. Pat. No. 4,592,830.

[0024] The operating conditions that can be used in processes of visbreaking in the presence of hydrogen are mentioned for example in the patent U.S. Pat. No. 4,708,784 by the company Philips Petroleum and in the patents U.S. Pat. No. 4,533,462, EP 0 113 284 B and EP 0 649 896 B.

[0025] The conversion rate of the compounds boiling above 540° C. in the feedstock during the visbreaking stage a) is generally lower than 60%, preferably lower than 50% and more preferably lower than 45%.

Stacie b): Separation of the Visbreaking Effluent

[0026] The effluent obtained at the end of the visbreaking stage a) can undergo at least one separation stage, optionally supplemented by other additional separation stages, making it possible to separate at least one light hydrocarbon fraction containing fuel bases and a heavy fraction containing compounds boiling at at least 350° C.

[0027] The separation stage can advantageously be implemented using any method known to a person skilled in the art, such as for example the combination of one or more high- and/or low-pressure separators, and/or high- and/or low-pressure distillation and/or stripping stages, and/or liquid/liquid extraction stages. Preferably, the separation stage b) makes it possible to obtain a gaseous phase, at least one light hydrocarbon fraction of the naphtha, kerosene and/or diesel type, a vacuum distillate fraction and a vacuum residue fraction and/or an atmospheric residue fraction.

[0028] The complexity of the separation stage depends on the complexity of the visbreaking stage a), in particular if this visbreaking stage is carried out under pressure and/or in the presence of hydrogen.

[0029] In the case of an implementation of the visbreaking stage in the absence of hydrogen and at low pressure (of less than 2 MPa), the effluent from the visbreaking stage a) is introduced into a distillation column making it possible to recover at least one is gaseous fraction and a liquid fraction of the atmospheric residue type. This column most often also makes it possible to extract a non-stabilized naphtha-type cut (which will optionally be treated subsequently in a stabilization column) as liquid distillate at the reflux drum. This column most often also makes it possible to extract, laterally, a gas-oil type fraction, optionally using a lateral stripper. The atmospheric residue type liquid fraction can optionally be treated in a vacuum column to recover a vacuum distillate and a vacuum residue.

[0030] In the case of an implementation of the visbreaking stage in the presence of hydrogen, the effluent originating from the visbreaking stage is at high pressure and contains at least one gas phase and a liquid phase. Thus, the separation can be carried out in a fractionation section which can firstly comprise a high-pressure high-temperature (HPHT) separator, and optionally a high-pressure low-temperature (HPLT) separator, and/or an atmospheric distillation and/or a vacuum distillation. During stage b), the effluent obtained at the end of stage a) is advantageously separated in a high-pressure high-temperature HPHT separator into a light fraction and a heavy fraction containing mainly compounds boiling at at least 350° C. The cut point of the separation is advantageously situated between 200 and 400° C.

[0031] In a variant of the process of the invention using hydrogen during the visbreaking stage, the effluent originating from the visbreaking stage a) can, during stage b), also undergo a succession of instantaneous (or flash) separation comprising at least one high-pressure high-temperature (HPHT) flask and a low-pressure high-temperature (LPHT) flask to separate a heavy fraction which is sent into a vapour stripping stage making it possible to eliminate from said heavy fraction at least one light fraction rich in hydrogen sulphide. The heavy fraction recovered at the bottom of the stripping column contains compounds boiling at at least 350° C. but also atmospheric distillates. According to the process of the invention, said heavy fraction separated from the light fraction rich in hydrogen sulphide is then sent into the maturation stage c) then into the sediment separation stage d).

[0032] In a variant, at least a part of the fraction known as heavy originating from stage b) is fractionated by atmospheric distillation into at least one atmospheric distillate fraction containing at least one light hydrocarbon fraction of the naphtha, kerosene and/or diesel type and an atmospheric residue fraction. At least a part of the atmospheric residue fraction can be sent into the maturation stage c) then into the sediment separation stage d).

[0033] The atmospheric residue can also be at least partially fractionated by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction. Said vacuum residue fraction is advantageously at least partially sent into the maturation stage c) then into the sediment separation stage d).

[0034] At least a part of the vacuum distillate and/or of the vacuum residue can also be recycled into the visbreaking stage a).

[0035] Whatever the separation method used, the light fraction(s) obtained can undergo other separation stages. Advantageously, it (or they) is (or are) subjected to an atmospheric distillation making it possible to obtain a gaseous fraction, at least one light hydrocarbon fraction of the naphtha, kerosene and/or diesel type and a vacuum distillate fraction.

[0036] A part of the atmospheric distillate and/or of the vacuum distillate can constitute a part of a fuel oil such as a fluxing agent. These cuts can also constitute low-viscosity marine fuels (Marine Diesel Oil (MDO) or Marine Gas Oil (MOO)). Another part of the vacuum distillate can also be upscaled by hydrocracking and/or by fluid catalytic cracking.

[0037] The gaseous fractions originating from the separation stage preferably undergo a purification treatment to recover the hydrogen, optionally the hydrogen, and to recycle it.

[0038] The upscaling of the different cuts of fuel bases (LPG, naphtha, kerosene, diesel and/or vacuum gas oil) obtained using the present invention is well known to a person skilled in the art. The products obtained can be incorporated in fuel reservoirs (also called fuel "pools") or can undergo additional refining stages. The naphtha, kerosene, gas oil fraction(s) and the vacuum gas oil can be subjected to one or more treatments (hydrotreatment, hydrocracking, alkylation, isomerization, catalytic reforming, catalytic or thermal cracking or others) to bring them up to the required specifications (sulphur content, smoke, octane and cetane point, etc.) separately or in a mixture.

[0039] Advantageously, the vacuum distillate leaving the visbreaking after separation can undergo a hydrotreatment.

[0040] This hydrotreated vacuum distillate can be used as fluxing agent for the fuel oil pool having a sulphur content of less than or equal to 0.5% by weight or be upscaled directly as fuel oil having a sulphur content of less than or equal to 0.1% by weight.

[0041] A part of the atmospheric residue, of the vacuum distillate and/or of the vacuum residue can undergo other additional refining stages such as a hydrotreatment, a hydrocracking, or a fluid catalytic cracking.

Stage c): Maturation of the Sediments

[0042] The heavy fraction obtained at the end of the separation stage b) contains organic sediments which result from the visbreaking conditions. A part of the sediments is constituted by asphaltenes precipitated under the visbreaking conditions and they are analyzed as existing sediments (IP375), and another part only forms after ageing (IP390), the ageing involving an additional precipitation.

[0043] Depending on the visbreaking conditions, the sediment content in the heavy fraction varies. From an analytical point of view, a distinction is made between the existing sediments (IP375) and the sediments after ageing (IP390) which include the potential sediments. Depending on the nature of the feedstock and of the more severe or less severe visbreaking conditions, i.e. when the conversion rate (of the compounds boiling above 540° C. in the feedstock) is for example greater than 40 or 50%, there is a formation of existing sediments and of potential sediments.

[0044] In order to obtain a fuel oil or a fuel-oil base complying with the recommendations of a sediment content after ageing (IP390) of less than or equal to 0.1%, the process according to the invention comprises a maturation stage making it possible to improve the effectiveness of separation of the sediments and thus to obtain stable fuel oils or fuel-oil bases, i.e. a sediment content after ageing of less than or equal to 0.1% by weight.

[0045] The maturation stage according to the invention makes it possible to form all of the existing and potential sediments (by converting the potential sediments into existing sediments) so as to separate them more effectively and thus to respect the sediment content after ageing (IP390) of 0.1% by weight at most.

[0046] The maturation stage according to the invention is advantageously implemented for a residence time comprised between 1 and 1500 minutes, preferably between 25 and 300 minutes, more preferably between 60 and 180 minutes, at a temperature between 50 and 350° C., preferably between 75 and 300° C. and more preferably between 100 and 250° C. The pressure of the maturation stage is advantageously less than 20 MPa, preferably less than 10 MPa, more preferably less than 3 MPa and even more preferably less than 1.5 MPa.

[0047] The maturation conditions are mild enough not to cause an excessive conversion of the hydrocarbons. During the maturation stage, the conversion rate of the compounds boiling above 540° C. is lower than 10%, preferably lower than 5% and more preferably lower than 2%.

[0048] The maturation stage can be carried out using an exchanger or heating furnace followed by one or more enclosure(s) in series or in parallel such as a horizontal or vertical drum, optionally with a decantation function for removing a part of the heaviest solids, and/or a piston reactor. A stirred and heated vessel can also be used, and can be equipped with a drawing-off device at the bottom for removing a part of the heaviest solids.

[0049] Advantageously, the stage c) of maturation of the heavy fraction originating from stage b) is carried out in the presence of an inert gas and/or an oxidizing gas.

[0050] The maturation stage c) can be carried out in the presence of an inert gas (nitrogen for example) or an oxidizing gas (oxygen for example), or in the presence of a mixture containing an inert gas and an oxidizing gas such as air or nitrogen-depleted air. The use of an oxidizing gas makes it possible to speed up the maturation process. According to this option, a gas is therefore introduced in a mixture with the liquid fraction originating from stage b) before the maturation, then this gas is separated after the maturation so as to obtain a liquid fraction at the outlet of the maturation stage c). Such a use of gas/liquid can for example be carried out in a bubble tower. According to a variant, the inert and/or oxidizing gas can also be introduced during the maturation stage c), for example by means of bubbling (injection of gas through the base) into a stirred tank, which makes it possible to promote the gas/liquid contact.

[0051] At the end of the maturation stage c), at least one hydrocarbon-containing fraction is obtained having a content enriched with existing sediments, which is sent into the stage d) of separating the sediments.

Stage d): Separation of the Sediments

[0052] The process according to the invention moreover comprises a stage d) of separating the sediments.

[0053] The heavy fraction obtained at the end of the maturation stage c) contains organic sediments of the precipitated asphaltenes type, which result from the visbreaking and maturation conditions.

[0054] Thus, at least a part of the heavy fraction originating from the maturation stage c) is subjected to a separation of the sediments, by means of at least one physical separation means selected from a filter, a separation membrane, a filtering bed of solids of the organic or inorganic type, an electrostatic precipitation, a centrifugation system, decantation, drawing-off by means of an endless screw. A combination, in series and/or in parallel, of several separation means of the same type or of different types can be used during this stage d) of separating the sediments and residues of catalysts. One of these solid-liquid separation techniques can require the periodic use of a light rinsing fraction, originating from the process or not, making it possible for example to clean a filter and remove the sediments.

[0055] The heavy fraction originating from stage d) with a reduced sediment content can advantageously serve as a fuel-oil base or as a fuel oil, in particular as a bunker oil base or as a bunker oil, having a sediment content after ageing of less than 0.1% by weight. Advantageously, said heavy fraction is mixed with one or more fluxing bases selected from the group constituted by the light cycle oils of a catalytic cracking, the heavy cycle oils of a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil.

Optional Stage e): Optional Separation Stage

[0056] The effluent obtained at the end of the stage d) of separating the sediments can undergo an optional separation stage making it possible to separate at least one light hydrocarbon fraction containing fuel bases and a heavy fraction containing mainly compounds boiling at at least 350° C.

[0057] This separation stage can advantageously be implemented using any method known to a person skilled in the art, such as for example the combination of one or more high- and/or low-pressure separators, and/or high- and/or low-pressure distillation and/or stripping stages. This optional separation stage e) is similar to the separation stage b) and will not be described further.

[0058] Preferably, this separation stage makes it possible to obtain at least one light hydrocarbon fraction of the naphtha, kerosene and/or diesel type, a vacuum distillate fraction and a vacuum residue fraction and/or an atmospheric residue fraction.

[0059] A part of the atmospheric residue and/or of the vacuum residue can also be recycled into the hydrocracking stage a).

Stage f): Optional Hydrotreatment Stage

[0060] The sulphur content of the heavy fraction originating from stage d) or e) when the latter is implemented, and containing mainly compounds boiling at at least 350° C., is a function of the operating conditions of the visbreaking stage but also, and above all, the sulphur content of the original feedstock.

[0061] Thus, for feedstocks with a low sulphur content, generally of less than 1% by weight, preferably less than 0.5% by weight, it is possible to directly obtain a heavy fraction with less than 0.5% by weight of sulphur, as required for vessels not equipped with fume treatment and operating outside the SECAs for the 2020-2025 time frame.

[0062] For feedstocks containing more sulphur, the sulphur content of which is generally greater than 1% by weight, preferably greater than 0.5% by weight, the sulphur content of the heavy fraction can exceed 0.5% by weight. In such a case, a fixed-bed hydrotreatment stage f) is made necessary in the case where the refiner desires to decrease the sulphur content, in particular for a bunker oil base or a bunker oil intended to be burned on a vessel not equipped with fume treatment.

[0063] According to the invention, the hydrotreatment stage described in stage f) is identical to the stage of hydrotreating the feedstock advantageously implemented before the visbreaking stage. In the case where a stage of hydrotreating the feedstock is implemented prior to the visbreaking stage, the conditions described in stage f) can therefore be adapted to this hydrotreatment stage.

[0064] The fixed-bed hydrotreatment stage f) is implemented on at least a part of the heavy fraction originating from stage d) or e) when stage e) is implemented. The heavy fraction originating from stage f) can advantageously serve as a fuel-oil base or as a fuel oil, in particular as a bunker oil base or as a bunker oil, having a sediment content after ageing of less than 0.1% by weight. Advantageously, said heavy fraction is mixed with one or more fluxing bases selected from the group constituted by the light cycle oils of a catalytic cracking, the heavy cycle oils of a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil.

[0065] The heavy fraction originating from the stage of separating the sediments d) or e) when stage e) is implemented is sent into the hydrotreatment stage f) comprising one or more fixed-bed hydrotreatment zones. Sending a heavy fraction depleted of sediments into a fixed bed constitutes an advantage of the present invention because the fixed bed will be less susceptible to clogging and to the increase in pressure drop.

[0066] By hydrotreatment (HDT) is meant in particular hydrodesulphurization (HDS) reactions, hydrodenitrogenation (HDN) reactions and hydrodemetallization (HDM) reactions, but also hydrogenation, hydrodeoxygenation, hydrodearomatization, hydroisomerization, hydrodealkylation, hydrocracking, hydrodeasphalting, reduction of Conradson carbon.

[0067] Such a process of hydrotreating heavy cuts is widely known and can resemble the process known as HYVAHL-F™ described in the patent U.S. Pat. No. 5,417,846.

[0068] A person skilled in the art will easily understand that in the hydrodemetallization stage mainly hydrodemetallization reactions are carried out, but also, in parallel, a part of the hydrodesulphurization reactions. Similarly, in the hydrodesulphurization stage, mainly hydrodesulphurization reactions are carried out, but also, in parallel, a part of the hydrodemetallization reactions.

[0069] According to a variant, a co-feedstock can be introduced with the heavy fraction in the hydrotreatment stage f). This co-feedstock can be selected from atmospheric residues, vacuum residues originating from direct distillation, deasphalted oils, aromatic extracts originating from lubricant base production chains, hydrocarbon-containing fractions or a mixture of hydrocarbon-containing fractions able to be selected from the products originating from a fluid catalytic cracking process: a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil, or able to originate from distillation, gas oil fractions, in particular those obtained by atmospheric or vacuum distillation, such as for example vacuum gas oil.

[0070] The hydrotreatment stage can advantageously be implemented at a temperature comprised between 300 and 500° C., preferably 350° C. to 420° C. and under a hydrogen partial pressure advantageously comprised between 5 MPa and 25 MPa, preferably between 10 and 20 MPa, an overall hourly space velocity (LHSV) situated in a range from 0.1 h-1 to 5 h-1 and preferably 0.1 h-1 to 2 h-1, a quantity of hydrogen mixed with the feedstock usually of 100 to 5000 Nm3/m3 (normal cubic metres (Nm3) per cubic metre (m3) of liquid feedstock), most often of 200 to 2000 Nm3/m3 and preferably 300 to 1500 Nm3/m3.

[0071] Normally, the hydrotreatment stage is carried out industrially in one or more reactors with a descending flow of liquid. The hydrotreatment temperature is generally adjusted as a function of the desired level of hydrotreatment.

[0072] The hydrotreatment catalysts used are preferably known catalysts and are generally granular catalysts comprising, on a support, at least one metal or metal compound having a hydrodehydrogenating function. These catalysts are advantageously catalysts comprising at least one metal of group VIII, generally selected from the group formed by nickel and/or cobalt, and/or at least one metal of group VIB, preferably molybdenum and/or tungsten. For example a catalyst comprising 0.5 to 10% by weight of nickel and preferably 1 to 5% by weight of nickel (expressed as nickel oxide NiO) and 1 to 30% by weight of molybdenum, preferably 5 to 20% by weight of molybdenum (expressed as molybdenum oxide MoO_3) on a mineral support will be used. This support will, for example, be selected from the group formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. Advantageously, this support includes other doping compounds, in particular oxides selected from the group formed by boron oxide, zirconia, cerite, titanium oxide, phosphoric anhydride and a mixture of these oxides. An alumina support is most often used, and a support of alumina doped with phosphorus and optionally boron is very often used. The concentration of phosphoric anhydride P_2O_5 is normally comprised between 0 or 0.1% and 10% by weight. The concentration of boron trioxide B_2O_5 is normally comprised between 0 or 0.1% and 10% by weight. The alumina used is normally a γ or η alumina. This catalyst is most often in the form of extrudates. The total content of oxides of metals of groups VIB and VIII is often 5 to 40% by weight and generally 7 to 30% by weight and the weight ratio expressed as metallic oxide between a metal (or metals) of group VIB and a metal (or metals) of group VIII is generally 20 to 1 and most often 10 to 2.

[0073] In the case of a hydrotreatment stage including a hydrodemetallization (HDM) stage, then a hydrodesulphurization (HDS) stage, specific catalysts adapted to each stage are most often used.

[0074] Catalysts that can be used in the hydrodemetallization (HDM) stage are for example indicated in the patents EP113297, EP113284, U.S. Pat. No. 5,221,656, U.S. Pat. No. 5,827,421, U.S. Pat. No. 7,119,045, U.S. Pat. No. 5,622,616 and U.S. Pat. No. 5,089,463. Hydrodemetallization (HDM) catalysts are preferably used in switchable reactors. Catalysts that can be used in the hydrodesulphurization (HDS) stage are for example indicated in the patents EP113297, EP113284, U.S. Pat. No. 6,589,908, U.S. Pat. No. 4,818,743 or U.S. Pat. No. 6,332,976. A mixed catalyst that is active in hydrodemetallization and in hydrodesulphurization can also be used both for the hydrodemetallization (HDM) section and for the hydrodesulphurization (HDS) section, as described in the patent FR2940143.

[0075] Prior to the injection of the feedstock, the catalysts used in the process according to the present invention are preferably subjected to an in situ or ex situ sulphurization treatment.

Stage g): Optional Stage of Separating the Hydrotreatment Effluent

[0076] The optional separation stage g) can advantageously be implemented using any method known to a person skilled in the art, such as for example the combination of one or more high- and/or low-pressure separators, and/or high- and/or low-pressure distillation and/or stripping stages. This optional separation stage g) is similar to the separation stage b) and will not be described further.

[0077] In a variant embodiment of the invention the effluent obtained at stage f) is at least partially, and often completely, sent into a separation stage g), comprising an atmospheric distillation and/or a vacuum distillation. The effluent from the hydrotreatment stage is fractionated by atmospheric distillation into a gaseous fraction, at least one atmospheric distillate fraction containing the fuel bases (naphtha, kerosene and/or diesel) and an atmospheric residue fraction. At least a part of the atmospheric residue can then be fractionated by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction.

[0078] The vacuum residue fraction and/or the vacuum distillate fraction and/or the atmospheric residue fraction can at least partially constitute the low-sulphur fuel-oil bases having a sulphur content of less than or equal to 0.5% by weight and a sediment content after ageing of less than or equal to 0.1%. The vacuum distillate fraction can constitute a fuel-oil base having a sulphur content of less than or equal to 0.1% by weight.

[0079] A part of the vacuum residue and/or of the atmospheric residue can also be recycled into the visbreaking stage a).

Fluxing

[0080] In order to obtain a fuel oil, the heavy fractions originating from stages d) and/or e) and/or f) and/or g) can be mixed with one or more fluxing bases selected from the group constituted by the light cycle oils of a catalytic cracking, the heavy cycle oils of a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil. Preferably, kerosene, gas oil and/or vacuum distillate produced in the process of the invention will be used. Advantageously, kerosene, gas oil and/or vacuum distillate obtained in the separation stages b) or g) of the process will be used.

[0081] 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 limitative of the remainder of the disclosure in any way whatsoever.

[0082] 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.

[0083] The entire disclosures of all applications, patents and publications, cited herein and of corresponding application No. FR 1460630, filed Nov. 4, 2014, are incorporated by reference herein.

EXAMPLES

[0084] The following example illustrates the invention but without limiting its scope. The feedstock treated is a vacuum residue (Ural VR), the characteristics of which are indicated in Table 1.

TABLE 1

Characteristics of the feedstock	
Cut	Ural VR
Sulphur % by mass	2.7
Conradson carbon	16
C7 asphaltenes (% by mass)	4.2
NI + V ppm	220
Viscosity at 100° C. (cSt)	548
350° C.+ (% by mass of compounds boiling above 350° C.)	99.0
540° C.+ (% by mass of compounds boiling above 540° C.)	86.5

[0085] The feedstock is subjected to a visbreaking stage. The operating conditions of the visbreaking section are given in Table 2.

TABLE 2

Visbreaking section operating conditions	
Temperature at furnace outlet (° C.)	457
Total pressure, MPa	0.8
Residence time in maturation chamber (soaker) (minutes)	35

[0086] The visbreaking effluents are then subjected to a separation comprising an atmospheric distillation and making it possible to recover a gaseous fraction and a heavy fraction. The heavy fraction (350° C.+ fraction) is then treated according to two variants:

[0087] A) No additional treatment (not according to the invention)

[0088] B) A stage of maturation of the sediments (4h at 150° C. carried out in a heated stirred tank in the presence of a 50/50 air/nitrogen mixture under a total pressure of 0.5 MPa) then a stage of physically separating the sediments using a filter (according to the invention)

[0089] According to the two preceding variants A) and B), the 350° C. fractions are distilled in the laboratory with a view to discovering the qualities and yields of vacuum distillate and vacuum residue. The yields and the sulphur content and the viscosity (for the heavy cuts) are indicated in Table 3.

TABLE 3

Yields, sulphur content and viscosity in visbreaking section

	Yield (% by weight/feedstock)	Sulphur content (% by weight)	Viscosity at 100° C. (cSt)
Gas	4.2		
Naphtha (80-180° C.)	2.8		
Diesel (180-350° C.)	7.5		
Vacuum distillates (350-540° C.)	39.4		
Vacuum residue (540+° C.)	46.2		
Atmospheric residue (350° C.+, Feedstock from the maturation stage)	85.6	2.3	85

[0090] The operating conditions of the visbreaking stage coupled with a stage of maturation and separation of the sediments according to the invention carried out on the heavy fraction originating from the atmospheric distillation have an impact on the stability of the effluents obtained. This is illustrated by the sediment contents after ageing measured in the atmospheric residues (350°C+ cut). The performances are summarized in Table 4 below.

TABLE 4

Summary of the performances with or without maturation and separation of the sediments		
	Visbreaking	
Conversion rate of the compounds boiling above 540° C. (%)	46	
Maturation	No	Yes
Separation of the sediments	No	Yes
Sediment content after ageing (IP390) in the 350° C.+ cut	0.6	<0.1

[0091] According to the invention, it is possible to obtain stable effluents with a low sediment content when a maturation stage then a stage of separating the sediments are implemented.

[0092] It is also possible to subject the effluents originating from the stages of maturation and separation of the sediments to a fixed-bed hydrotreatment stage. The operating conditions of the hydrotreatment stage are indicated in Table 5.

[0093] The CoMoNi on Alumina catalysts used are sold by the company Axens under the references HF858, HM848 and HT438.

TABLE 5

Operating conditions of the hydrotreatment stage carried out on the 350+ cuts originating from the visbreaking stage after passing to the stage of maturation and separation of the sediments

HDM, transition and HDS catalysts	CoMoNi on alumina
Cycle starting temperature (° C.)	370
H2 partial pressure (MPa)	15
LHSV (h−1, Sm3/h fresh feedstock/m3 of fixed-bed catalyst)	0.16
H2/HC at inlet of fixed-bed section not including H2 consumption (Nm3/m3 of fresh feedstock)	1000

[0094] The effluents originating from the hydrotreatment stage are then separated and analyzed. The vacuum distillate fractions contain less than 0.2% by weight of sulphur. The vacuum residue fractions contain less than 0.5% by weight of sulphur. Vacuum distillate fractions and vacuum residues (or atmospheric residue fractions) are thus obtained with a low sulphur content and a low sediment content after ageing. These fractions thus constitute excellent fuel-oil bases and in particular excellent bunker oil bases.

[0095] 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.

[0096] 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) Process for converting a hydrocarbon-containing feedstock containing at least one hydrocarbon fraction having a sulphur content of at least 0.1% by weight, an initial boiling temperature of at least 340° C. and a final boiling temperature of at least 440° C., making it possible to obtain a heavy fraction having a sediment content after ageing of less than or equal to 0.1% by weight, said process comprising the following stages:

a) a stage of visbreaking the feedstock in at least one maturation chamber (soaker),

b) a stage of separating the effluent obtained at the end of stage a) into at least one light hydrocarbon fraction containing fuel bases and a heavy fraction containing compounds boiling at at least 350° C.,

c) a stage of maturation of the heavy fraction originating from the separation stage b) making it possible to convert a part of the potential sediments to existing sediments, carried out for a duration comprised between 1 and 1500 minutes, at a temperature comprised between 50 and 350° C., and at a pressure of less than 20 MPa,

d) a stage of separating the sediments from the heavy fraction originating from the maturation stage c) in order to obtain said heavy fraction.

2) Process according to claim **1** in which the visbreaking stage is carried out at a temperature comprised between 370° C. and 500° C., for a duration comprised between 1 and 60 minutes, a total pressure of less than 10 MPa.

3) Process according to claim **1** in which a stage of hydrotreating the feedstock is carried out upstream of the visbreaking stage a).

4) Process according to claim **1** in which the visbreaking stage is carried out in the presence of hydrogen.

5) Process according to one of the preceding claims in which, during stage b), the effluent obtained at the end of stage a) is separated in a high-pressure high-temperature HPHT separator into a light fraction and a heavy fraction containing mainly compounds boiling at at least 350° C.

6) Process according to claim **1** in which at least a part of the fraction known as heavy originating from stage b) is fractionated by atmospheric distillation into at least one atmospheric distillate fraction containing at least one light hydrocarbon fraction of the naphtha, kerosene and/or diesel type and an atmospheric residue fraction.

7) Process according to claim **1** in which the stage of maturation of the heavy fraction originating from stage b) is carried out in the presence of an inert gas and/or an oxidizing gas.

8) Process according to claim **1** in which the separation stage d) is carried out by means of at least one separation means selected from a filter, a separation membrane, a filtering bed of solids of the organic or inorganic type, an electrostatic precipitation, a centrifugation system, decantation, drawing- off by means of an endless screw.

9) Process according to claim **1** also comprising a fixed-bed hydrotreatment stage f) implemented on at least a part of the heavy fraction originating from stage d) in which the heavy fraction and hydrogen are passed over a hydrotreatment catalyst under hydrotreatment conditions.

10) Process according to claim **9** in which the hydrotreatment stage is carried out at a temperature comprised between 300 and 500° C., an absolute pressure comprised between 5 MPa and 25 MPa, an overall hourly space velocity (LHSV) situated in a range from 0.1 h^{-1} to 5 h^{-1}, a quantity of hydrogen mixed with the feedstock of 100 to 5000 Nm^3/m^3.

11) Process according to claim **9** in which a co-feedstock is introduced with the heavy fraction in the hydrotreatment stage f).

12) Process according to claim **11** in which the co-feedstock is selected from atmospheric residues, vacuum residues originating from direct distillation, deasphalted oils, aromatic extracts originating from lubricant base production chains, hydrocarbon-containing fractions or a mixture of hydrocarbon-containing fractions able to be selected from the products originating from a fluid catalytic cracking process: a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil, or able to originate from distillation, gas oil fractions, in particular those obtained by atmospheric or vacuum distillation, such as for example vacuum gas oil.

13) Process according to claim **1** in which the feedstock treated is selected from atmospheric residues, vacuum residues originating from direct distillation, crude oils, topped crude oils, deasphalted oils, deasphalting resins, asphalts or deasphalting pitches, residues originating from conversion processes, aromatic extracts originating from lubricant base production chains, bituminous sands or derivatives thereof, oil shales or derivatives thereof, alone or in a mixture.

14) Process according to claim **1** in which the heavy fractions originating from stages d) and/or f) are mixed with one or more fluxing bases selected from the group constituted by the light cycle oils of a catalytic cracking, the heavy cycle oils of a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil.

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