

**PROCESS WITH SEPARATION FOR TREATING
PETROLEUM FEEDSTOCKS FOR THE PRODUCTION OF FUEL OILS
WITH A LOW SULFUR CONTENT**

FIELD OF THE INVENTION

The present invention relates to the refining and the conversion of heavy hydrocarbon fractions containing, inter alia, sulfur-based impurities. The invention more particularly relates to a process for treating heavy petroleum feedstocks for the production of fuel oils and fuel oil bases, especially bunker fuels and bunker fuel bases, with a low sulfur content.

TECHNOLOGICAL BACKGROUND

While the regulations regarding the sulfur contents in fuels for terrestrial use, typically petrols and diesels, became very rigorous in recent decades, the regulation regarding the sulfur content in marine combustibles was hitherto relatively unrestrictive. Specifically, the combustibles for marine use currently on the market may contain up to 3.5% or even 4.5% by weight of sulfur. As a result, ships have become the main source of emission of sulfur dioxide (SO₂).

In order to lower these emissions, the International Maritime Organization (IMO) submitted recommendations in terms of specifications regarding marine combustibles (annex VI of the MARPOL convention). These recommendations break down into the 2012 version of ISO standard 8217. The recommendations now relate to the emissions of SO_x by maritime combustibles. The equivalent sulfur content recommended for the 2020 or 2025 horizon is less than or equal to 0.5% by weight for ships operating outside the "Sulfur Emission Control Areas" (SECA). Within the SECA, the IMO envisages an equivalent sulfur content of less than or equal to 0.1% by weight at the 2015 horizon.

Moreover, another very restrictive recommendation relates to the content of sediments after ageing according to ISO standard 10307-2, which should be less than or equal to 0.1%.

The Applicant set itself the objective of producing fuel oils and fuel oil bases, especially bunker fuels and bunker fuel bases, which meet the recommendations of the MARPOL convention in terms of equivalent sulfur content, and which preferably also meet the recommendations regarding the content of sediments after ageing.

The fuel oils used in marine transport generally comprise atmospheric distillates, vacuum distillates, atmospheric residues and vacuum residues derived from direct distillation or derived from the refining process, especially hydrotreatment and conversion processes, these fractions possibly being used alone or as a mixture. One of the objects of the present invention is to propose a process for the conversion of heavy petroleum feedstocks for the preparation of fuel oils and fuel oil bases, especially bunker fuels and bunker fuel bases, with a very low sulfur content. Another object of the present invention is to jointly produce, by means of the same process, atmospheric distillates (naphtha, kerosene, diesel), vacuum distillates and/or light gases (C1 to C4). The bases of naphtha and diesel type may be upgraded in a refinery for the production of motor vehicle and aviation fuels, for instance superfuels, jet fuels and diesel oils.

Processes for refining and converting heavy petroleum feedstocks comprising a first step of fixed-bed hydrotreatment followed by a step of ebullated-bed hydroconversion were described in patents FR 2 764 300, CA 1238005, EP 1 343 857 and EP 0 665 282. EP 0 665 282, which describes a process for the hydrotreatment of heavy oils, is directed towards prolonging the service life of reactors. CA 1238005 describes a process for the conversion of a heavy liquid hydrocarbon-based feedstock using several reactors in series, in which the degree of conversion is improved by means of a particular recycling of the heavy fraction obtained. The process described in FR 2 764 300 is, itself, directed towards obtaining not fuel oil bases, especially bunker fuel bases, but fuels (petroleum and diesel) especially having a low sulfur content. Furthermore, the feedstocks treated in this process contain little or no asphaltenes. Finally, the process disclosed in EP 1 343 857 is described as a hydrotreatment process which may use a hydrodemetallation section, which may be preceded by a guard zone of permutable reactor type, and a hydrodesulfurization section.

None of these documents describes the production of a fuel oil or of fuel oil bases with a very low sulfur content meeting the new recommendations of the International Maritime Organization, and with a low content of sediments as required by the new version of ISO standard 8217:2012.

One of the objects of the present invention is to adapt and improve the conversion processes described in the prior art for the production of fuel oils and fuel oil bases, especially with a low sulfur content.

BRIEF DESCRIPTION OF THE INVENTION

The research studies led the Applicant to discover, surprisingly, that an improvement of the existing processes in terms of production of fuel oil bases and in terms of quality of the said fuel oil bases, especially of sulfur content and of sediment content, is possible by means of a combination of different steps, performed in a specific sequence.

The subject of the invention is, firstly, a process for treating a hydrocarbon feedstock having a sulfur content of at least 0.5% by weight, an initial boiling point of at least 340°C and a final boiling point of at least 440°C, which makes it possible to obtain at least one liquid hydrocarbon fraction with a sulfur content of less than or equal to 0.5% by weight, comprising the following successive steps:

a) a step of fixed-bed hydrotreatment, wherein the hydrocarbon feedstock and hydrogen are placed in contact over at least one hydrotreatment catalyst,

b) a step of separation of the effluent obtained from the hydrotreatment step (a) into at least one light fraction and at least one heavy fraction,

c) a step of hydroconversion of at least part of the heavy fraction of the effluent derived from step (b) in at least one ebullated-bed reactor containing a supported catalyst, and

d) a step of separation of the effluent derived from step (c) to obtain at least one gaseous fraction and at least the said liquid hydrocarbon fraction.

A subject of the invention is also the fuel oil which may be used in maritime transport, obtained from such a process, having a sulfur content of less than or equal to 0.5% by weight and preferably less than or equal to 0.1% by weight.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows one embodiment of the process according to the invention with intermediate separation of the effluent between the fixed-bed section and the ebullated-bed section, with decompression of the heavy fraction.

Figure 2 shows on a larger scale, for better readability, the guard zones of the hydrotreatment section of **Figure 1**.

Figure 3 shows another embodiment of the process according to the invention with intermediate separation of the effluent between the fixed-bed section and the ebullated-bed section, without decompression of the heavy fraction.

DETAILED DESCRIPTION OF THE INVENTION

It is pointed out that, throughout this description, the expression "between ... and ..." should be understood as including the cited limits.

The process according to the invention thus comprises a first step (a) of fixed-bed hydrotreatment, followed by a step (b) of separation of the hydrocarbon effluent into a light fraction and a heavy fraction, followed by a step (c) of ebullated-bed hydroconversion of the said heavy fraction, and finally a step (d) of separation.

The object of the hydrotreatment is, simultaneously, to refine, i.e. to substantially reduce the content of metals, sulfur and other impurities, while at the same time improving the ratio of hydrogen to carbon (H/C) and while also transforming the hydrocarbon feedstock more or less partially into lighter fractions. The effluent obtained in step (a) of fixed-bed hydrotreatment is then subjected to a separation step to obtain different fractions. This separation makes it possible to remove from the effluent obtained after the hydrotreatment step (a) the lighter fractions which do not require further treatment, or only a moderate treatment, from the heavier fractions. The latter fractions are sent into step (c) of ebullated-bed hydroconversion, which makes it possible to partially convert the hydrocarbon effluent obtained from the hydrotreatment step (a) so as to produce an effluent which may advantageously be used totally or partly as fuel oil or as fuel oil base, especially as bunker fuel or as bunker fuel base.

One of the advantages of performing in sequence a fixed-bed hydrotreatment and then an ebullated-bed hydroconversion lies in the fact that the feedstock of the ebullated-bed hydroconversion reactor is already at least partially hydrotreated. In this way, it is

possible to obtain an equivalent conversion of the hydrocarbon effluents of better quality, in particular with lower sulfur contents. Furthermore, the consumption of catalyst in the ebullated-bed hydroconversion reactor is greatly reduced relative to that of a process without prior fixed-bed hydrotreatment.

Moreover, the process according to the invention is characterized in that it comprises a step (b) of intermediate separation between the hydrotreatment step (a) and the hydroconversion step (c). This separation step advantageously makes it possible to minimize the fraction to be treated in the ebullated bed. In this way, the capacity of the ebullated-bed hydroconversion unit may be reduced. Similarly, overcracking of the light fractions and thus a loss of yield of fuel-type fractions is avoided.

The process according to the invention advantageously makes it possible to produce light fractions, fuel oils and fuel oil bases, especially for maritime use, with a low sulfur content, in high yield and with high energy efficiency, from a sulfur-containing heavy hydrocarbon feedstock.

The hydrocarbon feedstock

The hydrocarbon feedstock treated in the process according to the invention may be termed a "heavy feedstock". It has an initial boiling point of at least 340°C and a final boiling point of at least 440°C. Preferably, its initial boiling point is at least 350°C, preferentially at least 375°C, and its final boiling point is at least 450°C, preferentially at least 460°C, more preferentially at least 500°C and even more preferentially at least 600°C.

The hydrocarbon feedstock may be chosen from atmospheric residues, vacuum residues derived from direct distillation, crude petroleums, de-headed crude petroleums, de-asphalted oils, de-asphalting resins, de-asphalting pitches or asphalts, residues derived from conversion processes, aromatic extracts derived from lubricant base production lines, bituminous sands or derivatives thereof, bituminous shales or derivatives thereof, parent-rock oils or derivatives thereof, taken alone or as a mixture. In the present invention, the feedstocks that are treated are preferably atmospheric residues or vacuum residues, or mixtures of these residues.

In addition, the hydrocarbon feedstock treated in the process according to the invention contains sulfur. Its sulfur content is at least 0.5% by weight, preferentially at least 1% by weight, more preferentially at least 4% by weight and even more preferentially at least 5% by weight.

In addition, the hydrocarbon feedstock treated in the process according to the invention may contain asphaltenes. Its asphaltene content may be at least 2% by weight. In the present description, the term "asphaltene" means heavy hydrocarbon compounds which are insoluble in n-heptane (also referred to as C7 asphaltenes) but soluble in toluene. The quantification of asphaltenes generally involves normalized analyses as defined, for example, in standards AFNOR T 60-115 (France) or ASTM893-69 (United States).

The content of nickel and vanadium (Ni+V) metals of the feedstock is preferentially greater than 110 ppm and more preferentially greater than 150 ppm by weight.

These feedstocks may advantageously be used in unmodified form. Alternatively, they may be diluted with a co-feedstock. This co-feedstock may be a lighter hydrocarbon fraction or a mixture of lighter hydrocarbon fractions, which may be preferably chosen from products derived from a fluid catalytic cracking (FCC) process, a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil, an FCC residue, a gas oil fraction, especially a fraction obtained by atmospheric or vacuum distillation, for instance vacuum gas oil, or alternatively which may originate from another refining process. The co-feedstock may also advantageously be one or more fractions derived from the process of liquefaction of charcoal or biomass, aromatic extracts, or any other hydrocarbon fraction or alternatively non-petroleum feedstocks such as pyrolysis oil. The heavy hydrocarbon feedstock according to the invention may represent at least 50%, preferentially 70%, more preferentially at least 80% and even more preferentially at least 90% by weight of the total hydrocarbon feedstock treated via the process according to the invention.

Hydrotreatment step (a)

The said hydrocarbon feedstock is subjected, according to the process of the present invention, to a fixed-bed hydrotreatment step (a) in which the feedstock and hydrogen are placed in contact over a hydrotreatment catalyst.

The term "hydrotreatment", commonly referred to as HDT, means catalytic treatments with supply of hydrogen which makes it possible to refine, i.e. to substantially reduce the content of metals, sulfur and other impurities, the hydrocarbon feedstocks, while at the

same time improving the hydrogen-to-carbon ratio of the feedstock and while transforming the feedstock more or less partially into lighter fractions. The hydrotreatment especially comprises hydrodesulfurization reactions (commonly known as HDS), hydrodeazotization reactions (commonly known as HDN) and hydrodemetallation reactions (commonly known as HDM), accompanied by hydrogenation, hydrodeoxygenation, hydrodearomatization, hydroisomerization, hydrodealkylation, hydrocracking and hydrodeasphalting reactions and the Conradson carbon reduction reaction.

According to a preferred variant, the hydrotreatment step (a) comprises a first step (a1) of hydrodemetallation (HDM) performed in one or more fixed-bed hydrodemetallation zones and a second subsequent step (a2) of hydrodesulfurization (HDS) performed in one or more fixed-bed hydrodesulfurization zones. During the said first step (a1) of hydrodemetallation, the feedstock and hydrogen are placed in contact over a hydrodemetallation catalyst, under hydrodemetallation conditions, and then during the said second step (a2) of hydrodesulfurization, the effluent from the first step (a1) of hydrodemetallation is placed in contact with a hydrodesulfurization catalyst, under hydrodesulfurization conditions. This process, known as HYVAHL-FTM, is described, for example, in patent US 5 417 846.

A person skilled in the art will easily understand that, in the hydrodemetallation step, hydrodemetallation reactions are performed, but, in parallel, also some of the other hydrotreatment reactions and especially hydrodesulfurization reactions. Similarly, in the hydrodesulfurization step, hydrodesulfurization reactions are performed, but, in parallel, also some of the other hydrotreatment reactions and especially hydrodemetallation reactions. A person skilled in the art understands that the hydrodemetallation step begins when the hydrotreatment step begins, i.e. when the metal concentration is maximal. A person skilled in the art understands that the hydrodesulfurization step ends when the hydrotreatment step ends, i.e. when the removal of sulfur is the most difficult. Between the hydrodemetallation step and the hydrodesulfurization step, a person skilled in the art occasionally defines a transition zone in which all the types of hydrotreatment reaction take place.

The hydrotreatment step (a) according to the invention is performed under hydrotreatment conditions. It may advantageously be performed at a temperature of between 300°C and 500°C and preferably between 350°C and 420°C, and at an absolute

pressure of between 2 MPa and 35 MPa and preferably between 11 MPa and 20 MPa. The temperature is usually adjusted as a function of the desired level of hydrotreatment and of the targeted treatment duration. Usually, the hourly space velocity of the hydrocarbon feedstock, commonly known as the HSV, which is defined as being the volume flow rate of the feedstock divided by the total volume of catalyst, may be within a range from 0.1 h^{-1} to 5 h^{-1} , preferentially from 0.1 h^{-1} to 2 h^{-1} , more preferentially from 0.1 h^{-1} to 0.45 h^{-1} and even more preferentially between 0.1 h^{-1} and 0.2 h^{-1} . The amount of hydrogen mixed with the feedstock may be between 100 and 5000 normal cubic metres (Nm^3) per cubic metre (m^3) of liquid feedstock, preferentially between $200 \text{ Nm}^3/\text{m}^3$ and $2000 \text{ Nm}^3/\text{m}^3$ and more preferentially between $300 \text{ Nm}^3/\text{m}^3$ and $1500 \text{ Nm}^3/\text{m}^3$. The hydrotreatment step (a) may be performed industrially in one or more descending-liquid reactors.

The hydrotreatment catalysts used are preferably known catalysts. They may be granular catalysts comprising, on a support, at least one metal or metal compound having a hydro-dehydrogenating function. These catalysts may advantageously be catalysts comprising at least one group VIII metal, generally chosen from the group consisting of nickel and cobalt, and/or at least one group VIB metal, preferably molybdenum and/or tungsten. Use may be made, for example, of a catalyst comprising from 0.5% to 10% by weight of nickel, preferably from 1% to 5% by weight of nickel (expressed as nickel oxide NiO), and from 1% to 30% by weight of molybdenum, preferably from 5% to 20% by weight of molybdenum (expressed as molybdenum oxide MoO_3) on a mineral support. This support may be chosen, for example, from the group consisting of alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. Advantageously, this support may contain other dopant compounds, especially oxides chosen from the group consisting of boron oxide, zirconia, cerine, titanium oxide, phosphorus pentoxide and a mixture of these oxides. Use is usually made of an alumina support and very usually an alumina support doped with phosphorus and optionally with boron. When phosphorus pentoxide P_2O_5 is present, its concentration is less than 10% by weight. When boron trioxide B_2O_3 is present, its concentration is less than 10% by weight. The alumina used may be a γ (gamma) or η (eta) alumina. This catalyst is usually in the form of extrudates. The total content of group VIB and VIII metal oxides may be from 5% to 40% by weight and in general from 7% to 30% by weight, and the weight ratio expressed as metal oxide between group VIB metal(s) and group VIII metal(s) is generally between 20 and 1, and usually between 10 and 2.

In the case of a hydrotreatment step including a hydrodemetallation (HDM) step followed by a hydrodesulfurization (HDS) step, specific catalysts suited to each step are preferably used.

Catalysts that may be used in the HDM step are indicated, for example, in patents EP 0 113 297, EP 0 113 284, US 5 221 656, US 5 827 421, US 7 119 045, US 5 622 616 and US 5 089 463. HDM catalysts are preferably used in the permutable reactors.

Catalysts that may be used in the HDS step are indicated, for example, in patents EP 0 113 297, EP 0 113 284, US 6 589 908, US 4 818 743 or US 6 332 976.

A mixed catalyst, which is active in HDM and in HDS, may also be used, both for the HDM section and for the HDS section, as described in patent FR 2 940 143.

Prior to injecting the feedstock, the catalysts used in the process according to the present invention are preferably subjected to an *in-situ* or *ex-situ* sulfurization treatment.

According to a preferred embodiment of the present invention, the fixed-bed hydrotreatment step (a) uses a system of permutable reactors, also known as guard zones, upstream of the main hydrotreatment reactors. More particularly, the hydrotreatment step (a) may be performed in one or more fixed-bed hydrotreatment zones preceded by at least two hydrotreatment guard zones which are also in fixed beds, arranged in series so as to be used in a cyclic manner consisting of the successive repetition of steps a'') and a''') defined below:

a') a step wherein the guard zones are all used together for a duration that is at most equal to the deactivation and/or clogging time for one of them,

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

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

Preferably, after regeneration and/or replacement of the catalyst of a reactor, this reactor is reconnected downstream of the functioning reactor.

The system of permutable reactors is known in patents FR 2 681 871, FR 2 784 687 and EP 1 343 857. The function of permutable reactors is to protect the main downstream hydrotreatment reactors by preventing clogging and/or deactivation. Specifically, a problem encountered during the use of fixed beds is clogging, which takes place on account of the asphaltenes and sediments contained in the feedstock. Another problem is deactivation of the catalyst on account of the large deposition of metals which takes place during hydrotreatment reactions. Permutable reactors are thus used to increase the operation cycle of the hydrotreatment unit by allowing replacement of the deactivated and/or clogged catalyst only in the permutable reactors functioning in a cyclic manner, without stopping the entire unit for a certain time.

The deactivation and/or clogging time varies as a function of the feedstock, the operating conditions of the hydrotreatment step and the catalyst(s) used. It is generally expressed by a drop in catalytic performance, which may be observed by an increase in the concentration of metals and/or other impurities in the effluent, an increase in the temperature required to maintain activity of the catalyst or, in the specific case of clogging, by a significant increase in pressure loss. The pressure loss ΔP , expressing a degree of clogging, may be measured permanently throughout the cycle on each of the zones and may be defined by an increase in pressure resulting from the partially blocked passage of the flow through the zone. Similarly, the temperature may be permanently measured throughout the cycle on each of the two zones.

In order to define a deactivation and/or clogging time, a person skilled in the art first defines a maximum tolerable pressure loss value ΔP and/or temperature as a function of the feedstock to be treated, for the chosen operating conditions and catalysts, and from which point disconnection of the guard zone must be performed. The deactivation and/or clogging time is thus defined as the time at which the limit value of the pressure loss and/or temperature is reached. In the case of a heavy fraction hydrotreatment process, the limit value of the pressure loss is generally between 0.3 MPa and 1 MPa (3 and 10 bar), preferably between 0.5 MPa and 0.8 MPa (5 and 8 bar). The limit value of the temperature is generally between 400°C and 430°C, the temperature corresponding to the mean measured temperature of the catalytic bed.

The operating conditions of the permutable reactors are generally identical to those of the main hydrotreatment reactors. The hourly space velocity HSV value for each functioning permutable reactor is preferentially between 0.2 h^{-1} and 4 h^{-1} , more preferentially

between 1 h^{-1} and 2 h^{-1} . The overall hourly space velocity HSV value of the permutable reactors and that of each reactor is chosen so as to achieve the maximum hydrodemetallation while at the same time controlling the reaction temperature and thus limiting the exothermicity.

In a preferred embodiment of the invention, use is made of a catalyst conditioning section which allows permutation of these functioning guard zones, i.e. without stopping the functioning of the unit. The catalyst conditioning section may comprise the following elements:

- a system which operates at moderate pressure, preferentially between 1 MPa and 5 MPa (10 and 50 bar) and preferably between 1.2 MPa and 2.5 MPa (15 to 25 bar), which makes it possible to perform the washing, stripping and cooling operations on the disconnected guard reactor before discharging the spent catalyst, followed by heating and sulfurization after loading the fresh catalyst;

- another pressurization/depressurization and regulator-valve system of suitable technology, which makes it possible to permute these guard zones without stopping the unit, since all the operations of washing, stripping, discharging spent catalyst, recharging fresh catalyst, heating and sulfurization take place on the disconnected reactor or guard zone.

Alternatively, a presulfurized catalyst may be used in the conditioning section so as to simplify the functioning permutation procedure.

The effluent leaving the permutable reactors may then be sent to the main hydrotreatment reactors.

Each hydrotreatment zone or hydrotreatment guard zone may contain at least one catalytic bed, for example 1, 2, 3, 4 or 5 catalytic beds. Preferably, each guard zone contains a catalytic bed. Each catalytic bed may contain at least one catalytic layer containing one or more catalysts, optionally preceded by at least one inert layer, for example of alumina or of ceramic in the form of extrudates, beads or pellets. The catalysts used in the catalytic bed(s) may be identical or different.

According to a particular embodiment, the hydrocarbon feedstock passes at the inlet of each guard zone through a filter plate located upstream of the catalytic bed(s) contained in the guard zone. This filter plate, which is described, for example, in patent

FR 2 889 973, advantageously makes it possible to trap the clogging particles contained in the hydrocarbon feedstock by means of a specific distributing plate comprising a filtration medium.

Separation step (b)

The effluent obtained after the fixed-bed hydrotreatment step (a) undergoes at least one separation step, which is optionally completed with other additional separation steps, for separating at least one light fraction and at least one heavy fraction. The term "light fraction" means a fraction in which at least 90% of the compounds have a boiling point below 350°C. The term "heavy fraction" means a fraction in which at least 90% of the compounds have a boiling point of greater than or equal to 350°C. Preferably, the light fraction obtained during the separation step (b) comprises a gaseous phase and at least one light hydrocarbon fraction of naphtha, kerosene and/or diesel type. The heavy fraction preferably comprises a vacuum distillate fraction and a vacuum residue fraction and/or an atmospheric residue fraction.

The separation step (b) may be performed via any method known to those skilled in the art. This method may be chosen from high-pressure or low-pressure separation, high-pressure or low-pressure distillation, high-pressure or low-pressure stripping, liquid/liquid extraction, solid/liquid separation, centrifugation, and combinations of these various methods which may be performed at different pressures and temperatures.

According to a first embodiment of the present invention, the effluent derived from the hydrotreatment step (a) undergoes a step (b) of separation with decompression.

According to this embodiment, the separation is preferably performed in a fractionation section which may first comprise a high-pressure high-temperature (HPHT) separator, and optionally a high-pressure low-temperature (HPLT) separator, then optionally followed by an atmospheric distillation section and/or a vacuum distillation section. The effluent from step (a) may be sent to a fractionation section, generally to an HPHT separator, having a cutoff point of between 200°C and 400°C making it possible to obtain a light fraction and a heavy fraction. In general, the separation is preferably not made at a precise cutoff point, but rather resembles a separation of flash type.

Preferably, the said heavy fraction may then be fractionated by atmospheric distillation into at least one atmospheric distillate fraction, preferably containing at least one light hydrocarbon fraction of naphtha, kerosene and/or diesel type, and an atmospheric residue fraction. At least part of the atmospheric residue fraction may also be fractionated by vacuum distillation into a vacuum distillate fraction, preferably containing vacuum gas oil, and a vacuum residue fraction. At least part of the vacuum residue fraction and/or of the atmospheric residue fraction is advantageously sent to the hydroconversion step (c). Part of the vacuum residue may also be recycled into the hydrotreatment step (a).

According to a second embodiment, the effluent derived from the hydrotreatment step (a) undergoes a separation step (b) without decompression.

According to this embodiment, the effluent from the hydrotreatment step (a) is sent to a fractionation section, generally to an HPHT separator, with a cutoff point of between 200 and 400°C making it possible to obtain at least one light fraction and at least one heavy fraction. In general, the separation is preferably not made at a precise cutoff point, but rather resembles a separation of flash type.

The heavy fraction may then be sent directly into the hydroconversion step (c).

The light fraction may undergo other separation steps. Advantageously, it may be subjected to an atmospheric distillation making it possible to obtain a gaseous fraction, at least one light fraction of liquid hydrocarbons of naphtha, kerosene and/or diesel type and a vacuum distillation fraction, the latter possibly being at least partly sent into the hydroconversion step (c). Another part of the vacuum distillate may be used as a fuel oil flux. Another part of the vacuum distillate may be upgraded by being subjected to a fluidized-bed hydrocracking and/or catalytic cracking step.

The separation without decompression allows better thermal integration and is reflected by a saving in energy and equipment. In addition, this embodiment has technico-economical advantages, since it is not necessary to increase the pressure of the streams after separation before the subsequent hydroconversion step. Since the intermediate fractionation without decompression is simpler than fractionation with decompression, the investment cost is thus advantageously reduced.

The gaseous fractions derived from the separation step preferably undergo a purification treatment to recover the hydrogen and to recycle it into the hydrotreatment and/or hydroconversion reactors. The presence of the intermediate separation step, between the

hydrotreatment step (a) and the hydroconversion step (c), advantageously makes it possible to provide two independent hydrogen circuits, one connected to the hydrotreatment, the other to the hydroconversion, and which, according to need, may be connected together. The input of hydrogen may take place on the hydrotreatment section or on the hydroconversion section or on both. The recycling hydrogen may feed the hydrotreatment section or the hydroconversion section or both. A compressor may optionally be common to the two hydrogen circuits. The possibility of connecting the two hydrogen circuits allows optimization of the hydrogen management and limits the investments in terms of compressors and/or purification units for the gaseous effluents. The various embodiments of the hydrogen management that may be used in the present invention are described in patent application FR 2 957 607.

The light fraction obtained after the separation step (b), which comprises hydrocarbons of naphtha, kerosene and/or diesel type or the like, especially GPL and vacuum gas oil, may be upgraded according to the methods that are well known to those skilled in the art. The products obtained may be integrated into fuel formulations (also known as fuel "pools") or may undergo additional refining steps. The naphtha, kerosene, gas oil and vacuum gas oil fraction(s) may be subjected to one or more treatments, for example hydrotreatment, hydrocracking, alkylation, isomerization, catalytic reforming, catalytic or thermal cracking, to bring them separately or as a mixture to the required specifications which may relate to the sulfur content, the soak point, the octane number, the cetane number, and the like.

Ebullated-bed hydroconversion step (c)

At least part of the heavy fraction of the effluent derived from the separation step (b) is sent according to the process of the present invention into a hydroconversion step (c) which is performed in at least one ebullated-bed reactor containing a supported catalyst. The said reactor may function with an ascending stream of liquid and gas. The main object of the hydroconversion is to convert the heavy hydrocarbon feedstock into lighter fractions while at the same time partially refining it.

According to one embodiment of the present invention, part of the initial hydrocarbon feedstock may be injected directly into the inlet of the ebullated-bed hydroconversion section (c), as a mixture with the heavy fraction of the effluent derived from the

separation step (b), without this part of the hydrocarbon feedstock having been treated in the fixed-bed hydrotreatment section (a). This embodiment may resemble a partial short-circuit of the fixed-bed hydrotreatment section (a).

According to one variant, a co-feedstock may be introduced at the inlet of the ebullated-bed hydroconversion section (c) with the heavy fraction of the effluent derived from the separation step (b). This co-feedstock may be chosen from atmospheric residues, vacuum residues derived from direct distillation, de-asphalted oils, aromatic extracts derived from lubricant base production lines, hydrocarbon fractions or a mixture of hydrocarbon fractions which may be chosen from the products derived from a fluid-bed catalytic cracking process, especially a light cycle oil (LCO), a heavy cycle oil (HCO), a decanted oil, or which may originate from distillation, gas oil fractions, especially those obtained by atmospheric or vacuum distillation, for instance vacuum gas oil. According to another variant, and in the case where the hydroconversion section includes several ebullated-bed reactors, this co-feedstock may be partly or totally injected into one of the reactors downstream of the first reactor.

The hydrogen required for the hydroconversion reaction may be injected into the inlet of the ebullated-bed hydroconversion section (c). It may be recycling hydrogen and/or input hydrogen. In the case where the hydroconversion section includes several ebullated-bed reactors, the hydrogen may be injected into the inlet of each reactor.

The ebullated-bed technique is well known to those skilled in the art. Only the main operating conditions will be described herein. Ebullated-bed techniques conventionally use supported catalysts in the form of extrudates whose diameter is generally about 1 millimetre, for example 0.9 mm or 1.2 mm. The catalysts remain inside the reactors and are not removed with the products, except for during the phases of input and removal of catalysts necessary for maintaining the catalytic activity. The temperature levels may be high so as to obtain high conversions while at the same time minimizing the amounts of catalysts used. The catalytic activity may be kept constant by on-line replacement of the catalyst. It is therefore not necessary to stop the unit in order to change the spent catalyst, or to increase the reaction temperatures throughout the cycle in order to compensate for the deactivation. Furthermore, working under constant operating conditions advantageously makes it possible to obtain constant yields and product qualities throughout the cycle. Also, since the catalyst is kept in agitation by substantial recycling of liquid, the loss of pressure on the reactor remains low and constant. Due to

the attrition of the catalysts in the reactors, the products leaving the reactors may contain fine catalyst particles.

The conditions of the ebullated-bed hydroconversion step (c) may be standard conditions for the ebullated-bed hydroconversion of a liquid hydrocarbon fraction. The process may be performed at an absolute pressure of between 2.5 MPa and 35 MPa, preferentially between 5 MPa and 25 MPa, more preferentially between 6 MPa and 20 MPa, and even more preferentially between 11 MPa and 20 MPa at a temperature of between 330°C and 550°C and preferentially between 350°C and 500°C. The hourly space velocity (HSV) and the partial pressure of hydrogen are parameters that are set as a function of the characteristics of the product to be treated and of the desired conversion. The HSV (defined as being the volume flow rate of the feedstock divided by the total volume of the ebullated-bed reactor) is generally in a range from 0.1 h⁻¹ to 10 h⁻¹, preferentially from 0.2 h⁻¹ to 5 h⁻¹ and more preferentially from 0.2 h⁻¹ to 1 h⁻¹. The amount of hydrogen mixed with the feedstock is usually from 50 to 5000 normal cubic metres (Nm³) per cubic metre (m³) of liquid feedstock, usually from 100 Nm³/m³ to 1500 Nm³/m³ and preferably from 200 Nm³/m³ to 1200 Nm³/m³.

A standard granular hydroconversion catalyst may be used, comprising, on an amorphous support, at least one metal or metal compound having a hydro-dehydrogenating function. This catalyst may be a catalyst comprising group VIII metals, for example nickel and/or cobalt, usually in combination with at least one group VIB metal, for example molybdenum and/or tungsten. Use may be made, for example, of a catalyst comprising from 0.5% to 10% by weight of nickel and preferably from 1% to 5% by weight of nickel (expressed as nickel oxide NiO) and from 1% to 30% by weight of molybdenum and preferably from 5% to 20% by weight of molybdenum (expressed as molybdenum oxide MoO₃) on an amorphous mineral support. This support may be chosen, for example, from the group consisting of alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. This support may also contain other compounds, for example oxides chosen from the group consisting of boron oxide, zirconia, titanium oxide, phosphorus pentoxide. Use is usually made of an alumina support and very usually an alumina support doped with phosphorus and optionally with boron. When phosphorus pentoxide P₂O₅ is present, its concentration is usually less than 20% by weight and very usually less than 10% by weight. When boron trioxide B₂O₃ is present, its concentration is usually less than 10% by weight. The alumina used is usually a γ (gamma) or η (eta) alumina. This catalyst may be in the form of extrudates. The total

content of group VI and VIII metal oxides may be from 5% to 40% by weight and in general from 7% to 30% by weight, and the weight ratio expressed as metal oxide between group VI metal(s) and group VIII metal(s) is between 20 and 1, and preferably between 10 and 2.

The spent catalyst may be partly replaced with fresh catalyst, generally by removal from the bottom of the reactor and introduction into the top of the reactor of fresh or new catalyst at regular time intervals, i.e. for example in batches or continuously or virtually continuously. It is also possible to introduce the catalyst at the bottom and to remove it from the top of the reactor. It is possible, for example, to introduce fresh catalyst every day. The rate of replacement of the spent catalyst with fresh catalyst may be, for example, from about 0.05 kilogram to about 10 kilograms per cubic metre of feedstock. This removal and this replacement are performed by means of devices enabling continuous functioning of this hydroconversion step. The hydroconversion reactor usually comprises a recycling pump for maintaining the catalyst in the ebullated bed by continuous recycling of at least part of the liquid removed from the top of the reactor and reinjected into the bottom of the reactor. It is also possible to send the spent catalyst withdrawn from the reactor into a regeneration zone in which the carbon and sulfur it contains are removed, before reinjecting it into the hydroconversion step (c).

This hydroconversion step (c) according to the process of the invention may be performed under the conditions of the H-OIL® process as described, for example, in patent US 6 270 654.

The ebullated-bed hydroconversion may take place in a single reactor or in several reactors, preferably two, arranged in series. Using at least two ebullated-bed reactors in series makes it possible to obtain products of better quality and in a better yield. Furthermore, hydroconversion in two reactors makes it possible to have improved operability as regards the flexibility of the operating conditions and of the catalytic system. Preferably, the temperature of the second ebullated-bed reactor is at least 10°C higher than that of the first ebullated-bed reactor. The pressure of the second reactor may be from 0.1 MPa to 1 MPa lower than for the first reactor, to allow flow of at least some of the effluent derived from the first step without pumping being necessary. The various operating conditions in terms of temperature in the two hydroconversion reactors are selected so as to be able to control the hydrogenation and the conversion of the feedstock into desired products in each reactor.

In the case where the hydroconversion step (c) is performed in two sub-steps (c1) and (c2) in two reactors arranged in series, the effluent obtained from the first sub-step (c1) may optionally be subjected to a step for separation of the light fraction and of the heavy fraction, and at least part, preferably all, of the said heavy fraction may be treated in the second hydroconversion sub-step (c2). This separation is advantageously performed in an inter-stage separator, as described, for example, in patent US 6 270 654, and makes it possible especially to avoid overcracking of the light fraction in the second hydroconversion reactor. It is also possible totally or partly to transfer the spent catalyst withdrawn from the reactor of the first hydroconversion sub-step (c1), working at a lower temperature, directly into the reactor of the second sub-step (c2), working at a higher temperature, or totally or partly to transfer the spent catalyst withdrawn from the reactor of the second sub-step (c2) directly into the reactor of the first sub-step (c1). This cascade system is described, for example, in patent US 4 816 841.

Step (d) of separation of the hydroconversion effluent

The process according to the invention also comprises a separation step (d) for obtaining at least one gaseous fraction and at least one liquid hydrocarbon fraction.

The effluent obtained after the hydroconversion step (c) comprises a liquid fraction and a gaseous fraction containing gases, especially H_2 , H_2S , NH_3 and C_1 - C_4 hydrocarbons. This gaseous fraction may be separated from the hydrocarbon effluent by means of separation devices that are well known to those skilled in the art, especially using one or more separating flasks which may operate at different pressures and temperatures, optionally combined with a means for stripping with steam or with hydrogen. The effluent obtained after the hydroconversion step (c) is advantageously separated in at least one separating flask into at least one gaseous fraction and at least one liquid fraction. These separators may be, for example, high-pressure high-temperature (HPHT) separators and/or high-pressure low-temperature (HPLT) separators.

After optional cooling, this gaseous fraction is preferably treated in a hydrogen purification means so as to recover the hydrogen not consumed during the hydrotreatment and hydroconversion reactions. The hydrogen purification means may be an amine wash, a membrane, a system of PSA (Pressure Swing Adsorption) type or several of these means arranged in series. The purified hydrogen may then

advantageously be recycled into the process according to the invention, after optional recompression. The hydrogen may be introduced into the inlet of the hydrotreatment step (a) and/or into different points during the hydrotreatment step (a) and/or into the inlet of the hydroconversion step (c) and/or into different points during the hydroconversion step (c).

The separation step (d) may also comprise atmospheric distillation and/or vacuum distillation. Advantageously, the separation step (d) also comprises at least one atmospheric distillation, in which the liquid hydrocarbon fraction(s) obtained after separation are fractionated by atmospheric distillation into at least one atmospheric distillate fraction and at least one atmospheric residue fraction. The atmospheric distillate fraction may contain fuel bases (naphtha, kerosene and/or diesel) that are commercially upgradable, for example in a refinery for the production of motor vehicle and aviation fuels.

In addition, the separation step (d) of the process according to the invention may advantageously also comprise at least one vacuum distillation in which the liquid hydrocarbon fraction(s) obtained after separation and/or the atmospheric residue fraction obtained after atmospheric distillation are fractionated by vacuum distillation into at least one vacuum distillate fraction and at least one vacuum residue fraction. Preferably, the separation step (d) first comprises an atmospheric distillation, in which the liquid hydrocarbon fraction(s) obtained after separation are fractionated by atmospheric distillation into at least one atmospheric distillate fraction and at least one atmospheric residue fraction, followed by a vacuum distillation in which the atmospheric residue fraction obtained after atmospheric distillation is fractionated by vacuum distillation into at least one vacuum distillate fraction and at least one vacuum residue fraction. The vacuum distillate fraction typically contains fractions of vacuum gas oil type.

At least part of the vacuum residue fraction may be recycled into the hydroconversion step (c).

After the separation step (d), at least one liquid hydrocarbon fraction may be obtained having a sulfur content of less than or equal to 0.5% by weight, preferentially less than or equal to 0.3% by weight, more preferentially less than or equal to 0.1% by weight and even more preferentially less than or equal to 0.08% by weight. This liquid hydrocarbon fraction may advantageously serve as a fuel oil base, especially for a bunker fuel. Advantageously, all of the liquid hydrocarbon effluent obtained after the separation step

(d) may have a sulfur content of less than or equal to 0.5% by weight, preferentially less than or equal to 0.3% by weight, more preferentially less than or equal to 0.1% by weight and even more preferentially less than or equal to 0.08% by weight.

In the context of the present invention, the conversion of the hydrocarbon feedstock into lighter fractions may be between 10% and 95%, preferentially between 25% and 90% and more preferentially between 40% and 85%. The degree of conversion mentioned above is defined as being the amount of compounds with a boiling point of greater than 520°C in the initial hydrocarbon feedstock, minus the amount of compounds with a boiling point of greater than 520°C in the hydrocarbon effluent obtained after the hydroconversion step (c), the whole divided by the amount of compounds with a boiling point of greater than 520°C in the initial hydrocarbon feedstock. A high degree of conversion is advantageous insofar as this degree of conversion illustrates the production of conversion products, mainly atmospheric distillates and/or vacuum distillates of naphtha, kerosene and diesel type, in significant amount.

This liquid hydrocarbon effluent may, at least partly, advantageously be used as fuel oil bases or fuel oil, especially as bunker fuel base or bunker fuel, with a low sulfur content meeting the new recommendations of the International Maritime Organization.

In the invention, the term "fuel oil" means a hydrocarbon feedstock which may be used as fuel. In the invention, the term "fuel oil base" means a hydrocarbon feedstock which, when mixed with other bases, constitutes a fuel oil. As a function of the origin of these bases, especially as a function of the type of crude petroleum and of the type of refining, the properties of these bases, in particular their sulfur content and their viscosity, are very diverse.

Optional step (e) of separation of the sediments and fines

The hydrocarbon effluent obtained after the hydroconversion step (c), and especially the heaviest liquid fraction obtained, may contain sediments and catalyst residues derived from the fixed-bed step and/or from the ebullated-bed step in the form of fines. In order to obtain a fuel oil or a fuel oil base that meets the recommendations of a content of sediments after ageing of less than or equal to 0.1%, the process according to the invention may comprise an additional step that consists in separating the sediments and fines from the liquid hydrocarbon effluent after the separation step (d).

The process according to the invention may thus also comprise a step (e) of separation of the sediments and fines, in which at least part of the atmospheric residue fractions and/or vacuum distillate fractions and/or vacuum residue fractions is subjected to a separation of the sediments and of the catalyst fines, using at least one filter, a centrifugation system or on-line decantation.

Optional step (f) of catalytic cracking

According to an embodiment, the process according to the invention may also comprise a catalytic cracking step (f), in which at least part of the vacuum distillate fraction and/or of the vacuum residue fraction, optionally subjected beforehand to the step for separating out the sediments and fines (e), is sent to a catalytic cracking section in which it is treated under conditions enabling the production of a gaseous fraction, a petroleum fraction, a diesel fraction and a residual fraction.

The said catalytic cracking step (f) may be a step of fluidized-bed catalytic cracking, for example according to the process developed by the Applicant Company known as R2R. This step may be performed in a conventional manner known to those skilled in the art under suitable cracking conditions in order to obtain hydrocarbon products of lower molecular weight. Descriptions of functioning and of catalysts that may be used in the context of fluidized-bed cracking in this step (f) are described, for example, in patents US 4 695 370, EP 0 184 517, US 4 959 334, EP 0 323 297, US 4 965 232, US 5 120 691, US 5 344 554, US 5 449 496, EP 0 485 259, US 5 286 690, US 5 324 696, EP 0 542 604 and EP 0 699 224.

The fluidized-bed catalytic cracking reactor may function with an ascending stream or a descending stream. Although this is not a preferred embodiment of the present invention, it may also be envisaged to perform the catalytic cracking in a mobile-bed reactor. The catalytic cracking catalysts that are particularly preferred are those which contain at least one zeolite usually as a mixture with a suitable matrix, for instance alumina, silica or silica-alumina.

At least part of the residual fraction obtained after the catalytic cracking step (f), often referred by those skilled in the art as the "slurry" fraction, may be recycled into the inlet of the catalytic cracking step (f) and/or to the inlet of the hydrotreatment step (a) and/or

to the inlet of the hydroconversion step (c). The residual fraction may also be at least partly or even totally sent to a zone for storing heavy refinery fuel oil.

In one embodiment of the invention, part of the diesel fraction and/or of the residual fraction obtained after this catalytic cracking step (f) may be used to constitute a flux base.

Flux and fuel oils

One object of the present invention is to produce commercializable fuel oils, especially bunker fuels for maritime transport. It is preferable for this type of fuel oil to meet certain specifications, especially in terms of viscosity. Preferably, a very common type of bunker fuel has a viscosity of less than or equal to 380 cSt (at 50°C). Other qualities of fuel oils, known as "grades", meet different specifications, especially from the point of view of the viscosity. In particular for fuels of distillate type, the DMA grade imposes a viscosity of between 2 cSt and 6 cSt at 40°C and the DMB grade a viscosity of between 2 cSt and 11 cSt at 40°C. In order to obtain, inter alia, the target viscosity for the desired grade of fuel oil, fuel oil bases may be mixed, if necessary, with flux bases or "cutter stocks". Specifications for the fuel oils are described, for example, in standard ISO 8217 (last version in 2012).

The flux bases are generally of kerosene, gas oil or vacuum gas oil type. They may be chosen from oils from light cycle oils (LCO) from a catalytic cracking, heavy cycle oils (HCO) from a catalytic cracking, the residue of a catalytic cracking, kerosene, gas oil, vacuum distillate and/or a decanted oil.

In the process according to the invention, the atmospheric residue and/or the vacuum distillate and/or the vacuum residue obtained after the separation step (d), optionally subjected beforehand to step (e) for separating out the sediments and fines, may be mixed with one or more flux bases chosen from the group consisting of light cycle oils from a catalytic cracking, heavy cycle oils from a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil.

In a most particularly preferred manner, the said flux base is chosen from part of the light hydrocarbon fraction of kerosene or gas oil type obtained after the separation step (b), part of the heavy hydrocarbon fraction of vacuum distillate type obtained after the

separation step (b), and part of the petroleum fraction, of the diesel fraction and/or of the residual fraction obtained after the catalytic cracking step (f). Furthermore, or alternatively, the said flux base may be chosen from part of the kerosene and/or diesel fraction obtained after the ebullated-bed hydroconversion step.

After this step of mixing the atmospheric residue and/or the vacuum distillate and/or the vacuum residue obtained after the separation step (d), optionally subjected beforehand to step (e) of separating out the sediments and fines, with one or more flux bases, a fuel oil is obtained which may advantageously be used in maritime transport, also known as a bunker fuel, with a low sulfur content.

A subject of the present invention is thus also such a fuel oil which has a sulfur content of less than or equal to 0.5% by weight, and preferably less than or equal to 0.1% by weight. This fuel oil may advantageously have a sediment content of less than or equal to 0.1% by weight, so as to meet the new version of standard ISO 8217:2012.

Furthermore, the viscosity of this fuel oil may be between 1 cSt and 700 cSt at 50°C.

An advantageous embodiment of the process according to the invention is shown in **Figures 1, 2 and 3**.

Figure 1 shows a process according to the invention with intermediate separation with decompression. For better readability, the functioning of the guard zones in the hydrotreatment section of **Figure 1** is described in **Figure 2**.

In **Figure 1**, the feedstock (10), preheated in the chamber (12), mixed with recycled hydrogen (14) and input hydrogen (24) preheated in the chamber (16), is introduced via the pipe (18) into the guard zone system.

With reference to **Figure 2**, the functioning of the guard zones in the hydrotreatment section comprising two guard zones (or permutable reactors) Ra and Rb comprises a series of cycles each comprising four successive steps:

- a first step (step i) during which the feedstock successively passes through reactor Ra and then reactor Rb,
- a second step (step ii) during which the feedstock passes through only reactor Rb, reactor Ra being short-circuited for regeneration and/or replacement of the catalyst,

- a third step (step iii) during which the feedstock successively passes through reactor Rb and then reactor Ra,
- a fourth step (step iv) during which the feedstock passes through only reactor Ra, reactor Rb being short-circuited for regeneration and/or replacement of the catalyst.

The cycle can then recommence.

Steps i and iii are steps during which all the guard zones are used. Steps ii and iv are steps during which one guard zone is short-circuited while the other is used.

During step (i), the preheated feedstock is introduced via line (18) and line (19) comprising a valve V1 which is opened towards line (20) and the guard reactor Ra containing a fixed bed A of catalyst. During this period, valves V3, V4 and V5 are closed. The effluent from reactor Ra is sent via the pipe (21), the pipe (22) comprising an open valve V2 and the pipe (23) in the guard reactor Rb containing a fixed bed B of catalyst. The effluent from reactor Rb is sent via pipes (24) and (25) comprising an open valve V6 and the pipe (26) to the main hydrotreatment section, which will be described hereinbelow.

In the course of step (ii), valves V1, V2, V4 and V5 are closed and the feedstock is introduced via line (18) and line (27) comprising a valve V3 which is opened towards line (23) and reactor Rb. During this period, the effluent from reactor Rb is sent via pipes (24) and (25) comprising an open valve V6 and pipe (26) to the main hydrotreatment section.

During step (iii), valves V1, V2 and V6 are closed and valves V3, V4 and V5 are open. The feedstock is introduced via line (18) and lines (27) and (23) to reactor Rb. The effluent from reactor Rb is sent via line (24), line (28) comprising an open valve V4 and line (20) to the guard reactor Ra. The effluent from reactor Ra is sent via pipes (21) and (29) comprising an open valve V5 and pipe (26) to the main hydrotreatment section.

During step (iv), valves V2, V3, V4 and V6 are closed and valves V1 and V5 are open. The feedstock is introduced via line (18) and lines (19) and (20) to reactor Ra. During this period, the effluent from reactor Ra is sent via lines (21) and (29) comprising an open valve V5 and line (26) to the main hydrotreatment section.

Returning to **Figure 1**, the effluent leaving the guard reactor(s) is optionally remixed with hydrogen arriving via line (65) in an HDM reactor (30) which contains a fixed bed

(32) of catalyst. For reasons of readability, only one HDM reactor and only one HDS reactor are shown in the figure, but the HDM and HDS section may contain several HDM and HDS reactors in series. If need be, the recycled and/or input hydrogen may also be introduced into the hydrotreatment reactors between the various catalytic beds (not shown).

The effluent from the HDM reactor is withdrawn via line (34) and then sent to the first HDS reactor (36) where it passes through a fixed bed (38) of catalyst.

The effluent obtained from the hydrotreatment step is sent via line (42) to a high-pressure high-temperature (HPHT) separator (44) from which are recovered a gaseous fraction (46) and a liquid fraction (48). The cutoff point is generally between 200 and 400°C. The gaseous fraction (46) is sent, generally via an exchanger (not shown) or a cooling tower (50) for cooling, to a high-pressure low-temperature (HPLT) separator (52) from which are recovered a gaseous fraction (54) containing gases (H_2 , H_2S , NH_3 , C_1 - C_4 hydrocarbons, etc.) and a liquid fraction (56).

The gaseous fraction (54) obtained from the high-pressure low-temperature (HPLT) separator (52) is treated in the hydrogen purification unit (58), from which the hydrogen (60) is recovered and recycled via the compressor (62) and line (65) to the reactors (30) and/or (36) or via line (14) to the permutable reactors. The gases containing undesirable nitrogenous and sulfurous compounds are removed from the installation (stream (66)).

The liquid fraction (56) obtained from the high-pressure low-temperature (HPLT) separator (52) is depressurized in the device (68) and then sent to the fractionation system (70). Optionally, a medium-pressure separator (not shown) after the pressure-release device (68) may be installed to recover a gaseous fraction, which is sent to the purification unit (58), and a liquid phase, which is sent to the fractionation section (70).

The liquid fraction (48) obtained from the high-pressure high-temperature (HPHT) separator (44) is depressurized in the device (72) and then sent to the fractionation system (70). Fractions (56) and (48) may be sent together, after pressure release, to the system (70). According to a variant not shown, fractions (70) and (172) may be common and treated all the light fractions, including that coming from the inter-stage separator (108). The fractionation system (70) comprises an atmospheric distillation system for producing a gaseous effluent (74), at least one "light" fraction (76) especially containing naphtha, kerosene and diesel, and an atmospheric residue fraction (78). Part of the

atmospheric residue fraction may be sent via line (80) to the hydroconversion 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 and a vacuum distillate fraction (86) containing vacuum gas oil.

The vacuum residue fraction (84), optionally mixed with part of the atmospheric residue fraction (80) and/or with part of the vacuum distillate fraction (86), is mixed with recycled hydrogen (88) optionally made up with input hydrogen (90) preheated in the oven (91). It optionally passes through an oven (92). Optionally, a co-feedstock (94) may be introduced. The heavy fraction is then introduced via line (96) into the hydroconversion step at the bottom of the first ebullated-bed reactor (98) functioning with an ascending stream of liquid and gas and containing at least one hydroconversion catalyst. Reactor (98) usually comprises a recirculation pump (100) for maintaining the ebullated-bed catalyst by continuous recycling of at least part of the liquid withdrawn from the top of the reactor and reinjected into the bottom of the reactor. The input of fresh catalyst may take place via the top or via the bottom of the reactor (not shown). The input of catalyst may take place periodically or continuously. The spent catalyst may be withdrawn from the bottom of the reactor (not shown) to be either discarded or regenerated in order to remove the carbon and sulfur before being reinjected into the top of the reactor. The partially spent catalyst withdrawn from the bottom of the first reactor may also be transferred directly into the top of the second hydroconversion reactor (102) (not shown). Optionally, the converted effluent (104) obtained from reactor (98) may be subjected to a separation of the light fraction (106) in an inter-stage separator (108).

All or part of the effluent (110) obtained from the inter-stage separator (108) is advantageously mixed with additional hydrogen (157), which is preheated beforehand if need be (not shown). This mixture is then injected via pipe (112) into a second ebullated-bed hydroconversion reactor (102) functioning with an ascending stream of liquid and of gas containing at least one hydroconversion catalyst. The operating conditions, especially the temperature, in this reactor are chosen so as to achieve the desired level of conversion, as has been described previously. The input and withdrawal of the catalyst is performed in the same manner as that described for the first reactor. Reactor (102) also usually comprises a recirculation pump (114) functioning in the same manner as the pump of the first reactor.

The effluent from the ebullated-bed reactors is sent via line (134) to a high-pressure high-temperature (HPHT) separator (136), from which are recovered a gaseous fraction (138) and a liquid fraction (140). 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 (HPLT) separator (144), from which are recovered a gaseous fraction (146) containing the gases (H_2 , H_2S , NH_3 , C_1 - C_4 hydrocarbons, etc.) and a liquid fraction (148).

The gaseous fraction (146) from the high-pressure low-temperature (HPLT) separator (144) is treated in the hydrogen purification unit (150), from which is recovered hydrogen (152) for recycling via the compressor (154) and line (156) and/or line (157) to the hydroconversion section. The hydrogen purification unit may consist of an amine wash, a membrane or a system of PSA type. The gases containing the undesirable nitrogenous and sulfurous compounds are discharged from the installation (stream (158) which may represent several streams, especially an H_2S -rich stream and one or more purges containing light hydrocarbons (C_1 and C_2) which may be used as refinery fuel gas).

The liquid fraction (148) from the high-pressure low-temperature (HPLT) separator (144) is depressurized in the device (160) and then sent to the fractionation system (172). Optionally, a medium-pressure separator (not shown) after the pressure-release device (160) may be installed to recover a vapour phase which is sent to the purification unit (150) and/or to a dedicated medium-pressure purification unit (not shown), and a liquid phase which is conveyed to the fractionation section (172).

The liquid fraction (140) obtained from the high-pressure high-temperature (HPHT) separator (136) is depressurized in the device (174) and then sent to the fractionation system (172). Optionally, a medium-pressure separator (not shown) after the pressure-release device (174) may be installed to recover a vapour phase which is sent to the purification unit (150) and/or to a dedicated medium-pressure purification unit (not shown), and a liquid phase which is conveyed to the fractionation section (172).

Obviously, fractions (148) and (140) may be sent together, after depressurization, to the system (172). The fractionation system (172) comprises an atmospheric distillation system for producing a gaseous effluent (176), at least one "light" fraction (178), especially comprising naphtha, kerosene and diesel, and an atmospheric residue fraction (180). Part of the atmospheric residue fraction (180) may be withdrawn via line (182) to constitute the desired fuel oil bases. All or part of the atmospheric residue fraction (180)

may be sent to a vacuum distillation column (184) to recover a fraction containing the vacuum residue (186) and a vacuum distillate fraction (188) containing vacuum gas oil. At least part of the vacuum residue fraction is preferably recycled via line (190) into the hydroconversion step, or upstream of the hydrotreatment step (line not shown) so as to increase the conversion. Optionally, the atmospheric residue fraction (182), the vacuum distillate fraction (188) and/or the vacuum residue fraction (186) may be subjected to a step for separating out the fines and sediments via, for example, filters (191), (192) and (193), respectively.

An alternative scheme, not shown, for the separation and fractionation may be performed using a steam stripping column which treats the heavy fraction(s) from the high-pressure or medium-pressure or low-pressure separators. Via this means, the bottom of the stripping column directly feeds the vacuum column; the atmospheric distillation column remains for treating distillate mixtures but does not treat the unconverted fraction (the heaviest fraction).

Figure 3 represents another process according to the invention with intermediate separation without decompression. Essentially only the differences between the process according to **Figure 3** and the process according to **Figure 1** will be described below, the hydrotreatment and hydroconversion steps and the steps for separation after the hydroconversion (and the reference signs thereof) otherwise being strictly identical.

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

The residual fraction (48) is directly sent, after optional passage through an oven (92), into the hydroconversion section.

The lighter fraction (46) is sent, generally via an exchanger (not shown) or a cooling tower (50) for cooling, to a high-pressure low-temperature (HPLT) separator (52), from which are recovered a gaseous fraction (54) containing the gases (H_2 , H_2S , NH_3 , C_1 - C_4 hydrocarbons, etc.) and a liquid fraction (56).

The gaseous fraction (54) from the high-pressure low-temperature (HPLT) separator (52) is treated in the hydrogen purification unit (58), from which is recovered hydrogen (60), which is recycled via the compressor (154) and lines (64) and (156) to the hydrotreatment section and/or to the hydroconversion section. The gases containing

undesirable nitrogenous, sulfurous and oxygenated compounds are discharged from the installation (stream (66)). In this configuration, only one compressor (154) is used to feed all of the reactors requiring hydrogen.

The liquid fraction (56) obtained from the high-pressure low-temperature (HPLT) separator (52) is depressurized in the device (68) and then sent to the fractionation system (70). The fractionation system (70) comprises an atmospheric distillation system for producing a gaseous effluent (74), at least one "light" fraction (76) especially containing naphtha, kerosene and diesel, and an atmospheric residue fraction (195). Part of the atmospheric residue fraction may be sent via line (195) to the hydroconversion reactors, whereas another part of the atmospheric residue fraction (194) may be sent to another process (hydrocracking or FCC or hydrotreatment).

EXAMPLES

The following example illustrates the invention without, however, limiting its scope.

A vacuum residue (RSV Oural) was treated, containing 87.0% by weight of compounds boiling at a temperature above 520°C, with a density of 9.5°API and a sulfur content of 2.72% by weight. The feedstock contains 254 ppm of metals (Ni + V).

The feedstock was subjected to a hydrotreatment step including two permutable reactors. The HDM/HDS catalyst distribution of the feedstock is 63/27. The operating conditions are given in Table 1.

HDM and HDS catalysts	NiMo on alumina
T (°C)	370
Pressure (MPa)	15
HSV (h^{-1} , Sm^3/h fresh feedstock / m^3 of fixed-bed catalyst)	0.18
H_2 / HC fixed-bed section inlet excluding H_2 consumption (Nm^3 / m^3 of fresh feedstock)	1000

Table 1: Fixed-bed operating conditions

The hydrodemetallation HDM performance in the fixed-bed HDT section is greater than 80%.

The hydrotreatment effluent was then subjected to a flash flask separation at high pressure and high temperature (HPHT).

The heavy fraction (fraction 350°C⁺) was sent to a hydroconversion step comprising two successive ebullated-bed reactors. The operating conditions are given in Table 2.

Catalyst	NiMo on alumina
Ebullated-bed R1 T (°C)	418
Ebullated-bed R2 T (°C)	428
Pressure (MPa)	16
HSV (h ⁻¹ , Sm ³ /h fresh feedstock /m ³ of fixed-bed catalyst)	0.3
H ₂ / HC ebullated-bed section inlet excluding H ₂ consumption (Nm ³ / m ³ of fresh feedstock)	1000

Table 2: Ebullated-bed operating conditions

The yield and the sulfur content for each fraction obtained from the effluent leaving the overall chain are given in Table 3.

Products	Yield (weight %)	S (weight %)
NH ₃	0.7	0
H ₂ S	2.7	94.12
C ₁ -C ₄ (gas)	3.8	0
Naphtha (PI - 150°C)	8.0	0.02
Diesel (150°C - 350°C)	22.7	0.05
Vacuum distillate (350°C - 520°C)	29.5	0.26
Vacuum residue (520°C ⁺)	34.3	0.43

Table 3: Yields and sulfur content for the effluent of the ebullated-bed section (weight % / feedstock)

The hydrogen consumed represents 1.69% by weight of the fresh feedstock introduced at the inlet of the hydrotreatment section.

The above yields make it possible to calculate the degree of conversion of the fraction of the feedstock boiling at a temperature above 520°C being converted into products boiling at a temperature below 520°C, according to the following formula:

$$\text{Conversion} = \frac{(\text{amount of } 520^{\circ}\text{C}^{+} \text{ in the feedstock}) - (\text{amount of } 520^{\circ}\text{C}^{+} \text{ in the effluent})}{(\text{amount of } 520^{\circ}\text{C}^{+} \text{ in the feedstock})}$$

The numerical application gives: Conversion = (87.0-34.3) / 87.0 = 60.5%

This particularly high degree of conversion illustrates the production of conversion products (mainly distillates) in significant amount.

Thereafter, a mixture was prepared from 350-520°C and 520°C⁺ fractions obtained from the hydroconversion step in the following proportions:

- 350-540°C fraction: 48% by weight of the mixture, and
- 520°C⁺ fraction: 52% by weight of the mixture.

A fuel oil was thus obtained with a sulfur content of 0.35% by weight and a viscosity of 380 cSt at 50°C. Furthermore, its content of sediments after ageing is less than 0.1% by weight. With regard to these analyses, this fuel oil is particularly suitable for constituting a bunker fuel as recommended by the IMO outside of ZCES at the 2020-2025 horizon.

In addition to the first mixture leading to a fuel oil containing 0.35% sulfur, a second mixture was prepared composed of 80% by weight of a fraction obtained from the diesel cycle and of 20% by weight of a fraction obtained from the vacuum distillate cycle. In these proportions, the mixture has a sulfur content of 0.09% and a viscosity of 6 cSt at 40°C. This mixture thus constitutes a marine fuel of distillate type ("marine gas-oil" or "marine diesel") which may be likened to DMB grade (whose viscosity specification is between 2 cSt and 11 cSt at 40°C), for example. Due to its sulfur content of less than 0.1%, this mixture constitutes a fuel of choice for ZCES at the 2015 horizon.

CLAIMS

1. Process for treating a hydrocarbon feedstock having a sulfur content of at least 0.5% by weight, an initial boiling point of at least 340°C and a final boiling point of at least 440°C, which makes it possible to obtain at least one liquid hydrocarbon fraction with a sulfur content of less than or equal to 0.5% by weight, comprising the following successive steps:
 - a) a step of fixed-bed hydrotreatment, wherein the hydrocarbon feedstock and hydrogen are placed in contact over at least one hydrotreatment catalyst,
 - b) a step of separation of the effluent obtained from the hydrotreatment step (a) into at least one light fraction and at least one heavy fraction,
 - c) a step of hydroconversion of at least part of the heavy fraction of the effluent derived from step (b) in at least one ebullated-bed reactor containing a supported catalyst, and
 - d) a step of separation of the effluent derived from step (c) to obtain at least one gaseous fraction and at least the said liquid hydrocarbon fraction.

2. Process according to Claim 1, wherein the hydrotreatment step (a) comprises a first step (a1) of hydrodemetallation (HDM) performed in one or more fixed-bed hydrodemetallation zones and a subsequent second step (a2) of hydrodesulfurization (HDS) performed in one or more fixed-bed hydrodesulfurization zones.

3. Process according to either of Claims 1 and 2, wherein the hydrotreatment step (a) is performed at a temperature of between 300°C and 500°C, at an absolute pressure of between 2 MPa and 35 MPa, with an hourly space velocity of the hydrocarbon feedstock which is within a range from 0.1 h⁻¹ to 5 h⁻¹, and the amount of hydrogen mixed with the feedstock is between 100 Nm³/m³ and 5000 Nm³/m³.

4. Process according to any one of Claims 1 to 3, wherein the hydroconversion step (c) is performed at an absolute pressure of between 2.5 MPa and 35 MPa, at a temperature of between 330°C and 550°C, with an hourly space velocity which is in a range from

0.1 h⁻¹ to 10 h⁻¹, and the amount of hydrogen mixed with the feedstock is from 50 Nm³/m³ to 5000 Nm³/m³.

5. Process according to any one of Claims 1 to 4, wherein the hydrotreatment step (a) is performed in one or more fixed-bed hydrotreatment zones preceded by at least two hydrotreatment guard zones which are also in fixed beds, arranged in series so as to be used in a cyclic manner consisting of the successive repetition of steps a'') and a''') defined below:

a') a step wherein the guard zones are all used together for a duration that is at most equal to the deactivation and/or clogging time for one of them,

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

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

6. Process according to any one of Claims 1 to 5, wherein the hydrocarbon feedstock is chosen from atmospheric residues, vacuum residues obtained from direct distillation, crude petroleums, de-headed crude petroleums, deasphalted oils, deasphalting resins, deasphalting pitches or asphalts, residues obtained from conversion processes, aromatic extracts obtained from lubricant base production lines, bituminous sands or derivatives thereof, bituminous shales or derivatives thereof, parent-rock oils or derivatives thereof, taken alone or as a mixture.

7. Process according to any one of Claims 1 to 6, wherein the effluent obtained from the hydrotreatment step (a) undergoes a step (b) of separation with decompression, comprising the following steps:

- the said effluent from step (a) is sent to a fractionation section with a cutoff point of between 200°C and 400°C making it possible to obtain a light fraction and a heavy fraction,

- the said heavy fraction is fractionated by atmospheric distillation into at least one atmospheric distillate fraction, preferably containing at least one light fraction of

hydrocarbons of naphtha, kerosene and/or diesel type, and an atmospheric residue fraction,

- at least part of the atmospheric residue fraction is fractionated by vacuum distillation into a vacuum distillate fraction, preferably containing vacuum gas oil, and a vacuum residue fraction, and

- at least part of the vacuum residue fraction and/or of the atmospheric residue fraction is advantageously sent to the hydroconversion step (c).

8. Process according to one of Claims 1 to 6, wherein the effluent from the hydrotreatment step (a) undergoes a step (b) of separation without decompression, comprising the following steps:

- the effluent from the hydrotreatment step (a) is sent to a fractionation section having a cutoff point of between 200 and 400°C making it possible to obtain at least one light fraction and at least one heavy fraction,

- the heavy fraction is directly sent to the hydroconversion step (c);

- the light fraction is subjected to an atmospheric distillation making it possible to obtain a gaseous fraction, at least one light fraction of liquid hydrocarbons of naphtha, kerosene and/or diesel type, and a vacuum distillate fraction, and

- the said vacuum distillate fraction is at least partly sent to the hydroconversion step (c).

9. Process according to any one of Claims 1 to 8, wherein the separation step (d) also comprises at least one atmospheric distillation, wherein the liquid hydrocarbon fraction(s) obtained after separation are fractionated by atmospheric distillation into at least one atmospheric distillate fraction and at least one atmospheric residue fraction.

10. Process according to any one of Claims 1 to 9, wherein the separation step (d) also comprises at least one vacuum distillation in which the liquid hydrocarbon fraction(s) obtained after separation and/or the atmospheric residue fraction obtained after atmospheric distillation are fractionated by vacuum distillation into at least one vacuum distillate fraction and at least one vacuum residue fraction.

11. Process according to Claim 10, wherein part of the vacuum residue fraction is recycled into the hydroconversion step (c).

12. Process according to any one of Claims 9 to 11, also comprising a step (e) of separating out sediments and fines, wherein at least part of the atmospheric residue fraction and/or vacuum distillate fraction and/or vacuum residue fraction is subjected to a separation of the catalyst fines and sediments, using at least one filter, a centrifugation system or on-line decantation.

13. Process according to any one of Claims 10 to 12, also comprising a catalytic cracking step (f), wherein at least part of the vacuum distillate fraction and/or of the vacuum residue fraction, which has optionally been subjected beforehand to the step for separating out the sediments and fines (e), is sent to a catalytic cracking section in which it is treated under conditions enabling the production of a gaseous fraction, a petroleum fraction, a diesel fraction and a residual fraction.

14. Process according to any one of Claims 9 to 13, wherein the atmospheric residue and/or the vacuum distillate and/or the vacuum residue obtained after the separation step (d), which has optionally been subjected beforehand to the step (e) for separating out the sediments and fines, are mixed with one or more flux bases chosen from the group consisting of light cycle oils from a catalytic cracking, heavy cycle oils from a catalytic cracking, the residue of a catalytic cracking, a kerosene, a gas oil, a vacuum distillate and/or a decanted oil.

15. Process according to Claim 14, wherein the said flux base is chosen from part of the light hydrocarbon fraction of kerosene or gas oil type obtained from the separation step (b), part of the heavy hydrocarbon fraction of vacuum distillate type obtained from the separation step (b), and part of the petroleum fraction, of the diesel fraction and/or of the residual fraction obtained from the catalytic cracking step (f).

16. Fuel oil which may be used in maritime transport, obtained via the process as defined in either of Claims 14 and 15, having a sulfur content of less than or equal to 0.5% by weight and preferably less than or equal to 0.1% by weight.

17. Fuel oil according to Claim 16, characterized in that it has a sediment content of less than or equal to 0.1% by weight.

18. Fuel oil according to either of Claims 16 and 17, characterized in that its viscosity is between 1 cSt and 700 cSt at 50°C.