

METHOD FOR PRODUCING RENEWABLE KEROSENE BY TWO-STEP HYDROPROCESSING USING A SPECIFIC CATALYST IN THE HYDROCONVERSION STEP WITH RECYCLE OF A HEAVY FRACTION

Field of the invention

5 The search for new renewable energy sources for the production of fuels is a major challenge both for meeting fuel demand and for addressing environmental concerns.

In this respect, the upgrading as fuels of feedstocks derived from renewable sources has received substantial renewed interest in recent years. Among these feedstocks, examples that may be mentioned include plant oils (for example, palm, rapeseed, soybean), animal fats, used
10 cooking oils, oils of microbial origin (for example, derived from algae), fish oils, long-chain paraffins (waxes) derived from the Fischer-Tropsch process, whether crude or pretreated, and also mixtures thereof. These feedstocks contain, for the most part, chemical structures of triglyceride or fatty acid or ester type, the structure and length of the hydrocarbon chain of these feedstocks being compatible with the hydrocarbons present in gas oils and kerosene.

15 One possible route is catalytic transformation of the feedstock obtained from a renewable source into paraffinic fuel deoxygenated in the presence of hydrogen (hydrotreating). There are many metal or sulfide catalysts that are known to be active for this type of reaction.

These processes for hydrotreating feedstocks derived from renewable sources are already well known and are described in numerous patents. Mention may be made, for example, of the
20 following patents: US 4 992 605, US 5 705 722, EP 1 681 337 and EP 1 741 768.

The use of solids based on transition metal sulfides allows the production of paraffins from molecules of ester type according to two reaction pathways:

- hydro-deoxygenation leading to the formation of water by consumption of hydrogen and to the formation of hydrocarbons with a carbon number (C_n) equal to that of the initial fatty acid
25 chains,

- decarboxylation/decarbonylation leading to the formation of carbon oxides (carbon monoxide and dioxide: CO and CO₂) and to the formation of hydrocarbons containing one carbon less (C_{n-1}) relative to the initial fatty acid chains.

The liquid effluent obtained from these hydrotreating processes, after separation, consists
30 essentially of n-paraffins and is substantially free of sulfur-based, nitrogen-based and oxygen-

based impurities. After hydrotreating and separation of the gases, the sulfur content is typically between 1 and 20 ppm by weight, the nitrogen content is generally between 0.2 and 30 ppm by weight and the oxygen content is generally less than 2000 ppm by weight. The paraffins have a number of carbon atoms typically between 9 and 25, which is mainly dependent on the composition of the feedstock to be hydrotreated.

However, this liquid effluent generally cannot be incorporated as such into the kerosene or gas oil pool notably on account of insufficient cold properties and/or excessively high boiling points. Specifically, the paraffins present lead to high pour points and thus to setting phenomena for uses at low temperatures. For example, eicosane (linear paraffin of 20 carbon atoms, $C_{20}H_{42}$) has a boiling point equal to 340°C and a melting point of 37°C. The boiling point of eicosane is thus compatible with its incorporation in a gas-oil pool but its melting point may give rise to setting problems and limit its use. By way of illustration, the limit filterability temperature for a winter gas oil is a maximum of -15°C. Moreover, the boiling point of eicosane renders it ineligible for incorporation into a kerosene pool, for which the final temperature of the distillation curve must be less than 300°C.

Depending on the degree of incorporation and the favored fuel pool (gas oil or kerosene) targeted, it may be necessary to perform a hydroconversion step (hydroisomerization and/or hydrocracking reactions) to transform the linear paraffins of the hydrotreated liquid effluent. Hydroisomerization makes it possible to convert a linear paraffin into a branched paraffin with conservation of the number of carbon atoms of the molecule. This makes it possible to improve the cold properties of the effluent since branched paraffins have better cold properties than linear paraffins. For example, nonadecane has a melting point of 32°C, whereas one of its singly branched isomers, 7-methyloctadecane, has a melting point of -16°C. Hydrocracking enables a linear paraffin to be converted into linear or branched paraffins of smaller molecular weight. This makes it possible to adjust, as need be, the distillation curve of the effluent to render it compatible with the kerosene pool. By way of illustration, the hydrocracking of an eicosane molecule can lead to the production of two 2-methylnonane molecules. The boiling point of 2-methylnonane is 167°C, which is compatible with incorporation into the kerosene pool. The hydroconversion step is performed on a bifunctional catalyst containing both a hydro/dehydrogenating function and a Brønsted acid function. The operating conditions may be adapted to promote the hydroisomerization or hydrocracking reactions as need be. In any case, it is desirable to minimize the production of cracking products that are too light to be incorporated into the kerosene or gas oil pool.

The appropriate choice of the acid phase makes it possible to promote the isomerization of long linear paraffins and to minimize the cracking. Thus, the form selectivity of medium-pore (10 MR) one-dimensional zeolites such as zeolites ZSM-22, ZSM-23, NU-10, ZSM-48 and ZBM-30 makes them particularly suitable for use for obtaining catalysts that are selective toward isomerization. Other acidic phases of zeolite or non-zeolite type such as halogenated (notably chlorinated or fluorinated) aluminas, phosphorus-based aluminas, silica-aluminas or siliceous aluminas may also be used.

However, it is well known that factors other than the acid phase have an impact on the activity and selectivity of a bifunctional catalyst. Hydroisomerization and hydrocracking of normal paraffins have thus been the subject of numerous academic studies since the original investigations in the 1960s by Weisz or Coonradt and Garwood. The most commonly accepted mechanism first involves dehydrogenation of the n-paraffin to an n-olefin on the hydrogenating-dehydrogenating phase and then, after diffusion to the acid phase, protonation to a carbenium ion. After structural rearrangement and/or β -scission, the carbenium ions are desorbed from the acidic phase in the form of olefins after deprotonation. Next, after diffusion to the hydro-dehydrogenating phase, the olefins are hydrogenated to form the final reaction products. It is then appropriate to have a hydro/dehydrogenating function that is sufficiently active toward the acid function firstly to rapidly supply the acidic phase with olefins and secondly to rapidly hydrogenate the olefinic intermediates after they have reacted on the acidic phase. This makes it possible firstly to maximize the activity of the catalyst and secondly to promote hydroisomerization relative to hydrocracking when the first reaction is desired, or to limit the production of excessively light cracking products when the hydrocracking reaction is desired. The use of a sufficiently active hydrogenating function is also desirable so as to limit the deactivation of the bifunctional catalyst by coking during the hydroconversion of n-paraffins (Alvarez et al., Journal of Catalysis, 162, 2, 179-189) for a range of set operating conditions.

The proximity between the two functions on the catalyst may also have an impact on the performance of the difunctional catalyst. Thus, Zecevic et al. (Nature, 2015, 528, 245-254) recently studied the impact of the localization of platinum on the hydroisomerization performance of long paraffins (n-decane, n-nonadecane, pristane) by a difunctional catalyst using the zeolite USY as acidic phase and an alumina matrix. It is observed that the difunctional catalyst for which platinum is deposited on alumina is systematically more selective towards isomerization than the catalyst for which platinum is deposited in the zeolite. In the light of these results, a person skilled in the art is thus inclined to favour localization of the

hydrogenating function on the alumina matrix rather than on the acidic phase to improve the selectivity towards isomerization. From the point of view of the activity, localizing platinum on the aluminium matrix has a variable impact depending on the long paraffin under consideration: a positive impact as regards n-decane, a marginal impact as regards n-nonadecane and finally a negative impact as regards pristane.

Noble metals (Pt, Pd) or transition metals from group VIB (Mo, W) combined with transition metals from group VIII (Ni, Co) can act as hydrogenating function for the catalyst. The noble metals are used in their reduced form whereas the transition metals are used in a sulfide form. For the latter, there is a known synergistic effect between the transition metals of group VIA and the transition metals of group VIII, generally attributed to the decoration of the sulfide phases of group VIB with the transition metals of group VIII. These are then referred to as molybdenum or tungsten sulfide phases promoted with nickel or cobalt ("CoMoS", "NiMoS", "NiWS"). This synergistic effect is reflected by an increase in the catalytic activity of the promoted phase in comparison with an unpromoted phase.

The choice of the nature of the hydrogenating function, of noble metal or sulfide type, depends on various criteria, of economic nature (the price of noble metals is markedly higher than that of transition metals of groups VIA and VIII) or of chemical nature (impact of the presence of contaminants). Thus, the hydrogenating activity of noble metals is higher than that of transition metal sulfides when the partial pressure of hydrogen sulfide (H₂S) in the reaction medium is low or even zero. Conversely, the hydrogenating activity of transition metal sulfides is higher than that of noble metals when the partial pressure of H₂S in the reaction medium becomes high (C. Marcilly, Catalyse acido-basique [Acid-base catalysis], volume 2, 2003, published by Technip).

Patent US2022/0127537 discloses a process for hydrotreating a renewable feedstock. Said process comprises a step of hydrotreating the feedstock in the presence of hydrogen and a hydrotreating catalyst to deoxygenate said feedstock and thus produce a hydrotreated effluent. Said process comprises a step of hydroisomerization, in the presence of hydrogen and a hydroisomerization catalyst, of an effluent derived from the hydrotreated effluent to obtain a hydroisomerized effluent. The hydroisomerization catalyst used may comprise a Group VIII metal chosen from Pt and Pd, alone or in combination, and a support which may be amorphous or crystalline, chosen from alumina, amorphous alumina-silica, ferrierite, ALPO-31, SAPO-11, SAPO-31, SAPO-37, SAPO-41, SM-3, MgAPSO-31, FU-9, NU-10, NU-23, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, ZSM-57, MeAPO-11, MeAPO-31, MeAPO-41, MgAPSO-

11, MgAPSO-31, MgAPSO-41, MgAPSO-46, ELAPSO-11, ELAPSO-3, EMAPSO-41, ELAPSO-11, ELAPSO-31, ELAPSO-41, alone or in combination.

In a first embodiment claimed in claim 1, said process comprises a step of separating the hydrotreated effluent and/or the isomerized effluent to obtain a vapour effluent and a liquid effluent; a step of distilling the liquid effluent or the hydroisomerized effluent to produce a kerosene cut and a gas oil cut; and a step of hydrocracking the gas oil cut to obtain a hydrocracked effluent comprising a kerosene cut. In contrast with the present invention, said process thus allows the co-production of gas oil and kerosene cuts, which are separated via a distillation step, and the gas oil cut obtained then undergoes a hydrocracking step.

In a second embodiment claimed in claim 16, said process involves obtaining a gas oil cut from the hydroisomerized effluent, said gas oil cut being characterized in that the concentration of normal paraffin of a given carbon number is at least twice that of the corresponding normal paraffin concentration in said hydroisomerized effluent. Said gas oil cut undergoes a hydrocracking or hydroisomerization step to obtain a hydrocracked effluent comprising a kerosene cut. Unlike the present invention, said process thus comprises either a step of hydrocracking the gas oil cut obtained, or a step of recycling said gas oil cut into the hydroisomerization step.

In a third embodiment claimed in claim 19, said process comprises a step of separating said hydroisomerized effluent into a vapour effluent and a liquid effluent; a step of distilling the liquid effluent or the hydroisomerized effluent to obtain a kerosene cut and a gas oil cut, and a step of hydrocracking said gas oil cut to obtain a hydrocracked effluent comprising a kerosene cut. In contrast with the present invention, said process thus allows the co-production of gas oil and kerosene cuts, which are separated via a distillation step, and the gas oil cut obtained then undergoes a hydrocracking step.

Patent US 8 324 439 B2 discloses a process for treating renewable feedstocks of plant or animal origin. Said process comprises a step of hydrotreating the renewable feedstock, and a step of separating the hydrotreated effluent to obtain hydrogen, other gases and at least one effluent containing hydrocarbons. Said process then comprises a step of hydroisomerizing at least a portion of said hydrocarbon-based effluent in the presence of a selective hydroisomerization catalyst, said catalyst comprising at least one 10 MR one-dimensional zeolite and at least one metal from Group VIII and/or Group VIB. Finally, said process comprises a step of separating the hydroisomerized effluent so as to obtain hydrogen, other

gases and at least one gas oil type cut. Said patent also discloses a process comprising a step of hydroisomerization of an effluent obtained from the step of hydrotreating a renewable feedstock of animal or plant origin over a hydroisomerization catalyst. Said catalyst comprises at least one 10 MR one-dimensional zeolite of TON or EUO structure code, or a zeolite ZSM-48, ZBM-30, IZM-1, COK-7, EU-2 and EU-11, alone or as a mixture. The structural framework codes are defined in the International Zeolite Association classification (IZA: <http://www.iza-structure.org/databases/>).

Patent application US2014/0291200 A1 describes a process for producing gas oil with a sulfur content of less than 10 ppm from renewable feedstocks, including the following steps:

- 10 a) a step of hydrotreating renewable feedstocks,
- b) a step of separating the hydrotreated effluent from step a) into a hydrogen-rich gaseous fraction and a liquid hydrocarbon fraction,
- c) a step of removing H₂S dissolved in the hydrocarbon liquid effluent obtained from step b),
- 15 d) a step of hydroisomerizing at least a portion of the liquid effluent from step b) over a catalyst comprising at least one Group VIII metal or a combination of a Group VIII metal and a Group VIB metal on an amorphous support of the alumina or silica-alumina type or a crystalline support, i.e. a support comprising a 10 MR zeolite chosen from zeolites of the TON or EU structure type or chosen from the zeolites ZSM-48, ZBM-30, IZM-1,
- 20 COK-7, EU-2 and EU-11, alone or as a mixture,
- e) a step of separating the effluent obtained into a hydrogen-rich gaseous fraction and at least a gas oil fraction.

The recycling of the gaseous fractions from separation steps b) and/or e) into steps a) and/or d) is mentioned with the aim of better controlling the exothermicity of the reactions within step a). No recycling of part of the gas oil fraction obtained or of a fraction heavier than gas oil into step a) and/or e) is mentioned.

Patent application US 2021/0395620 A1 describes a process for producing kerosene from renewable feedstocks. The process includes a first step of hydrotreating the renewable feedstock in dilution with a hydrocarbon cut, followed by a hydrocracking step. The

hydrocracked effluent is then separated into at least a gaseous fraction and at least a liquid fraction. More specifically, the separation step enables the production of a kerosene-type cut and a heavy gas oil type cut. At least a portion of the hydrocracked effluent, more specifically the kerosene-type cut, is then directed towards the hydrodearomatization step so as to make it compatible with the product specifications in force, notably by reducing the aromatic content.

Patent applications WO 2010/000934 A1 and US 2010/000908 describe a process for producing kerosene from renewable feedstocks, including a first step of hydrodeoxygenation of renewable feedstocks to allow the production of n-paraffins. A second step according to the process allows the hydroisomerization of the n-paraffins obtained from the first step and the production of an isoparaffin-rich effluent. The latter effluent is sent to a separation and fractionation step to allow the production of a cut boiling in the gasoline range, a cut boiling in the kerosene range and, where applicable, a cut boiling in the gas oil range, as well as a cut with a boiling point greater than or equal to 200°C. The cut with a boiling point greater than or equal to 200°C, possibly in admixture with the cut boiling in the gas oil range, is then specifically recycled into a hydroisomerization step, which may be identical to or distinct from the first step of hydroisomerization, in order to be re-isomerized therein. The isomerization catalyst(s) comprise a Group VIII metal and a support comprising a zeolite chosen from SAPO-11, SAPO-41, ZSM-22, ZSM-23 or ferrierite

Patent application US 2014/0005450 A1 describes a method for manufacturing synthetic distillates, based on the hydrotreating of a feedstock and then its hydroisomerization/hydrocracking, followed by a step involving the separation of the paraffins (n-paraffins and i-paraffins) performed over molecular sieves. More particularly, passing the feedstock over molecular sieves allows the separation of an n-paraffin-rich cut and an i-paraffin-rich cut. The i-paraffin-rich cut is then fractionated by distillation, enabling the production of at least a heavy distillate fraction and at least a light distillate or gas oil fraction. Recycling of the n-paraffins into the hydroisomerization/hydrocracking step is described. Recycling of a part of the heavy distillate fraction is also described. This involves selective recycling of a stream based on its chemical family rather than its distillation range. The hydroisomerization catalyst used may comprise a Group VIII metal chosen from Pt and Pd, alone or in combination, and a support which may be amorphous or crystalline, chosen from alumina, amorphous alumina-silica, ferrierite, ALPO-31, SAPO-11, SAPO-31, SAPO-37, SAPO-41, SM-3, MgAPSO-31, FU-9, NU-10, NU-23, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, ZSM-57, MeAPO-11, MeAPO-31, MeAPO-41, MgAPSO-11, MgAPSO-31,

MgAPSO-41, MgAPSO-46, ELAPSO-11, ELAPSO-3, EMAPSO-41, ELAPSO-11, ELAPSO-31, ELAPSO-41, laumontite, cancrinite, offretite, stilbite in hydrogen form, mordenite in magnesium or calcium form, and partheite in calcium or magnesium form, alone or in combination.

- 5 US patent application 2017/0022424 A1 describes a process for hydrotreating renewable feedstocks that allows the production of an n-paraffinic hydrocarbon cut. Said patent claims a very specific implementation process for performing the injection of renewable feedstock into different catalytic beds, in admixture with a recycle gas stream (rich in hydrogen) and/or with a recycle liquid stream. The recycled streams (gas and liquid) are obtained from an effluent
10 separation section located downstream of the hydrotreating step and are injected in a ratio relative to the renewable feedstock that is advantageously selected to control the reaction exothermicity and the reactor temperature profile. A portion of the liquid stream comprising paraffins is sent to a hydroisomerization step in the presence of a hydroisomerization catalyst comprising at least one Group VIII metal chosen from platinum and palladium, nickel and cobalt
15 and/or at least one Group VIB metal chosen from molybdenum and tungsten, and at least one amorphous support of the doped alumina, alumina-silica or zeolite type, preferably comprising a zeolite of the TON (NU-10), FER (ferrierite) or EUO (EU-1 or ZSM-50) structure type or the zeolites ZSM-48, ZBM-30, IZM-1, COK-7, EU-2 and EU-11, alone or as a mixture. All or part of the hydroisomerized effluent is then sent to a fractionation step to obtain a gaseous fraction,
20 a naphtha fraction and a middle distillates fraction comprising gas oil and kerosene. Part of the middle distillates fraction (150°C+) may be recycled into the hydrotreating step or to the hydroisomerization step. In another variant, part of the 300°C+ fraction may be recycled into the hydroisomerization step so as to upgrade this cut into lighter products and improve the cold properties.
- 25 Patent application US 2011/0105812 A1 describes a process for improving the cold properties of a diesel cut produced from renewable feedstocks. The process includes a step of hydrogenating/deoxygenating renewable feedstocks to allow the production of an n-paraffinic effluent, followed by a step of hydroisomerization and selective hydrocracking of the n-paraffinic effluent. The effluent collected after hydroisomerization and selective hydrocracking
30 is then selectively separated to produce at least one gas oil stream comprising a portion of the paraffins with a boiling point within the gas oil range, at least one recycle stream comprising another portion of the paraffins with a boiling point within the gas oil range (preferably C16+), the composition of the gas oil stream being different from that of the recycle stream, at least

one light stream containing at least the LPGs and at least one naphtha-type stream. The recycle stream is advantageously recycled into the step of hydroisomerization and selective hydrocracking. The hydroisomerization catalyst used may comprise a Group VIII metal chosen from Pt and Pd, alone or in combination, and a support which may be amorphous or crystalline,
 5 chosen from alumina, amorphous alumina-silica, ferrierite, ALPO-31, SAPO-11, SAPO-31, SAPO-37, SAPO-41, SM-3, MgAPSO-31, FU-9, NU-10, NU-23, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50, ZSM-57, MeAPO-11, MeAPO-31, MeAPO-41, MgAPSO-11, MgAPSO-31, MgAPSO-41, MgAPSO-46, ELAPSO-11, ELAPSO-3, EMAPSO-41, ELAPSO-11, ELAPSO-31, ELAPSO-41, laumontite, cancrinite, offretite, stilbite in hydrogen form,
 10 mordenite in magnesium or calcium form, and partheite in calcium or magnesium form, alone or in combination.

Patent application WO 2021/099343 A1 describes the composition of an isoparaffin-rich hydrocarbon cut and, more specifically, the composition of a hydrocarbon cut having an excellent pour point, suitable for use as aviation fuel. More particularly, the object of the
 15 invention is to provide an aviation fuel-type hydrocarbon cut with increased yield and density, produced from a renewable feedstock. Said composition is obtained via a process comprising the hydrodeoxygenation of a renewable plant oil-type feedstock followed by a step of isomerizing the n-paraffins formed to produce isoparaffins, the isomerization catalyst comprising a Group VIII metal chosen from platinum, palladium and nickel, and a support
 20 comprising a zeolite chosen from SAPO-11, SAPO-41, ZSM-22, ZSM-23 or ferrierite. The isoparaffins formed can then be fractionated so as to obtain said composition.

For the purposes of the present invention, the various embodiments presented can be used alone or in combination with each other, without any limit to the combinations.

For the purposes of the present invention, the various ranges of parameters for a given step,
 25 such as the pressure ranges and the temperature ranges, can be used alone or in combination. For example, for the purposes of the present invention, a preferred range of pressure values may be combined with a more preferred range of temperature values.

In the remainder of the text, the term “naphtha” or “naphtha cut” means the hydrocarbon fraction with a boiling point lower than the middle distillate cut. The middle distillate cut
 30 generally has an initial cut point of between 120°C and 160°C, preferentially 120°C. The naphtha cut may have boiling points between that of the hydrocarbon compounds containing

five carbon atoms per molecule (or 36°C boiling point) up to 216°C and includes the gasoline cut.

Throughout the remainder of the text, the term “kerosene” or “kerosene cut” means the cut having initial and final boiling points of between 120°C and 300°C and the term “gas-oil” or “gas-oil cut” means the cut having initial and final boiling points in a range from 120°C to 400°C and preferably between 120°C and 380°C.

In the remainder of the text, the groups of chemical elements are given according to the CAS classification (CRC Handbook of Chemistry and Physics, published by CRC Press, editor-in-chief D.R. Lide, 81st edition, 2000-2001). For example, group VIII according to the CAS classification corresponds to the metals from columns 8, 9 and 10 according to the new IUPAC classification, and group VIB corresponds to the metals from column 6.

In the continuation of the text, the expressions “of between ... and ...” and “between ... and ...” are equivalent and mean that the limiting values of the range are included in the range of values described. If such were not the case and if the limiting values were not included in the range described, such a detail will be provided by the present invention.

In the present description, the term “greater than...” is understood as strictly greater than, and is symbolized by the sign “>”, and the term “less than...” is understood as strictly less than, and is symbolized by the sign “<”.

ADVANTAGES OF THE PROCESS ACCORDING TO THE INVENTION

Whilst attempting to develop a process for treating a feedstock from a renewable source for the selective production of a kerosene cut, the Applicant discovered that the use of a specific bifunctional catalyst comprising a noble metal (Pt)-based hydrogenating/dehydrogenating phase and a support comprising a specific zeolite chosen from zeolites with the structure code MTW, and IZM-2 zeolite, either alone or as a mixture, for the step of hydroconversion (hydroisomerization and/or hydrocracking reactions) of linear paraffins obtained from the step of hydrodeoxygenation of renewable feedstocks, combined with the implementation of a step of recycling, into the hydroconversion step, of all or a portion of a heavy cut with an initial boiling point of between 250 and 300°C separated on conclusion of the hydroconversion step, was of great interest.

Subject of the invention

More specifically, the present invention relates to a process for treating a feedstock from a renewable source to produce a kerosene cut, said process comprising at least the following steps and preferably consisting of the following steps:

- 5 a) a step of hydrotreating said feedstock in the presence of a catalyst in a fixed bed, said catalyst comprising a hydrogenating function and an oxide support, at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly space velocity of between 0.1 h⁻¹ and 10 h⁻¹ and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 2000 Nm³ of
10 hydrogen/m³ of feedstock,
 - b) a step of separating at least a portion of the effluent obtained from step a) into at least a light gaseous fraction, at least a hydrocarbon liquid effluent, and at least an aqueous liquid effluent,
 - c) a step of hydroconversion of at least a portion of the hydrocarbon liquid effluent obtained
15 from step b) in the presence of at least one difunctional hydroconversion catalyst in a fixed bed, said catalyst comprising a hydrogenating phase comprising at least one noble metal from group VIII of the Periodic Table chosen from platinum and palladium, and a support comprising at least one zeolite chosen from zeolites with the structure code MTW and the zeolite IZM-2, either alone or as a mixture, and at least one binder, said hydroconversion step being
20 performed at a temperature of between 250°C and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly space velocity of between 0.1 and 10 h⁻¹ and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1000 Nm³/m³ of feedstock,
 - d) a step of separating at least a portion of the effluent obtained from step c) making it possible
25 to separate at least a gaseous fraction and at least a hydrocarbon liquid effluent,
 - e) a step of fractionating the hydrocarbon effluent obtained from step d) into at least a kerosene cut and at least a heavy cut with an initial boiling point of between 250 and 300°C,
- Said process comprises a step of recycling all or a portion of said heavy cut with an initial boiling point of between 250 and 300°C, obtained from said fractionation step e), into said
30 hydroconversion step c).

One advantage of the present invention is that it provides a two-step process for treating a feedstock obtained from a renewable source to produce a kerosene cut, using a specific catalyst in the hydroconversion step to afford a gain in activity and selectivity. The use of the specific catalyst makes it possible, all other things being equal, to reduce the temperature required to obtain the target cold properties on the kerosene cut produced. Performing the hydroconversion step with the specific catalyst according to the invention also makes it possible, whilst meeting the target cold properties, to maximize the yield of said kerosene cut of interest produced in said process.

Another advantage of the present invention is that it provides a process for treating a feedstock derived from a renewable source to produce at least a kerosene cut, in two steps, comprising a hydrotreating step and a hydroconversion step, enabling an increase in kerosene yield to be achieved by using a specific catalyst in the hydroconversion step and by recycling, into said hydroconversion step, a heavy cut with an initial boiling point of between 250 and 300°C.

The implementation of the process, and in particular of such recycling, maximizes the selectivity of the process towards the kerosene cut of interest while at the same time maximizing the conversion of the renewable feedstock. More particularly, the operating conditions of the hydroconversion step and also the cut-off point of said kerosene cut can be jointly adapted to maximize the yields of the kerosene cut of interest.

Another advantage of the present invention is that it provides a method for fractionating the hydroconversion effluent which offers flexibility in adjusting the distillation ranges of the kerosene cut (the cut-off point being advantageously adjustable within the 120-300°C range for maximum kerosene production).

An advantage of the present invention is that it enables the processing of heavier feedstocks from renewable sources within said process by means of performing the fractionation step e) and recycling said heavy cut back into the hydroconversion step c), as compared to prior art processes which do not perform such a fractionation step.

Detailed description of the invention

Feedstocks

The present invention is particularly dedicated to the preparation of gas oil and/or kerosene fuel bases which meet the new environmental standards, starting with feedstocks obtained from renewable sources.

The feedstocks derived from renewable sources used in the process according to the present invention are advantageously chosen from plant oils (for example palm, rapeseed, soybean) and animal fats, used cooking oils, oils of microbial origin (for example derived from algae), fish oils, long-chain paraffins (waxes) derived from the Fischer-Tropsch process, whether crude or pretreated, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters. The vegetable oils may advantageously be crude or wholly or partially refined and obtained from the following plants: rapeseed, sunflower, soybean, palm, palm kernel, olive, coconut, jatropha, this list not being limiting. Algal oils or fish oils are also relevant. The animal fats are advantageously chosen from lard or fats composed of residues from the food industry or resulting from the catering industries.

These feedstocks essentially contain chemical structures of triglyceride type that a person skilled in the art also knows under the name fatty acid triester, and also free fatty acids. A fatty acid triester is thus composed of three fatty acid chains. These fatty acid chains in triester form or in free fatty acid form have a number of unsaturations per chain, also known as the number of carbon-carbon double bonds per chain, generally between 0 and 3, but which may be higher notably for oils derived from algae which generally contain from 5 to 6 unsaturations per chain.

The molecules present in the feedstocks obtained from renewable sources used in the present invention thus have a number of unsaturations, expressed per triglyceride molecule, advantageously between 0 and 18. In these feedstocks, the degree of unsaturation, expressed as the number of unsaturations per hydrocarbon fatty chain, is advantageously between 0 and 6.

The feedstocks obtained from renewable sources generally also include various impurities and notably heteroatoms such as nitrogen. The nitrogen contents in plant oils are generally between 1 ppm and 1000 ppm by weight approximately, depending on their nature.

Process and catalysts

Advantageously, the feedstock may undergo, prior to step a) of the process according to the invention, a pretreatment or pre-refining step so as to remove, via a suitable treatment, contaminants such as metals, for instance alkali metal compounds, for example on ion-exchange resins, alkaline-earth metal compounds and phosphorus. Suitable treatments may be, for example, heat treatments and/or chemical treatments that are well known to those skilled in the art.

In accordance with step a) of the process according to the invention, the optionally pretreated feedstock is placed in contact with a catalyst in a fixed bed at a temperature of between 200 and 450°C, preferably between 220 and 350°C, preferably between 220 and 320°C and even more preferably between 220 and 310°C. The pressure is between 1 MPa and 10 MPa, preferably between 1 MPa and 6 MPa and even more preferably between 1 MPa and 4 MPa. The hourly space velocity, i.e. the volume of feedstock per volume of catalyst and per hour, is between 0.1 h⁻¹ and 10 h⁻¹. The feedstock is placed in contact with the catalyst in the presence of hydrogen. The total amount of hydrogen mixed with the feedstock is such that the hydrogen/feedstock ratio is between 70 and 2000 Nm³ of hydrogen/m³ of feedstock and preferably between 150 and 1000 Nm³ of hydrogen/m³ of feedstock.

In step a) of the process according to the invention, the fixed-bed catalyst is advantageously a hydrotreating catalyst comprising a hydro-dehydrogenating function comprising at least one metal from group VIII and/or from group VIB, taken alone or as a mixture, and a support chosen from the group formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals. This support may also advantageously contain other compounds, for example oxides chosen from the group consisting of boron oxide, zirconia, titanium oxide and phosphorus pentoxide. The preferred support is an alumina support and very preferably η , δ or γ alumina.

Said catalyst is advantageously a catalyst comprising metals from group VIII preferably chosen from nickel and cobalt, taken alone or as a mixture, preferably in combination with at least one metal from group VIB preferably chosen from molybdenum and tungsten, taken alone or as a mixture.

The content of oxides of metals from group VIII and preferably of nickel oxide is advantageously between 0.5% and 10% by weight of nickel oxide (NiO) and preferably

between 1% and 5% by weight of nickel oxide, and the content of oxides of metals from group VIB and preferably of molybdenum trioxide is advantageously between 1% and 30% by weight of molybdenum trioxide (MoO_3), preferably from 5% to 25% by weight, the percentages being expressed as weight percentages relative to the total mass of the catalyst.

- 5 The total content of oxides of metals from groups VIB and VIII in the catalyst used in step a) is advantageously between 5% and 40% by weight and preferably between 6% and 30% by weight relative to the total mass of the catalyst.

Said catalyst used in step a) of the process according to the invention must advantageously be characterized by a high hydrogenating power so as to orient the reaction selectivity as much
10 as possible toward a hydrogenation conserving the number of carbon atoms in the fatty chains, i.e. the hydro-deoxygenation route, so as to maximize the yield of hydrocarbons included in the distillation range of kerosenes and/or gas oils. This is why the process is preferably performed at a relatively low temperature. Maximizing the hydrogenating function also makes it possible to limit the polymerization and/or condensation reactions leading to the formation of
15 coke which would degrade the stability of the catalytic performance. A catalyst of Ni or NiMo type is preferably used.

Said catalyst used in the hydrotreating step a) of the process according to the invention may also advantageously contain a doping element chosen from phosphorus and boron, taken alone or as a mixture. Said doping element may be introduced into the matrix or, preferably,
20 may be deposited on the support. Silicon may also be deposited on the support, alone or with phosphorus and/or boron and/or fluorine.

The weight content of oxide of said doping element is advantageously less than 20% by weight and preferably less than 10% by weight and is advantageously at least 0.001% by weight.

Preferred catalysts are the catalysts described in patent application FR 2 943 071 that
25 describes catalysts having a high selectivity for hydro-deoxygenation reactions.

Other preferred catalysts are the catalysts described in patent application EP 2 210 663 that describes supported or bulk catalysts comprising an active phase consisting of a group VIB sulfide element, in which the group VIB element is molybdenum.

The metals of the catalysts used in the hydrotreating step a) of the process according to the
30 invention are metal sulfides or metallic phases and preferably metal sulfides.

It would not constitute a departure from the context of the present invention to use in step a) of the process according to the invention, simultaneously or successively, a single catalyst or several different catalysts. This step may be performed industrially in one or more reactors with one or more catalytic beds, preferably with a descending flow of liquid.

- 5 Said hydrotreating step a) allows the hydrogenation, hydro-deoxygenation, hydro-denitrogenation and hydro-desulfurization of said feedstock.

In accordance with step b) of the process according to the invention, a step of separating at least a portion and preferably all of the effluent obtained from step a) is performed. Said step b) enables the separation of at least one hydrogen-rich "light" gas fraction, at least one
10 hydrocarbon liquid effluent composed of n-paraffins, and at least one liquid aqueous effluent.

Said light gaseous fraction comprises at least the hydrogen not converted in the reactions performed in step a), at least the gases containing one or more oxygen atoms resulting from the decomposition of oxygenated compounds in step a), and at least the C₄⁻ compounds, i.e. C₁ to C₄ compounds preferably having a final boiling point below 20°C. The aim of this step is
15 to separate the gases from the liquids. More particularly, the aim is to recover at least the hydrogen-rich gases, which may also contain compounds such as CO and CO₂, at least one hydrocarbon liquid effluent consisting of n-paraffins, and at least one liquid aqueous effluent containing the water produced in the reactions performed in step a). Said hydrocarbon liquid effluent preferably has a sulfur content of less than 10 ppm by weight and a nitrogen content
20 of less than 2 ppm by weight.

The separation step b) may advantageously be performed via any method known to those skilled in the art, for instance the combination of one or more high-pressure and/or low-pressure separators operated under hot or cold conditions, and/or steps of distillation and/or high-pressure and/or low-pressure stripping.

25 Step b) also allows the separation of at least one liquid aqueous effluent, preferably water. The removal of at least a portion of the water and preferably all of the water may be performed via any method or technique known to those skilled in the art. Preferably, the removal of water is performed by decantation into a separating vessel, by drying, by passing through a desiccant, by flash distillation, or via a combination of at least two of these techniques. The atomic oxygen
30 content of the hydrocarbon liquid effluent containing the paraffinic hydrocarbons obtained from step b) of the process according to the invention, expressed in parts per million by weight

(ppm), is preferably less than 10 000 ppm, preferably less than 6000 ppm, very preferably less than 1000 ppm and more preferably less than 500 ppm by weight. The content in ppm by weight of atomic oxygen in said hydrocarbon liquid effluent is measured via the infrared absorption technique, for instance the technique described in patent application US 2009/0018374 A1.

In accordance with the invention, the process comprises a step c) of hydroconversion of at least a portion, and preferably all, of the liquid hydrocarbon effluent obtained from step b) of the process in the presence of at least one difunctional hydroconversion catalyst in a fixed bed, said catalyst comprising a hydrogenating phase comprising at least one noble metal from group VIII of the Periodic Table chosen from platinum and palladium, alone or as a mixture, and a support comprising at least one zeolite chosen from zeolites with the structure code MTW and IZM-2, either alone or as a mixture, and at least one binder, said hydroconversion step being performed at a temperature of between 250°C and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly space velocity of between 0.1 and 10 h⁻¹ and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1000 Nm³/m³ of feedstock, and preferably between 150 and 750 Nm³/m³ of feedstock.

The operating conditions of the hydroconversion step c) are adjusted to promote the hydroisomerization or hydrocracking reactions as need be. Preferably, the hydroconversion step c) of the process according to the invention is a hydroisomerization step and advantageously operates at a temperature of between 250°C and 450°C and very preferably between 250°C and 400°C, at a pressure of between 2 MPa and 10 MPa and very preferably of between 3 MPa and 9 MPa, at an hourly space velocity advantageously between 0.2 and 7 h⁻¹ and very preferably between 0.5 and 5 h⁻¹ (defined relative to the feedstock flow rate of step c), excluding recycling), at a hydrogen flow rate such that the hydrogen/feedstock volume ratio is advantageously between 100 and 1000 normal m³ of hydrogen per m³ of feedstock and preferably between 150 and 1000 normal m³ of hydrogen per m³ of feedstock (ratio defined relative to the feedstock flow rate of step c), excluding recycling).

The process according to the invention is a flexible process which, by applying adjusted operating conditions in hydroconversion step c), combined with the use of a specific catalyst in said step c) and a final fractionation step e) allowing the separation of at least a heavy cut

with an initial boiling point of between 250 and 300°C, which is recycled into said step c), makes it possible to maximize the yield of the kerosene cut obtained.

According to the invention, a portion and preferably all of the liquid hydrocarbon effluent obtained in step b) is sent into said hydroconversion step c) in admixture with all or a portion
5 of the heavy cut with an initial boiling point of between 250 and 300°C, which is recycled into said step c) and is obtained from the final fractionation step e).

Said hydroconversion step may advantageously comprise one or more catalytic beds, which may comprise one or more different catalysts in each of the beds.

According to a preferred embodiment, the heavy cut with an initial boiling point of between 250
10 and 300°C obtained from the fractionation step e) is advantageously mixed with all or a portion of the liquid hydrocarbon effluent from step b) upstream of the hydroconversion reactor, and this mixture is then injected into the first catalytic bed of step c) in the case where said hydroconversion step comprises several catalytic beds.

In another embodiment, the heavy cut with an initial boiling point of between 250 and 300°C
15 obtained from the fractionation step e) is advantageously injected into an intermediate bed of the hydroconversion reactor in the case where said hydroconversion step comprises several catalytic beds. In this optional mode, the beds preceding the recycle injection then process only all or a portion of the liquid hydrocarbon effluent from step b) of the process of the invention.

20 In all cases, the operating conditions of the hydroconversion step c) are adjusted to promote the hydroisomerization or hydrocracking reactions as need be. More particularly, the operating conditions of the hydroconversion step c) and the degree of recycling of the heavy cut with an initial boiling point of between 250 and 300°C obtained from the fractionation step e) may be advantageously adjusted so as to maximize the yields of the desired kerosene cut at the outlet
25 of said process.

In accordance with the invention, the catalyst used in step c) is a difunctional catalyst comprising a hydrogenating phase comprising at least one noble metal from group VIII of the Periodic Table chosen from platinum and palladium, alone or as a mixture, and a support
30 comprising at least one zeolite chosen from zeolites of the MTW structure type, and IZM-2 zeolite, either alone or as a mixture, and at least one binder.

The hydro-dehydrogenating function

Preferably, the Group VIII metal of the catalyst used in step c) is platinum.

Advantageously, the hydro-dehydrogenating (metal) element, preferably platinum, may be introduced onto the catalyst support via any method known to those skilled in the art, for instance co-kneading, dry impregnation or impregnation by exchange.

According to one or more embodiments, the content of group VIII metal, and preferably the content of platinum, in the catalyst used in step c) is between 0.01% by weight and 4% by weight, preferably between 0.05% by weight and 2% by weight, relative to the total weight of said catalyst.

The catalyst used in step c) may also advantageously comprise at least one additional metal chosen from the group formed by metals from groups IIIA, IVA and VIIB of the Periodic Table of the Elements, preferably chosen from gallium, indium, tin and rhenium. Said additional metal is preferably chosen from indium, tin and rhenium.

Preferably, the content of the at least one additional metal in the catalyst used in step c) is between 0.01% by weight and 2% by weight, preferably between 0.05% by weight and 1% by weight, relative to the total weight of said catalyst.

According to one embodiment, the sulfur content in the hydroconversion catalyst is such that the ratio of the number of moles of sulfur to the number of moles of at least one group VIIB metal is between 0.3 and 3. According to one or more embodiments, the presence of sulfur in the catalyst results from an optional sulfurization step of the hydroconversion catalyst. According to one or more embodiments, the presence of sulfur in the catalyst results from impurities that may be present, for instance in the alumina binder. According to another embodiment, the catalyst does not contain any sulfur.

The acid function

In accordance with the invention, the catalyst used in step c) comprises a support comprising at least one zeolite chosen from zeolites of the MTW structure type and zeolite IZM-2, either alone or as a mixture, and at least one binder.

The acid function of the difunctional catalyst used in step c) is provided by the zeolite chosen from zeolites of the MTW structure type and zeolite IZM-2, either alone or as a mixture.

Preferably, the zeolites of structure type MTW are chosen from ZSM-12, TPZ-12, Theta-3, NU-13, CZH-5 zeolites, alone or as a mixture, and preferably the zeolite of structure type MTW is ZSM-12.

5 According to a preferred embodiment, the catalyst used in step c) comprises a support comprising an IZM-2 zeolite alone, or a support comprising a ZSM-12 zeolite alone.

IZM-2 zeolite is a crystalline microporous solid, the crystal structure and preparation process of which are described in patent application FR2918050A1. The structure code of IZM-2 zeolite is unknown to date. ZSM-12 zeolite is a crystalline microporous solid, the crystal structure of
10 which is described on the International Zeolite Association website (<http://www.iza-structure.org/>). It is a monodimensional 12 MR zeolite; its structure code is MTW. A process for preparing this zeolite is described, for example, in the article "Synthesis of zeolite ZSM-12 in the system $(\text{MTEA})_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ " by S. Ernst et al. (Zeolites, 7, 5, 458-462, DOI10.1016/0144-2449(87)90015-7).

15 The zeolites are preferably essentially in acid form, i.e. the atomic ratio between the monovalent compensation cation (for example sodium) and the aluminium inserted into the crystal lattice of the solid is advantageously less than 0.1, preferably less than 0.05 and very preferably less than 0.01. According to one or more embodiments, the zeolites included in the
20 composition of said hydroisomerization catalyst are advantageously calcined. According to one or more embodiments, said zeolites are exchanged by means of 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, leads to the acid form of said zeolites.

25 In a preferred embodiment, the catalyst used in step c) comprises a hydrogenating phase comprising platinum and a support comprising IZM-2 zeolite alone and an alumina binder.

In another preferred embodiment, the catalyst used in step c) comprises a hydrogenating phase comprising platinum and a support comprising ZSM-12 zeolite alone and an alumina binder.

30 Preferably, the catalyst used in step c) comprises a zeolite content of between 1% by weight and 90% by weight, preferably between 3% by weight and 80% by weight, more preferentially between 4% by weight and 60% by weight, preferably between 4% and 30% by weight and more preferably between 4% and 20% by weight relative to the total weight of said catalyst.

The binder

Preferably, the binder of the catalyst support of step c) is amorphous or crystalline. Preferably, the binder used in the catalyst support of step c) is advantageously chosen from the group
 5 formed by alumina, silica, silica-alumina, clays, titanium oxide, boron oxide, zirconia and aluminates, taken alone or as a mixture. Preferably, the binder is alumina. Preferably, said binder may contain alumina in all its forms known to those skilled in the art, for instance aluminas of alpha, gamma, eta and delta type.

10 Preferably, the catalyst used in step c) comprises a binder content of between 10% by weight and 99% by weight relative to the total weight of said catalyst, i.e. so as provide the balance up to 100% by weight of the elements constituting the catalyst used in step c).

According to the invention, the catalyst support comprises the zeolite as a mixture with a
 15 binder. The support is preferably formed into a mixture by co-kneading, extrusion and then heat treatment of the zeolite with the binder or a precursor of the binder, for instance boehmite, which is transformed into alumina by heat treatment.

A preferred catalyst for step c) comprises, and preferably consists of, platinum, and a support
 20 comprising, and preferably consisting of, a ZSM-12 zeolite and an alumina binder.

Another preferred catalyst for step c) comprises, and preferably consists of, platinum, and a support comprising, and preferably consisting of, an IZM-2 zeolite and an alumina binder.

According to a preferred embodiment, the catalyst used in step c) more particularly comprises,
 25 and preferably consists of:

- from 1% to 90% by weight, preferably from 3% to 80% by weight and even more preferably from 4% to 60% by weight of zeolite;
- from 0.01% to 4% by weight and preferably from 0.05% to 2% by weight of at least one metal from group VIIIB, preferably platinum;
- 30 - optionally from 0.01% to 2% by weight and preferably from 0.05% to 1% by weight of at least one additional metal chosen from the group formed by metals from groups IIIA, IVA and VIIB;
- optionally a sulfur content, preferably such that the ratio of the number of moles of sulfur to the number of moles of the group VIIIB metal(s) is between 0.3 and 3; and

- optionally at least one binder, preferably alumina, providing the balance up to 100% by weight in the catalyst, relative to the total weight of the catalyst of step c).

Preferably, the catalyst used in step c) is formed into cylindrical or polylobal extrudates such as straight or twisted bilobal, trilobal or polylobal extrudates. According to one or more embodiments, the catalyst used in step c) is formed into crushed powders, tablets, rings, beads or wheels. Techniques other than extrusion, such as pelletizing or coating, may advantageously be used.

Preferably, the noble metal contained in said catalyst used in step c) may advantageously be reduced. One of the preferred methods for reducing the metal is treatment at a temperature of between 150°C and 650°C and a total pressure of between 0.1 and 25 MPa. For example, a reduction may comprise a steady stage at 150°C for two hours, then a rise in temperature up to 450°C at a rate of 1°C/min and then a steady stage of two hours at 450°C; during the reduction step, the hydrogen flow rate may be 1000 normal m³ of hydrogen per m³ of catalyst and the total pressure may be kept constant at 0.1 MPa. Any reduction method can advantageously be envisaged, either *in situ* (the reduction of the catalyst is performed in the unit where the catalytic reaction is performed), or *ex situ* (the reduction is performed outside the unit where the catalytic reaction is performed, therefore before the catalyst is loaded into the unit).

In accordance with the invention, the process comprises a step d) of separating at least a portion and preferably all of the effluent obtained from step c).

Said step d) makes it possible to separate at least a "light" gaseous fraction and at least a hydrocarbon liquid effluent. Optionally, step d) also makes it possible to separate at least a portion of the residual water and preferably all of the residual water.

Said "light" gaseous fraction comprises at least the hydrogen not converted by the reactions described in step c) and at least a portion of the C₄⁻ cracking products, that is to say C₁ to C₄ compounds preferably having a final boiling point below 20°C. The aim of this step is to separate the gases from the liquids. More particularly, the aim is to recover at least the hydrogen-rich gases, at least one hydrocarbon liquid effluent rich in branched paraffins and optionally an aqueous liquid effluent containing a small amount of residual water (residual water generated either by the hydrodeoxygenation of the residual oxygen compounds present in the feedstock of step c) or by slight entrainment of water from step b) to step c)).

The separation step d) described may advantageously be performed via any method known to those skilled in the art, for instance the combination of one or more high-pressure and/or low-pressure separating vessels operated under hot or cold conditions, and/or steps of distillation and/or high-pressure and/or low-pressure stripping.

- 5 In accordance with the process of the invention, the liquid hydrocarbon effluent from step d) undergoes a step e) of fractionation into at least a kerosene cut and at least a heavy cut with an initial boiling point of between 250 and 300°C, and preferably between 270 and 300°C.

Advantageously, said fractionation step e) also makes it possible to separate at least one gaseous cut consisting mainly of C1-C4 light hydrocarbons, and at least one lighter
10 hydrocarbon cut, referred to as naphtha.

The fractionation step e) may be performed via any method known to those skilled in the art and may preferably be performed in a distillation column or in a steam stripping step followed by a distillation column.

Said heavy cut with an initial boiling point of between 250 and 300°C separated in said step e)
15 is advantageously composed mainly of long-chain n-paraffins that have not been converted, i.e. that have not been isomerized or cracked in step c), and is advantageously obtained at the bottom of the distillation column.

More particularly, the cut-off point between the kerosene cut and the naphtha cut is adjustable within the range between 100 and 150°C, and preferably around 120°C. More particularly, the
20 cut-off point between the kerosene cut and the heavy cut is adjustable in the range between 250 and 300°C if the aim is to target kerosene production, and preferably around 300°C.

The naphtha cut thus contains compounds with a boiling point below 120°C, while the kerosene cut contains compounds with a boiling point between 120°C and 300°C.

More particularly, fractionation according to step e) of the process advantageously allows the
25 processing of atypical feedstocks which generate, for example, long-chain n-paraffins (number of carbon atoms greater than C20) during the hydroconversion step c). This is the case, for instance, with n-paraffins derived from waxes produced by the Fischer-Tropsch process: these feedstocks can advantageously be processed in admixture with plant oil-type feedstocks in the process according to the invention.

In this case, the specific hydroconversion catalyst used in step c), combined with the fractionation step e) of the process according to the invention, advantageously allows, on the one hand, the conversion of the long-chain paraffins contained in Fischer-Tropsch waxes to be maximized and, on the other hand, the selectivity of the process towards the product of interest, namely the kerosene cut, to be maximized.

The upgrading of the bio-naphtha cut is not the subject of the present invention, but this cut may advantageously be sent to a steam cracking or reforming unit or else upgraded as a gasoline base in admixture with other gasoline bases.

In accordance with the invention, said process comprises a step of recycling all or a portion of said unconverted heavy fraction from said fractionation step e) into said hydroisomerization step c).

The process according to the invention advantageously does not comprise a hydrocracking step downstream of step c) of hydroconversion of part or all of the effluent obtained from step c).

15 **Description of the figures**

Figure 1 represents the various steps in the two-step process for producing renewable kerosene or gas oil with recycling, using a specific catalyst for the hydroconversion step c).

The feedstock from renewable sources is sent via pipe 1, in admixture with supplemental and/or recycled hydrogen (pipe 2), into a hydrotreating step a) (enabling the hydrogenation, hydrodeoxygenation, hydrodenitrogenation and hydrodesulfurization of the feedstock). The hydrotreated effluent obtained from the hydrotreating step a) is drawn off via pipe 3 and sent to the three-phase separation step b), which allows the separation of at least a hydrogen-rich gaseous effluent (pipe 4) and at least a hydrocarbon liquid effluent (pipe 5). Step b) also allows the removal of at least a portion of the water produced by the hydrodeoxygenation reactions and, preferably, all of this water (pipe 6).

The hydrocarbon liquid effluent (5) is sent to a hydroconversion (hydroisomerization and/or hydrocracking) step c), in the presence of a supplemental and/or recycled hydrogen stream (pipe 7) and a heavy cut with an initial boiling point of between 250 and 300°C, which is recycled (pipe 15) from the fractionation step e) to produce a second effluent (pipe 8) which is sent to a three-phase separation step d) which allows the separation of a hydrogen-rich

gaseous effluent (9) which may also contain light fractions such as the C₁-C₄ cut, and at least one liquid hydrocarbon effluent (10). Said step also allows the removal of at least a portion of the water, and preferably all of the residual water (11).

5 The liquid hydrocarbon effluent obtained from step d) (10) is sent to step e), in which the hydrocarbon effluent obtained from step d) is fractionated by distillation to allow the separation of a light gaseous fraction (12), a naphtha hydrocarbon cut (13), a kerosene cut (14) and a heavy cut with an initial boiling point of between 250 and 300°C (15), which is recycled into the hydroconversion step c). Optionally, the fractionation allows the co-production of a kerosene cut (14) with a gas oil cut (15).

10 The examples below illustrate the invention without limiting the scope thereof.

EXAMPLES

Example 1: preparation of a hydrotreating catalyst (C1)

15 The catalyst is an industrial catalyst based on nickel, molybdenum and phosphorus on alumina with contents of molybdenum oxide MoO₃ of 22% by weight, of nickel oxide NiO of 4% by weight and of phosphorus oxide P₂O₅ of 5% by weight relative to the total weight of the finished catalyst.

Example 2: Preparation of a hydroconversion catalyst in accordance with the invention (C2)

Synthesis of the IZM-2 zeolite

20 The IZM-2 zeolite was synthesized in accordance with the teaching of patent FR 2 918 050 B. A colloidal silica suspension known under the trade name Ludox HS-40, sold by Aldrich, is incorporated into a solution composed of sodium hydroxide (Prolabo), 1,6-bis(methylpiperidinium)hexane dibromide structuring agent, aluminum hydroxide (Aldrich) and deionized water. The molar composition of the mixture is as follows: 1 SiO₂; 0.0060 Al₂O₃;
25 0.1666 Na₂O; 0.1666 1,6-bis(methylpiperidinium)hexane; 33.3333 H₂O. The mixture is stirred vigorously for 30 minutes. The mixture is then transferred, after homogenization, into a Parr autoclave. The autoclave is heated for 5 days at 170°C with spindle stirring (30 rpm). The product obtained is filtered, washed with deionized water to reach neutral pH and then dried overnight at 100°C in an oven. The solid is then introduced into a muffle furnace and calcined

therein so as to remove the structuring agent. The calcination cycle comprises a temperature increase up to 200°C, a hold of two hours at this temperature, a temperature increase up to 550°C, followed by a hold of eight hours at this temperature and finally a return to ambient temperature. The temperature rises are performed at a rate of 2°C/minute. The solid thus obtained is then refluxed for 2 hours in an aqueous ammonium nitrate solution (10 ml of solution per gram of solid, ammonium nitrate concentration of 3M) so as to exchange the sodium alkaline cations with ammonium ions. This refluxing step is performed four times with fresh ammonium nitrate solution, and the solid is then filtered off, washed with deionized water and dried in an oven overnight at 100°C. Finally, to obtain the zeolite in its acid (protonated H⁺) form, a step of calcination is performed at 550°C for 10 hours (temperature increase ramp of 2°C/minute) in a traversed bed under dry air (2 normal litres per hour and per gram of solid). The solid thus obtained was analysed by X-ray diffraction and identified as consisting of IZM-2 zeolite. Characterizations via the ²⁷Al NMR, x-ray fluorescence and ICP methods afford the following results for IZM-2:

- weight percentage of hexacoordinated aluminium atoms Al^{VI}: 5%,
- ratio of the number of moles of silicon divided by the number of moles of lattice aluminium, in mol/mol, Si/Al: 72
- ratio of the number of moles of sodium divided by the number of moles of lattice aluminium, in mol/mol, Na/Al: 0.03.

Preparation of the IZM-2/alumina support

The IZM-2/alumina support is obtained by blending and extrusion of the zeolite IZM-2 with a Pural SB3 alumina gel. The blended paste is extruded through a quadrilobal die 1.8 mm in diameter. After drying in an oven overnight at 110°C, the extrudates are calcined at 500°C for two hours (temperature increase ramp of 5°C/min) in a crossed bed under dry air (2 normal litres per hour and per gram of solid). The weight content of IZM-2 zeolite in the support after calcination is 13% by weight.

Platinum impregnation onto the IZM-2/alumina support

Platinum is impregnated by dry impregnation of the support with an aqueous solution containing platinum tetramine nitrate Pt(NH₃)₄(NO₃)₂. 50 g of support are used, and are dry-impregnated in a pan. After impregnation, the solid is left to mature for at least five hours in the

laboratory air and is then dried overnight in an oven at 110°C. Finally, a calcination step is performed under a flow of dry air (2 normal litres per hour and per gram of solid) in a tubular oven under the following conditions:

- temperature rise from room temperature to 450°C at 5°C/min;
- 5 - steady stage of two hours at 450°C;
- decrease to room temperature.

The Pt content measured by XRF on the calcined catalyst C2 is 0.29% by weight, its dispersion measured by H₂/O₂ assay is 52%, and its coefficient of distribution measured by Castaing microprobe is 0.91.

10 **Example 3: Preparation of a hydroconversion catalyst in accordance with the invention (C3)**

ZSM-12 Zeolite

ZSM-12 zeolite is supplied by the company Zeolyst. The solid was analysed by X-ray diffraction and identified as consisting of ZSM-12 zeolite. Characterizations via the ²⁷Al NMR, x-ray
15 fluorescence and ICP methods afford the following results for ZSM-12:

- weight percentage of hexacoordinated aluminium atoms Al^{VI}: 0%;
- ratio of the number of moles of silicon divided by the number of moles of lattice aluminium, in mol/mol, Si/Al: 43;
- ratio of the number of moles of sodium divided by the number of moles of lattice aluminium,
20 in mol/mol, Na/Al: 0.009.

Preparation of the ZSM-12/alumina support

The ZSM-12/alumina support is obtained by blending and extrusion of the zeolite ZSM-12 with a Pural SB3 alumina gel. The blended paste is extruded through a quadrilobal die 1.8 mm in diameter. After drying in an oven overnight at 110°C, the extrudates are calcined at 500°C for
25 two hours (temperature increase ramp of 5°C/min) in a crossed bed under dry air (2 normal litres per hour and per gram of solid). The weight content of ZSM-12 zeolite in the support after calcination is 6% by weight.

Platinum impregnation onto the ZSM-12/alumina support

Platinum is impregnated by dry impregnation of the support with an aqueous solution containing platinum tetramine nitrate $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. 50 g of support are used, and are dry-impregnated in a pan. After impregnation, the solid is left to mature for at least five hours in the laboratory air and is then dried overnight in an oven at 110°C. Finally, a calcination step is performed under a flow of dry air (2 normal litres per hour and per gram of solid) in a tubular oven under the following conditions:

- temperature rise from room temperature to 450°C at 5°C/min;

- steady stage of two hours at 450°C;

- decrease to room temperature.

The Pt content measured by XRF on the calcined catalyst C3 is 0.31% by weight, its dispersion measured by H_2/O_2 assay is 38%, and its coefficient of distribution measured by Castaing microprobe is 0.87.

Example 4: hydrotreating of a feedstock obtained from a renewable source according to a process in accordance with the invention

Pre-refined rapeseed oil with a density of 920 kg/m³, having an oxygen content of 11% by weight, is hydrotreated in a reactor which is temperature-regulated so as to ensure isothermal functioning and with a fixed bed containing 190 ml of hydrotreating catalyst C1, the catalyst being sulfide-treated beforehand. The cetane number is 35 and the fatty acid distribution of the rapeseed oil is detailed in table 1. Prior to the hydrotreating step, said feedstock is supplemented with dimethyl disulfide so as to adjust its sulfur content to 50 ppm by weight.

Table

Fatty acid composition	(%)
14:0	0.1
16:0	5.0
16:1	0.3
17:0	0.1
17:1	0.1
18:0	1.5
18:1 trans	< 0.1
18:1 cis	60.1
18:2 trans	< 0.1
18:2 cis	20.4
18:3 trans	< 0.1
18:3 cis	9.6
20:0	0.5
20:1	1.2
22:0	0.3
22:1	0.2
24:0	0.1
24:1	0.2

Table 1: Characteristics of the rapeseed oil renewable feedstock used as feedstock for the hydrotreating step

Before hydrotreating the feedstock, the catalyst is sulfide-treated *in situ* in the unit, with a distillation gas oil supplemented with 2% by weight of dimethyl disulfide, under a total pressure of 5.1 MPa, a hydrogen/supplemented gas oil ratio of 700 Nm³ per m³. The volume of supplemented gas oil per volume of catalyst and per hour is set at 1 h⁻¹. Sulfurization is performed for 12 hours at 350°C, with a temperature increase ramp of 10°C per hour.

After sulfurization, the operating conditions of the unit are adjusted so as to perform the hydrotreating of the feedstock:

- HSV (volume of feedstock/volume of catalyst/hour): 1 h⁻¹,

- total working pressure: 5.1 MPa,
- hydrogen/feedstock ratio: 700 Nm³ of hydrogen/m³ of feedstock,
- temperature: 310°C.

5 The hydrogen employed is supplied by Air Products and has a purity of greater than 99.999% by volume.

Step b): separation of the effluent obtained from step a)

10 All of the hydrotreated effluent obtained from step a) is separated using a gas/liquid separator so as to recover a light fraction predominantly containing hydrogen, propane, water in vapor form, carbon oxides (CO and CO₂) and ammonia, and a liquid hydrocarbon effluent predominantly consisting of linear hydrocarbons. The water present in the hydrocarbon liquid effluent is removed by decantation. The hydrocarbon liquid effluent thus obtained has an atomic oxygen content of less than 80 ppm by weight, said atomic oxygen content being measured via the infrared adsorption technique described in patent application US 2009/0018374, and a sulfur content of 2 ppm by weight and a nitrogen content of less than 1
15 ppm by weight, said nitrogen and sulfur contents being measured, respectively, by chemiluminescence and by UV fluorescence. Said hydrocarbon liquid effluent has a density of 791 kg/m³. The hydrocarbon liquid effluent is composed of paraffins; its composition, measured by gas chromatography, is given in table 2.

Table 2

Distribution of the n-paraffins by carbon number	(% m/m)
nC8	0.01
nC9	0.00
nC10	0.01
nC11	0.01
nC12	0.01
nC13	0.02
nC14	0.06
nC15	0.97
nC16	4.09
nC17	17.70
nC18	72.77
nC19	0.67
nC20	1.56
nC21	0.18
nC22	0.56
nC23	0.09
nC24	0.23
nC25	0.02
nC26	0.02

Table 2: composition of the hydrocarbon liquid effluent used as feedstock for the hydroconversion

5 Non-compliant Example 5: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C2, producing a kerosene cut and a gas oil cut without recycling the gas oil cut.

Example 5 is not in accordance with the invention in that it illustrates a process not in accordance with the invention but using a C2 catalyst that is in accordance with the invention in the hydroconversion step c).

The hydroconversion catalyst C2 was evaluated in a pilot plant, representative in terms of implementation (reaction operating conditions, effluent separation quality), of the industrial process according to the invention. The various steps and unit operations of the pilot plant, which mimic the industrial implementation of the process according to the invention, are described hereinbelow.

The hydroconversion of the hydrocarbon liquid effluent obtained from Example 4 is performed in a reactor which is temperature-regulated so as to ensure isothermal functioning and with a fixed bed containing 50 ml of hydroconversion catalyst C2, the catalyst being preactivated by reduction. Given the nature of the catalyst C2 (noble metal), any injection of sulfur is to be avoided.

The catalyst C2 undergoes a reduction step under hydrogen performed at 5.1 MPa and 400°C (2-hour steady stage).

After reduction, the operating conditions of the unit are adjusted so as to perform the hydroconversion of the hydrocarbon liquid effluent under the following range of operating conditions:

- HSV (volume of feedstock/volume of catalyst/hour): 0.5 h^{-1} ,
- total working pressure: 5.1 MPa,
- hydrogen/feedstock ratio: 350 Nm^3 of hydrogen/ m^3 of feedstock.

The hydrogen used and entering the hydroconversion step is supplied by Air Products: it has a purity of greater than 99.999% by volume and is free of hydrogen sulfide.

On leaving the hydroconversion reactor, the reaction effluent is sent to a gas-liquid separation step performed using a flash vessel operated at a pressure comparable to that of the hydroconversion reactor. The hydrogen-rich gas phase is sent to the unit's gas outlet. The liquid hydrocarbon phase is depressurized and sent to a stripper for stabilizing the liquid effluent; the gas phase collected at the top of the stripper is also sent to the unit's gas outlet.

At the unit's gas outlet, inline analysis by gas chromatography and a gas meter makes it possible to calculate the mass of light hydrocarbons produced (essentially hydrocarbons containing 1 to 5 carbon atoms) and present in the hydrogen stream. The liquid effluent is weighed separately, topped off at 120°C to remove the naphtha fraction; the 120°C+ liquid

effluent is then reweighed and distilled into two sub-cuts: a 120-X°C kerosene cut and an X°C+ gas oil cut, in which X is a temperature that can be adjusted by the refiner as a function of their specific requirements and the targets they wish to achieve. A classic example of a value of X may be 280 or 290°C.

- 5 Temperature steady stages in the 250-400°C range were applied in order to determine the maximum yield of the 120-X°C kerosene cut. At low temperatures, hydroconversion is very low and does not allow for the production of a large amount of the 120-X°C kerosene cut. At high temperatures, hydroconversion is too high and leads to the formation of a large amount of gas and C5-120°C naphtha cut, to the detriment of the 120-X°C cut of interest.

- 10 The yield of C1-C4 gas is calculated as follows:

C1-C4 yield = [(mass of C1-C4 compounds) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of C5-120°C naphtha is calculated as follows:

- 15 C5-120°C yield (naphtha cut yield) = [(C5-120°C mass of the liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of 120-X°C kerosene is calculated as follows:

- 20 120-X°C yield (kerosene cut yield) = [(120-X°C mass of the liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of X°C+ gas oil is calculated as follows:

X°C+ yield (gas oil cut yield) = [(X°C+ mass of the liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

- 25 The various masses of gases and of liquid effluents correspond to the amounts of gas and liquid accumulated over a certain period of time, typically 24 hours, and the mass of feedstock corresponds to the amount of feedstock injected into the hydroconversion reactor over the same period of time.

At an HSV of 0.5 h^{-1} , a total pressure of 5.1 MPa and an $\text{H}_2/\text{feedstock}$ ratio of $350 \text{ Nm}^3/\text{m}^3$, the incremental variation in temperature between 250 and 400°C made it possible to determine the optimum temperature (denoted T_{base}) at which the yield of the $120\text{--}X^\circ\text{C}$ kerosene cut is maximal.

5 At the temperature T_{base} , for a $120\text{--}280^\circ\text{C}$ kerosene cut, the structure-yield is as follows:

- C1-C4 gas yield: 19 wt%
- C5- 120°C naphtha cut yield: 20 wt%
- $120\text{--}280^\circ\text{C}$ kerosene cut yield: 43 wt%
- $280^\circ\text{C}+$ gas oil cut yield: 18 wt%

10 At the same temperature T_{base} , for a $120\text{--}290^\circ\text{C}$ kerosene cut, the structure-yield is as follows:

- C1-C4 gas yield: 19 wt%
- C5- 120°C naphtha cut yield: 20 wt%
- $120\text{--}290^\circ\text{C}$ kerosene cut yield: 47 wt%
- $290^\circ\text{C}+$ gas oil cut yield: 14 wt%

15 In both cases ($X = 280$ and 290°C), the features obtained for the kerosene cut of interest and the gas oil cut, along with the associated operating conditions, are reported in the Summary Table 3. In both cases ($X = 280$ and 290°C), the $120\text{--}X^\circ\text{C}$ kerosene cut has a crystal disappearance point below -60°C and a smoke point above 25 mm.

20 **Compliant Example 6: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C2, producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 25 vol%.**

Example 6 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C2 in accordance with the invention. The combination of the process and catalyst C2 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

5 The use of a hydroconversion reactor simulator enabled calculation of the impact of recycling on cut yields as a function of the degree of recycling selected by the refiner.

The degree of recycling is defined as the ratio between the volume of recycled X°C+ gas oil cut in the hydroisomerization reactor and the volume of fresh feedstock (obtained from Example 4). With a degree of recycling of 25 vol%, the HSV, which was 0.5 h⁻¹ in non-compliant Example 5, thus increases to 0.63 h⁻¹ as it integrates 25 vol% of X°C+ cut in addition to the
10 fresh feedstock. Similarly, in order to maintain a constant hydrogen flow rate at the inlet of the hydroisomerization reactor, the H₂/feedstock ratio changes from 350 Nm³/m³ in the non-compliant Example 5 to 278 Nm³/m³ in the case of 25 vol% recycling. The temperature is then adjusted to afford, under these operating conditions, 25 vol% of the X°C+ cut, which will be recycled into the hydroisomerization reactor.

15 In the case of a cut-off at 280°C, the temperature required to produce and recycle 25 vol% of the 280°C+ cut is equal to the base temperature of non-compliant Example 5 minus 2°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.63 h⁻¹
- 20 • H₂/(fresh + recycled 280°C+ feedstock) ratio: 278 Nm³/m³
- Temperature: T_{base} – 2°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 10 wt%
- 25 • C5-120°C naphtha cut yield: 36 wt%
- 120-280°C kerosene cut yield: 54 wt%

The operation consisting in recycling the 280°C+ cut with a degree of recycling of 25 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 43% by weight (non-compliant Example 5) to 54% by weight, representing an 11% by weight gain in kerosene cut yield. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 3.

In the case of a cut-off at 290°C, the temperature required to produce and recycle 25 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 5 minus 2.8°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.63 h⁻¹
- H₂/(fresh + recycled 290°C+ feedstock) ratio: 278 Nm³/m³
- Temperature: T_{base} – 2.8°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 8 wt%
- C5-120°C naphtha cut yield: 31 wt%
- 120-290°C kerosene cut yield: 61 wt%

The operation consisting in recycling the 290°C+ cut with a degree of recycling of 25 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 5) to 61% by weight, representing an 14% by weight gain in kerosene cut yield. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 3.

Compliant Example 7: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C2,

producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 50 vol%.

Example 7 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C2 in accordance with the invention. The combination of the process and catalyst C2 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

Example 7 is identical to Example 6, but uses a degree of recycling of 50 vol% instead of 25 vol%.

In the case of a cut-off at 280°C, the temperature required to produce and recycle 50 vol% of the 280°C+ cut is equal to the base temperature of non-compliant Example 5 minus 2.5°C.

The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.75 h⁻¹
- H₂/(fresh + recycled 280°C+ feedstock) ratio: 233 Nm³/m³
- Temperature: T_{base} – 2.5°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 9 wt%
- C5-120°C naphtha cut yield: 32 wt%
- 120-280°C kerosene cut yield: 59 wt%

The operation consisting in recycling the 280°C+ cut with a degree of recycling of 50 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 43% by weight (non-compliant Example 5) to 59% by weight, representing an 16% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–280°C yield is 5% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 3.

In the case of a cut-off at 290°C, the temperature required to produce and recycle 50 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 5 minus 3.8°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- 5 • Overall HSV: 0.75 h⁻¹
- H₂/(fresh + recycled 290°C+ feedstock) ratio: 233 Nm³/m³
- Temperature: T_{base} – 3.8°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- 10 • C1-C4 gas yield: 7 wt%
- C5-120°C naphtha cut yield: 26 wt%
- 120-290°C kerosene cut yield: 66 wt%

The operation consisting in recycling the 290°C+ cut with a degree of recycling of 50 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 5) to 66% by weight, representing an 19% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–290°C yield is 5% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 3.

20 **Compliant Example 8: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C2, producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 100 vol%.**

25 Example 8 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C2 in accordance with the invention. The combination of the process and catalyst C2 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

Example 8 is identical to Examples 6 and 7, but uses a degree of recycling of 100 vol% instead of 25 vol% and 50 vol%, respectively.

In the case of a cut-off at 280°C, the temperature required to produce and recycle 100 vol% of the 280°C+ cut is equal to the base temperature of non-compliant Example 5 minus 3.3°C.

5 The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 1.0 h⁻¹
- H₂/(fresh + recycled 280°C+ feedstock) ratio: 175 Nm³/m³
- Temperature: T_{base} – 3.3°C

10 Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 8 wt%
- C5-120°C naphtha cut yield: 28 wt%
- 120-280°C kerosene cut yield: 64 wt%

15 The operation consisting in recycling the 280°C+ cut with a degree of recycling of 100 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 43% by weight (non-compliant Example 5) to 64% by weight, representing an 21% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–280°C yield is 10% by weight. Relative to the case where the degree of recycling is 50
20 vol%, the gain in 120–280°C yield is 5% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 3.

In the case of a cut-off at 290°C, the temperature required to produce and recycle 100 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 5 minus 4.7°C.

25 The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa

- Overall HSV: 1.0 h^{-1}
- H_2 /(fresh + recycled 290°C+ feedstock) ratio: $175 \text{ Nm}^3/\text{m}^3$
- Temperature: $T_{\text{base}} - 4.7^\circ\text{C}$

5 Under these conditions, the yields obtained at the terminals of the HDI hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 6 wt%
- C5-120°C naphtha cut yield: 22 wt%
- 120-290°C kerosene cut yield: 72 wt%

10 The operation consisting in recycling the 290°C+ cut with a degree of recycling of 100 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 5) to 72% by weight, representing an 25% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–290°C yield is 11% by weight. Relative to the case where the degree of recycling is 50 vol%, the gain in 120–290°C yield is 6% by weight. The properties of the kerosene cut are only
15 very minimally affected by the introduction of this recycle, as shown in Table 3.

Table 3

		Example 5 (not compliant)	Example 6 (compliant)	Example 7 (compliant)	Example 8 (compliant)
Degree of recycling	(vol%)	0	25	50	100
Total pressure	(MPa)	5.1	5.1	5.1	5.1
HSV (fresh feedstock)	(h ⁻¹)	0.5	0.5	0.5	0.5
HSV (fresh + recycled feedstock)	(h⁻¹)	-	0.63	0.75	1.00
H ₂ /fresh feedstock ratio	(Nm ³ /m ³)	350.0	350.0	350.0	350.0
H₂/(fresh + recycled feedstock) ratio	(Nm³/m³)	-	277.8	233.3	175.0
<u>Case of a cut-off at 280°C:</u>					
Temperature	(°C)	Tbase	Tbase-2.0	Tbase-2.5	Tbase-3.3
C1-C4 (gas) yield	(wt%)	19	10	9	8
C5-120°C (naphtha) yield	(wt%)	20	36	32	28
120-280°C (kerosene) yield	(wt%)	43	54	59	64
- Crystal disappearance point	(°C)	< -60	< -60	< -60	< -60
- Density at 15°C	(g/cm ³)	0.7464	0.7454	0.7450	0.7445
- Smoke point	(°C)	> 25	> 25	> 25	> 25
- Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10
- Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1
280°C+ (gas oil) yield	(wt%)	18	0	0	0
- Cold filter plugging point	(°C)	< -48	-	-	-
- Density at 15°C	(g/cm ³)	0.7865	-	-	-
- Cetane number	(-)	> 60	-	-	-
- Sulfur content	(ppm by weight of S)	< 10	-	-	-
- Nitrogen content	(ppm by weight of N)	< 1	-	-	-
<u>Case of a cut-off at 290°C:</u>					
Temperature	(°C)	Tbase	Tbase-2.8	Tbase-3.8	Tbase-4.7
C1-C4 (gas) yield	(wt%)	19	8	7	6
C5-120°C (naphtha) yield	(wt%)	20	31	26	22
120-290°C (kerosene) yield	(wt%)	47	61	66	72
- Crystal disappearance point	(°C)	< -60	< -60	< -60	< -60
- Density at 15°C	(g/cm ³)	0.7488	0.7476	0.7472	0.7470
- Smoke point	(°C)	> 25	> 25	> 25	> 25
- Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10
- Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1
290°C+ (gas oil) yield	(wt%)	14	0	0	0
- Cold filter plugging point	(°C)	-48	-	-	-
- Density at 15°C	(g/cm ³)	0.7877	-	-	-
- Cetane number	(-)	> 60	-	-	-
- Sulfur content	(ppm by weight of S)	< 10	-	-	-
- Nitrogen content	(ppm by weight of N)	< 1	-	-	-

Table 3: Yields and properties of the C1–C4, naphtha, kerosene and gas oil cuts for the various examples of the invention using the catalyst C2.

Non-compliant Example 9: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C3, producing a kerosene cut and a gas oil cut without recycling the gas oil cut.

5 Example 9 is not in accordance with the invention in that it illustrates a process not in accordance with the invention but using a C3 catalyst that is in accordance with the invention in the hydroconversion step c).

10 The hydroconversion catalyst C3 was evaluated in a pilot plant, representative in terms of implementation (reaction operating conditions, effluent separation quality), of the industrial process according to the invention. The various steps and unit operations of the pilot plant, which mimic the industrial implementation of the process according to the invention, are described hereinbelow.

15 The hydroconversion of the hydrocarbon liquid effluent obtained from Example 4 is performed in a reactor which is temperature-regulated so as to ensure isothermal functioning and with a fixed bed containing 50 ml of hydroconversion catalyst C3, the catalyst being preactivated by reduction. Given the nature of the catalyst C3 (noble metal), any injection of sulfur is to be avoided.

The catalyst C3 undergoes a reduction step under hydrogen performed at 5.1 MPa and 400°C (2-hour steady stage).

20 After reduction, the operating conditions of the unit are adjusted so as to perform the hydroconversion of the hydrocarbon liquid effluent under the following range of operating conditions:

- HSV (volume of feedstock/volume of catalyst/hour): 0.5 h^{-1} ,
- total working pressure: 5.1 MPa,
- hydrogen/feedstock ratio: 350 Nm^3 of hydrogen/ m^3 of feedstock.

25 The hydrogen used and entering the hydroconversion step is supplied by Air Products: it has a purity of greater than 99.999% by volume and is free of hydrogen sulfide.

On leaving the hydroconversion reactor, the reaction effluent is sent to a gas-liquid separation step performed using a flash vessel operated at a pressure comparable to that of the

hydroconversion reactor. The hydrogen-rich gas phase is sent to the unit's gas outlet. The liquid hydrocarbon phase is depressurized and sent to a stripper for stabilizing the liquid effluent; the gas phase collected at the top of the stripper is also sent to the unit's gas outlet.

At the unit's gas outlet, inline analysis by gas chromatography and a gas meter makes it possible to calculate the mass of light hydrocarbons produced (essentially hydrocarbons containing 1 to 5 carbon atoms) and present in the hydrogen stream. The liquid effluent is weighed separately, topped off at 120°C to remove the naphtha fraction; the 120°C+ liquid effluent is then reweighed and distilled into two sub-cuts: a 120-X°C kerosene cut and an X°C+ gas oil cut, in which X is a temperature that can be adjusted by the refiner as a function of their specific requirements and the targets they wish to achieve. A classic example of a value of X may be 280 or 290°C.

Temperature steady stages in the 250-400°C range were applied in order to determine the maximum yield of the 120-X°C kerosene cut. At low temperatures, hydroconversion is very low and does not allow for the production of a large amount of the 120-X°C kerosene cut. At high temperatures, hydroconversion is too high and leads to the formation of a large amount of gas and C5-120°C naphtha cut, to the detriment of the 120-X°C cut of interest.

The yield of C1-C4 gas is calculated as follows:

C1-C4 yield = [(mass of C1-C4 compounds) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of C5-120°C naphtha is calculated as follows:

C5-120°C yield (naphtha cut yield) = [(C5-120°C mass of the liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of 120-X°C kerosene is calculated as follows:

120-X°C yield (kerosene cut yield) = [(120-X°C mass of the liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

The yield of X°C+ gas oil is calculated as follows:

$X^{\circ}\text{C}+$ yield (gas oil cut yield) = $[(X^{\circ}\text{C}+ \text{mass of the liquid effluent}) / (\text{mass of feedstock})] \times 100$, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 4.

5 The various masses of gases and of liquid effluents correspond to the amounts of gas and liquid accumulated over a certain period of time, typically 24 hours, and the mass of feedstock corresponds to the amount of feedstock injected into the hydroconversion reactor over the same period of time.

At an HSV of 0.5 h^{-1} , a total pressure of 5.1 MPa and an $\text{H}_2/\text{feedstock}$ ratio of $350 \text{ Nm}^3/\text{m}^3$, the incremental variation in temperature between 250 and 400°C made it possible to determine the optimum temperature at which the yield of the $120\text{--}X^{\circ}\text{C}$ kerosene cut is maximal.

10 At a temperature $T_{\text{base}} - 7^{\circ}\text{C}$, for a $120\text{--}280^{\circ}\text{C}$ kerosene cut, the structure-yield is as follows:

- C1-C4 gas yield: 19 wt%
- C5- 120°C naphtha cut yield: 20 wt%
- $120\text{--}280^{\circ}\text{C}$ kerosene cut yield: 44 wt%
- $280^{\circ}\text{C}+$ gas oil cut yield: 17 wt%

15 At a temperature $T_{\text{base}} - 7^{\circ}\text{C}$, for a $120\text{--}290^{\circ}\text{C}$ kerosene cut, the structure-yield is as follows:

- C1-C4 gas yield: 19 wt%
- C5- 120°C naphtha cut yield: 19 wt%
- $120\text{--}290^{\circ}\text{C}$ kerosene cut yield: 47 wt%
- $290^{\circ}\text{C}+$ gas oil cut yield: 15 wt%

20 In both cases ($X = 280$ and 290°C), the features obtained for the kerosene cut of interest and the gas oil cut, along with the associated operating conditions, are reported in the Summary Table 4. In both cases ($X = 280$ and 290°C), the $120\text{--}X^{\circ}\text{C}$ kerosene cut has a crystal disappearance point below -60°C and a smoke point above 25 mm.

Compliant Example 10: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C3, producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 25 vol%.

- 5 Example 10 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C3 in accordance with the invention. The combination of the process and catalyst C3 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

The use of a hydroconversion reactor simulator enabled calculation of the impact of recycling on cut yields as a function of the degree of recycling selected by the refiner.

- 10 The degree of recycling is defined as the ratio between the volume of recycled X°C+ gas oil cut in the hydroisomerization reactor and the volume of fresh feedstock (obtained from Example 4). With a degree of recycling of 25 vol%, the HSV, which was 0.5 h⁻¹ in non-compliant Example 9, thus increases to 0.63 h⁻¹ as it integrates 25 vol% of X°C+ cut in addition to the fresh feedstock. Similarly, in order to maintain a constant hydrogen flow rate at the inlet of the
- 15 hydroisomerization reactor, the H₂/feedstock ratio changes from 350 Nm³/m³ in the non-compliant Example 9 to 278 Nm³/m³ in the case of 25 vol% recycling. The temperature is then adjusted to afford, under these operating conditions, 25 vol% of the X°C+ cut, which will be recycled into the hydroisomerization reactor.

- In the case of a cut-off at 280°C, the temperature required to produce and recycle 25 vol% of
- 20 the 280°C+ cut is equal to the base temperature of non-compliant Example 5 minus 10°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.63 h⁻¹
- H₂/(fresh + recycled 280°C+ feedstock) ratio: 278 Nm³/m³
- 25 • Temperature: T_{base} – 10°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 10 wt%

- C5-120°C naphtha cut yield: 36 wt%
- 120-280°C kerosene cut yield: 54 wt%

5 The operation consisting in recycling the 280°C+ cut with a degree of recycling of 25 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 44% by weight (non-compliant Example 9) to 54% by weight, representing an 10% by weight gain in kerosene cut yield. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

In the case of a cut-off at 290°C, the temperature required to produce and recycle 25 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 5 minus 9.3°C.

10 The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.63 h⁻¹
- H₂/(fresh + recycled 290°C+ feedstock) ratio: 278 Nm³/m³
- Temperature: T_{base} – 9.3°C

15 Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 7 wt%
- C5-120°C naphtha cut yield: 30 wt%
- 120-290°C kerosene cut yield: 63 wt%

20 The operation consisting in recycling the 290°C+ cut with a degree of recycling of 25 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 9) to 63% by weight, representing an 16% by weight gain in kerosene cut yield. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

Compliant Example 11: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C3, producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 50 vol%.

- 5 Example 11 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C3 in accordance with the invention. The combination of the process and catalyst C3 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

Example 11 is identical to Example 10, but uses a degree of recycling of 50 vol% instead of 25 vol%.

- 10 In the case of a cut-off at 280°C, the temperature required to produce and recycle 50 vol% of the 280°C+ cut is equal to the base temperature of non-compliant Example 5 minus 10.5°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.75 h⁻¹
- 15 • H₂/(fresh + recycled 280°C+ feedstock) ratio: 233 Nm³/m³
- Temperature: T_{base} – 10.5°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 10 wt%
- 20 • C5-120°C naphtha cut yield: 32 wt%
- 120-280°C kerosene cut yield: 58 wt%

- The operation consisting in recycling the 280°C+ cut with a degree of recycling of 50 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 44% by weight (non-compliant Example 9) to 58% by weight, representing an 14% by weight gain in
- 25 kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in

120–280°C yield is 4% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

5 In the case of a cut-off at 290°C, the temperature required to produce and recycle 50 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 5 minus 10.8°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- Overall HSV: 0.75 h⁻¹
- H₂/(fresh + recycled 290°C+ feedstock) ratio: 233 Nm³/m³
- 10 • Temperature: T_{base} – 10.8°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- C1-C4 gas yield: 7 wt%
- C5-120°C naphtha cut yield: 26 wt%
- 15 • 120-290°C kerosene cut yield: 67 wt%

The operation consisting in recycling the 290°C+ cut with a degree of recycling of 50 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 9) to 67% by weight, representing an 20% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in
20 120–290°C yield is 4% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

Compliant Example 12: Hydroconversion of the liquid hydrocarbon effluent obtained from Example 4 according to a process using the hydroconversion catalyst C3, producing a kerosene cut and a gas oil cut which is entirely recycled into the isomerization step (c) with a degree of recycling of 100 vol%.
25

Example 12 is in accordance with the invention insofar as it combines a process in accordance with the invention with catalyst C3 in accordance with the invention. The combination of the process and catalyst C3 maximizes the yield of the cut of interest, namely 120–X°C kerosene.

5 Example 12 is identical to Examples 10 and 11, but uses a degree of recycling of 100 vol% instead of 25 vol% and 50 vol%, respectively.

In the case of a cut-off at 280°C, the temperature required to produce and recycle 100 vol% of the 280°C+ cut is equal to the base temperature of non-compliant Example 9 minus 11.2°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- 10 • Overall HSV: 1.0 h⁻¹
- H₂/(fresh + recycled 280°C+ feedstock) ratio: 175 Nm³/m³
- Temperature: T_{base} – 11.2°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- 15 • C1-C4 gas yield: 8 wt%
- C5-120°C naphtha cut yield: 29 wt%
- 120-280°C kerosene cut yield: 63 wt%

The operation consisting in recycling the 280°C+ cut with a degree of recycling of 100 vol% thus made it possible to increase the yield of the 120-280°C kerosene cut of interest from 44% by weight (non-compliant Example 9) to 63% by weight, representing an 19% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–280°C yield is 9% by weight. Relative to the case where the degree of recycling is 50 vol%, the gain in 120–280°C yield is 5% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

In the case of a cut-off at 290°C, the temperature required to produce and recycle 100 vol% of the 290°C+ cut is equal to the base temperature of non-compliant Example 9 minus 11.6°C. The conditions at the hydroconversion reactor terminals are then as follows:

- Total pressure: 5.1 MPa
- 5 • Overall HSV: 1.0 h⁻¹
- H₂/(fresh + recycled 290°C+ feedstock) ratio: 175 Nm³/m³
- Temperature: T_{base} – 11.6°C

Under these conditions, the yields obtained at the terminals of the hydroconversion section (hydroconversion reactor + distillation + recycling) are as follows:

- 10 • C1-C4 gas yield: 7 wt%
- C5-120°C naphtha cut yield: 23 wt%
- 120-290°C kerosene cut yield: 70 wt%

The operation consisting in recycling the 290°C+ cut with a degree of recycling of 100 vol% thus made it possible to increase the yield of the 120-290°C kerosene cut of interest from 47% by weight (non-compliant Example 9) to 70% by weight, representing an 23% by weight gain in kerosene cut yield. Relative to the case where the degree of recycling is 25 vol%, the gain in 120–290°C yield is 7% by weight. Relative to the case where the degree of recycling is 50 vol%, the gain in 120–290°C yield is 3% by weight. The properties of the kerosene cut are only very minimally affected by the introduction of this recycle, as shown in Table 4.

Table 4

		Example 9 (not compliant)	Example 10 (compliant)	Example 11 (compliant)	Example 12 (compliant)
Degree of recycling	(vol%)	0	25	50	100
Total pressure	(MPa)	5.1	5.1	5.1	5.1
HSV (fresh feedstock)	(h ⁻¹)	0.5	0.5	0.5	0.5
HSV (fresh + recycled feedstock)	(h⁻¹)	-	0.63	0.75	1.00
H ₂ /fresh feedstock ratio	(Nm ³ /m ³)	350.0	350.0	350.0	350.0
H₂/(fresh + recycled feedstock) ratio	(Nm³/m³)	-	277.8	233.3	175.0
<u>Case of a cut-off at 280°C:</u>					
Temperature	(°C)	Tbase-7.1	Tbase-10.0	Tbase-10.5	Tbase-11.2
C1-C4 (gas) yield	(wt%)	19	10	10	8
C5-120°C (naphtha) yield	(wt%)	20	36	32	29
120-280°C (kerosene) yield	(wt%)	44	54	58	63
- Crystal disappearance point	(°C)	< -60	< -60	< -60	< -60
- Density at 15°C	(g/cm ³)	0.7464	0.7456	0.7451	0.7445
- Smoke point	(°C)	> 25	> 25	> 25	> 25
- Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10
- Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1
280°C+ (gas oil) yield	(wt%)	17	0	0	0
- Cold filter plugging point	(°C)	< -48	-	-	-
- Density at 15°C	(g/cm ³)	0.7863	-	-	-
- Cetane number	(-)	> 60	-	-	-
- Sulfur content	(ppm by weight of S)	< 10	-	-	-
- Nitrogen content	(ppm by weight of N)	< 1	-	-	-
<u>Case of a cut-off at 290°C:</u>					
Temperature	(°C)	Tbase-7.7	Tbase-9.3	Tbase-10.8	Tbase-11.6
C1-C4 (gas) yield	(wt%)	19	7	7	7
C5-120°C (naphtha) yield	(wt%)	19	30	26	23
120-290°C (kerosene) yield	(wt%)	47	63	67	70
- Crystal disappearance point	(°C)	< -60	< -60	< -60	< -60
- Density at 15°C	(g/cm ³)	0.7486	0.7474	0.7471	0.7471
- Smoke point	(°C)	> 25	> 25	> 25	> 25
- Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10
- Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1
290°C+ (gas oil) yield	(wt%)	15	0	0	0
- Cold filter plugging point	(°C)	-48	-	-	-
- Density at 15°C	(g/cm ³)	0.7875	-	-	-
- Cetane number	(-)	> 60	-	-	-
- Sulfur content	(ppm by weight of S)	< 10	-	-	-
- Nitrogen content	(ppm by weight of N)	< 1	-	-	-

Table 4: Yields and properties of the C1–C4, naphtha, kerosene and gas oil cuts for the various examples of the invention using the catalyst C3.

CLAIMS

1. Process for treating a feedstock from a renewable source to produce a kerosene cut, said process comprising at least the following steps and preferably consisting of the following steps:

- 5 a) a step of hydrotreating said feedstock in the presence of a catalyst in a fixed bed, said catalyst comprising a hydrogenating function and an oxide support, at a temperature of between 200 and 450°C, at a pressure of between 1 MPa and 10 MPa, at an hourly space velocity of between 0.1 h⁻¹ and 10 h⁻¹ and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 2000 Nm³ of hydrogen/m³ of feedstock,
- 10 b) a step of separating at least a portion of the effluent obtained from step a) into at least a light gaseous fraction, at least a hydrocarbon liquid effluent, and at least an aqueous liquid effluent,
- 15 c) a step of hydroconversion of at least a portion of the hydrocarbon liquid effluent obtained from step b) in the presence of at least one difunctional hydroconversion catalyst in a fixed bed, said catalyst comprising a hydrogenating phase comprising at least one noble metal from group VIII of the Periodic Table chosen from platinum and palladium, and a support comprising at least one zeolite chosen from zeolites with the structure code MTW and the zeolite IZM-2, either alone or as a mixture, and at least one binder, said hydroconversion step being performed at a temperature of between 250°C and 500°C, at a pressure of between 1 MPa and 10 MPa, at an hourly space velocity of between 0.1 and 10 h⁻¹ and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 70 and 1000 Nm³/m³ of feedstock,
- 20 d) a step of separating at least a portion of the effluent obtained from step c) making it possible to separate at least a gaseous fraction and at least a hydrocarbon liquid effluent,
- 25 e) a step of fractionating the hydrocarbon effluent obtained from step d) into at least a kerosene cut and at least a heavy cut with an initial boiling point of between 250 and 300°C,

Said process comprises a step of recycling all or a portion of said heavy cut with an initial boiling point of between 250 and 300°C, obtained from said fractionation step e), into said hydroconversion step c).

- 30 2. Process according to Claim 1, in which the feedstock derived from renewable sources is chosen from oils and fats of plant or animal origin, used cooking oils, oils of microbial origin,

fish oils, long-chain paraffins derived from the Fischer-Tropsch process, whether crude or pretreated, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters.

3. Process according to either of Claims 1 and 2, in which, in step a), the feedstock is placed
5 in contact with a catalyst in a fixed bed at a temperature of between 220 and 350°C, at a pressure of between 1 MPa and 6 MPa, and at an hourly space velocity of between 0.1 h⁻¹ and 10 h⁻¹, and in the presence of a total amount of hydrogen mixed with the feedstock such that the hydrogen/feedstock ratio is between 150 and 1000 Nm³ of hydrogen/m³ of feedstock.

4. Process according to one of Claims 1 to 3, in which the hydrotreating catalyst used in step
10 a) comprising a hydro-dehydrogenating function comprising at least one metal from group VIII and/or from group VIB, taken alone or as a mixture, and a support chosen from the group formed by alumina, silica, silica-aluminas, magnesia, clays and mixtures of at least two of these minerals.

5. Process according to one of Claims 1 to 4, in which the hydroconversion step c) operates
15 at a temperature of between 250°C and 450°C and very preferably between 250°C and 400°C, at a pressure of between 2 MPa and 10 MPa and very preferably of between 3 MPa and 9 MPa, at an hourly space velocity advantageously 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/feedstock volume ratio is advantageously between 100 and 1000 normal m³ of hydrogen per m³ of feedstock and
20 preferably between 150 and 1000 normal m³ of hydrogen per m³ of feedstock.

6. Process according to one of Claims 1 to 5, in which the Group VIII metal of the catalyst used in step c) is platinum.

7. Process according to one of Claims 1 to 6, in which the zeolite of structure code MTW used in the catalyst of step c) is ZSM-12.

25 8. Process according to one of Claims 1 to 7, in which the catalyst used in step c) comprises a hydrogenating phase comprising platinum and a support comprising an IZM-2 zeolite alone and an alumina binder.

9. Process according to one of Claims 1 to 7, in which the catalyst used in step c) comprises a hydrogenating phase comprising platinum and a support comprising an ZSM-12 zeolite alone
30 and an alumina binder.

10. Process according to one of Claims 1 to 9, in which the fractionation step e) is performed in a distillation column or in a step of steam stripping followed by a distillation column.

5 11. Process according to one of Claims 1 to 10, in which the heavy cut with an initial boiling point of between 250 and 300°C obtained from the fractionation step e) is mixed with all or a portion of the liquid hydrocarbon effluent obtained from step b) upstream of the hydroconversion reactor, and this mixture is then injected into the first catalytic bed of step c) in the case where said hydroconversion step comprises several catalytic beds.

10 12. Process according to one of Claims 1 to 10, in which the heavy cut with an initial boiling point of between 250 and 300°C obtained from the fractionation step e) is injected into an intermediate bed of the hydroconversion reactor in the case where said hydroconversion step comprises several catalytic beds.

13. Process according to one of Claims 1 to 12, in which the process does not comprise a hydrocracking step downstream of step c) of hydroconversion of part or all of the effluent obtained from step c).