

METHOD OF CONVERTING FEEDS FROM RENEWABLE SOURCES IN CO-PROCESSING WITH A PETROLEUM FEED USING A CATALYST BASED ON NICKEL AND MOLYBDENUM

The present invention relates to a method of hydrotreatment of a feed constituted by a mixture of feeds obtained from renewable sources and in particular oils of vegetable or animal origin, combined with petroleum cuts with the aim of producing gas oil fuel bases.

It relates to a method enabling the required environmental specifications to be met, for example for an atmospheric gas oil obtained by direct distillation of a crude oil, in a mixture with a feed obtained from a renewable source, in order to produce gas oil and/or kerosene fuels of good quality, i.e. complying with the 2009 specifications, i.e. having less than 10 ppm of sulphur and an improved cetane number in the case of gas oil fuel.

10 The hydrotreatment conversion of feeds obtained from renewable sources uses complex reactions, which are promoted by a hydrogenating catalytic system. These reactions in particular comprise:

- hydrogenation of unsaturations,
- deoxygenation according to two reaction pathways:
- 15 - hydrodeoxygenation (HDO): elimination of oxygen by consumption of hydrogen and leading to formation of water
- decarboxylation/decarbonylation (DCO): elimination of oxygen by formation of carbon monoxide and carbon dioxide: CO and CO₂

The invention relates to the processing of these feeds of renewable origin in a mixture with petroleum cuts of fossil origin, such as for example gas oils from various origins in the refining process.

25 The chemical structures of the triglyceride and/or fatty acid type contained in the feeds obtained from renewable sources can, under the operating conditions of hydrotreatment and with the catalysts used according to the invention, be converted totally to hydrocarbons of the paraffin type. In principle, the processing of feeds of this type in a mixture with gas oil cuts of petroleum origin typically processed in the refinery, offers the following advantages:

- limitation of polymerizations linked to the preheating of renewable feed in furnace systems, the required temperature of the 'renewable feed plus petroleum feed' mixture being attained by adjusting the temperature of the petroleum feed that is thermally more stable before mixing. In fact, it is known by a person skilled in the art that raising the temperature (>180°C) of the vegetable oils alone is highly favourable to the formation of gums or heavy polymers by thermal degradation or by thermo-oxidation of a vegetable oil (A. Rosssignol-Castera. "La thermo-oxydation des huiles végétales" Institut des corps gras ITERG -2006). This phenomenon is accentuated by the

presence of unsaturations of fatty acids and traces of metals (such as Cu, Fe, Zn, Al). These reactions mainly produce polymers of triglycerides or previously oxidized triglycerides either by epoxide bridge formation or by oligomerization of the double bonds (radical mechanism) (J.L. PERRIN et al. "Etude analytique profonde d'huiles chauffées - Techniques analytiques et essais préliminaires" Revue française des corps gras, 1992, Vol. 32, No. 4, p. 151-158). These compounds are troublesome for process management as they are liable to clog the reactor or generate unwanted degradation products. Heating the feed obtained from renewable sources by mixing with the stream of petroleum origin and in the presence of hydrogen avoids the risks of thermal degradation of vegetable oils in the equipment for preheating in this process.

- decreasing, by dilution, the contents of sulphur, nitrogen and aromatics in the feed to be processed globally in the hydrotreatment stage of the method according to the invention. The feeds of renewable origin are in fact generally free from aromatic compounds, and have lower sulphur and nitrogen contents than the feeds of petroleum origin and in particular the gas oils typically processed in the refining process. This permits a significant relaxation of the operating conditions required for this treatment, and a decrease in consumption of hydrogen in this stage.
- limitation of the exothermic effects linked to the hydrotreatment of these feeds of vegetable and/or animal origin. Processing in a mixture with a fraction of petroleum origin and in particular gas oil therefore permits better management of this exothermic effect, and thus protects the catalyst, for which the formation of hot spots would tend to promote the formation of coke, and therefore degrade performance stability and reduce the cycle time. Moreover, the thermal gradient is used advantageously for heating the mixture to the temperature required for inlet to the second hydrotreatment stage, in which the reactions of hydrodesulphurization take place.
- improve the quality of the gas oil cut produced overall, and in particular the cetane number, owing to the formation, by hydrogenation of the triglyceride and/or fatty acid structures, of hydrocarbons of the paraffin type, characterized by an excellent cetane number.
- increase in solubility of hydrogen in the mixture to be treated during the deoxygenation stage. In fact, the solubility of hydrogen is higher in the feeds of petroleum origin than in feeds obtained from renewable sources alone. Thus, by mixing a feed obtained from a renewable source with a conventional petroleum feed it is possible to increase the solubility of hydrogen in the mixture to be hydrotreated and thus limit the use of high pressures for increasing the quantity of hydrogen in solution, necessary for the reactions of hydrogenation and deoxygenation. By controlling in this way the level of

hydrogen dissolved in the liquid phase it is possible to promote the reactions of hydrodeoxygenation, and limit the formation of coke on the catalyst and the phenomena of polymerization of the oxygenated compounds.

5 Prior art

Patent application EP 1,693,432 A1 (Petrobras) describes a method permitting the hydroconversion of a mixture of 1% to 75% by volume of vegetable oils and of 99% to 25% by volume of hydrocarbons in a single hydrotreatment reactor, at a pressure from 4 MPa to 10 MPa and operating at a temperature comprised between 320°C and 400°C in the presence of
10 a hydrotreatment catalyst comprising sulphides of group VIB transition metals promoted by group VIII metals. The benefit of this approach is the gain in terms of cetane number and decrease in density provided by mixing with vegetable oil relative to the properties obtained by direct processing of the petroleum base. Moreover, mixing hydrocarbon feeds with vegetable oils makes it possible to improve the low-temperature properties of the effluents obtained
15 relative to those that would be obtained by processing vegetable oils alone.

Patent FR2904324 (Total) describes a similar application in a method of catalytic hydrotreatment on catalysts of the type NiMo, NiW, CoMo, Pt, Pd, of a feed of petroleum origin of the gas oil type in which animal oils or fats are incorporated at a maximum content of 30 wt.%.

20 However, these applications have several drawbacks. The first drawback is the application of a single stage for co-processing the vegetable oil and the petroleum base. In fact, this is limiting for optimum operation of the aforementioned hydrotreatment catalysts, which must effect the reactions of deoxygenation and of hydrodesulphurization simultaneously. The activity and stability of the catalyst as used in these patents are adversely affected by the formation of the
25 by-products carbon monoxide and carbon dioxide resulting from the reactions of decarboxylation/decarbonylation (elimination of oxygen from feed of renewable origin by formation of carbon monoxide and dioxide) promoted on this type of catalyst under the conditions of pressure and temperature described. These molecules are in fact well known by a person skilled in the art for their effect, respectively of deactivation and inhibition, on the
30 hydrotreatment catalysts (US 2003/0221994). Moreover, application as described in these documents (EP 1,693,432 A1 and FR2904324) would lead the refiner to work with large quantities of catalyst and at higher temperatures to achieve the current specifications. This would lead to overconsumption of utilities for maintaining the high temperatures and accelerated ageing of the catalyst. Taking into account the cost of the operations of loading
35 and unloading, the price of the raw materials of the catalysts and their recycling, it seems

important for the refiners to maximize the cycle time of the unit and consequently the working life of the hydrotreatment catalyst for obtaining fuels that meet the specifications.

In addition, patent application WO08/084145 proposes using the co-processing of a mixture formed from oils of vegetable or animal origin and petroleum bases received from distillation or a conversion unit in order to produce gas oil fuel bases directly to the specifications, in particular in terms of sulphur content, density and properties of low-temperature stability, in a method of hydrotreatment comprising two units in series with intermediate stripping. The first unit is more particularly dedicated to the reactions of hydrodeoxygenation on the oils of vegetable or animal origin mixed together, while pretreating the hydrocarbon feed, whereas the second unit functions at higher severity to promote hydrodesulphurization. The intermediate stripping makes it possible to remove carbon monoxide, carbon dioxide and water, resulting from the hydrotreatment of the triglycerides constituting the oil of vegetable or animal origin on the first catalyst bed, before the final desulphurization stage. However, installation of intermediate stripping is expensive, as it requires additional capital expenditure and more complex management of the gases. Moreover, the main drawback of this application is still the control of corrosion, linked to the presence of carbon monoxide and dioxide. The investment in terms of special materials necessary for the application of co-processing with production of CO and CO₂ by decarboxylation and decarbonylation of the triglycerides is very high.

There is a great industrial need for using co-processing of petroleum feed and feed obtained from renewable sources while limiting the capital expenditure, the operating costs linked to deactivation of the catalysts and deterioration of the units by corrosion. In order to overcome these drawbacks, the applicant therefore endeavoured to find a method to enable reduction of the presence of carbon monoxide and dioxide during the operations of co-processing of a feed from obtained renewable sources and a feed of petroleum origin while providing production of a gas oil and/or kerosene fraction of excellent quality.

The method according to the invention consists of mixing a feed obtained from a renewable source and a petroleum fraction typically processed in the refinery. As the conditions required for carrying out the conversion of the triglyceride and/or fatty acid structures contained in the feeds obtained from renewable sources are generally milder than those required for deep desulphurization of the fractions of petroleum origin, and preferably the gas oil cuts, the total feed is sent to a first hydrotreatment reaction zone, where the reactions of hydrogenation of the unsaturations of the fatty acid chains of the triglycerides constituting the feed obtained from a

renewable source as well as the reactions of deoxygenation and preferably the reactions of hydrodeoxygenation (HDO) are mostly carried out.

The liquid and gaseous effluent leaving this first reaction zone is then fed into a second catalytic zone intended for hydrotreatment of said effluent, i.e. for hydrodesulphurization, for hydrodenitrogenation and for hydrogenation of the aromatic compounds, so that the effluent meets the required environmental specifications, namely below 10 ppm by weight of sulphur. Preferably, the second catalytic zone is intended essentially for hydrodesulphurization of any sulphur-containing compounds present. Now, the presence of carbon monoxide (CO) and of carbon dioxide (CO₂) produced during the reactions of deoxygenation in the first catalytic zone is a poison of the hydrotreatment catalysts conventionally used in deep hydrodesulphurization. We discovered that by using a particular catalyst in the first catalytic zone, the refining process according to the hydrodeoxygenation route (HDO) was greatly promoted, leading to a considerable decrease in the production of CO and CO₂, and therefore avoiding the occurrence of marked inhibition of the hydrotreatment reactions in the second catalytic zone.

The application of this sequence using, in a first hydrotreatment stage, a particular hydrogenation and hydrodeoxygenation catalyst favouring the HDO route followed by a second hydrotreatment stage using a conventional hydrodesulphurization catalyst, makes it possible, owing to the absence of CO and CO₂ formed in the first stage, and relative to application based on a conventional hydrotreatment catalyst:

- to avoid the loss of activity in HDS in the second stage.
- to avoid the phenomena of corrosion, so that existing refining units can be used more easily. In fact, the presence of CO and of CO₂ would mean using more expensive corrosion-resistant materials, and possibly modifying the existing units in the refinery quite appreciably, with a consequent increase in the total investment required.
- to improve the yield of fuel base, since the excellent selectivity for the hydrodeoxygenation route (HDO) makes it possible to form paraffins with the same number of carbon atoms as the fatty acid chains present in the feeds from renewable sources.
- to reduce the size of the section for purification of the recycle gas. In fact, in the presence of CO and CO₂ formed in the first reaction zone, it would be necessary on the one hand to increase the size of the section for washing with amines for purification of the recycle gas, so as to remove the H₂S but also the CO₂ and on the other hand to provide a methanation or Water Gas Shift section for removing the CO that cannot be treated by washing with amines.

Summary of the invention

More precisely, the invention relates to a method of hydrotreatment in co-processing of petroleum feeds, in a mixture with at least one feed obtained from renewable sources, for producing fuel bases (kerosene and/or gas oil) having a sulphur content below 10 ppm, said method comprising the following stages:

- a) a first hydrotreatment stage in which said feed passes through at least one first fixed-bed catalytic zone comprising at least one bulk or supported catalyst comprising an active phase constituted by at least one group VIB element and at least one group VIII element, said elements being in the form of sulphide and the atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals), being strictly greater than 0 and less than 0.095,
- b) a second hydrotreatment stage into which the effluent from the first hydrotreatment stage is sent directly, and in which said effluent passes through at least one second fixed-bed catalytic zone comprising at least one hydrotreatment catalyst.

The effluent from the first hydrotreatment stage is preferably sent without an intermediate separation stage and very preferably, without an intermediate stripping stage.

Description of the invention

According to the invention, said method of hydrotreatment processes a mixture of petroleum feeds, with at least one feed obtained from renewable sources, for producing fuel bases.

The petroleum feeds treated in the method of hydrotreatment according to the invention are advantageously feeds of the middle distillate type. Within the meaning of the present description, the term middle distillate denotes hydrocarbon fractions with a boiling point in the range from about 130°C to about 410°C, generally from about 140°C to about 375°C and for example from about 150°C to about 370°C and containing at least 0.01 wt.% of sulphur. A middle distillate feed can also comprise a gas oil or diesel cut, or can be designated with one of these names. The gas oils from direct distillation or obtained from catalytic cracking (LCO) or from another method of conversion (coking, visbreaking, hydroconversion of residue etc.) constitute a part of the typical feeds of the method according to the invention.

Preferably, the petroleum feeds are selected from the group comprising atmospheric gas oils from direct distillation, gas oils obtained from conversion processes, for example those obtained from coking, from fixed-bed hydroconversion (such as those from HYVAHL® processes for treatment of heavy fractions developed by the applicant) or processes for fluidized-bed hydrotreatment of heavy fractions (such as those from H-OIL® processes), or oils deasphalted with a solvent (for example with propane, with butane, or with pentane)

obtained from deasphalting of vacuum residue from direct distillation, or of residues obtained from processes for conversion of heavy feeds, for example HYVAHL® and H-OIL®. The feeds can also advantageously be formed by mixing these various fractions. They can also advantageously contain light gas oil or kerosene cuts with a distillation profile from about 100°C to about 370°C. They can also advantageously contain aromatic extracts and paraffins obtained within the manufacture of lubricating oils.

The feeds obtained from renewable sources used in the present invention are advantageously selected from oils and fats of vegetable or animal origin, or from mixtures of said feeds, containing triglycerides and/or free fatty acids and/or esters. The vegetable oils can advantageously be raw or refined, wholly or partly, and derived from the following plants: rape, sunflower, soya, palm, cabbage palm, olive, coconut, jatropha, this list not being limitative. Oils from algae or from fish are also suitable. The oils can also be obtained from genetically modified organisms. The animal fats are advantageously selected from lard or fats composed of residues from the food industry or obtained from the catering industry.

These feeds essentially contain chemical structures of the triglyceride type that a person skilled in the art also knows by the names fatty acid triesters as well as free fatty acids. A fatty acid triester is thus composed of three esterified fatty acid chains with a glycerol root. These fatty acid chains in the form of triester or in the form of free fatty acids have a number of unsaturations per chain, also called number of carbon-carbon double bonds per chain, generally comprised between 0 and 3 but which can be higher in particular for the oils obtained from algae, which generally have a number of unsaturations per chain from 5 to 6.

The molecules present in the feeds obtained from renewable sources used in the present invention therefore have a number of unsaturations, expressed per molecule of triglyceride, advantageously comprised between 0 and 18. In these feeds, the degree of unsaturation, expressed in number of unsaturations per hydrocarbon fatty chain, is advantageously comprised between 0 and 6. The feeds obtained from renewable sources have an iodine number from 0 to 600 generally 5 to 200 and an oxygen content from 5 to 20% and preferably 8% and 13%. The feeds obtained from renewable sources can have nitrogen contents comprised between 1 ppm and 500 ppm by weight.

The mixture of conventional petroleum feed and feed from a renewable source can advantageously be constituted by from 1 to 99 wt.% of petroleum bases and from 99 to 1 wt.% of oils of vegetable or animal origin and preferably 60 to 99 wt.% of conventional petroleum feed and from 1 to 40 wt.% of oils of vegetable or animal origin and very preferably, from 70 to

99 wt.% of conventional petroleum feed and from 1 to 30 wt.% of oils of vegetable or animal origin.

The gas oil bases produced according to the invention are of excellent quality:

- they have a low sulphur content i.e. below 10 ppm by weight, and the content of diaromatics+ is below 2 wt.%
- they have an excellent cetane number above 51, preferably above 55.
- they have good properties of low-temperature stability.
- the density obtained is low, generally comprised between 825 and 845 kg/m³.

Detailed description of the invention

According to the invention, the method of hydrotreatment uses a mixture of petroleum feeds with at least one feed obtained from renewable sources in a first hydrotreatment stage in which said feed passes through at least one first fixed-bed catalytic zone comprising at least one particular catalyst carrying out the reactions of hydrogenation of the unsaturations of the fatty acid chains of the triglycerides constituting the feed obtained from a renewable source as well as the reactions of deoxygenation and preferably the reactions of hydrodeoxygenation (HDO) followed by a second hydrotreatment stage into which the effluent from the first hydrotreatment stage is sent directly, and preferably without an intermediate separation stage and very preferably, without an intermediate stripping stage, and in which said effluent passes through at least one second fixed-bed catalytic zone comprising at least one hydrotreatment catalyst, preferably carrying out hydrosulphurization.

During hydrotreatment (HDT), the total feed constituted by the mixture of petroleum feeds and at least one feed from a renewable source is subjected to the following reactions:

- the reaction of hydrogenation of the unsaturations of the unsaturated chains of the fatty acids of the triglycerides and esters constituting the feed obtained from renewable sources.

- the reactions of deoxygenation, which can be separated into:

- the reaction of decarbonylation, which represents all of the reactions for removing an oxygen and a carbon from a carboxyl group, forming carbon monoxide (CO).

- the reaction of decarboxylation, which represents all of the reactions for removing a carboxyl group from a carboxylic acid group, forming carbon dioxide (CO₂)

- the reaction of hydrodeoxygenation (HDO) which corresponds to the reactions leading to the formation of water in the presence of hydrogen.

- the reaction of hydrodesulphurization (HDS), which denotes the reactions for removing sulphur from the petroleum feed with production of H_2S .

- the reaction of hydrodenitrogenation (HDN), which denotes the reactions for removing nitrogen from the petroleum feed with production of NH_3 .

5 - the reaction of hydrogenation of aromatic compounds, which denotes the conversion of aromatic compounds in the petroleum feed to naphthenic and naphthenoaromatic compounds.

Each stage can comprise one or more reactors, and one or more catalytic zones (or
10 beds). It is thus possible to adapt the processing conditions in each of the units and/or zones so as to separate the reactions taking place in the different units and/or zones. Thus, the hydrotreatment of the mixture of feeds obtained from renewable sources and of hydrocarbons can be carried out at lower temperature and lower pressure than the reactions of hydrotreatment, hydrodesulphurization, hydrodenitrogenation and the reactions of
15 hydrogenation of the aromatic compounds.

Stage 1) - hydrotreatment of the total feed

The feed from a renewable source and the petroleum feed, preferably hot, are advantageously mixed.

20 Preferably, the temperature conditions of the stream at inlet to the first catalytic zone of the first hydrotreatment stage a) of the method according to the invention are adjusted by adding the previously heated petroleum feed. The temperature of the stream entering the first catalytic zone of the first hydrotreatment stage a), said stream being constituted by the mixture of the feed obtained from a renewable source and of the petroleum feed is advantageously
25 comprised between 150 and 260°C and preferably between 180 and 220°C and very preferably between 180 and 210°C. These temperature conditions of said ingoing stream can initiate the reaction of hydrogenation of the unsaturations of the triglycerides contained in the feed obtained from a renewable source, while controlling the exothermic effect of these reactions. Thus, the temperature change between said ingoing stream and the effluent leaving
30 the first catalytic zone is advantageously limited so that the temperature of the effluent leaving the first catalytic zone is advantageously comprised between 280 and 370°C, preferably between 280 and 330°C and more preferably above 300°C.

This principle thus makes it possible to operate at reduced temperature at the top of the first
35 catalytic zone of the first hydrotreatment stage a) and therefore achieve an overall lowering of

the mean temperature level of the reaction zone, which promotes the reactions of hydrodeoxygenation and therefore the yield of gas oil base.

In the case when the first hydrotreatment stage a) uses more than one catalytic zone and preferably at least two catalytic zones, the temperatures of the streams entering and leaving the catalytic zones following the first, are within the ranges defined for the first catalytic zone, preferably by using:

- either a stream constituted by feed from a renewable source or of total feed constituted by a mixture of petroleum feeds and at least one feed from a renewable source,
- or a stream of the hydrotreated effluent from hydrotreatment stage a) or b), at a recycle ratio comprised between 1:10 and 8:1,

the temperature of the stream being comprised between 20 and 100°C. This makes it possible to manage the exothermic effect in the various catalytic zones and therefore the temperature rise.

The feed containing at least the petroleum feed can be preheated by any means known by a person skilled in the art before it is fed into the first hydrotreatment stage. Without limiting the scope of the invention, the use of heat exchangers and/or a preheating furnace may be mentioned.

Mixing of the feed obtained from a renewable source and the petroleum feed can take place at various points in the refining process.

A first possibility consists of injecting the feed obtained from a renewable source after preheating of the petroleum feed by passage in the presence of hydrogen through a feed-effluent exchanger and then through a preheating furnace.

A second method consists of mixing the petroleum feed and the feed obtained from a renewable source in the presence of hydrogen after preheating of the petroleum feed by passage through a feed-effluent exchanger, the effluent being from the first zone. In this case, the mixing of the petroleum feeds and of the feed obtained from a renewable source can optionally be completed by passage through a preheating furnace.

Finally, mixing of the feed obtained from a renewable source and the petroleum feed can take place in the presence of hydrogen before heating, in which case the temperature of the mixture increases firstly by passage through a feed-effluent exchanger and then optionally through a preheating furnace.

The feeds can also be mixed prior to the introduction of hydrogen or subsequently. Preferably, the mixing of the feed obtained from a renewable source with the petroleum feed takes place in the presence of hydrogen, either before the feed-effluent exchanger, before the

preheating furnace or before entering the reactor. Very preferably, mixing of the feed obtained from a renewable source with the petroleum feed takes place in the presence of hydrogen after raising the temperature of the petroleum feed by at least one heating stage.

5 In the case when the second hydrotreatment stage b) uses more than one catalytic zone and preferably at least two catalytic zones, petroleum feed can advantageously be injected in each catalytic zone of said second hydrotreatment stage b).

10 The mixture of conventional petroleum feed and feed from a renewable source can advantageously be constituted by 1 to 99 wt.% of petroleum bases and 99 to 1 wt.% of feed from a renewable source and preferably 60 to 99 wt.% of conventional petroleum feed and 1 to 40 wt.% of feed from a renewable source and very preferably, 70 to 99 wt.% of conventional petroleum feed and 1 to 30 wt.% of feed from a renewable source.

15 According to a first preferred embodiment, in the case when the mixture of conventional petroleum feed and feed from a renewable source is constituted by 60 to 99 wt.% of conventional petroleum feed and 1 to 40 wt.% of feed from a renewable source and very preferably, 70 to 99 wt.% of conventional petroleum feed and 1 to 30 wt.% of feed from a renewable source, no recycling of the hydrotreated liquid effluent resulting from the method
20 according to the invention is used for management of the exothermic effect of the hydrodeoxygenation reactions.

In fact, owing to the heat released by the exothermic effects of the reactions of hydrogenation of the unsaturations and deoxygenation and of the proportion of the feed obtained from a renewable source in the total feed, the effluent from the first hydrotreatment stage a) which
25 constitutes the feed of the second hydrotreatment stage b), advantageously reaches the temperature required for entering the second hydrotreatment stage b), i.e. a temperature comprised between 280 and 370°C, preferably between 280 and 330°C and more preferably above 300°C so as to permit, in particular, the reactions of hydrodesulphurization, without any recycling of the hydrotreated liquid effluent being necessary. Moreover, this makes it possible
30 to avoid exceeding the temperatures that lead to risks of formation of coke in the first deoxygenation stage, i.e. temperatures above 350°C.

According to a second preferred embodiment, in the case when the mixture of conventional petroleum feed and feed from a renewable source is constituted by 40 to 99 wt.% of feed from
35 a renewable source and 1 to 60 wt.% of petroleum bases, recycling of the hydrotreated liquid effluent resulting from the method according to the invention is implemented for management

of the exothermic effect of the reactions of hydrogenation of the unsaturations and of deoxygenation of the feed obtained from a renewable source at a recycle ratio advantageously comprised between 1:10 and 8:1. This application also aims to maintain the level of hydrogen dissolved in the liquid phase, in order to promote the reactions of hydrodeoxygenation, to limit the formation of coke on the catalyst and the phenomena of polymerization of the oxygen-containing compounds. The amount of recycle used is such that the heat released during the reactions of hydrogenation and of deoxygenation means that at the outlet of the first hydrotreatment stage a) said stage of hydrodeoxygenation does not exceed the temperature required for entering the second hydrotreatment stage b), i.e. a temperature comprised between 280 and 370°C, preferably between 280 and 330°C and more preferably above 300°C so as to permit, in particular, the reactions of hydrodesulphurization.

In this second preferred embodiment and in the case when the first hydrotreatment stage uses more than one catalytic zone and preferably at least two catalytic zones, an injection of a stream at a temperature comprised between 20 and 100°C, constituted by feed from a renewable source or of total feed constituted by a mixture of petroleum feeds and of at least one feed from a renewable source, can also advantageously be applied in each catalytic zone following the first catalytic zone of the first hydrotreatment stage a), so as to manage the exothermic effect in the different catalytic zones and therefore the temperature rise.

Thus, the temperature of the stream entering each catalytic zone following the first catalytic zone in the first hydrotreatment stage a), is advantageously always comprised between 150 and 260°C and preferably between 180 and 220°C and very preferably between 180 and 210°C.

Advantageously, prior to the first hydrotreatment stage a), the total feed can be pretreated or pre-refined so as to remove, by an appropriate treatment, contaminants that are present naturally in the feeds from renewable sources such as alkali metals, alkaline-earth metals, and transition metals, as well as nitrogen. Appropriate treatments can be for example thermal and/or chemical treatments well known by a person skilled in the art and preferably the application of a guard bed advantageously located in the same reactor or in a reactor different from that used for the hydrotreatment stage of the method according to the invention. The catalysts for the guard bed are known by a person skilled in the art.

According to the invention, the total feed, optionally pretreated beforehand, is subjected to the first hydrotreatment stage a) in which said feed passes through at least one first fixed-bed

catalytic zone comprising at least one bulk or supported catalyst comprising an active phase constituted by at least one group VIB element and at least one group VIII element, said elements being in the form of sulphide and the atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals), being strictly greater than 0 and less than 0.095.

5 The "active phase" is the phase containing the element or elements in the form of sulphide of the groups of metals, in the present case the active phase of the catalyst used in the first hydrotreatment stage a) is constituted by at least one sulphide of a group VIB element and at least one sulphide of a group VIII element.

10 According to the present invention, the catalyst used in the method according to the invention can be supported, i.e. it has an amorphous mineral support selected from the group comprising alumina, silica, aluminosilicates, magnesia, clays and mixtures of at least two of these minerals. Said support can also advantageously contain other compounds, for example
15 oxides selected from the group comprising boron oxide, zirconia, titanium dioxide, phosphoric anhydride.

Preferably, the amorphous mineral support is an alumina support (η , δ or γ).

According to the present invention, said catalyst used in the method according to the invention can alternatively be a bulk catalyst, i.e. unsupported.

20 According to the method of the invention, the active phase of said catalyst in supported or bulk form is constituted by at least one group VIB element and at least one group VIII element, said group VIB element being selected from molybdenum and tungsten and preferably, said group VIB element is molybdenum and said group VIII element is selected from nickel and cobalt and
25 preferably said group VIII element is nickel.

According to the method of the invention, the atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals), is strictly greater than 0 and less than 0.095, preferably comprised between 0.01 and 0.08, preferably between 0.01 and 0.05 and very preferably between 0.01 and 0.03.

30 Preferably, the group VIB metal is molybdenum and the group VIII metal is nickel and the atomic ratio of the group VIII metal to the group VIB metal, i.e. the atomic ratio Ni/Mo, is strictly greater than 0 and less than 0.095, preferably comprised between 0.01 and 0.08, preferably between 0.01 and 0.05 and very preferably between 0.01 and 0.03.

35 In the case when said catalyst is in supported form, the oxide content of group VIB element is advantageously comprised between 1 and 30 wt.% relative to the total weight of the catalyst,

preferably comprised between 10 and 25 wt.%, very preferably between 15 and 25 wt.% and even more preferably between 17 and 23 wt.% and the oxide content of group VIII element is advantageously strictly greater than 0% and less than 1.5 wt.% relative to the total weight of the catalyst, preferably comprised between 0.05 and 1.1 wt.%, very preferably between 0.07 and 0.65 wt.% and even more preferably between 0.08 and 0.36 wt.%.

The minimum value of the atomic ratio Ni/Mo equal to 0.01, for a content of molybdenum oxide of 1 wt.%, within the scope of the invention, corresponds to a nickel content of 50 ppm by weight, detectable by the usual techniques of elemental analysis by ICP (inductively coupled plasma), said limits of detection of nickel being of the order of 1 ppm.

In the case when said catalyst is in bulk form, the oxide contents of elements of groups VIB and VIII are defined by the atomic ratios of the group VIII metal (or metals) to group VIB metal (or metals) defined according to the invention.

For an atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) strictly greater than 0 and less than 0.095, the content of group VIB element is advantageously greater than 95.3% and strictly below 100 wt.% in oxide equivalent of the group VIB element and the content of group VIII element is advantageously strictly greater than 0 and less than 4.7 wt.% in oxide equivalent of the group VIII element.

For an atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) comprised between 0.01 and 0.08, the content of group VIB element is advantageously comprised between 96 and 99.4 wt.% in oxide equivalent of the group VIB element and the content of group VIII element is advantageously comprised between 0.6 and 4 wt.% in oxide equivalent of the group VIII element.

For an atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) comprised between 0.01 and 0.05, the content of group VIB element is advantageously comprised between 97.4 and 99.4 wt.% in oxide equivalent of the group VIB element and the content of group VIII element is advantageously comprised between 0.6 and 2.6 wt.% in oxide equivalent of the group VIII element.

For an atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) comprised between 0.01 and 0.03, the content of group VIB element is advantageously comprised between 98.4 and 99.4 wt.% in oxide equivalent of the group VIB element and the content of group VIII element is advantageously comprised between 0.6 and 1.6 wt.% in oxide equivalent of the group VIII element.

The catalyst used in the method according to the invention can also advantageously contain at least one doping element in order to reach a high level of conversion while maintaining a

selectivity of reaction for the hydrodeoxygenation (HDO) route. The active phase in the case when said catalyst is in the bulk form and/or the support in the case when said catalyst is in the supported form can therefore also advantageously contain at least one doping element selected from phosphorus, fluorine and boron and preferably, the doping element is phosphorus. It is known by a person skilled in the art that these elements have indirect effects on catalytic activity: a better dispersion of the sulphide active phase and an increase in acidity of the catalyst which is favourable to the hydrotreatment reactions (Sun et al., Catalysis Today 86(2003) 173).

Said doping element can be introduced into the matrix or can be deposited on the support. Advantageously, silicon can also be deposited on the support, alone or with phosphorus and/or boron and/or fluorine.

The content of doping element, preferably of phosphorus, is advantageously strictly greater than 1% and less than 8 wt.% of oxide P_2O_5 relative to the total weight of the catalyst and preferably greater than 1.5% and less than 8% and very preferably greater than 3% and less than 8 wt.%.

Use of the catalyst described above in the method according to the invention makes it possible to limit the formation of carbon monoxide for the reasons mentioned previously by limiting the reactions of decarboxylation / decarbonylation.

Within the scope of the present invention, it is thus possible to obtain selectivity in hydrodeoxygenation (HDO) in the first hydrotreatment stage a), advantageously greater than or equal to 90% and preferably greater than or equal to 95% and preferably greater than or equal to 96%.

The selectivity in decarboxylation/decarbonylation of the feed obtained from renewable sources is advantageously limited to at most 10%, and preferably limited to at most 5% and more preferably to at most 4% in the first hydrotreatment stage a).

The selectivity in hydrodeoxygenation (HDO) is calculated as follows:

Using R_{DCO} to denote the theoretical yield of $CO+CO_2$ for a feed obtained from a given renewable source, which is transformed exclusively according to the decarboxylation (DCO) route, expressed as percentage by weight relative to the feed, and R to denote the yield of $CO + CO_2$ obtained experimentally during the hydrotreatment of a feed obtained from a pure renewable source, then S_{HDO} is defined as the selectivity in HDO by the following simple equation.

$$S_{\text{hydro}} = 100 * (R_{\text{DCO}} - R) / R_{\text{DCO}}$$

It has thus been demonstrated that it is possible to control the selectivity of the reactions of hydrodeoxygenation of feeds obtained from renewable sources and to minimize the reactions of decarboxylation/decarbonylation in relation to the nature of the active phase and more particularly in relation to the atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) of said active phase.

Surprisingly, the use of a catalyst having an atomic ratio of the group VIII metal (or metals) to group VIB metal (or metals) of said active phase and in particular the use of an Ni/Mo atomic ratio strictly greater than 0 and less than 0.095 makes it possible to control and increase the selectivity for the reactions of hydrodeoxygenation and thus limit the reactions of decarboxylation / decarbonylation and therefore limit the drawbacks resulting from the formation of oxides of carbon.

Moreover, increasing the content of group VIII element and in particular nickel tends to promote the reaction of decarboxylation / decarbonylation, even if the reaction of hydrodeoxygenation is still the main reaction. Thus, it was demonstrated that the selectivity in hydrodeoxygenation is optimum in particular for values of the atomic ratio Ni/Mo comprised between 0.01 and 0.03.

In the case when a supported catalyst is used in the method according to the invention, the hydrogenating function can be introduced on said catalyst by any method known by a person skilled in the art, for example co-mixing or dry impregnation, and the sulphurization is then carried out in-situ or ex-situ according to a method known by a person skilled in the art.

In the case when a bulk catalyst is used in the method according to the invention, said catalyst is prepared according to methods known by a person skilled in the art, for example the decomposition of metal thiosalts.

In the case when the first hydrotreatment stage a) comprises at least two catalytic zones, said catalytic zones can use catalysts that may be identical or different, and preferably said catalysts are identical.

Use of such a catalyst in the first hydrotreatment stage a) therefore makes it possible to obtain a high selectivity for the reactions of hydrodeoxygenation (HDO) and makes it possible to limit the reactions of decarboxylation / decarbonylation (DCO) and thus limit the drawbacks resulting from the formation of oxides of carbon.

Moreover, the co-processing of the feed obtained from a renewable source with a petroleum feed makes possible better control of the exothermic effects during the reactions of hydrogenation of the unsaturations of the fatty acid hydrocarbon chains of the triglycerides and of HDO. This makes it possible to limit the use of recycling. Moreover, the thermal gradient is advantageously used for bringing the effluent from the first hydrotreatment stage, which constitutes the feed of the second hydrotreatment stage, to the temperature required for entering the second hydrotreatment stage and to permit in particular the initiation of the reactions of hydrodesulphurization. The temperature of the effluent from the first hydrotreatment stage a) constituting the feed of the second hydrotreatment stage b) is therefore advantageously comprised between 280 and 340°C and preferably between 280 and 320°C and preferably a temperature above 300°C so as to permit, in particular, the reactions of hydrodesulphurization.

The first hydrotreatment stage a) operates advantageously at a temperature comprised between 120 and 450°C, preferably between 120 and 350°C, preferably between 150 and 320°C, and even more preferably between 180 and 310°C at a pressure comprised between 1 MPa and 10 MPa, preferably between 1 MPa and 6 MPa, at an hourly space velocity comprised between 0.1 h⁻¹ and 10 h⁻¹ and preferably between 0.2 and 5 h⁻¹, and at a hydrogen/feed ratio comprised between 50 and 3000 Nm³ of hydrogen/m³ of feed, preferably between 70 and 2000 Nm³ of hydrogen/m³ of feed and preferably between 150 and 1500 Nm³ of hydrogen/m³ of feed.

The method according to the invention offers the option, in order to limit the inhibition of the catalytic system in the first stage of hydrodeoxygenation by the production of water and dilution of the hydrogen by the water and the propane formed, of operating the first reactor in counterflow for the introduction of hydrogen. In fact, as it is a fixed-bed process, there is a concentration gradient of the gases produced towards the bottom of the reactor. The introduction of hydrogen in counterflow permits better activity of the catalyst by increasing the H₂/HC ratio.

The first hydrotreatment stage a) is therefore advantageously predominantly the place of hydrogenation of the unsaturations of the fatty acid chains of the triglycerides and of hydrodeoxygenation of feed from a renewable source.

The second hydrotreatment stage b) is predominantly the place of the reactions of hydrodesulphurization, hydrodenitrogenation and hydrogenation of the aromatic compounds and predominantly of the reactions of hydrodesulphurization of the petroleum feed.

The second hydrotreatment stage b), called the hydrodesulphurization stage, operates under harsher conditions than the first hydrotreatment stage a), called the hydrodeoxygenation zone.

5 Stage 2) Hydrotreatment of the effluent from the first hydrotreatment stage

The hydrodeoxygenated effluent obtained from hydrotreatment stage a) is then sent directly, preferably without an intermediate separation stage and preferably without an intermediate stripping stage, into the second hydrotreatment stage.

10 Owing to the temperature gradient in the hydrotreatment stage a), the effluent from the first hydrotreatment stage a) constituting the feed of the second hydrotreatment stage b) leaves said first stage at a temperature advantageously comprised between 280 and 370°C, preferably between 280 and 330°C and more preferably above 300°C and is then injected
15 directly into at least one and preferably at least two catalytic zones comprising at least one hydrotreatment catalyst.

The thermal gradient is therefore used advantageously for heating the effluent from the first hydrotreatment stage a) to the temperature required for entering the second hydrotreatment stage b) and to permit in particular the initiation of the reactions of hydrodesulphurization.

20 The hydrotreatment catalyst used in the second hydrotreatment stage b) of the method according to the invention advantageously comprises a hydro-dehydrogenating function and a support. Preferably, the support is selected from the group comprising alumina, silica, aluminosilicates, magnesia, clays and mixtures of at least two of these minerals. This support can also advantageously contain other compounds and for example oxides selected from the
25 group comprising boron oxide, zirconia, titanium dioxide, phosphoric anhydride. Preferably, the support is constituted by alumina and very preferably η , δ or γ alumina.

Said hydrogenating function of the catalyst used in the second hydrotreatment stage b) of the method according to the invention advantageously comprises at least one group VIII metal and/or at least one group VIB metal.

30 Preferably, said catalyst advantageously comprises at least one group VIII metal selected from nickel and cobalt and at least one group VIB metal selected from molybdenum and tungsten.

Preferably, the group VIII element is nickel and the group VIB element is molybdenum and said catalyst comprises a content of nickel oxide comprised between 0.5 and 10 wt.% and
35 preferably between 1 and 5 wt.% and a content of molybdenum trioxide comprised between 1

and 30 wt.% and preferably between 5 and 25 wt.%, on an alumina amorphous mineral support, the percentages being expressed in wt.% relative to the total weight of the catalyst. Preferably, the hydrotreatment catalyst used in the second hydrotreatment stage b) has an Ni/Mo atomic ratio greater than 0.1.

- 5 Said catalyst used in the second hydrotreatment stage b) of the method according to the invention can also advantageously contain at least one element selected from phosphorus and boron. This element can advantageously be introduced into the matrix or preferably be deposited on the support. Advantageously, silicon can also be deposited on the support, alone or with phosphorus and/or boron and/or fluorine.
- 10 The content by weight of oxide of said element is usually advantageously below 20% and preferably below 10% and it is usually advantageously at least 0.001%.

The metals of the catalysts used in the second hydrotreatment stage b) of the method according to the invention are advantageously metal sulphides or metallic phases.

15

In the case when the second hydrotreatment stage b) comprises at least two catalytic zones, said catalytic zones can use catalysts that may be identical or different.

- 20 Hydrotreatment stage b) operates advantageously at a temperature comprised between 250 and 450°C and preferably between 300 and 400°C, at a total pressure from 0.5 to 30 MPa (preferably between 1 and 25 MPa), an hourly space velocity of 0.1 to 20 h⁻¹ (preferably between 0.2 and 4 h⁻¹), a hydrogen/feed ratio expressed in volume of hydrogen, measured under normal conditions of temperature and pressure, per volume of liquid feed generally from 50 NI/I to 2000 NI/I.

25

With the aim of producing a gas oil fuel with improved properties, the hydrocarbon effluent is then processed according to the following optional stages:

- The hydrotreated effluent resulting from the method according to the invention is then subjected to at least one stage of separation and preferably a stage of gas/liquid separation
- 30 optionally followed by separation of water and of at least one liquid hydrocarbon base, said stages being optional and can be applied in any order relative to one another.

- Preferably, the hydrotreated effluent resulting from the method according to the invention is first subjected to a stage of gas/liquid separation. The aim of this stage is to separate the gases
- 35 from the liquid, and in particular to recover the hydrogen-rich gases, which can also contain gases such as H₂S, traces of CO and of CO₂, and propane and at least one liquid effluent, and

said gases can advantageously also be purified by methods known by a person skilled in the art.

Preferably, the liquid effluent resulting from the preceding optional gas/liquid separation is then subjected to separation of at least some and preferably all of the water formed, of at least one liquid hydrocarbon base, the water being produced during the reactions of hydrodeoxygenation that take place during the first hydrotreatment stage a) of the method according to the invention.

The aim of this stage is to separate the water from the liquid hydrocarbon effluent. Removal of water means removal of the water produced by the reactions of hydrodeoxygenation (HDO). The more or less complete removal of the water is advantageously a function of the water tolerance of the hydroisomerization catalyst used in the next optional stage of the method according to the invention. The water can be removed by any methods and techniques known by a person skilled in the art, such as for example by drying, passing over a drying agent, flash, solvent extraction, distillation and decanting or by a combination of at least two of these methods.

At least a portion of the hydrotreated liquid effluent, having optionally undergone a stage of removal of water, can advantageously be recycled to the top of each catalytic zone of the hydrotreatment stage a) following the first catalytic zone and/or to the top of each catalytic zone of the second hydrotreatment stage b) in the case when the mixture of conventional petroleum feed and feed from a renewable source is constituted by 40 to 99 wt.% of feed from a renewable source and 1 to 40 wt.% of petroleum bases.

At least a portion of the hydrogen-rich gaseous effluent from the optional stage of separation and that has preferably undergone a purification treatment for the purpose of lowering the concentration of impurities resulting from the reactions present in the gaseous effluent at the time of the separation stage, can advantageously be injected, either mixed with at least a portion of the hydrotreated liquid effluent from the stage of separation in the case when recycling of the hydrotreated liquid effluent is envisaged, or separately, to the top of each catalytic zone of hydrotreatment stages a) and b).

The separation stage can advantageously be applied by any method known by a person skilled in the art, such as for example a combination of one or more high and/or low pressure separators, and/or of stages of high and/or low pressure distillation and/or stripping.

Stage 3): Hydroisomerization of the hydrotreated effluent

The hydrotreated liquid effluent resulting from the method according to the invention is essentially constituted by n-paraffins, which can be incorporated in the gas oil pool. To improve the low-temperature properties of this hydrotreated liquid effluent, a hydroisomerization stage is necessary for transforming the n-paraffins to branched paraffins, which have better low-temperature properties.

At least a portion of the hydrotreated liquid effluent, and preferably all of it, having optionally undergone a stage of separation as above, is then subjected to an optional hydroisomerization stage in the presence of a selective hydroisomerization catalyst.

The hydroisomerization stage is advantageously applied in a separate reactor. The hydroisomerization catalysts used are advantageously of the bifunctional type, i.e. they have a hydro/dehydrogenating function and a hydroisomerizing function.

Said hydroisomerization catalyst advantageously comprises at least one group VIII metal and/or at least one group VIB metal as hydrodehydrogenating function and at least one molecular sieve or an amorphous mineral support as hydroisomerizing function.

Said hydroisomerization catalyst advantageously comprises either at least one group VIII precious metal preferably selected from platinum or palladium, active in their reduced form, or at least one group VIB metal, preferably selected from molybdenum or tungsten, in combination with at least one group VIII base metal, preferably selected from nickel and cobalt, preferably used in their sulphide form.

Preferably, said hydroisomerization catalyst comprises at least one group VIB metal, preferably selected from molybdenum or tungsten, in combination with at least one group VIII base metal, preferably selected from nickel and cobalt, preferably used in their sulphide form. Very preferably, the group VIB element is molybdenum and the group VIII base metal is nickel.

In the case when the hydroisomerization catalyst comprises at least one group VIII precious metal, the total content of precious metal in the hydroisomerization catalyst is advantageously comprised between 0.01 and 5 wt.% relative to the finished catalyst, preferably between 0.1 and 4 wt.% and very preferably between 0.2 and 2 wt.%.

Preferably, the hydroisomerization catalyst comprises platinum or palladium and more preferably the hydroisomerization catalyst comprises platinum.

In the case when the hydroisomerization catalyst comprises at least one group VIB metal in combination with at least one group VIII base metal, the content of group VIB metal of the

hydroisomerization catalyst is advantageously, in oxide equivalent, comprised between 5 and 40 wt.% relative to the finished catalyst, preferably between 10 and 35 wt.% and very preferably between 15 and 30 wt.% and the content of group VIII metal of said catalyst is advantageously, in oxide equivalent, comprised between 0.5 and 10 wt.% relative to the finished catalyst, preferably between 1 and 8 wt.% and very preferably between 1.5 and 6 wt.%.

The metallic hydro/dehydrogenating function can advantageously be introduced on said catalyst by any method known by a person skilled in the art, for example co-mixing, dry impregnation, exchange impregnation.

According to a preferred embodiment, said hydroisomerization catalyst comprises at least one amorphous mineral support as hydroisomerizing function, said one amorphous mineral support being selected from the silica-aluminas and aluminosilicates and preferably the silica-aluminas.

A preferred hydroisomerization catalyst comprises an active phase based on nickel and tungsten and a silica-alumina amorphous mineral support.

According to another preferred embodiment, said hydroisomerization catalyst comprises at least one molecular sieve, preferably at least one zeolite molecular sieve and more preferably, at least one 10 MR one-dimensional zeolite molecular sieve as hydroisomerizing function.

The zeolite molecular sieves are defined in the classification "Atlas of Zeolite Structure Types", W.M. Meier, D.H. Olson and Ch. Baerlocher, 5th revised edition, 2001, Elsevier, to which the present application also makes reference. The zeolites are classified there according to the size of their pore or channel openings.

The 10 MR one-dimensional zeolite molecular sieves have pores or channels the opening of which is defined by a ring with 10 oxygen atoms (10 MR opening). The channels in the zeolite molecular sieve having a 10 MR opening are advantageously non-interconnected one-dimensional channels which open directly onto the outside of said zeolite. The 10 MR one-dimensional zeolite molecular sieves present in said hydroisomerization catalyst advantageously comprise silicon and at least one element T selected from the group comprising aluminium, iron, gallium, phosphorus and boron, preferably aluminium. The Si/Al ratios of the zeolites described above are advantageously those obtained during synthesis or

else obtained after post-synthesis dealuminating treatments that are well known by a person skilled in the art, such as, non-limitatively, hydrothermal treatments whether or not followed by attack with acids or alternatively direct acid attack with solutions of mineral or organic acids. Preferably, they are practically completely in the form of acid, i.e. the atomic ratio of the monovalent compensation cation (for example sodium) to the element T inserted in the crystal lattice of the solid is advantageously less than 0.1, preferably less than 0.05 and very preferably less than 0.01. Thus, the zeolites included in the composition of said selective hydroisomerization catalyst are advantageously calcined and exchanged by at least one treatment with a solution of at least one ammonium salt so as to obtain the ammonium form of the zeolites which, once calcined, lead to the acid form of said zeolites.

Said 10 MR one-dimensional zeolite molecular sieve of said hydroisomerization catalyst is advantageously selected from the zeolite molecular sieves of structural type TON, such as NU-10, FER, such as ferrierite, EUO, selected from EU-1 and ZSM-50, used alone or in a mixture, or the zeolite molecular sieves ZSM-48, ZBM-30, IZM-1, COK-7, EU-2 and EU-11, used alone or in a mixture. Preferably, said 10 MR one-dimensional zeolite molecular sieve is selected from the zeolite molecular sieves ZSM-48, ZBM-30, IZM-1 and COK-7, used alone or in a mixture. Even more preferably, said 10 MR one-dimensional zeolite molecular sieve is selected from the zeolite molecular sieves ZSM-48 and ZBM-30, used alone or in a mixture. Very preferably, said 10 MR one-dimensional zeolite molecular sieve is ZBM-30 and even more preferably, said 10 MR one-dimensional zeolite molecular sieve is ZBM-30 synthesized with the organic structurizing agent triethylenetetramine.

Preferably, the hydroisomerization catalyst comprises a metallic active phase constituted by platinum and a hydroisomerizing function based on ZBM-30, and preferably the hydroisomerization catalyst comprises a metallic active phase constituted by platinum and a hydroisomerizing function based on ZBM-30 synthesized with the organic structurizing agent triethylenetetramine.

Zeolite ZBM-30 is described in patent EP-A-46 504, and zeolite COK-7 is described in patent applications EP 1 702 888 A1 or FR 2 882 744 A1.

Zeolite IZM-1 is described in patent application FR-A-2 911 866.

The zeolites of structural type TON are described in the work "Atlas of Zeolite Structure Types", W.M. Meier, D.H. Olson and Ch. Baerlocher, 5th Revised edition, 2001, Elsevier.

The zeolite of structural type TON is described in the work "Atlas of Zeolite Structure Types", cited above and, with respect to zeolite NU-10, in patents EP-65400 and EP-77624.

- 5 The zeolite of structural type FER is described in the work "Atlas of Zeolite Structure Types", cited above.

The content of 10 MR one-dimensional zeolite molecular sieve is advantageously comprised between 5 and 95 wt.%, preferably between 10 and 90 wt.%, more preferably between 15 and 85 wt.% and very preferably between 20 and 80 wt.% relative to the finished catalyst.

10

Preferably, said hydroisomerization catalyst also comprises a binder constituted by a porous mineral matrix. Said binder can advantageously be used during the stage of forming of said hydroisomerization catalyst.

- 15 Preferably, forming is carried out with a binder constituted by a matrix containing alumina, in all its forms known by a person skilled in the art, and very preferably with a matrix containing gamma alumina.

The hydroisomerization catalysts obtained are advantageously formed as grains of various shapes and sizes. They are generally used in the form of cylindrical extrudates or multilobed
20 extrudates such as bilobed, trilobed, multilobed of straight or twisted shape, but can optionally be manufactured and used in the form of pulverized powders, tablets, rings, spheres, wheels. Techniques other than extrusion, such as tableting or particle coating, can advantageously be used.

- 25 In the case when the hydroisomerization catalyst contains at least one precious metal, the precious metal contained in said hydroisomerization catalyst must advantageously be reduced. One of the preferred methods for carrying out reduction of the metal is treatment under hydrogen at a temperature comprised between 150°C and 650°C and a total pressure comprised between 1 and 250 bar. For example, a reduction stage consists of a plateau at
30 150°C for two hours then a temperature rise to 450°C at a rate of 1°C/min then a plateau of two hours at 450°C; throughout this reduction stage, the hydrogen flow rate is 1000 normal m³ hydrogen / m³ catalyst with the total pressure maintained constant at 1 bar. Any method of reduction ex-situ can advantageously be envisaged.

- 35 In the hydroisomerization stage, the feed is advantageously contacted, in the presence of hydrogen, with said hydroisomerization catalyst, at operating temperatures and pressures

advantageously permitting hydroisomerization of the non-converting feed to be carried out. This means that the hydroisomerization is carried out with a conversion of the 150°C⁺ fraction to 150°C⁻ fraction of less than 20 wt.%, preferably less than 10 wt.% and very preferably less than 5 wt.%.

5

Thus, the optional hydroisomerization stage of the method according to the invention operates advantageously at a temperature comprised between 150 and 500°C, preferably between 150°C and 450°C, and very preferably, between 200 and 450°C, at a pressure between 1 MPa and 10 MPa, preferably between 1 MPa and 10 MPa and very preferably, between 2 MPa and 9 MPa, at an hourly space velocity advantageously comprised between 0.1 h⁻¹ and 10 h⁻¹, preferably between 0.2 and 7 h⁻¹ and very preferably, between 0.5 and 5 h⁻¹, at a hydrogen flow rate such that the hydrogen/hydrocarbons volume ratio is advantageously comprised between 70 and 1000 Nm³/m³ of feed, between 100 and 1000 normal m³ of hydrogen per m³ of feed and preferably between 150 and 1000 normal m³ of hydrogen per m³ of feed.

15

Preferably, the optional hydroisomerization stage operates in counter-current.

The hydroisomerized effluent is then advantageously subjected at least partly, and preferably wholly, to one or more separations. The aim of this stage is to separate the gases from the liquid, and in particular, to recover the hydrogen-rich gases which can also contain light fractions such as the C₁-C₄ cut and at least one gas oil cut complying with the specifications and a naphtha cut. Utilization of the naphtha cut is not the object of the present invention, but this cut can advantageously be sent to a steam cracking or catalytic reforming unit.

25 Description of the drawing

The drawing illustrates a preferred embodiment of the method according to the invention. The feed obtained from renewable sources (1) is mixed with hydrogen (2) and with the preheated feed of petroleum origin (3), the heating means not being shown in Fig. 1. The mixture is fed into the first hydrotreatment stage a) comprising two catalytic zones (10) and (11) in which the reactions of hydrogenation of the unsaturations and of deoxygenation according to the so-called hydrodeoxygenation route of the feed from a renewable source take place, thus limiting the formation of CO and of CO₂. The effluent leaving the second catalytic zone (11) of the first hydrotreatment stage a) is then injected into the second hydrotreatment stage comprising a catalytic zone (12) in which the conventional reactions of hydrotreatment and in particular of hydrodesulphurization take place. The effluent leaving the second catalytic zone (12) is then fed via pipe (5) into a zone for gas/liquid separation and separation of water

(13) in which the gaseous stream (6), and water (8) are separated from the hydrocarbon liquid effluent (7). A staged injection of feed from a renewable source is applied via pipe (14) into the second catalytic zone (11). The hydrocarbon effluent (7) is sent to a last catalytic zone for hydroisomerization (14). The effluent (9) produced is, after separation of the gases, a fuel base (kerosene and/or gas oil) having a sulphur content below 10 ppm.

Example

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

10 **Comparative example 1:** Method of hydrotreatment of a petroleum gas oil in one stage using a hydrotreatment catalyst of the NiMoP/alumina type (not according to the invention).

It is therefore not a method of hydrotreatment in co-processing of a petroleum feed mixed with a feed obtained from renewable sources – only a petroleum feed is processed.

15 The petroleum feed processed in comparative example 1 is an atmospheric gas oil from direct distillation, obtained from a Middle East crude. Its main characteristics are as follows:

- Density at 15°C 0.8522 g/cm³
- Sulphur 13000 ppm by weight
- Nitrogen 120 ppm by weight
- Total aromatics 29.5 wt. %
- 20 - Diaromatics+ 12 wt. %
- Motor cetane number 56
- TLF (*) +1°C

(*) Temperature Limit of Filterability

25 The hydrotreatment of this feed is carried out in a fixed-bed isothermal unit of the descending flow type containing 100 ml of densely packed catalyst of the NiMoP/alumina type. The catalyst contains 21.0 wt.% of MoO₃, 5.0 wt.% of P₂O₅ and 4.3 wt.% of NiO, supported on gamma alumina and has an Ni/Mo atomic ratio equal to 0.4. The catalyst was sulphided in situ in the unit under pressure, by adding 2 wt.% of dimethyl disulphide to the petroleum gas oil.

30 The effluent leaving the hydrotreatment stage is then hydroisomerized on 50 ml of catalyst of the NiW/silica-alumina type characterized by an NiO content of 3.5 wt.% and a content of WO₃ of 27 wt.% positioned downstream of the catalytic zone containing the NiMoP hydrotreatment catalyst.

35 The Table 1 below gives the operating conditions used in hydrotreatment as well as the characteristics of the gas oil cut produced.

Table 1

Characteristics of the gas oil cut produced by hydrotreatment of a petroleum gas oil on NiMoP/alumina catalyst

Operating conditions	
Total pressure (MPa rel)	5
H ₂ /HC reactor inlet (N l/l)	700
LHSV (h ⁻¹)	1.6
Temperature (°C)	350
Characteristics of fuel base (150°C+ cut)	
Sulphur (ppm by weight)	8
Nitrogen (ppm by weight)	5
Total aromatics (wt.%)	25.0
Diaromatics+ (wt.%)	6.0
Motor cetane number	58
TLF (°C)	+1

- 5 **Comparative example 2:** Method of two-stage hydrotreatment of a mixture constituted by a petroleum feed and a vegetable oil using a conventional catalyst of the NiMo / alumina type in both hydrotreatment stages (not according to the invention) without intermediate stripping

The petroleum feed is identical to the atmospheric gas oil from direct distillation, derived from a Middle East crude, the characteristics of which are shown in Table 1 of Example 1.

The feed from a renewable source is a rapeseed vegetable oil of DND grade (degummed, neutralized and dried) the main characteristics of which are as follows:

- Density at 15°C 0.920 g/cm³
- 15 - Sulphur 5 ppm by weight

The method of hydrotreatment according to Example 2 processes a feed constituted by a mixture of 70 wt.% of the above petroleum feed mixed with 30 wt.% of the DND rapeseed oil. The sulphur content of the total feed to be treated is thus 9100 ppm by weight, its nitrogen content is 84 ppm by weight, its content of total aromatics is 20.7 wt.% and its content of diaromatics+ is 8.4 wt.%.

The co-processing of this mixture is carried out in a fixed-bed isothermal unit of the descending flow type containing 100 ml of densely packed catalyst of the NiMoP/alumina type. The NiMoP catalyst is of the same composition as that described in Example 1, namely 21.0 wt.% of MoO₃, 5.0 wt.% of P₂O₅ and 4.3 wt.% of NiO, supported on gamma alumina and with an Ni/Mo atomic ratio equal to 0.4. The same catalyst is used in both hydrotreatment stages of the method according to Example 2 for carrying out the reactions of HDO (deoxygenation) and of

HDS (hydrodesulphurization) and therefore in two catalytic zones. The two stages of hydrotreatment are applied without an intermediate stripping stage. All of the hydrotreated effluent is then subjected to a stage of separation of water by decanting and the hydrocarbon liquid effluent is then subjected to a hydroisomerization stage in order to improve, by hydroisomerization, the low-temperature properties of the gas oil cut, and in particular the temperature limit of filterability, on 50 ml of catalyst of the NiW/silica-alumina type characterized by an NiO content of 3.5 wt.% and a content of WO₃ of 27 wt.%, said catalyst being positioned downstream of the catalytic zones containing the NiMoP hydrotreatment catalyst.

After sulphurization in situ of the catalysts at 350°C in the unit under pressure, carried out by adding 2 wt.% of dimethyl disulphide to the petroleum gas oil, hydrotreatment was then carried out under the following conditions, summarized in Table 2.

Table 2

Operating conditions of the various catalytic zones

Total feed rate (cm ³ /h)	160
Total pressure (MPa rel)	5
<u>Zone 1 (HDO)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiMoP (h ⁻¹)	3.2
Temperature (°C)	300
<u>Zone 2 (HDS)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiMoP (h ⁻¹)	3.2
Temperature (°C)	350
<u>Zone 3 (hydroisom.)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiW (h ⁻¹)	3.2
Temperature (°C)	340

Table 3 below shows the yields obtained in the various catalytic zones (expressed in wt.% relative to the fresh starting feed), as well as the main characteristics of the fuel cut produced at the outlet from each zone.

Table 3

Yields obtained in each hydrotreatment zone and characteristics of the cut obtained

Hydrotreatment zone	Zone 1 NiMoP (HDO)	Zone 2 NiMoP (HDS)	Zone 3 NiW (Hydroisom.)
Degree of deoxygenation (%)	100	-	-
Selectivity HDO (wt.%)	70	-	-
Yields (wt.%/fresh feed)			
H ₂ S		0.9	0.9
C1+C2		0.2	0.2
C3		1.5	1.5
C4		0.1	0.1
CO + CO ₂		1.4	1.4
H ₂ O		2.6	2.6
Naphtha (150°C-)		-	7.0
Kerosene + Gas oil (150°C+)		94.7	87.7
H ₂ consumption		1.4	1.4
Characteristics of fuel base (150°C+ cut)			
Sulphur (ppm by weight)	1250	240	200
Nitrogen (ppm by weight)	40	10	10
Total aromatics (wt.%)	19.3	18.0	18.0
Diaromatics+ (wt.%)	7.5	6.5	6.5
Motor cetane number	59	60	60
TLF (°C)	+1	+1	-1

In hydrotreatment stage 1, essentially for the purpose of deoxygenation of the rapeseed oil, the degree of deoxygenation is total, but the selectivity of the HDO route (hydrodeoxygenation with elimination of oxygen in the form of water) is 70%.

The selectivity in hydrodeoxygenation (HDO) is calculated as follows:

Using R_{DCO} to denote the theoretical yield of CO+CO₂ for a feed obtained from a given renewable source, which is transformed exclusively according to the decarboxylation (DCO) route, expressed as percentage by weight relative to the feed, and R to denote the yield of CO + CO₂ obtained experimentally during hydrotreatment of a feed obtained from a pure renewable source, S_{HDO} is then defined as the selectivity for HDO by the following simple equation.

$$S_{hydro} = 100 * (R_{DCO} - R) / R_{DCO}$$

It can be seen that, relative to the results described in Example 1 processing a petroleum feed only, and obtained under the same operating conditions of hydrotreatment, there is a clear degradation of HDS performance, since the sulphur content of the middle distillate cut obtained is 200 ppm. To satisfy the required specifications of max. 10 ppm by weight for the

gas oil cut, it is necessary to increase the operating temperature by 20°C. However, increasing the operating temperature like this has adverse effects especially in terms of rate of deactivation of the catalyst by coking, and under industrial conditions leads to a considerable reduction in the cycle time of the catalyst.

5

Example 3 according to the invention: Method of hydrotreatment of a mixture constituted by a petroleum feed and a vegetable oil using a series of NiMo/alumina catalysts having an Ni/Mo atomic ratio equal to 0.02 + conventional NiMo/alumina having an Ni/Mo atomic ratio equal to 0.4 in both hydrotreatment stages a) and b).

10

The petroleum feed and the rapeseed oil feed are strictly identical to those described in Example 2. The mixture processed is also strictly identical to that described in Example 2 and constituted by 70 wt.% of petroleum gas oil and 30 wt.% of DND rapeseed oil.

15 The co-processing of this mixture is carried out in a fixed-bed isothermal unit of the descending flow type:

The total feed is subjected to a first hydrotreatment stage a) in which the feed passes through a catalytic zone comprising 50 ml of NiMoP/alumina catalyst having an Ni/Mo atomic ratio equal to 0.02 intended to promote the reactions of HDO of the vegetable oil.

20 The effluent from the first hydrotreatment stage a) is sent directly without an intermediate stripping stage to a second hydrotreatment stage b) comprising 50 ml of NiMoP/alumina catalyst having an Ni/Mo atomic ratio equal to 0.4 and intended to promote the reactions of HDS of the feed.

25 All of the hydrotreated effluent is then subjected to a stage of separation of water by decanting and the hydrocarbon liquid effluent is then subjected to a hydroisomerization stage on 50 ml of catalyst of the NiW/alumina type, intended to improve the low-temperature properties and in particular the temperature limit of filterability, of the gas oil cut.

30 The NiMoP/alumina catalyst used in the catalytic zone of the first hydrotreatment stage a) is characterized by an NiO content of 0.22 wt.%, a content of MoO₃ of 21 wt.% and a content of P₂O₅ of 5 wt.%, and therefore by an Ni/Mo atomic ratio equal to 0.02, said catalyst being supported on gamma alumina.

35 The NiMoP/alumina catalyst used in the catalytic zone of the second hydrotreatment stage b) is of the same composition as that described in Example 1, namely 21.0 wt.% of MoO₃, 5.0 wt.% of P₂O₅ and 4.3 wt.% of NiO, and therefore an Ni/Mo atomic ratio equal to 0.4, said catalyst being supported on gamma alumina.

The NiW/silica-alumina catalyst, used essentially for hydroisomerization of the paraffins resulting from the transformation of the vegetable oil at the end of the first and second stages of hydrotreatment a) and b), is characterized by an NiO content of 3.5 wt.% and a WO₃ content of 27 wt.%.

- 5 The catalysts are prepared by dry impregnation of the oxide precursors in aqueous solution. The method of preparation of the catalysts does not limit the scope of the invention. After in-situ sulphurization of the catalysts at 350°C in the unit under pressure, carried out by adding 2 wt.% of dimethyl disulphide to the petroleum gas oil, hydrotreatment was then carried out under the following conditions, summarized in Table 4. The operating conditions are identical to those used for Example 2. The only change is the nature of the catalyst used
- 10 essentially for the deoxygenation stage and in particular the first hydrotreatment stage a) of hydrodeoxygenation.

Table 4

Operating conditions of the various catalytic zones

Total feed rate (ml/h)	160
Total pressure (MPa rel)	5
<u>Zone 1 (HDO)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiMoP [Ni/Mo 0.02] (h ⁻¹)	3.2
Temperature (°C)	300
<u>Zone 2 (HDS)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiMoP [Ni/Mo 0.4] (h ⁻¹)	3.2
Temperature (°C)	350
<u>Zone 3 (hydroisom.)</u>	
H ₂ /HC inlet (N l/l)	700
LHSV catalyst NiW (h ⁻¹)	3.2
Temperature (°C)	340

Table 5 below shows the yields obtained in the various catalytic zones (expressed in wt.% relative to the fresh starting feed), as well as the main characteristics of the fuel cut produced at the outlet from each zone.

20

Table 5

Yields obtained in each hydrotreatment stage and characteristics of the cut obtained

Hydrotreatment zone	Zone 1 (HDO)	Zone 2 (HDS)	Zone 3 (Hydroisom.)
Catalyst Ni/Mo [at/at.]	NiMoP 0.02	NiMoP 0.4	NiW -
Degree of deoxygenation (%)	100	-	-
Selectivity HDO (wt.%)	96.8	-	-

Yields (wt.%/fresh feed)			
H ₂ S		0.9	0.9
C1+C2		0.2	0.2
C3		1.5	1.5
C4		0.1	0.1
CO +CO ₂		0.3	0.3
H ₂ O		3.5	3.5
Naphtha (150°C-)		-	6.0
Kerosene + Gas oil (150°C+)		95.0	89.0
H ₂ consumption		1.5	1.5
Characteristics of fuel base (150°C+ cut)			
Sulphur (ppm by weight)	1500	8	6
Nitrogen (ppm by weight)	50	6	6
Total aromatics (wt.%)	19.5	17.5	17.5
Diaromatics+ (wt.%)	8.0	6.0	6.0
Motor cetane number	58	63	62
TLF (°C)	+1	+1	-3

Relative to the results described in Example 2 (not according to the invention), the following is observed:

- an improvement in the yield of gas oil base, owing to the better yields by weight of gas oil base obtained by promoting the hydrodeoxygenation route (HDO).
- better quality of the gas oil base produced.
- a considerable improvement in the hydrodesulphurization (HDS) performance, which makes it possible to produce, at a temperature of 350°C for the second hydrotreatment stage b) of HDS, a gas oil base complying with the specifications for sulphur of max. 10 ppm by weight.

This result is achievable owing to the particularly high selectivity of the NiMo catalyst according to the invention, having a well defined Ni/Mo atomic ratio, used in the first hydrotreatment stage a) which is very favourable to deoxygenation of the vegetable oil according to the hydrodeoxygenation route (HDO) (which is accompanied by formation of water) rather than according to the decarboxylation route (which is accompanied by formation of CO and CO₂) relative to the conventional NiMo catalyst used in the first hydrotreatment stage in comparative example 2. The very small amount of CO and CO₂ formed provides evidence of this very good selectivity for hydrodeoxygenation (HDO).

CLAIMS

1. Method of hydrotreatment in co-processing of petroleum feeds, in a mixture with at least one feed obtained from renewable sources, for producing fuel bases having a sulphur content below 10 ppm, said method comprising the following stages:
 - 5 a) a first hydrotreatment stage in which said feed passes through at least one first fixed-bed catalytic zone comprising at least one bulk or supported catalyst comprising an active phase constituted by at least one group 6 element and at least one group 8 to 10 element, said elements being in the form of sulphide and the atomic ratio of the group 8 to 10 metal or metals to group 6 metal or metals is comprised between 0.01 and 0.03,
 - 10 b) a second hydrotreatment stage into which the effluent from the first hydrotreatment stage is sent directly, and in which said effluent passes through at least one second fixed-bed catalytic zone comprising at least one hydrotreatment catalyst.
- 15 2. Method according to claim 1 in which the temperature of the stream entering the first catalytic zone of the first hydrotreatment stage a), said stream being constituted by the mixture of the feed obtained from a renewable source and of the petroleum feed, is comprised between 180 and 220°C.
- 20 3. Method according to one of claims 1 or 2 in which the active phase of said catalyst is constituted by at least one group 6 element, said group 6 element being molybdenum and at least one group 8 to 10 element, said group 8 to 10 element being nickel.
- 25 4. Method according to one of claims 1 to 3 in which in the case when the catalyst is in the supported form, the oxide content of group 6 element is comprised between 1 and 30 wt.% relative to the total weight of the catalyst and the oxide content of group 8 to 10 element is

strictly greater than 0% and less than 1.5 wt.% of oxide relative to the total weight of the catalyst.

5 5. Method according to one of claims 1 to 4 in which the first hydrotreatment stage a) is a stage of hydrogenation of the unsaturations of the fatty acid chains of the triglycerides and hydrodeoxygenation of the feed.

10 6. Method according to one of claims 1 to 5 in which the first hydrotreatment stage a) operates at a temperature comprised between 120 to 450°C, at a total pressure comprised between 1 and 10 MPa, at an hourly space velocity comprised between 0.1 and 10 h⁻¹ and at a hydrogen/feed ratio expressed as volume of hydrogen, measured under normal conditions of temperature and pressure, per volume of liquid feed generally comprised between 50 NI/l and 3000 NI/l.

15 7. Method according to one of claims 1 to 6 in which the selectivity for hydrodeoxygenation (HDO) of the first hydrotreatment stage a) is greater than 95%.

20 8. Method according to one of claims 1 to 7 in which the effluent from the first hydrotreatment stage a) is sent directly, without an intermediate stripping stage, to the second hydrotreatment stage b).

9. Method according to one of claims 1 to 8 in which the temperature of the effluent leaving the first hydrotreatment stage a) is above 300°C.

25 10. Method according to one of claims 1 to 8 in which the hydrotreatment catalyst used in the second hydrotreatment stage b) comprises nickel as group 8 to 10 element and molybdenum as group 6 element and said catalyst comprises a content of nickel oxide comprised between

0.5 and 10 wt.% and a content of molybdenum trioxide comprised between 1 and 30 wt.% on an alumina amorphous mineral support, the percentages being expressed in wt.% relative to the total weight of the catalyst.

5 11. Method according to one of claims 1 to 10 in which the hydrotreated effluent is subjected to a stage of separation of water and of at least one liquid hydrocarbon base.

12. Method according to one of claims 1 to 11 in which all of the hydrotreated liquid effluent is then subjected to a hydroisomerization stage in the presence of a selective
10 hydroisomerization catalyst.

13. Method according to one of claims 1 to 12 in which the petroleum feeds are selected from the group comprising atmospheric gas oils from direct distillation, gas oils obtained from conversion processes, and the feeds obtained from renewable sources are selected from oils
15 and fats of vegetable or animal origin, or mixtures of said feeds, containing triglycerides and/or free fatty acids and/or esters.

14. Method according to one of claims 1 to 13 in which the mixture of conventional petroleum feed and feed from a renewable source is constituted by 60 to 99 wt.% of conventional
20 petroleum feed and 1 to 40 wt.% of feed from a renewable source.