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(54) PROCESS FOR CONVERSION OF PETROLEUM FEED COMPRISING AN EBBULATED BED HYDROCONVERSION STEP IN A FIXED BED HYDROTREATMENT STEP FOR THE PRODUCTION OF LOW SULPHUR CONTENT FUEL

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(57) ABSTRACT
Process for conversion of petroleum feed for production of low sulphur content fuel comprising the following steps: a step of ebullated bed hydroconversion of the feed in the presence of a supported catalyst, a separation step allowing a residual fraction to be obtained, a step of fixed bed hydrotreatment of the residual fraction using an upstream system of permutable reactors.
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EBULLATED BED HYDROCONVERSION
STEP IN A FIXED BED HYDROTREATMENT
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SULPHUR CONTENT FUEL

[0001] The present invention concerns the refining and conversion of heavy hydrocarbon fractions containing amongst others sulphurated impurities. More particularly it concerns a conversion method for heavy petroleum feeds for the production of fuel bases of the type vacuum distillate, atmospheric residue and vacuum residue, in particular bunker fuel bases with low sulphur content. The method according to the invention also allows the production of atmospheric distillates (naphtha, kerosene and diesel), vacuum distillates and light gases (C1 to C4).

[0002] Whereas land-based industry has been subjected to stringent regulations on the sulphur content contained in fuel bases (petrol, diesel) in recent decades, the sulphur content in marine fuel has so far been subjected to few constraints. In fact the fuels presently available on the market contain up to 4.5% weight sulphur. As a result ships have become the main source of sulphur dioxide emissions (SO₂).

[0003] In order to reduce these emissions, the International Maritime Organisation has submitted recommendations in terms of specifications concerning marine fuels. These recommendations are given in the 2010 version of standard ISO 8217 (Annex VI of the MARPOL Convention). The specification concerning sulphur henceforth applies to SO₂ emissions and is reflected by a recommendation of a sulphur content equivalent to less than or equal to 0.5% weight. Another highly restrictive recommendation is the content of sediment after ageing according to ISO 10307-2 which must be less than or equal to 0.1%.

[0004] The present invention allows the production of fuel bases, in particular bunker fuel bases, complying with the recommendations of the MARPOL agreement.

[0005] U.S. Pat. No. 6,447,671 describes a method for converting heavy petroleum fractions comprising a first ebullated bed hydroconversion step, a step of eliminating catalyst particles contained in the hydroconversion effluent, and then a fixed bed hydrotreatment step. This method is designed to give fuel bases (petrol and diesel) having in particular a low sulphur content. The method, however, also leads to a heavy fuel with sulphur contents higher than the new recommendations.

[0006] The present invention adapts and improves the conversion method described by the applicant in U.S. Pat. No. 6,447,671 for the production of fuel bases by integrating in this method a system of permutable reactors (or storage zones) functioning in fixed beds in the hydrotreatment step.

[0007] More particularly the invention concerns a method converting a hydrocarbon-containing feed comprising at least one fraction of hydrocarbons with a sulphur content of at least 0.1% weight, an initial boiling temperature of at least 340° C. and a final boiling temperature of at least 440° C., comprising the following steps:

a) a step of hydroconversion in the presence of hydrogen in at least one reactor containing a catalyst supported in an ebulliated bed,

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

c) a step of fixed bed hydrotreatment of at least part of the heavy fraction from step b) in which, under hydrotreatment conditions, the heavy fraction and hydrogen are passed over a hydrotreatment catalyst and in which the hydrotreatment step comprises a plurality of fixed bed hydrotreatment zones preceded by at least two storage zones also with fixed bed hydrotreatment, arranged in series to be used in a cyclic manner comprising the successive repetition of steps c) and e) defined below:

d) a step in which the storage zones are used together for a duration at most equal to the deactivation and/or clogging time of one of them,

e) a step during which the deactivated and/or clogged storage zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh catalyst, and during which the other storage zone(s) is/are used, and

f) a step during which the storage zones are all used together, wherein the storage zone of which the catalyst has been regenerated during the preceding step is reconnected and said step is continued for a duration equal at most to the deactivation and/or clogging time of one of the storage zones.

[0012] The system of permutable reactors is known from patents FR 2681871, FR 2784687 and EP 1343857. It is conventionally used to extend the operating cycle of a hydrotreatment unit by allowing replacement of a deactivated and/or clogged catalyst in the permutable reactors without stopping the entire unit.

[0013] The present invention is targeted at the production of fuel bases complying with the recommendations of the International Maritime Organisation and atmospheric distillates and/or vacuum distillates.

[0014] The hydroconversion step allows partial conversion of the heavy feed in order to produce atmospheric distillates and/or vacuum distillates. Although the ebulliated bed technology is known to be suitable for heavy feeds with impurities, the ebulliated bed by its nature produces catalyst fines and sediments which must be removed before the subsequent fixed bed treatment in order to prevent clogging of the catalytic bed(s). The fines come principally from wear on the catalyst in the ebulliated bed. The sediment can be precipitated asphaltenes. Initially the hydroconversion conditions and in particular the temperature to which they are subjected causes them to undergo reactions in the feed (dealkylation, polymerization) leading to their precipitation.

[0015] The permutable reactors in the method according to the invention solve this problem of fines and sediments at the same time as the problem of sulphur content, without pushing excessively the operating conditions in the hydrotreatment step.

[0016] In fact the permutable reactors receiving the heavy fraction from the hydroconversion limit the content of fines and sediment by their filter function (fixed bed).

[0017] In order to achieve the recommendation of a sulphur content of less than or equal to 0.5% weight, the operating conditions of the hydrotreatment section must be severe, which is conventionally reflected by an increase in temperature in the fixed beds. However this increase in temperature promotes the deposit of coke, accelerating the process of clogging and deactivation. The permutable reactors are intended to protect the hydrotreatment section and thus relieve the load on the main hydrotreatment reactors suffi-
ciently to perform the necessarily extensive desulphuration of the heavy fraction obtained after hydroconversion, without the operating conditions becoming excessively harsh.

[0020] In other words, the integration of the permutable reactors in a sequence of ebullated bed hydroconversion then fixed bed hydrotreatment allows the obtaining of fuel bases complying with future specifications. The fuel bases produced by the method according to the invention have a sulphur content of less than or equal to 0.5% weight and a sediment content after ageing of less than or equal to 0.1%. Furthermore if the base fuel is constituted by vacuum distillate from the process, the sulphur content can be less than or equal to 0.1% weight.

[0021] Another important point in the process is the partial conversion of the feed allowing production, in particular by ebullated bed hydroconversion, of low sulphur content distillates (naphtha, kerosene and diesel). In the context of the present invention, the rate of conversion of the feed into lighter fractions lies habitually between 10 and 90% and more often between 25 and 60% or even limited to around 50%. The conversion rate mentioned above is defined as being the mass fraction of organic compounds with a boiling point higher than 350°C at the entry to the reaction section, minus the mass fraction of organic compounds with a boiling point higher than 350°C at the outlet from the reaction section, all divided by the mass fraction of organic compounds with a boiling point higher than 350°C at the entry to the reaction section.

[0022] In order to constitute the fuel meeting the requirements of viscosity, the fuel bases obtained by the present method may be mixed with flux bases so as to achieve the target viscosity of the desired fuel grade. The viscosity of bunker fuel must be less than or equal to 380 cSt (50°C).

[0023] In a variant of the method, the effluent obtained after hydrotreatment may be subjected to a separation step (step d) from which normally at least one fraction of fuel bases (naphtha, kerosene, diesel) and heavy fractions such as vacuum distillate or vacuum residue are recovered.

[0024] According to a variant of the method, at least part of one of these heavy fractions can be sent to a catalytic cracking section (step e) in which it is processed under conditions allowing production amongst others of a light cycle oil (LCO) and a heavy cycle oil (HCO). These oils can be used as flux for mixing the fuel bases resulting from the method according to the invention to constitute the fuel, so as to achieve the target viscosity.

**DETAILED DESCRIPTION**

**Feed**

[0025] The feeds processed in the method according to the invention are advantageously selected from atmospheric residues, vacuum residues from direct distillation, crude petroleum, topped crude petroleum, deasphalted oils, resin from deasphaltation, asphalt or deasphaltation pitch, residues from conversion processes, aromatic extracts from production chains of lubricant bases, bituminous sands or their derivatives, oil shales or their derivatives, taken alone or in combination. These feeds can advantageously be used as such or diluted with a hydrocarbonated fraction or a mixture of hydrocarbonated fractions which can be selected from products resulting from fluid catalytic cracking (FCC), a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil (DO), an FCC residue, or can come from distillation, the gas oil fractions in particular being those obtained by atmospheric or vacuum distillation such as for example vacuum gas oil. The heavy feeds can also advantageously comprise cuts from the coal or biomass liquefaction process, aromatic extracts or any other hydrocarbonated cuts or even non-petroleum feeds such as pyrolysis oil.

[0026] Said heavy feeds generally have a sulphur content of at least 0.1% weight, an initial boiling temperature of at least 340°C and a final boiling temperature of at least 440°C.

[0027] According to the present invention the feeds treated are preferably atmospheric residues or vacuum residues or mixtures of these residues.

**Ebullated Bed Hydroconversion (Step a)**

[0028] According to the present invention the feed is subjected to a hydroconversion step performed in at least one reactor containing a supported catalyst in an ebullated bed functioning with liquid and gas upflow. The main objective of hydroconversion is to convert the heavy fraction into lighter cuts while partially refining the feed.

[0029] Ebullated bed technology is widely known so only the main operating conditions are described here. Ebullated bed technologies use supported catalysts in the form of extrusions, the diameter of which is generally of the order of 1 mm or less than 1 mm. The catalysts remain inside the reactors and are not evacuated with the products. The temperature levels are high in order to obtain high conversion while minimising the quantities of catalysts used. The catalytic activity can be held constant thanks to in-line replacement of the catalyst. It is therefore not necessary to stop the unit in order to replace exhausted catalyst nor to increase the reaction temperatures throughout the cycle in order to compensate for deactivation. Furthermore, by working under constant operating conditions, constant yields and product quality are obtained throughout the cycle. Thus, because the catalyst is held in agitation by significant liquid recycling, the load loss over the reactor remains low and constant.

[0030] The conditions of the feed processing in step a) in the presence of hydrogen are normally conventional conditions of ebullated bed hydroconversion of a liquid hydrocarbonated fraction. This is operated normally at an absolute pressure of 2.5 to 35 MPa, often 5 to 25 MPa, and most often 6 to 20 MPa, at a temperature of 330 to 550°C and often 350 to 500°C. The hourly spatial velocity (VHV) and the hydrogen partial pressure are significant factors which are selected as a function of characteristics of the product to be processed and the desired conversion. The VHV is defined as the volumetric flow of the feed divided by the total volume of the reactor, and generally lies in a range from 0.1 h⁻¹ to 10 h⁻¹ and preferably 0.2 h⁻¹ to 5 h⁻¹. The quantity of hydrogen mixed into the feed is normally 50 to 5000 standard cubic metres (Nm³) per cubic metre (m³) of liquid feed and most often 100 to 1000 Nm³/m³ and preferably 200 to 500 Nm³/m³.

[0031] A conventional granular hydroconversion catalyst can be used comprising, on an amorphous support, at least one metal or metal compound with a hydro-dehydrogenating function. This catalyst may be a catalyst comprising metals of group VIII, for example nickel and/or cobalt, most often in association with at least one metal of group VIb, for example molybdenum and/or tungsten. For example a catalyst can be used comprising 0.5 to 10% weight nickel and preferably 1 to 5% weight nickel (expressed as nickel oxide NiO) and 1 to 50% weight molybdenum, preferably 5 to 20% weight molybdenum (expressed as molybdenum oxide MoO₃) on an
amorphous mineral support. This support is selected for example from the group formed from alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. The support can also contain other compounds and for example oxides selected from the group formed by boron oxides, zircon, titanium oxide, phosphoric anhydride. Usually an alumina support is used, and very often a support of alumina doped with phosphorus and where applicable boron. When phosphoric anhydride \( P_2O_5 \) is present, its concentration is usually less than 20% by weight and most often less than 10% by weight. The concentration of boron trioxide \( B_2O_3 \) is normally 0 to 10% by weight. The alumina used is normally a gamma or eta alumina. This catalyst is most often present in the form of extrusions. The total content of oxides of metals of groups VI and VIII is often 5 to 40% by weight and generally 7 to 30% by weight, and the weight ratio expressed in metal oxide between the metal (or metals) of group VI to the metal (or metals) of group VIII is generally 20 to 1 and most often 10 to 2.

[0032] The exhausted catalyst is partly replaced by fresh catalyst, generally by extraction from the bottom of the reactor and introduction of fresh or new catalyst at the top of the reactor at regular intervals i.e. for example in batches or quasi-continuously. The catalyst can also be introduced at the bottom and extracted at the top of the reactor. For example fresh catalyst can be introduced every day. The rate of replacement of exhausted catalyst with fresh catalyst may for example be around 0.05 kilograms to around 10 kilograms per cubic metre of feed. This extraction and replacement are performed using devices allowing continuous function of this hydroconversion step. The unit normally comprises a recirculation pump allowing the catalyst to be maintained in the ebulliated bed by continuous recycling of at least part of the liquid extracted at the head of the reactor and re-injected at the base of the reactor. It is also possible to send the exhausted catalyst extracted from the reactor to a regeneration zone in which the carbon and sulphur it contains are eliminated, before it is re-injected into hydroconversion step a).

[0033] Most often this hydroconversion step a) is implemented under the conditions of the Fluid Oil Process as described for example in U.S. Pat. No. 6,270,654.

[0034] The ebulliated bed hydroconversion can be carried out in a single reactor or in several reactors (generally two) arranged in series. By using at least two ebulliated bed reactors in series, products of better quality can be obtained with a better yield, thus limiting the requirements for energy and hydrogen in any post-treatment. Also hydroconversion in two reactors allows improved operability in relation to the flexibility of the operating conditions and the catalytic system. Generally the temperature of the second reactor is preferably at least 10°C higher than that of the first ebulliated bed reactor. The pressure of the second reactor is 0.1 to 1 MPa lower than for the first reactor to allow the flow of at least part of the effluent from the first step without pumping being necessary. The different operating conditions in terms of temperature in the two hydroconversion reactors are selected in order to be able to control the hydrogenation and conversion of the feed into the desired products in each reactor.

[0035] Where applicable the effluent obtained at the end of the first hydroconversion step is subjected to separation of the light fraction, and at least part, preferably all, of the residual effluent is treated in the second hydroconversion step. This separation is advantageously performed in an inter-stage separator described in U.S. Pat. No. 6,270,654 and in particular allows avoidance of over-cracking of the light fraction in the second hydroconversion reactor.

[0036] It is also possible to transfer all or part of the exhausted catalyst extracted from the reactor in the first hydroconversion step, operating at lower temperature, directly to the reactor of the second step, operating at higher temperature, or to transfer all or part of the exhausted catalyst extracted from the reactor in the second step directly to the reactor of the first step. This cascade system is described in U.S. Pat. No. 4,816,841.

Separation of the Hydroconversion Effluent (Step b)

[0037] The effluent obtained after the ebulliated bed hydroconversion undergoes at least one separation step, where applicable supplemented by other further separation steps allowing separation of at least one light hydrocarbon fraction containing fuel bases and a heavy fraction containing predominantly compounds boiling at minimum 350°C. The separation step can advantageously be implemented by any method known to the person skilled in the art, such as for example the combination of one or a plurality of high- and/or low-pressure separators and/or distillation steps and/or high- and/or low-pressure stripping, and/or liquid/liquid extraction steps and/or solid/liquid separation steps and/or centrifuging steps. Preferably the separating step b) leads to the acquisition of a gaseous phase, at least one light hydrocarbon fraction of the type naphtha, kerosene and/or diesel, a vacuum distillate fraction and a vacuum residue fraction and/or an atmospheric residue fraction.

[0038] According to a first embodiment the effluent from the hydroconversion undergoes a separation step with decompression between the ebulliated bed hydroconversion and the fixed bed hydrotreatment. This configuration can be described as a non-integrated system.

[0039] According to the non-integrated system, separation is preferably performed in a fractioning section which can firstly comprise a high-pressure, high-temperature separator (HP/HTT) and where applicable a high-pressure, low-temperature separator (HPLT) and/or an atmospheric distillation and/or a vacuum distillation. The effluent obtained from step a) is separated (generally in an HP/HTT separator) into a light fraction and a heavy fraction containing predominantly compounds boiling at minimum 350°C. Separation is not made following a precise cutting point, it rather resembles a flash. If we have to define a cutting point, we could say that this lies between 200 and 400°C.

[0040] Preferably the so-called heavy fraction is then fractioned by atmospheric distillation into at least one atmospheric distillate fraction containing at least one light fraction of hydrocarbons of the type naphtha, kerosene and/or diesel, and an atmospheric residue fraction. At least part of the atmospheric residue fraction can be sent for hydrotreatment. The atmospheric residue can also at least be partly fractioned by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction. Said vacuum residue fraction is advantageously sent at least partly to the hydrotreatment step c). Part of the vacuum residue can also be recycled in hydroconversion step a).

[0041] According to a second embodiment the effluent from the ebulliated bed hydroconversion undergoes a separation step without decompression between hydroconversion and hydrotreatment. This configuration can be called an integrated system.
According to the integrated system, the effluent obtained after step a) is separated (generally in an HPHT separator) into a light fraction and a heavy fraction containing predominantly compounds boiling at minimum 350°C. Separation is not made according to a precise cutting point but is similar to a flash. If we have to define a cutting point, we could say that this lies between 200 and 400°C.

Preferably the heavy fraction is then sent to the hydrotreatment step. The light fraction can undergo further separation steps, where applicable in the presence of the light fraction from the inter-stage separator between the two hydroconversion reactors. Advantageously it is subjected to atmospheric distillation giving a gaseous fraction, at least one light fraction of hydrocarbons of the type naphtha, kerosene and/or diesel, and a vacuum distillate fraction, wherein the latter can be sent at least partly to the hydrotreatment step c).

Another part of the vacuum distillate can constitute part of a fuel as a flux agent. Another part of the vacuum distillate can be refined by hydrocracking and/or by fluid catalytic cracking.

Separation according to the integrated system allows better thermal integration and is reflected by a saving in energy and equipment. Also this system has technical and economic advantages given that the high-pressure flux will not require an increase in pressure in view of the subsequent hydrotreatment. This embodiment therefore, by its simplified intermediate fractioning, allows a reduction in the consumption of utilities and hence the investment costs.

The gaseous fractions from the separation step (either the integrated or non-integrated system) preferably undergo purification treatment to recover the hydrogen and recycle it towards hydroconversion and/or hydrotreatment reactors. The same applies to gaseous effluent from hydrotreatment. The gas phase from the optional inter-stage separator can also be added.

The separation step in the non-integrated or integrated system allows the arrangement of two independent hydrogen circuits, one linked to hydroconversion and the other to hydrotreatment, and which depending on need can be linked together. The hydrogen can be added to one or the other or to both reaction sections, the recycling gas can supply one or the other or both reaction sections. The compressor may where applicable be common to both sections. The possibility of linking the two hydrogen circuits allows optimisation of hydrogen management and limits the investment in terms of compressors and/or purification units for the gaseous effluent. The various embodiments of hydrogen management which can be used in the present invention are described in application FR 2957607.

The processing of the various fuel base cuts (LPG, naphtha, kerosene, diesel and/or vacuum gas oil) obtained in the non-integrated or integrated system is not the subject of the present invention and these methods are well known to the person skilled in the art. The products obtained can be integrated in fuel reservoirs (also called fuel pools) or undergo additional refining steps. The naphtha, kerosene, gas oil and vacuum gas oil fractions may be subjected to one or a plurality of treatments (hydrotreatment, hydrocracking, alkylation, isomerisation, catalytic reforming, catalytic cracking or thermal cracking or other) to bring these to the required specifications (sulphur content, smoke point, octane, cetane etc.) either separately or combined.

Advantageously the vacuum distillate from the ebullated bed, after separation, can undergo hydrotreatment. This hydrotreated vacuum distillate can be used as a flux for the fuel pool having a sulphur content of less than or equal to 0.5% weight or be used directly as fuel with a sulphur content of less than or equal to 0.1% weight. Part of the atmospheric residue, the vacuum distillate and/or vacuum residue can undergo other additional refining steps such as hydrocracking or fluid catalytic cracking.

Hydrotreatment (Step c)

The heavy fraction containing compounds boiling at minimum 350°C from separation step b) is then sent to the hydrotreatment step comprising one or a plurality of fixed bed hydrotreatment zones preceded by at least two storage zones also with fixed bed hydrotreatment.

Hydrotreatment (HDT) in particular means reactions of hydrodesulphurisation (HDS), hydrodenitrogenation (HDN) and hydrodemetallation (HDM), but also hydrogenation, hydrodeoxygenation, hydrodearomatization, hydroisomerization, hydrodialkylation, hydrocracking, hydrodesulphation and Conndrad carbon reduction.

According to a preferred variant, the hydrotreatment step comprises a first hydrodemetallation step comprising one or a plurality of fixed bed hydrodemetallation zones preceded by at least two of said hydrotreatment storage zones, and a second subsequent hydrodesulphurization step comprising one or a plurality of fixed bed hydrodesulphurization zones and in which, during the first said hydrodemetallation step, under hydrodemetallation conditions, the feed of hydrocarbons and hydrogen is passed over a hydrodemetallation catalyst, then during the second subsequent step, under hydrodesulphuration conditions, the effluent from the first step is passed over a hydrodesulphuration catalyst. This process known under the name HYVAHL-FTM is described in U.S. Pat. No. 5,417,846.

The person skilled in the art will easily understand that in the hydrodemetallation step, predominantly hydrodemetallation reactions are performed but in parallel also part of the hydrodesulphuration reactions. Similarly in the hydrodesulphuration step predominantly hydrodesulphuration reactions are performed but in parallel also part of the hydrodemetallation reactions.

The catalytic beds in the fixed bed reactors, in particular the upper parts of the catalytic beds and more particularly the upper parts of the first catalytic bed in contact with the feed, are susceptible to clogging fairly quickly due to the asphaltenes and sediments contained in the feed, which is reflected initially by an increase in the load loss and sooner or later requires a stoppage of the hydrotreatment unit for replacement of the catalyst in the main hydrotreatment reactors.

The function of the permeable reactors is to filter the sediments and the catalyst fines from the hydroconversion step, which prevents clogging in the main reactors.

Another problem traditionally found when using fixed beds is deactivation of the catalyst due to the high deposits of metals occurring during the hydrotreatment reactions. To compensate for this deactivation, the reactor temperature is then increased. Nonetheless this increase in temperature promotes coke deposits. The deposition of impurities is supplemented by that of coke, the whole then tending rapidly to deactivate and clog the catalytic system. These phenomena lead to stoppages of the hydrotreatment...
units for replacement of catalysts and to overconsumption of catalysts, which the person skilled in the art wishes to minimise.

[0056] The function of the permutable reactors is to protect the main hydrotreatment reactors downstream by preventing clogging and/or deactivation. The permutable reactors are thus used to extend the operating cycle of the hydrotreatment unit by allowing replacement of deactivated and/or clogged catalyst in the permutable reactors working in a cyclic fashion, without stopping the entire unit for a specific period. According to the method of the invention, extended hydrotreatment of the heavy fraction thus becomes possible in order in particular to obtain fuel bases with known sulphur content.

[0057] The function of the storage zones in the HDM section is described in FIG. 1 comprising two storage zones (or permutable reactors) Ra and Rb. This hydrotreatment process consists of a series of cycles each comprising four successive steps:

[0058] a first step (step c') during which the feed passes successively through reactor Ra then reactor Rb;

[0059] a second step (step c") during which the feed passes only through reactor Rb, reactor Ra being short-circuited for regeneration and/or replacement of the catalyst;

[0060] a third step (step c") during which the feed passes successively through reactor Rb then reactor Ra;

[0061] a fourth step (step c"') during which the feed passes only through reactor Ra, reactor Rb being short-circuited for regeneration and/or replacement of the catalyst.

[0062] Preferably after regeneration and/or replacement of the catalyst of one reactor, this reactor is reconnected downstream of the running reactor.

[0063] During step c') of the method, the effluent from the step of ebulliated bed hydroconversion is introduced via the conduit (96) and the conduit (98) which comprises an open valve V1 towards the conduit (100), and the storage reactor Ra containing a fixed bed of catalyst. During this period the valves V3, V4 and V5 are closed. The effluent from the reactor Ra is sent via the conduit (102), the conduit (104) which comprises an open valve V2 and conduit (106) into the storage reactor Rb containing a fixed bed of catalyst. The effluent from the reactor Rb is sent via the conduits (108) and (110) comprising an open valve V6 and the conduit (112) to the main hydrotreatment section which will be described below.

[0064] During step c") of the method, the valves V1, V2, V4 and V5 are closed and the feed is introduced via the conduit (96) and the conduit (114) comprising an open valve V3 towards the conduit (106) and the reactor Rb. During this period the effluent from the reactor Rb is sent via the conduits (108) and (110) comprising an open valve V6 and conduit (112) to the main hydrotreatment section.

[0065] During step c"') the valves V1, V2 and V6 are closed and the valves V3, V4 and V5 are open. The feed is introduced via the conduit (96) and the conduits (114) and (116) to the reactor Rb. The effluent from reactor Rb is sent via the conduit (108), the conduit (116) containing an open valve V4 and the conduit (100) to the storage reactor Ra. The effluent from reactor Ra is sent via the conduits (102) and (118) comprising an open valve V5 and the conduit (112) to the main hydrotreatment section.

[0066] During step c"''), the valves V2, V3, V4 and V6 are closed and the valve V1 and V5 are open. The feed is introduced via the conduit (96) and the conduits (98) and (100) to the reactor Ra. During this period the effluent from the reactor Ra is sent via the conduits (102) and (118) comprising an open valve V5 and the conduit (112) to the main hydrotreatment section. The cycle then begins again.

[0067] The deactivation and/or clogging time varies depending on the feed, the operating conditions of the hydroconversion step, the operating conditions of the hydrotreatment step and the catalyst(s) used. It is generally expressed in a fall in catalytic performance (an increase in concentration of metals and/or other impurities in the effluent), an increase in the temperature necessary to maintain a catalytic activity or—in the specific case of clogging—via a significant increase in the load loss. The load loss Δp expressing a degree of clogging is measured permanently throughout the cycle over each of the zones and can be defined by a pressure increase resulting from a partially blocked passage of the outflow through the zone. Similarly the temperature is measured permanently throughout the cycle on each of the two zones.

[0068] In order to define a deactivation and/or clogging time, the person skilled in the art will first define a maximum permitted value for the load loss Δp and/or temperature as a function of the feed to be treated, the selected operating conditions and catalysts, and above which the storage zone must be disconnected. The deactivation and/or clogging time is thus defined as the time when the limit value for load loss and/or temperature is reached. In the case of a heavy fraction hydrotreatment process, the limit value for load loss is generally between 0.3 and 1 MPa (3 and 10 bar), preferably between 0.5 and 0.8 MPa (5 and 8 bar). The limit value for temperature is generally between 400 and 430°C, where the temperature here and throughout the text corresponds to the mean temperature measured in the catalytic bed.

[0069] In a preferred embodiment a catalyst conditioning section is used allowing switching of these storage zones during operation i.e. without stopping the operation of the unit. Firstly a system which operates at a moderate pressure (10 to 50 bar but preferably 15 to 25 bar) allows the performance of the following operations on the disconnected storage reactor: washing, stripping, cooling, before discharge of worn catalyst; then heating and sulphuration after loading of fresh catalyst; then another system of pressurisation/depressurisation and slide valves of appropriate technology effectively allows switching of these storage zones without stopping the unit, i.e. without affecting the operating factor, since all operations of washing, stripping, discharge of worn catalyst, reload of fresh catalyst, heating and sulphuration are performed on the disconnected reactor or storage zone. Alternatively a pre-sulphurated catalyst can be used in the conditioning section so as to simplify the process of switching during operation.

[0070] The effluent from the permutable reactors is then sent into the main hydrotreatment reactors.

[0071] Each hydrotreatment zone or hydrotreatment storage zone contains at least one catalytic bed (for example 1, 2, 3, 4 or 5 catalytic beds). Preferably each storage zone contains one catalytic bed. Each catalytic bed contains at least one catalytic layer containing one or a plurality of catalysts, where applicable preceded by at least one inert layer, for
example alumina or ceramic in the form of extrusions, balls or discs. The catalyst used in the catalytic bed(s) can be identical or different.

[0072] In another variant, the heavy fraction obtained in step b) can be subjected, before being sent to the hydrorefining step, to separation of the sediments and catalyst fines using at least one rotating filter or at least one basket filter, or a centrifuging system such as a hydrocyclone associated with filters or in-line decantation.

[0073] In another variant the heavy fraction obtained in step b), at the inlet to each storage zone, passes through a filtering plate located upstream of the catalytic bed(s) contained in the storage zone. This filtering plate described in patent FR 2889973 can trap the clogging particles contained in the feed by means of a specific distributor plate comprising a filtering medium.

[0074] According to a variant, a co-feed can be introduced with the residual fraction in the hydrorefining step. This co-feed can be selected from atmospheric residues, vacuum residues from direct distillation, desphalted oils, aromatic extracts from the production chains of lubricant bases, hydrocarbonated fractions or a mixture of hydrocarbonated fractions which can be selected from the products resulting from a fluid catalytic cracking process: a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil, or which can come from distillation, the gas oil fractions in particular being those obtained by atmospheric or vacuum distillation, such as for example vacuum gas oil.

[0075] The hydrorefining step can advantageously be implemented at a temperature between 300 and 500°C, preferably 350 to 420°C, and at an absolute pressure advantageously between 2 MPa and 35 MPa, preferably between 10 and 20 MPa. The temperature is normally adjusted as a function of the desired hydrorefining level. Usually the global VHV lies in a range from 0.1 h⁻¹ to 5 h⁻¹ and preferably 0.1 h⁻¹ to 2 h⁻¹. The quantity of hydrogen mixed with the feed is normally 100 to 5000 standard cubic metres (Nm³) per cubic metre (m³) of liquid feed and most often 200 to 2000 Nm³/m³ and preferably 300 to 1500 Nm³/m³. Normally this hydrorefining step is performed industrially in one or a plurality of liquid downflow reactors.

[0076] The operating conditions of the permutable reactors are generally identical to those of the main hydrorefining reactors. The VHV value of each permutable reactor in operation is preferably 0.25 to 4 h⁻¹ and more often 1 to 2 h⁻¹. The global VHV value of the permutable reactors and that of each reactor is selected to achieve the maximum HDM while controlling the reaction temperature (limitation of exothermicity).

[0077] The hydrorefining catalysts used are preferably known catalysts and are generally granular catalysts comprising on a support at least one metal or metal compound with a hydro-dehydrogenating function. These catalysts are advantageously catalysts comprising at least one metal from group VIII, selected generally from the group formed by nickel and/or cobalt, and/or at least one metal from group VIB, preferably molybdenum and/or tungsten. For example a catalyst is used comprising 0.5 to 10% weight nickel and preferably 1 to 5% weight nickel (expressed in nickel oxide NiO) and 1 to 30% of weight molybdenum, preferably 5 to 20% of weight molybdenum (expressed as molybdenum oxide MoO₃) on a mineral support. This support is for example selected from the group formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. Advantageously the support contains other doping compounds, in particular oxides selected from the group formed by boron oxide, zircon, cerine, titanium oxide, phosphoric anhydride and a mixture of these oxides. Most often an alumina support is used, and very often an alumina support doped with phosphorus and where applicable boron. The concentration of phosphoric anhydride P₂O₅ is normally between 0 or 0.1% and 10% by weight. The concentration of boron trioxide B₂O₃ is conventionally between 0 or 0.1% and 10% by weight. The alumina used is normally γ or η alumina. The catalyst is most often in the form of extrusions. The total content of metal oxides of the groups VII and VIII is often 5 to 40% by weight and generally 7 to 30% by weight, and the weight ratio expressed in metal oxide between the metal (or metals) of group VII and the metal (or metals) of group VIII is generally 20 to 1 and most often 10 to 2.

[0078] In the case of a hydrorefining step including an HDM step then an HDS step, most often specific catalysts are used adapted to each step.


[0080] The catalysts which can be used in the HDS step are for example indicated in patents EP 1132927, EP 1132884, U.S. Pat. No. 6,589,908, U.S. Pat. No. 4,816,743 or U.S. Pat. No. 6,332,976.

[0081] Also a mixed catalyst can be used which is active in HDM and HDS both for the HDM section and for the HDS section as described in patent FR 2940143.

[0082] Before injection of the feed, the catalysts used in the method according to the present invention are preferably subjected to sulphonation treatment (in situ or ex situ).

Separation of the Hydrorefining Effluent (Step d)

[0083] In a current form of implementation of the invention, the effluent obtained in step c) is at least partly and often fully sent to a separation step d) comprising an atmospheric distillation and a vacuum distillation. The effluent from the hydrorefining step is fractioned by atmospheric distillation into a gaseous fraction, at least one atmospheric distillate fraction containing fuel bases (naphthas, kerosene and/or diesel) and an atmospheric residue fraction. At least part of the atmospheric residue can then be fractioned by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction.

[0084] The vacuum residue fraction and/or vacuum distillate fraction and/or atmospheric residue fraction can constitute at least partly the basis for fuel with low sulphur content, with a sulphur content of less than or equal to 0.5% weight and a sediment content after ageing of less than or equal to 0.1%. The vacuum distillate fraction can constitute a fuel base with a sulphur content of less than or equal to 0.1% weight. Part of the vacuum residue can also be recycled into hydroconversion step a).

[0085] The separation stage of step b) in the integrated system, according to which the heavy fraction is recovered for hydrorefining and a light fraction, may be separate from the separation step d), but preferably the light fraction obtained without decompression in separation step b) is sent to separation step d).
Although the fuel bases produced according to the present method contain very little sediment, a supplementary filtration step may be provided.

Catalytic Cracking (Step e)

According to a variant at least part of the vacuum distillate fraction and/or vacuum residue fraction resulting from step d) is sent to a catalytic cracking section known as step e) in which it is treated under conditions allowing production of a gaseous fraction, a petrol fraction, a diesel fraction and a residual fraction.

In one embodiment of the invention at least part of the residual fraction obtained in catalytic cracking step e), often called the slurry fraction by the person skilled in the art, is recycled to the inlet of step e) and/or a) and/or c). The residual fraction can thus be sent at least partly or fully to the heavy fuel storage zone of the refinery.

In a particular embodiment of the invention, part of the gas oil fraction (or LCO) and/or part of the residual fraction (containing the HCO) obtained during step e) can be used to constitute flux bases which will be mixed with the fuel bases obtained by the present method.

The catalytic cracking step e) is most often a fluid catalytic cracking step, for example using the method developed by the applicant known as R2R. This step can be performed in a conventional manner known to the person skilled in the art under adequate cracking conditions with a view to obtaining hydrocarbon-containing products of lower molecular weight. This step can use processes and devices for thermal exchange, in particular of solid particles, with a view to reducing the catalyst temperature at the entry to the reaction zone. Descriptions of the function and catalysts which can be used in the context of fluid cracking in this step e) are given for example in the documents of patents U.S. Pat. No. 4,695,370, EP-B-184517, U.S. Pat. No. 4,959,334, EP-B-323297, U.S. Pat. No. 4,965,232, U.S. Pat. No. 5,120,691, U.S. Pat. No. 5,344,554, U.S. Pat. No. 5,449,496, EP-A-485259, U.S. Pat. No. 5,286,690, U.S. Pat. No. 5,324,696, EP-B-542604 and EP-A-699224, the descriptions of which are regarded as incorporated in the present description by reference.

The fluid catalytic cracking reactor can function with upflow or downflow. Although not a preferred form of embodiment of the present invention, it is also possible to perform catalytic cracking in a mobile bed reactor. Particularly preferred catalysts for catalytic cracking are those which contain at least one zeolite normally mixed with an appropriate matrix such as for example alumina, silica or silica-alumina.

Fluxing

In order to constitute a fuel meeting the viscosity recommendations which must be less than or equal to 380 cSt (50°C), the fuel bases obtained by the present method can be mixed if necessary with flux bases to achieve the target viscosity of the desired fuel grade.

The flux bases can be selected from light cycle oils (LCO) from catalytic cracking, heavy cycle oils (HCO) from catalytic cracking, residue from catalytic cracking, kerosene, gas oil, vacuum distillate and/or decanted oil (DO).

Preferably kerosene, gas oil and/or vacuum distillate obtained from the separation step b) of the method after hydroconversion, or gas oil and/or a fraction of the residual fraction obtained in catalytic cracking step e) is used.

DESCRIPTION OF THE FIGURES

The following figures show advantageous embodiments of the invention. The installation and the method according to the invention are described in essence. The operating conditions described above are not repeated.

FIG. 2 shows the process according to the invention with intermediate separation with decompression (non-integrated system).

In FIG. 2 the feed (10) preheated in the enclosure (12) and mixed with the recycled hydrogen (14) and heated in the enclosure (16) is introduced via the conduit (18) at the bottom of the first ebullated bed reactor (20) working with liquid and gas upflow and containing at least one hydroconversion catalyst. The reactor (20) normally comprises a recirculation pump (22) allowing the catalyst to be maintained in the ebullated bed by continuous recycling of at least part of the liquid extracted from the upper part of the reactor and re-injected at the base of the reactor. The hydrogen can also be introduced into the oven (12), thus eliminating the enclosure (16). The hydrogen is supplied via the hydrogen recycled from the process (64), supplemented with added hydrogen (24). Fresh catalyst can be added at the top of the reactor (not shown). The catalyst can be added periodically or continuously. The exhausted catalyst can be extracted from the base of the reactor (not shown) to be either eliminated or regenerated to eliminate the carbon and sulphur before being re-injected at the top of the reactor. The partly exhausted catalyst extracted at the bottom of the first reactor can also be transferred directly to the top of the second hydroconversion reactor (40) (cascading) (not shown). Where applicable the converted effluent (26) from the reactor (20) can also be subjected to separation of the light fraction (28) in an inter-stage separator (30).

All or part of the effluent (32) from the first hydroconversion reactor (20) is advantageously mixed with additional hydrogen (34), if required first preheated (not shown). This mixture is then injected via the conduit (36) into a second ebullated bed hydroconversion reactor (40) functioning with liquid and gas upflow and containing at least one hydroconversion catalyst. The operational conditions, in particular temperature, in this reactor are selected to achieve the desired conversion level as already described. The addition and extraction of catalyst is performed in the same way as described for the first reactor. The reactor (40) normally comprises a recirculation pump (38) allowing maintenance of the ebullated bed catalyst by continuous recycling of at least part of the liquid extracted from the upper part of the reactor and re-injected at the base of the reactor. The effluent treated in the reactor (40) is sent via the conduit (42) to a high-pressure, high-temperature separator (HPHT) (44) from which a gaseous fraction (46) and a liquid fraction (48) are recovered.

The cutting point is generally between 200 and 400°C. The gaseous fraction (46) is sent, optionally mixed with the light fraction (28) from the optional inter-stage separator (30) between the two hydroconversion reactors, generally via an exchanger (not shown) or a cooling tower (50) for cooling, to a high-pressure, low-temperature separator (HPLT) (52) from which a gaseous fraction (54) is recovered containing the gases (H₂, H₂S, NH₃, Cl₂, C₂H₄, acetylene, etc.) and a liquid fraction (56).

The gaseous fraction (54) from the high-pressure, low-temperature separator (HPLT) (52) is treated in the hydrogen purification unit (58) from which the hydrogen (60) is recovered to be recycled via the compressor (62) and the
conduit (64) to the reactors (20) and/or (40). The gases containing the undesirable nitrated and sulphurated compounds are evacuated from the installation (flux (66)).

[0100] The liquid fraction (56) from the high-pressure, low-temperature separator (HPHT) (52) is decompressed in the device (68) then sent to the fractioning system (70). Optionally a medium-pressure separator (not shown) may be installed after the decompressor (68) to recover a gaseous fraction which is sent to the purification unit (58), and a liquid phase which is brought to the fractioning section (70).

[0101] The liquid fraction (48) from the high-pressure, high-temperature separator (HPHT) (44) is decompressed in the device (72) then sent to the fractioning system (70). Evidently the fractions (56) and (48) can be sent together, after decompression, to the system (70). Depending on a variant not shown, the fractions (70) and (172) can be common and treat all the light fractions including that from the inter-stage separator. The fractioning system (70) comprises an atmospheric distillation system to produce a gaseous effluent (74), at least one so-called light fraction (76) containing in particular naphtha, kerosene and diesel, and an atmospheric residue fraction (78). Part of the atmospheric residue fraction can be sent via the conduit (80) to the hydrotreatment reactors. All or part of the atmospheric residue fraction (78) is sent to a vacuum distillation column (82) to recover a fraction (84) containing the vacuum residue containing the fines and sediments, and a vacuum distillates phase (86) containing vacuum gas oil.

[0102] The vacuum residue fraction (84), where applicable mixed with part of the atmospheric residue fraction (80), is mixed with the recycled hydrogen (88), possibly supplemented by added hydrogen (90). It passes optionally through an oven (92) and a filter (94). Optionally a co-feed (198) may be introduced. The effluent thus heated and filtered is introduced via the conduit (96) at the top of the permeable reactor system of the hydrotreatment step. The operation of the permeable reactors has been described with reference to FIG. 1.

[0103] The effluent leaving the storage reactors is optionally re-mixed with the hydrogen (91) arriving through the conduit (112) in a main HDM reactor (120) which contains a fixed bed catalyst (122). For reasons of legibility, a single HDM and HDS reactor is shown in the figure but the HDM and HDS sections conventionally comprises a plurality of HDM and HDS reactors. If necessary the recycled and/or added hydrogen can also be introduced into the hydrotreatment reactors between the various catalytic beds (not shown).

[0104] The effluent from the HDM reactor is extracted via the conduit (124) then sent to the first HDS reactor (130) where it passes through a fixed bed catalyst (132).

[0105] The effluent is sent via the conduit (134) into a high-pressure, high-temperature separator (HPHT) (136) from which a gaseous fraction (138) and a liquid fraction (140) are recovered. The gaseous fraction (138) is generally sent via an exchanger (not shown) or a cooling tower (142) for cooling, to a high-pressure, low-temperature separator (HPHT) (144) from which a gaseous fraction (146) is recovered containing the gases (H₂, H₂S, NH₃, C₁-C₄ hydrocarbons etc.) and a liquid fraction (148).

[0106] The gaseous fraction (146) from the high-pressure, low-temperature separator (HPHT) (144) is treated in the hydrogen purification unit (58) from which the hydrogen (152) is recovered to be recycled via the compressor (154) and the conduit (156) to the hydrotreatment section. The gases containing the undesirable nitrated and sulphurated compounds are evacuated from the installation (flux (158)).

[0107] The liquid fraction (148) from the high-pressure, low-temperature separator (HPHT) (144) is decompressed in the device (160) then sent to the fractioning system (172). Optionally a medium-pressure separator (not shown) can be installed after the decompressor (160) to recover a vapour phase which is sent to the purification unit (150) and a liquid phase which is brought to the fractioning section (172).

[0108] The liquid fraction (140) from the high-pressure, high-temperature separator (HPHT) (136) is decompressed in the device (174) then sent to the fractioning system (172). Evidently fractions (148) and (140) can be sent together, after decompression, to the system (172). The fractioning system (172) comprises an atmospheric distillation system to produce a gaseous effluent (176), at least one so-called light fraction (178) containing in particular naphtha, kerosene and diesel, and an atmospheric residue fraction (180). Part of the atmospheric residue fraction (180) can be extracted via the conduit (182) to constitute the desired fuel base. All or part of the atmospheric residue fraction (180) is sent to a vacuum distillation column (184) to recover a fraction containing the vacuum residue (186), and a vacuum distillates fraction (188) containing vacuum gas oil. At least part of the vacuum residue fraction (186) is preferably recycled via the conduit (190) to the conversion step, not in order to increase the yield.

[0109] FIG. 3 describes the method according to the invention with an intermediate separation without decompression (integrated system). In reference to FIG. 3, essentially the differences of the installation and process (separation step) are described in relation to the process of FIG. 2, the steps of hydroconversion, hydrotreatment and separation after hydrotreatment (and their reference symbols) being strictly identical to those in FIG. 2.

[0110] The effluent treated in the hydroconversion reactors is sent via the conduit (42) to a high-pressure, high-temperature separator (HPHT) (44) from which a lighter fraction (46) and a residual fraction (48) are recovered. The cutting point is generally between 200 and 400°C.

[0111] The residual fraction (48) is sent directly to the hydrotreatment section, following any possible passing through a filter (94).

[0112] The lighter fraction (46) is sent, optionally mixed with the gaseous fraction (28) from the optional inter-stage separator (30) between the two hydroconversion reactors, generally via an exchanger (not shown) or a cooling tower (50) for cooling, to a high-pressure, low-temperature separator (HPHT) (52) from which are recovered a gaseous fraction (54) containing the gases (H₂, H₂S, NH₃, C₁-C₄ hydrocarbons etc.) and a liquid fraction (56).

[0113] The gaseous fraction (54) from the high-pressure, low-temperature separator (HPHT) (52) is treated in the hydrogen purification unit (58) from which the hydrogen (60) is recovered for recycling via the compressor (156) and the conduits (88) and (64) to the hydrotreatment section and/or hydroconversion section. The gases containing the undesirable nitrated, sulphurated and oxygenated compounds are evacuated from the installation (flux (66)). In this configuration a single compressor (156) is used to supply all reactors requiring hydrogen.

[0114] The liquid fraction (56) from the high-pressure, low-temperature separator (HPHT) (52) is decompressed in the device (68) then sent to the fractioning system (70). Optionally a medium-pressure separator (not shown) can be
installed after the decompressor (68) to recover a gaseous fraction which is sent to the purification unit (58), and a liquid fraction which is brought to the fractioning section (70).

The fractioning system (70) comprises an atmospheric distillation system to produce a gaseous effluent (74), at least one so-called light fraction (76) containing in particular naphtha, kerosene and diesel, and an atmospheric residue fraction (192). Part of the atmospheric residue fraction can be sent via the conduit (192) to the hydrotreatment reactors while another part of the atmospheric residue fraction (194) can be sent to another process (hydrocracking or FCC or hydrotreatment).

The following examples illustrate the invention without however limiting its scope.

Example 1

A vacuum residue (RSV Oural), see table 1, is treated. The feed is subjected to a hydroconversion step in two successive ebulated bed reactors. The operating conditions and the yield, the sulphur content and the viscosity of the effluent leaving the hydroconversion section are given in tables 2 and 3.

### Table 1: Characteristics of the feed

<table>
<thead>
<tr>
<th>Cut</th>
<th>RSV Oural 530+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density 15/4</td>
<td>1.002</td>
</tr>
<tr>
<td>Sulphur % mass</td>
<td>2.55</td>
</tr>
<tr>
<td>Conrad carbon</td>
<td>16</td>
</tr>
<tr>
<td>Asphaltene C7 (% mass)</td>
<td>3.8</td>
</tr>
<tr>
<td>N%+V ppm</td>
<td>253</td>
</tr>
</tbody>
</table>

### Table 2: Operating conditions for ebulated bed section

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NiMo on alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C) ebulated bed R1</td>
<td>415</td>
</tr>
<tr>
<td>T (°C) ebulated bed R2</td>
<td>417</td>
</tr>
<tr>
<td>Pressure, MPa.</td>
<td>18</td>
</tr>
<tr>
<td>VVH (Sm/h)</td>
<td>0.243</td>
</tr>
<tr>
<td>H2 inlet (Nm3/m3 feed)</td>
<td>348</td>
</tr>
</tbody>
</table>

### Table 3: Yield, sulphur content and viscosity of ebulated bed section (% weight/feed)

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (% weight)</th>
<th>S (% weight)</th>
<th>Viscosity at 50°C (Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>0.26</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H2S</td>
<td>2.11</td>
<td>94.12</td>
<td></td>
</tr>
<tr>
<td>C1-C4 (gas)</td>
<td>2.06</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Naphtha (IBP=180°C) C.</td>
<td>7.30</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Diesel (180-350°C) C.</td>
<td>19.80</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Vacuum distillates (350-480°C C.)</td>
<td>24.50</td>
<td>0.55</td>
<td>44</td>
</tr>
<tr>
<td>Vacuum residue (480-540°C C.)</td>
<td>45.60</td>
<td>0.89</td>
<td>5000</td>
</tr>
<tr>
<td>Residue (350°C+) - fixed bed feed</td>
<td>70.10</td>
<td>0.77</td>
<td>400</td>
</tr>
</tbody>
</table>

### Table 4: Operating conditions of fixed bed

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CoMoNi on alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>380</td>
</tr>
<tr>
<td>Pressure, MPa.</td>
<td>15</td>
</tr>
<tr>
<td>VVH (Sm/h)</td>
<td>0.15</td>
</tr>
<tr>
<td>H2/JC (Nm3/h)</td>
<td>1000</td>
</tr>
</tbody>
</table>

### Table 5: Yield, sulphur content and viscosity of ebulated bed section (% weight/hydroconversion effluent)

<table>
<thead>
<tr>
<th>Products</th>
<th>Yield (% weight)</th>
<th>S (% weight)</th>
<th>Viscosity at 50°C (Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>0.59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H2S</td>
<td>2.65</td>
<td>94.12</td>
<td></td>
</tr>
<tr>
<td>C1-C4 (gas)</td>
<td>2.81</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Naphtha (IBP=180°C) C.</td>
<td>7.30</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Naphtha (IBP=150°C) ex fixed bed</td>
<td>1.28</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Gas oil (150-350°C C.) ex ebullied bed</td>
<td>19.80</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Vacuum distillates (350-550°C C.) ex fixed bed</td>
<td>4.89</td>
<td>0.02</td>
<td>120</td>
</tr>
<tr>
<td>Vacuum residue (550°C+) ex fixed bed</td>
<td>33.32</td>
<td>0.09</td>
<td>7000</td>
</tr>
</tbody>
</table>

with H2 consumed representing 1.20% of the intermediate feed.

### Table 6: Yield, sulphur content and viscosity of complete chain (% weight/feed)

<table>
<thead>
<tr>
<th>Products</th>
<th>Yield (% weight)</th>
<th>S (% weight)</th>
<th>Viscosity at 50°C (Ct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH3</td>
<td>0.59</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H2S</td>
<td>2.65</td>
<td>94.12</td>
<td></td>
</tr>
<tr>
<td>C1-C4 (gas)</td>
<td>2.81</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Naphtha (IBP=180°C) ex ebullied bed</td>
<td>7.30</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Naphtha (IBP=150°C) ex fixed bed</td>
<td>1.28</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Gas oil (150-350°C C.) ex fixed bed</td>
<td>19.80</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Vacuum distillates (350-550°C C.) ex fixed bed</td>
<td>4.89</td>
<td>0.02</td>
<td>120</td>
</tr>
<tr>
<td>Vacuum residue (550°C+) ex fixed bed</td>
<td>33.32</td>
<td>0.09</td>
<td>7000</td>
</tr>
</tbody>
</table>

with H2 consumed representing 1.47% of the feed.

To obtain a bunker fuel compliant with specifications, the fuel is made up of 50% vacuum distillates ex fixed bed, 48% vacuum residue ex fixed bed and 2% gas oil ex fixed bed. It has a viscosity of 380 cSt at 50°C, a sulphur content of 0.27% weight and a sediment content of <0.1% weight. Not all the vacuum distillate ex fixed bed is used and it could directly constitute a fuel with 0.1% S.
Example 2

Comparative

TABLE 7

| Operating conditions, fines content, load loss and operating factor in case 1 (according to invention fixed bed with PRS) and case 2 (comparative fixed bed without PRS) |
|---|---|
| Case | 1 (according to invention) | 2 (comparative) |
| Configuration of fixed bed section | With PRS | Without PRS |
| Catalyst | CoMoNi on aluminia | CoMoNi on aluminia |
| T (°C) | 380 | 380 |
| Pressure MPa | 15 | 15 |
| H2/HC (Nm³/h H2/Sm³ intermediate feed) | 1000 | 1000 |
| Duration of cycle (months) | 11 | 5 |
| Number of cycles | 2 | 1 |
| Number of permeable reactors | 3 | 3 |
| Number of permeations per cycle | 0.25 | 0.25 |
| VVH HDS | 0.38 | 0.38 |
| VVH global fixed bed | 0.15 | 0.15 |
| % HDS section HDM | 70 | 70 |
| Sediment at outlet of ebullated bed section (% weight) | 0.5 | 0.5 |
| Sediment at outlet of PRS (case with PRS) or entry to fixed bed (case without PRS) % weight | 0.2 | 0.5 |
| Sediment at outlet of fixed bed section (% weight) | <0.1 | <0.1 |
| Catalyst fines at outlet of ebullated bed section (ppm weight) | 70 | 70 |
| Catalyst fines at outlet from PRS (case with PRS) or entry to fixed bed (case without PRS) (ppm weight) | 25 | 70 |
| Catalyst fines at outlet of fixed bed section (ppm weight) | 10 | 10 |
| Delta P section HDM start of cycle or permeation (in bar) | 1.5 | 1.5 |
| Delta P section HDM end of cycle or permeation (in bar) | 5.0 | 7.5 |
| Operational factor (%) | 0.92 | 0.83 |

The comparative example is intended to show the benefit of using the permeable reactors between the ebulated bed section and the remainder of the fixed bed section in order to capture the majority of catalyst fines and sediments from the first ebullated bed step.

Case 1 corresponds to example 1 according to the invention which, thanks to the permeable reactors (PRS), allows a high operating factor and a lower catalyst quantity (size of reactor). This operational factor corresponds to a stoppage of 1 month and 11 months' operation.

Case 2 corresponds to a case without PRS where the quantity of catalysts installed is the same as case 1. Because of the catalyst fines and the sediments from the ebullated bed section, the load loss of the fixed bed section increases greatly to a point where it is no longer possible to operate, and the unit must then be stopped and the catalyst changed. The operational factor is degraded because with this installation it is only possible to perform two cycles of 5 months in one year. Furthermore, to overcome these additional load losses, the feed pump, the additional hydrogen compressor and the recyling gas compressor must be over-dimensioned, which leads to greater investment costs and greater consumption of utilities.

1. Method of conversion of a hydrocarbon-containing feed comprising at least one fraction of hydrocarbons with a sulphur content of at least 0.1% weight, an initial boiling temperature of at least 340°C and a final boiling temperature of at least 440°C, comprising the following steps:

   a) a step of hydroconversion in the presence of hydrogen in at least one reactor containing a supported catalyst in an ebullated bed,

   b) a step of separating the effluent obtained from step a) into at least one light fraction of hydrocarbon fuel bases and a heavy fraction containing predominantly compounds boiling at minimum 350°C,

   c) a step of fixed bed hydrotreatment of at least part of the heavy fraction from step b) in which, under hydrotreatment conditions, the heavy fraction and hydrogen are passed over a hydrotreatment catalyst and in which the hydrotreatment step comprises one or a plurality of fixed bed hydrotreatment zones preceded by at least two storage zones also with fixed bed hydrotreatment, arranged in series to be used in a cyclic manner comprising the successive repetition of steps c') and c") defined below:

   c') a step in which the storage zones are used together for a duration at most equal to the deactivation and/or clogging time of one of them,

   c") a step during which the deactivated and/or clogged storage zone is short-circuited and the catalyst it contains is regenerated and/or replaced by fresh catalyst, and during which the other storage zone(s) is/are used, and

   c"') a step during which the storage zones are all used together, wherein the storage zone of which the catalyst has been regenerated during the preceding step is reconnected and said step is continued for a duration equal at most to the deactivation and/or clogging time of one of the storage zones.

2. Method according to claim 1 in which the hydrotreatment step comprises a first hydrometallisation step comprising one or a plurality of fixed bed hydrometallisation zones preceded by at least two of said hydrotreatment storage zones and a second subsequent hydrosulphurisation step comprising one or a plurality of fixed bed hydrosulphurisation zones in which, during the first hydrometallisation step, under hydrometallisation conditions, the feed of hydrocarbons and hydrogen is passed over a hydrometallisation catalyst, then during the second subsequent step, under hydrosulphurisation conditions, the effluent from the first step is passed over a hydrosulphurisation catalyst.

3. Method according to claim 1, in which during step a) the treatment in the presence of hydrogen is carried out under an absolute pressure of 2.5 to 35 MPa, at a temperature of 330 to 550°C with an hourly spatial velocity of 0.1 to 10 h⁻¹, and the quantity of hydrogen mixed in the feed is from 50 to 5000 Nm³/m³.

4. Method according to claim 1, in which the hydrotreatment step c) is performed under an absolute pressure of around 2 to 35 MPa, at a temperature of 300 to 500°C with an hourly spatial velocity of 0.1 to 5 h⁻¹ and a quantity of hydrogen mixed in the feed is from 100 to 5000 Nm³/m³.

5. Method according to claim 1, in which the hydrocarbon-containing feed is selected from the atmospheric residues, the vacuum residues from direct distillation, crude petroleum,
tapped crude petroleum, deasphalted oil, deasphalted resin, asphalts or deasphaltation pitch, residues from the conversion processes, aromatic extracts from the production chain of lubricant bases, bituminous sands or their derivatives, oil shales or their derivatives, taken alone or in combination.

6. Method according to claim 1, in which the separation step b) is performed without decompression, the effluent from step a) is sent to the fractioning section with a cutting point between 200 and 400 °C, so as to obtain a light fraction and said heavy fraction, said heavy fraction being sent to the hydrotreatment step while the light fraction is subjected to atmospheric distillation to give a gaseous fraction, at least one light fraction of hydrocarbons of the type naphtha, kerosene and/or diesel, and a vacuum distillate fraction, the latter being at least partly sent to the hydrotreatment step c).

7. Method according to claim 1, in which the separation step b) is performed with decompression, the effluent from step a) is sent to a fractioning section with a cutting point between 200 and 400 °C, to give a light fraction and said heavy fraction, and in which the heavy fraction is fractioned by atmospheric distillation into at least one atmospheric distillate fraction containing at least one light fraction of hydrocarbons of the type naphtha, kerosene and/or diesel, and an atmospheric residue fraction, said atmospheric residue fraction being at least partly fractioned by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction, at least part of said atmospheric residue fraction and/or vacuum residue fraction being sent to the hydrotreatment step c).

8. Method according to claim 1, in which the heavy fraction obtained in step b) is subjected, before being sent to the hydrotreatment step, to separation of the sediment and catalyst fines using at least one rotating filter or also at least one basket filter or also a centrifuging system such as a hydrocyclone associated with filters or in-line decantation, or in which the heavy fraction obtained in step b) at the inlet to each storage zone passes through a filtering plate situated upstream from the catalytic bed(s) contained in the storage zone.

9. Method according to claim 1, in which at least part of the effluent obtained in step c) is sent to a separation step, called step d), comprising an atmospheric distillation and a vacuum distillation and in which the effluent from the hydrotreatment step is fractioned by atmospheric distillation into a gaseous fraction, at least one atmospheric distillate fraction containing fuel bases (naphtha, kerosene and/or diesel) and an atmospheric residue fraction, at least part of the atmospheric residue is then fractioned by vacuum distillation into a vacuum distillate fraction containing vacuum gas oil and a vacuum residue fraction.

10. Method according to claim 9, in which the light fraction obtained without decompression in the separation step b) is sent to the separation step d).

11. Method according to claim 9, in which part of the vacuum residue fraction is recycled in the hydroconversion step a).

12. Method according to claim 9, in which at least part of the vacuum distillate fraction and/or the vacuum residue fraction is/are sent to a catalytic cracking section, called step e), in which it is/they are treated under conditions allowing production of a gaseous fraction, a petrol fraction, a diesel fraction and a residual fraction.

13. Method according to claim 12, in which at least part of the residual fraction obtained in catalytic cracking step e) is recycled to the inlet of step e) and/or a) and/or c).

14. Method according to claim 9, in which the atmospheric residue and/or the vacuum distillate and/or the vacuum residue are mixed with flux bases selected from the light cycle oils from catalytic cracking, heavy cycle oils from catalytic cracking, the residue from catalytic cracking, kerosene, gas oil, vacuum distillate and/or a decanted oil.

15. Method according to claim 14, in which the flux base is selected from kerosene, gas oil and/or vacuum distillate obtained from separation step b) of the process after hydroconversion, or gas oil and/or a fraction of the residual fraction obtained in the catalytic cracking step e).

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