

METHOD FOR PRODUCING RENEWABLE KEROSENE COMPRISING TWO HYDROCONVERSION STEPS AND USING A SPECIFIC CATALYST IN THE SECOND HYDROCONVERSION STEP

Field of the invention

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, pine oils, 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, 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.

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 the hydrotreating of feedstocks derived from renewable sources are already well known and are described in numerous patents. Mention may be made, for example, of the 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 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 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 VIB 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 VIB 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 (H_2S) 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 H_2S in the reaction medium becomes high (C. Marcilly, *Catalyse acido-basique [Acid-base catalysis]*, volume 2, 2003, published by Technip).

Patent application 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. In the case of a two-step process, 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 silica-alumina, 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.

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. The hydrocracking catalyst comprises a Group VIII metal or a Group VIB metal on an amorphous silica-alumina support or on a zeolite-based support. In the case where the hydrocracking catalyst is zeolite-based, the active phase comprises a Group VIII metal, optionally in combination with a Group VIB metal. The zeolites are preferably chosen from mordenite, stilbite, heulandite, ferrierite, dachiardite, chabazite, erionite and faujasite, and preferably zeolites B, X, Y and L, preferably zeolite Y. 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.

Figure 1 of patent application US2022/0127537 describes a process for hydrotreating a plant oil followed by separation of the hydrotreated effluent in a hot separator to recover a liquid effluent which is hydroisomerized. The hydroisomerized effluent is then fractionated in a distillation column to produce a kerosene cut, a light gas oil cut and a heavy gas oil cut comprising n-paraffins. Said heavy gas oil cut is then sent to a hydrocracking step to convert the heavy gas oil cut into kerosene. The hydrocracked effluent may be sent to the hydroisomerization step at different points: either directly upstream of the hydroisomerization reactor, i.e. without prior gas/liquid separation, or after prior separation of the effluent by a flash vessel producing a gas fraction and a liquid fraction, the liquid fraction of the hydrocracked effluent being directed either upstream of the hydroisomerization reactor or downstream. According to an optional mode, said process shown in Figure 1 thus comprises a step of hydrocracking the heavy gas oil cut followed by its recycling into the hydroisomerization step. The present invention does not comprise any recycling of the effluent from the second hydroconversion step upstream of the first hydroconversion step.

Figure 2 of patent application US2022/0127537 describes a process for treating a plant oil in which the hydrocracking and hydroisomerization steps are performed successively in the same reactor. The process comprises a step of hydrotreating a plant oil followed by separation of the hydrotreated effluent in a hot separator to recover a first liquid hydrotreated effluent, which is then hydroisomerized in a reactor comprising a bed of hydroisomerization catalyst, this being positioned downstream of a bed of hydrocracking catalyst. The hydrocracking catalyst, positioned upstream of the hydroisomerization catalyst, is fed with the heavy gas oil fraction

recycled from the step of fractionating the hydroisomerized effluent. The hydrotreated liquid effluent is thus sent between the hydrocracking catalyst bed and the hydroisomerization catalyst bed. The hydroisomerized effluent is then fractionated in a distillation column to produce a kerosene cut, a light gas oil cut and a heavy gas oil cut comprising n-paraffins. Said heavy gas oil cut is then sent to the catalytic bed containing the hydrocracking catalyst located upstream of the hydroisomerization catalyst to convert the heavy gas oil cut into kerosene. The hydrocracked effluent can be sent to the hydroisomerization step. Unlike the present invention, said process shown in Figure 1 comprises a step of hydrocracking the heavy gas oil cut prior to its recycling into the hydroisomerization step, and the hydrocracking and hydroisomerization reactions are performed successively in the same reactor.

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. 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.

Figure 3 of patent application US2022/0127537 describes a process for treating a plant oil in which the hydrotreating and hydroisomerization steps are performed in the same reactor, the catalytic bed comprising the hydrotreating catalyst being located upstream of the catalytic bed comprising the hydroisomerization catalyst. The process comprises a step of hydrotreating a plant oil followed by a step of hydroisomerization of the hydrotreated effluent in a reactor comprising a bed of hydroisomerization catalyst downstream of a bed of hydrotreating catalyst. The hydroisomerized effluent is then sent to a hydrocracking step, in admixture with a heavy gas oil fraction produced by fractionating the hydrocracked effluent in a distillation column. Fractionation produces a kerosene cut, a light gas oil cut and a heavy gas oil cut comprising n-paraffins. Said heavy gas oil cut is then recycled into the hydrocracking step. In contrast to the present invention, said process according to Figure 3 involves recycling the heavy gas oil

cut as feedstock for the hydrocracking step, in admixture with the effluent from the hydroisomerization step performed in the same reactor as the hydrotreatment. In contrast to the present invention, the hydrotreating and hydroisomerization steps are performed successively in the same reactor.

Figure 4 of patent application US2022/0127537 describes a process for treating a plant oil in which the hydroisomerization and hydrocracking steps are performed in the same reactor as shown in Figure 2. The process comprises a step of hydrotreating a plant oil, followed by separation of the hydrotreated effluent in a hot separator and then in a stripping column to recover a light gas oil cut (C_{17-}) and a heavy gas oil cut (C_{18+}). The heavy gas oil cut is sent to a hydrocracking step in a reactor comprising a hydrocracking catalyst bed upstream of a hydroisomerization catalyst bed, and the light gas oil cut is sent to the hydroisomerization catalyst bed present in the same reactor. The effluent comprising kerosene from said reactor is sent to a stripping column to produce a kerosene cut which is then recycled, only partly, into the catalytic bed comprising the hydroisomerization catalyst. In contrast to the present invention, said process shown in Figure 4 comprises a step of separating the hydrotreated effluent into light and heavy gas oil cuts before sending said light and heavy gas oil cuts respectively to the hydroisomerization and hydrocracking catalyst.

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 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. Unlike the process according to the invention, the heavy fraction of the hydroisomerized effluent is not sent to a second hydroisomerization step that is different from the first.

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:

- 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),
- d) a step of hydroisomerizing at least a portion of the liquid effluent from step c), 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 EUO structure type or chosen from the zeolites ZSM-48, ZBM-30, IZM-1, COK-7, EU-2 and EU-11, alone or as a mixture,
- e) a step of separating the effluent from d) 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). Unlike the process of the invention, the heavy cut of the hydroisomerized effluent is not sent to a second hydroisomerization step separate from the first.

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 a separate hydrodearomatization step comprising a hydroisomerization catalyst bed and a hydrodearomatization catalyst bed so as to make it compatible with the product specifications in force, notably by reducing the aromatic content of the kerosene-type cut. In contrast to the process according to the invention, the kerosene cut is directed towards a second hydroconversion step (rather than the gas oil cut), whilst the gas oil cut is recycled into the first step of hydrotreating followed by hydrocracking.

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 from the first step and the production of an isoparaffin-rich effluent. This effluent is sent to a separation and fractionation step that

allows the production of a cut boiling in the gasoline range, a cut boiling in the kerosene range and, optionally, a cut boiling in the gas oil range. The cut with a boiling point greater than or equal to 200°C, or possibly the cut boiling in the gas oil range, is then specifically recycled into a hydroisomerization step, which may be identical to or different from the first hydroisomerization step, for re-isomerization. In the event that the second hydroisomerization step is different from the first, the effluent from the second hydroisomerization step is returned to the separation and fractionation step as described in Figure 3. 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. In the case where the second hydroisomerization step is separate from the first, the hydroisomerization catalysts may be identical to or different from each other in the two hydroisomerization steps. Preferably, in the first hydroisomerization, the catalyst may be selected so as to be less cracking-promoting, and in the second hydroisomerization, the second catalyst may be chosen so as to promote cracking reactions.

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) generated 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 fraction. Recycling of the n-paraffins separated from the molecular sieve back into the hydroisomerization/hydrocracking step is described. This involves selective recycling of a stream based on its chemical family rather than its distillation range. Recycling of a part of the heavy distillate fraction is also described. 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.

US patent application 2017/0022424 A1 describes a process for hydrotreating renewable feedstocks that allows the production of an n-paraffinic hydrocarbon fraction. 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 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 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, 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. Unlike the process according to the invention, the heavy cut of the effluent obtained from the hydroisomerization step is not sent to a second hydroisomerization step separate from the first.

Patent application US 2011/0105812 A1 describes a process for improving the cold properties of a gas oil 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 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 the composition 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, 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. Unlike the process according to the invention, the recycle stream of the effluent from the hydroisomerization step is not sent to a second hydroisomerization step separate from the first.

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 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 comprising a zeolite chosen from SAPO-11, SAPO-41, ZSM-22, ZSM-23 or ferrierite. The hydroisomerized effluent obtained is then fractionated so as to obtain said composition. Unlike the process according to the invention, no cut resulting from the fractionation of the hydroisomerized effluent is sent to a second hydroisomerization step separate from the first.

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, 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 generally has an initial cut point of between 120°C and 180°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

In an endeavour 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 difunctional catalyst, comprising a noble metal (Pt)-based hydrogenation/dehydrogenation phase and a support comprising silica-alumina or comprising one or more specific zeolites chosen from zeolites of structure codes MTW and IZM-2, combined with the implementation of the specific process including two steps of hydroconversion, was of great interest.

Advantageously, the process according to the invention includes three conversion steps, including a step of hydrodeoxygenation of renewable feedstocks producing an effluent rich in linear paraffins and two separate steps of hydroconversion of the paraffinic effluent (hydroisomerization and/or hydrocracking reactions), the second hydroconversion step utilising a specific catalyst.

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, comprising at least the following steps and preferably including:

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 Nm^3 of hydrogen/ m^3 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 first 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 containing at least one metal from group VIII and/or at least one metal from group VIB of the Periodic Table, an acidic support comprising a silica-alumina or one or more zeolites and optionally at least one binder, said first 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 $1000 \text{ Nm}^3/\text{m}^3$ of feedstock,

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,

e) a step of fractionating the hydrocarbon liquid effluent obtained from step d) into at least one light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C , and a heavy cut with an initial boiling point of between 250 and 300°C , or a step of stabilizing the hydrocarbon liquid effluent obtained from step d) to enable the separation of at least a light gaseous fraction, a naphtha hydrocarbon cut and a heavy cut with an initial boiling point of between 100 and 180°C ,

f) a second step of hydroconversion, separate from step c), of all or part of the heavy cut with an initial boiling point of between 250 and 300°C obtained from step e) in the case where step e) is a fractionation step, or of all or part of the heavy cut with an initial boiling point of between 100 and 180°C obtained from step e) in the case where step e) is a stabilization step, said second hydroconversion step being performed in a fixed bed in the presence of a difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum, and a support comprising a silica-alumina, or a difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum and a support comprising a zeolite chosen from zeolites of structure codes MTW and IZM-2, alone or as a mixture, said hydroconversion step being performed at a temperature of between 250 and 500°C , at a pressure of between 1 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 processed in said step f), to produce a hydroconverted effluent,

g) a step of separating at least a portion of the hydroconverted effluent obtained from step f) making it possible to separate at least a gaseous fraction and at least a hydrocarbon liquid effluent,

h) a step of fractionating the hydrocarbon liquid effluent obtained from step g) into at least one light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and a heavy cut with an initial boiling point of between 250 and 300°C, or a step of stabilizing the hydrocarbon liquid effluent obtained from step g) to separate at least one light gaseous fraction, a naphtha hydrocarbon cut and a kerosene cut with an initial boiling point of between 100 and 180°C, said steps d) and g) and e) and h) being possibly performed in the same equipment or in separate equipment.

An advantage of the present invention is that it provides a process for treating a feedstock from a renewable source to produce one or more kerosene cuts, using a specific catalyst in a second step of hydroconversion of all or part of the heavy cut from the first hydroconversion step, making it possible, whilst meeting the targeted cold properties, to maximize the overall yield of said kerosene cut(s) of interest produced in said process.

Another advantage of the present invention is that it provides the flexibility to co-produce a gas oil cut at the outlet of the first hydroconversion step, said gas oil cut with an initial boiling point of between 100 and 180°C in the case where step e) is a stabilization, or between 250 and 300°C in the case where step e) is a fractionation, with a kerosene cut at the outlet of the second hydroconversion step in the case where step e) is a stabilization, or two kerosene cuts, one at the outlet of the first hydroconversion step and one at the outlet of the second hydroconversion step, in the case where step e) is a fractionation.

Another advantage of the present invention is that it enables the processing of heavier feedstocks from renewable sources within said process by using a specific catalyst that promotes the cracking of long-chain paraffins in the first hydroconversion step, followed by a second hydroconversion step that is more selective for hydroisomerization using another specific catalyst.

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, pine 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

Step a)

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 (MoO₃), preferably from 5% to 25% by weight, the percentages being expressed as weight percentages relative to the total mass of the catalyst.

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 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 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, 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 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 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.

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

Step b)

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 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 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 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 high-pressure and/or low-pressure stripping.

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 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.

Step c)

In accordance with the invention, the process comprises a first step c) of hydroconversion of at least a portion and preferably all of the hydrocarbon liquid effluent from step b) of the process in the presence of a difunctional hydroconversion catalyst in a fixed bed, said catalyst comprising a hydrogenating phase comprising at least one metal from group VIII and/or at least one metal from group VIB of the Periodic Table alone or as a mixture, an acidic support comprising a silica-alumina or one or more zeolites and optionally at least one binder, said first 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 first hydroconversion step c) are adjusted to promote the hydroisomerization or hydrocracking reactions as need be. Preferably, the hydroconversion step c) 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 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 Nm³/m³ of feedstock and preferably between 150 and 1000 Nm³/m³ of feedstock.

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

In accordance with the invention, the catalyst used in step c) is a difunctional catalyst comprising a hydrogenating phase comprising at least one Group VIII metal and/or at least one Group VIB metal of the Periodic Table, alone or as a mixture, an acidic support comprising silica-alumina or one or more zeolites, and optionally at least one binder.

The hydro-dehydrogenating function

The Group VIII metals are advantageously chosen from iron, cobalt, nickel, platinum and palladium, taken alone or as a mixture, and preferably from nickel, cobalt, platinum and palladium.

The group VIB metals are chosen from tungsten and molybdenum, taken alone or as a mixture. In the case where the Group VIII metals are chosen from non-noble metals, the following metal combinations are preferred: nickel-molybdenum, cobalt-molybdenum, nickel-tungsten, cobalt-

tungsten, and very preferably: nickel-molybdenum, nickel-tungsten. It is also possible to use combinations of three metals, for instance nickel-cobalt-molybdenum.

The content of non-noble metal of group VIII in the catalyst is advantageously between 0.5% and 8% by weight of oxide, relative to the total weight of said catalyst, preferably between 0.5% and 6% by weight of oxide and very preferably between 1% and 4% by weight of oxide.

The content in the catalyst of group VIB metal is advantageously between 1% and 30% by weight of oxide relative to the total weight of said catalyst, preferably between 2% and 25% by weight of oxide and very preferably between 5% and 20% by weight of oxide, and even more preferably between 5% and 16% by weight of oxide.

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% and 2% by weight, preferably between 0.05% 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 the at least one group VIII noble 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.

In the case where the Group VIII metals are chosen from noble metals, the content of Group VIII noble metal, and preferably the platinum content, in the catalyst used in step c) is between 0.01% and 4% by weight, preferably between 0.05% and 2% by weight, relative to the total weight of said catalyst.

In a preferred embodiment, the catalyst comprises at least one Group VIII metal, preferably nickel, and at least one Group VIB metal, preferably tungsten, preferably active in their sulfide form.

In another embodiment, the catalyst comprises at least one Group VIII metal, preferably a Group VIII noble metal chosen from platinum and palladium. Preferably, the Group VIII metal of the catalyst used in step c) is platinum, preferably active in its reduced form.

The metal function is advantageously introduced into the catalyst via any method known to those skilled in the art, for instance co-kneading, dry impregnation or impregnation by exchange.

The acid function

In accordance with the invention, the catalyst used in step c) comprises at least one acidic support comprising alumina-silica or one or more zeolites.

In the case where the acidic support is composed of one or more zeolites, said zeolites are chosen from zeolites of the structure types FAU, *BEA, ISV, IWR, IWW, MEI, UWY, taken alone or as a mixture, and preferably chosen from zeolites of the structure types FAU and *BEA, taken alone or as a mixture. In a preferred embodiment, the zeolite is chosen from zeolite Y and zeolite beta, taken alone or as a mixture, and preferably the zeolite is zeolite Y and very preferably dealuminated zeolite USY.

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

Preferably, the acidic support of the catalyst used in step c) comprises, and is preferably composed of, silica-alumina.

The binder

Optionally, said catalyst support used in step c) may also comprise a binder. Preferably, said support comprises a binder when said support comprises a zeolite. Said binder is advantageously chosen from silica (SiO_2), alumina (Al_2O_3), clays, titanium oxide (TiO_2), boron oxide (B_2O_3) and zirconia (ZrO_2), taken alone or as a mixture. Preferably, said binder is chosen from silica and alumina and even more preferably said binder is alumina in all its forms known to those skilled in art, for instance γ -alumina.

A preferred hydroconversion catalyst used in the first step c) of hydroconversion includes nickel and tungsten, and a silica-alumina as acidic support, without any other binder. In this case, said catalyst is in sulfide form.

A preferred catalyst comprises a silica-alumina and at least tungsten and/or molybdenum and at least nickel and/or cobalt, said catalyst being a sulfide. The content of tungsten and/or molybdenum is advantageously, as oxide equivalent, between 5% and 50% by weight relative to the finished catalyst, preferably between 10% and 40% by weight and very preferably between 15% and 35% by weight, and the nickel and/or cobalt content of said catalyst is advantageously, as oxide equivalent, between 0.5% and 10% by weight relative to the finished catalyst, preferably between 1% and 8% by weight and very preferably between 1.5% and 6% by weight. The content of elements is perfectly measured by means of X-ray fluorescence.

A preferred catalyst used in the first hydroconversion step c) comprises a particular silica-alumina, said silica-alumina having:

- alumina and silica with a mass content of silica (SiO_2) of greater than 5% by weight and less than or equal to 95% by weight, preferably between 10% and 80% by weight, preferably a silica content of greater than 20% by weight and less than 80% by weight and even more preferably greater than 25% by weight and less than 75% by weight; the silica content is advantageously between 10% and 50% by weight,
- a BET specific surface area of from $100 \text{ m}^2/\text{g}$ to $500 \text{ m}^2/\text{g}$, preferably between $200 \text{ m}^2/\text{g}$ and $450 \text{ m}^2/\text{g}$ and very preferably between $200 \text{ m}^2/\text{g}$ and $300 \text{ m}^2/\text{g}$,
- a mean diameter of the mesopores, measured by mercury porosimetry, of between 3 nm and 12 nm, preferably of between 3 nm and 11 nm and very preferably between 4 nm and 10.5 nm,
- a total pore volume, measured by mercury porosimetry, of between 0.4 and 1.2 ml/g, preferably between 0.4 and 1.0 ml/g and very preferably between 0.4 and 0.8 ml/g,
- a volume of macropores, the diameter of which is greater than 50 nm, of less than 0.002 ml/g.

The mean diameter of the mesopores is defined as being the diameter corresponding to the cancellation of the curve derived from the mercury intrusion volume obtained from the mercury porosity curve for pore diameters of between 2 and 50 nm.

Preferably, the coefficient of distribution of the metals of said preferred catalyst is greater than 0.1, preferably greater than 0.2 and very preferably greater than 0.4. The coefficient of distribution represents the distribution of the metal inside the catalyst grain. The coefficient of distribution of the metals may be measured with a Castaing microprobe.

Another preferred hydroconversion catalyst used in the first step c) of hydroconversion includes at least one noble metal, said noble metal being platinum, and a silica-alumina as acidic support, without any other binder. In this case, said catalyst is in reduced form.

In this case, the silica content of the silica/alumina, expressed as a weight percentage, is advantageously between 1% and 95%, advantageously between 5% and 95%, preferably between 10% and 80%, very preferably between 20% and 70% and even more preferably between 22% and 45%. This silica content is perfectly measured by means of X-ray fluorescence.

A preferred hydroconversion catalyst used in the first hydroconversion step c) comprises a particular silica-alumina. Preferably, said catalyst comprises from 0.05% to 10% by weight, preferably between 0.1% and 5% by weight, of at least one noble metal from Group VIII, preferably chosen from platinum and palladium (in a preferred manner platinum), deposited on the silica-alumina, without any other binder, containing an amount of silica (SiO_2) of between 1% and 95%, expressed as weight percentage, preferably between 5% and 95%, in a preferred manner between 10% and 80%, in a very preferred manner between 20% and 70% and in an even more preferred manner between 22% and 45%, said catalyst having:

- a BET specific surface area of from $100 \text{ m}^2/\text{g}$ to $500 \text{ m}^2/\text{g}$, preferably between $200 \text{ m}^2/\text{g}$ and $450 \text{ m}^2/\text{g}$ and very preferably between $200 \text{ m}^2/\text{g}$ and $300 \text{ m}^2/\text{g}$,
- a mean diameter of the mesopores, measured by mercury porosimetry, of between 4 nm and 12 nm, preferably of between 4 nm and 11 nm and very preferably between 5 nm and 11 nm,
- a total pore volume, measured by mercury porosimetry, of between 0.2 and 1.2 ml/g, preferably between 0.3 and 1.0 ml/g and very preferably between 0.3 and 0.9 ml/g,
- a volume of macropores measured by mercury porosimetry, the diameter of which is greater than 50 nm, of less than 0.02 ml/g,
- a content of alkali metal or alkaline-earth metal compounds of less than 300 ppm by weight and preferably less than 200 ppm by weight.

The mean diameter of the mesopores is defined as being the diameter corresponding to the cancellation of the curve derived from the mercury intrusion volume obtained by mercury porosimetry for pore diameters of between 3.7 and 50 nm.

Preferably, the dispersion of the noble metal of said preferred catalyst is advantageously between 5% and 100%, preferably between 5% and 90% and very preferably between 10% and 90%. The dispersion, representing the fraction of metal accessible to the reagent relative

to the total amount of metal of the catalyst, is advantageously measured, for example, by H_2/O_2 titration or by transmission electron microscopy.

Preferably, the coefficient of distribution of the noble metal of said preferred catalyst is greater than 0.1, preferably greater than 0.2 and very preferably greater than 0.4. The distribution of the noble metal represents the distribution of the metal inside the catalyst grain, it being possible for the metal to be well or poorly dispersed. Thus, it is possible to obtain platinum which is poorly distributed (for example detected in a ring, the thickness of which is markedly less than the radius of the grain) but well dispersed, that is to say that all the platinum atoms, located in the ring, will be accessible to the reactants. The coefficient of distribution of the noble metal can be measured with a Castaing microprobe.

Preferably, the catalyst used in the first 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.

Advantageously, the catalyst used in the first step of hydroconversion may be difunctional, comprising a hydrogenating/dehydrogenating phase of the type such as nickel-tungsten oxide or reduced platinum on a silica-alumina acidic support. This specific choice advantageously allows atypical feedstocks to be co-processed in admixture with renewable feedstocks, for example waxes from the Fischer-Tropsch process known to be rich in heavy paraffins, and to maximize their conversion by hydrocracking into the middle distillate distillation range. Sending the converted n-paraffins obtained to a second hydroconversion step operating with a specific Pt-type catalyst on a crystalline support that promotes hydroisomerization also allows the conversion to the kerosene cut to be maximized.

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).

Step d)

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 C_4^- cracking products, that is to say C_1 to C_4 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 high-pressure and/or low-pressure stripping.

Step e)

In accordance with the process according to the invention, the hydrocarbon liquid effluent obtained from step d) undergoes a step e) of fractionation into at least a light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and preferably between 110 and 130°C, and a heavy cut with an initial boiling point of between 250 and 300°C and preferably between 270 and 300°C, or a step e) of stabilization allowing the separation of at least a light gaseous fraction, a naphtha hydrocarbon cut and a heavy cut with an initial boiling point of between 100 and 180°C, and preferably between 110 and 130°C.

The fractionation step e) may advantageously 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), 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 180°C, and preferably around 120°C. More particularly, the 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 280°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 and 280°C.

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 the case where step e) is a stabilization step, said step e) enables the separation of three hydrocarbon cuts: a light gaseous fraction, a naphtha hydrocarbon cut and a heavy cut with an initial boiling point of between 100 and 180°C, and preferably between 110 and 130°C.

The stabilization step e) may be performed via any method known to those skilled in the art, for instance, a gas stripping step, advantageously using steam, and/or separation in separating vessels, and/or a combination of these options.

Preferably, said stabilization step is a step of stripping at least a portion, and preferably all, of the hydrocarbon liquid effluent obtained from step d).

Optionally, the heavy cut obtained from step d) is sent, totally or only partially, to the second hydroconversion step f). In the case where part of the heavy cut obtained from step e) is not directed to step f), said process advantageously allows for the co-production of a bio-gas oil cut with the required fuel properties and thus offers the operator of said process the flexibility to produce various biofuel bases on the one hand (road bio-gas oil and bio-kerosene), and, on the other hand, to adjust their respective yields by adapting the proportion of the heavy cut that is sent to the second hydroconversion step f).

Step f)

In accordance with the invention, said process comprises a second hydroconversion step f), separate from step c), of all or part, and preferably all, of the heavy cut with an initial boiling point of between 250 and 300°C obtained from step e) in the case where said step e) is a fractionation step, or all or part, and preferably all of the heavy cut with an initial boiling point of between 100°C and 180°C obtained from step e) in the case where step e) is a stabilization step.

Optionally, according to the invention, a second external paraffinic feedstock may advantageously be sent into said second hydroconversion step f). Said second paraffinic feedstock external to said process according to the invention is advantageously sent into said step f) in admixture with said heavy feedstock. For example, this second feedstock may originate from a step of hydrodeoxygenation of a renewable feedstock separate from step a)

described in said process. The origin described here is not limiting and other sources of external feedstocks are conceivable.

According to the invention, said hydroconversion step f) is performed in the presence of a fixed-bed difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum, and a support comprising a silica-alumina, or a fixed-bed difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum, and a support comprising a zeolite chosen from zeolites of structure code MTW and IZM-2, alone or as a mixture, said hydroconversion step being performed at a temperature of between 250 and 500°C, at a pressure of between 1 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 total feedstock processed in said step f) to produce a hydroconverted effluent.

The operating conditions of the second hydroconversion step f) are adjusted to promote the hydroisomerization or hydrocracking reactions as need be. Preferably, the second hydroconversion step f) 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 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 Nm³ of hydrogen per m³ of feedstock and preferably between 150 and 1000 Nm³ of hydrogen per m³ of total feedstock treated in said step f).

In accordance with the invention, the difunctional catalyst used in said second hydroconversion step f) comprises at least one noble metal, said noble metal being platinum, and a support comprising a silica-alumina, or said catalyst comprises at least one noble metal, said noble metal being platinum, and a support comprising a zeolite chosen from zeolites of structure code MTW and IZM-2, alone or as a mixture.

Preferably, the content of Group VIII noble metal, and preferably the content of platinum, in the catalyst used in step f) is between 0.01% and 4% by weight, preferably between 0.05% and 2% by weight, relative to the total weight of said catalyst.

In the case where the difunctional catalyst comprises a support comprising a silica-alumina, the silica content of the silica-alumina, expressed as a weight percentage, is advantageously between 1% and 95%, advantageously between 5% and 95%, preferably between 10% and 80%, very preferably between 20% and 70%, and even more preferably between 22% and 45%. This silica content is perfectly measured by means of X-ray fluorescence.

A preferred hydroconversion catalyst used in step f) of the process according to the invention comprises a particular silica-alumina. Preferably, said catalyst comprises from 0.05% to 10% by weight, preferably between 0.1% and 5% by weight, of at least one noble metal from Group VIII, preferably chosen from platinum and palladium (in a preferred manner platinum), deposited on a silica-alumina support, without any other binder, containing an amount of silica (SiO_2) of between 1% and 95%, expressed as weight percentage, preferably between 5% and 95%, in a preferred manner between 10% and 80%, in a very preferred manner between 20% and 70% and in an even more preferred manner between 22% and 45%, said catalyst having:

- a BET specific surface area of from $100 \text{ m}^2/\text{g}$ to $500 \text{ m}^2/\text{g}$, preferably between $200 \text{ m}^2/\text{g}$ and $450 \text{ m}^2/\text{g}$ and very preferably between $200 \text{ m}^2/\text{g}$ and $300 \text{ m}^2/\text{g}$,
- a mean diameter of the mesopores, measured by mercury porosimetry, of between 4 nm and 12 nm, preferably of between 4 nm and 11 nm and very preferably between 5 nm and 11 nm,
- a total pore volume, measured by mercury porosimetry, of between 0.2 and 1.2 ml/g, preferably between 0.3 and 1.0 ml/g and very preferably between 0.3 and 0.9 ml/g,
- a volume of macropores measured by mercury porosimetry, the diameter of which is greater than 50 nm, of less than 0.02 ml/g,
- a content of alkali metal or alkaline-earth metal compounds of less than 300 ppm by weight and preferably less than 200 ppm by weight.

The mean diameter of the mesopores is defined as being the diameter corresponding to the cancellation of the curve derived from the mercury intrusion volume obtained by mercury porosimetry for pore diameters of between 3.7 and 50 nm.

Preferably, the dispersion of the metal of said preferred catalyst is advantageously between 5% and 100%, preferably between 5% and 90% and very preferably between 10% and 90%. The dispersion, representing the fraction of metal accessible to the reagent relative to the total amount of metal of the catalyst, is advantageously measured, for example, by H_2/O_2 titration or by transmission electron microscopy.

Preferably, the coefficient of distribution of the noble metal of said preferred catalyst is greater than 0.1, preferably greater than 0.2 and very preferably greater than 0.4. The distribution of the noble metal represents the distribution of the metal inside the catalyst grain, it being

possible for the metal to be well or poorly dispersed. Thus, it is possible to obtain platinum which is poorly distributed (for example detected in a ring, the thickness of which is markedly less than the radius of the grain) but well dispersed, that is to say that all the platinum atoms, located in the ring, will be accessible to the reactants. The coefficient of distribution of the noble metal can be measured with a Castaing microprobe.

Another preferred catalyst for the second hydroconversion step f) comprises, and is preferably composed of, platinum, and a support comprising, and preferably composed of, a zeolite of structure code MTW, preferably ZSM-12, and an alumina binder.

Another preferred catalyst for the second hydroconversion step f) comprises, and is preferably composed of, platinum, and a support comprising, and preferably composed of, an IZM-2 zeolite and an alumina binder.

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 composition of said hydroconversion 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.

According to a preferred embodiment, the catalyst used in step f) more particularly comprises, and is preferably composed 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 group VIIIB metal, preferably platinum;
- 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 remainder to 100% in the catalyst, relative to the total weight of the catalyst of step e).

The catalysts used in the first step c) and the second step f) may advantageously be identical or different, and are preferably different.

In a preferred embodiment, the use of said specific catalyst in the second step f) of hydroconversion of all or part of the heavy cut with an initial boiling point of between 250 and 300°C resulting from step e) in the case where step e) is a fractionation step, or of all or part of the heavy cut with an initial boiling point of between 100 and 140°C from step e), in the case where step e) is a stabilization step, as an optional mixture with a second external paraffinic feedstock, enables the targeted cold properties to be achieved while maximizing the yield of said kerosene cut of interest produced in said process.

Step g)

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

Said step g) makes it possible to separate at least a “light” gaseous fraction and at least a hydrocarbon liquid effluent. Optionally, step g) 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 f) and at least a portion of the C_4^- cracking products, that is to say C_1 to C_4 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 f) or by slight entrainment of water from step e) to step f)).

The separation step g) 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 high-pressure and/or low-pressure stripping.

Step h)

In accordance with the invention, the process comprises a step h) of fractionating the hydrocarbon liquid effluent from step g) into at least one light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and a heavy cut with an initial boiling point of between 250 and 300°C, or a step of stabilizing the hydrocarbon liquid effluent obtained from step g) to separate at least one light gaseous fraction, a naphtha hydrocarbon cut and a kerosene cut with an initial boiling point of between 100 and

180°C, said steps d) and g) and e) and h) being possibly performed in the same equipment or in separate equipment.

In the case where step h) is a stabilization step, the stabilization step h) may be performed via any method known to those skilled in the art, for instance, a stripping step, advantageously using steam, and/or separation in separating vessels, and/or a combination of these options.

Preferably, said stabilization step is a step of stripping at least a portion, and preferably all, of the hydrocarbon liquid effluent obtained from step g).

According to the invention, said stripping step enables the separation of a light gas fraction, a naphtha hydrocarbon cut and a kerosene cut.

More particularly, the cut-off point between the kerosene and naphtha cuts is adjustable within the range from 100 to 180°C, preferably about 120°C. The naphtha cut thus contains compounds with a boiling point below 120°C, and the kerosene cut contains compounds with a boiling point above 120°C. In the presence of the specific catalyst in accordance with the invention, the operating conditions of the second hydroconversion step f) may advantageously be adjusted to selectively produce a bio-kerosene cut.

In a variant, step h) is a step of fractionating the hydrocarbon liquid effluent obtained from step g) into at least a light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and preferably between 110 and 130°C, and a heavy cut with an initial boiling point of between 250 and 300°C, and preferably between 270 and 300°C.

The fractionation step h) may advantageously 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 h), 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 in the range between 100 and 180°C, and preferably about 120°C. More particularly, the cut-off point between the kerosene cut and the heavy cut is adjustable in the range between 250 and 300°C, and preferably about 280°C, if the aim is to target kerosene production.

The upgrading of the bio-naphtha cut obtained from step h) 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 steps d) and g) and e) and h) may be performed in the same equipment or in separate equipment. Thus, said steps d) and g) may be performed in the same equipment or in separate equipment, and said steps e) and h) may be performed in the same equipment or in separate equipment.

In one embodiment, said second hydroconversion step f) and also steps g) and h) may be performed at the same site as the preceding steps a) to e) of the process according to the invention or at a different site, i.e. *ex-situ* or relocated to a dedicated hydroconversion unit not belonging to the process according to the invention.

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).

Description of the figures

Figure 1 represents the various steps of the process for producing renewable kerosene, comprising a hydrodeoxygenation step and two hydroconversion steps, and using a specific catalyst for the second hydroconversion step f).

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

The hydrocarbon liquid effluent (5) is sent to a first hydroconversion unit c), in the presence of a supplemental and/or recycled hydrogen stream (7) to produce a second effluent (8) which is sent to a three-phase separation unit 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 hydrocarbon liquid effluent (10). Said unit d) also allows the removal of at least a portion of the water and preferably all of the residual water (11).

The hydrocarbon liquid effluent (10) from unit d) is sent to a stripping stabilization unit e) which allows the separation of a light gaseous fraction (12), a naphtha hydrocarbon cut (13), and a gas oil cut (15) with an initial boiling point of between 100 and 180°C. Optionally, unit e) is a fractionation unit enabling the production of a first bio-kerosene cut (14) and a gas oil cut with an initial boiling point of between 250 and 300°C (15) by distillation of the hydrocarbon effluent (10) from unit d).

The gas oil cut (15) is then sent to a second hydroconversion unit f) in the presence of a supplemental and/or recycled hydrogen stream (18) to produce a third effluent (19).

Optionally, a part of the gas oil cut is sent to a finished product storage unit (16) that allows the co-production of a bio-gas oil road fuel base.

Optionally, a second external stream rich in n-paraffins (17) may be mixed with the gas oil cut (15) obtained from unit e) so as to be co-treated with the gas oil cut (15) in the second hydroconversion unit f).

The third effluent (19) is sent to a unit g) for three-phase separation, allowing the separation of a hydrogen-rich gaseous effluent (20) which may also contain light fractions such as the C₁–C₄ cut, and at least one hydrocarbon liquid effluent (21). Said unit g) also allows the removal of at least a portion of the water, and preferably all of the residual water (22).

The hydrocarbon liquid effluent (21) from unit g) is sent to a stripping stabilization unit h) to allow the separation of a light gaseous fraction (23), a naphtha hydrocarbon cut (24), and a bio-kerosene cut (25) with an initial boiling point of between 100 and 180°C.

Optionally, unit h) involves the fractionation of the hydrocarbon liquid effluent (21) obtained from unit g) into a light gaseous fraction (23), a naphtha hydrocarbon cut (24), a bio-kerosene cut (25) with an initial boiling point of between 100 and 180°C and a bio-gas oil hydrocarbon cut with an initial boiling point of between 250 and 300°C.

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

EXAMPLES

Example 1: preparation of a hydrotreating catalyst (C1)

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 P_2O_5 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)

The silica-alumina powder is prepared according to the synthetic protocol described in patent EP 1 415 712 A. The amounts of orthosilicic acid and of aluminium hydrate are chosen so as to have a composition containing 70% by weight of alumina Al_2O_3 and 30% by weight of silica SiO_2 in the final solid.

This mixture is rapidly homogenized in a commercial colloidal mill in the presence of nitric acid so that the nitric acid content of the suspension leaving the mill is 8% relative to the silica-alumina mixed solid. Next, the suspension is dried conventionally in an atomizer conventionally from 300°C to 60°C. The powder thus prepared is formed in a Z-shaped blade mixer in the presence of 8% nitric acid relative to the anhydrous product. The extrusion is performed by passing the paste through a die equipped with orifices 1.4 mm in diameter. The extrudates thus obtained are oven-dried at 140°C, then calcined under a stream of dry air at 550°C and then calcined at 850°C in the presence of steam.

The characteristics of the support thus prepared are as follows:

- a mean mesopore diameter, measured by mercury porosimetry, of 7.7 nm,
- a total pore volume of 0.49 ml/g,
- a mesopore volume of 0.47 ml/g,
- a volume of macropores, the diameter of which is greater than 50 nm, of less than 0.01 ml/g,
- a BET surface area of 240 m²/g.

The silica-alumina extrudates are then subjected to a step of dry impregnation with an aqueous solution of ammonium metatungstate and nickel nitrate, left to mature in a water maturator for 24 hours at room temperature and then calcined for 2 hours in dry air in a crossed bed at 450°C (temperature increase ramp of 5°C/minute). The weight content of tungsten oxide WO_3 of the finished catalyst after calcination is 27%, and the content of nickel oxide NiO is 3.5%. The distribution coefficient of the metals, measured with a Castaing microprobe, is equal to 0.93.

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

Synthesis of the IZM-2 zeolite

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 SiO_2 ; 0.0060 Al_2O_3 ; 0.1666 Na_2O ; 0.1666 1,6-bis(methylpiperidinium)hexane; 33.3333 H_2O . 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 ^{27}Al isotope 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 $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. 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 0.29% by weight, its dispersion measured by H_2/O_2 assay is 52%, and its coefficient of distribution measured by Castaing microprobe is 0.91.

Example 4: Preparation of a hydroconversion catalyst in accordance with the invention (C4)

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 ^{27}Al isotope NMR, x-ray 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, 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 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 C4 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 5: hydrotreatment using catalyst (C1) of a feedstock obtained from a renewable source according to a process in accordance with the invention

The hydrotreating catalyst C1 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.

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 1

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 Nm^3 of hydrogen/ m^3 of feedstock,
- temperature: 310°C .

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

Step of separating the effluent obtained from the hydrotreating step according to Example 5

All of the hydrotreated effluent obtained from the hydrotreating step according to Example 5 is separated using a gas/liquid separator so as to recover a light fraction predominantly containing hydrogen, propane, water in vapour form, carbon oxides (CO and CO_2) and ammonia, and a hydrocarbon liquid 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 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/m^3 . 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

Example 6 in accordance with the invention: Two-step hydroconversion of the hydrocarbon liquid effluent from Example 5 according to a compliant process, and using catalyst (C2) in the first hydroconversion step and catalyst (C3) in the second hydroconversion step

The hydroconversion catalysts C2 and C3 were 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.

First hydroconversion step using catalyst (C2)

The first hydroconversion of the hydrocarbon liquid effluent obtained from Example 5 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 sulfurization. Given the nature of the catalyst C2 (sulfide form), sulfur in the form of dialkyl pentasulfide is first introduced into said hydrocarbon liquid effluent, so as to obtain a total sulfur content of 25 ppm by weight.

The catalyst C2 undergoes a step of *in situ* sulfurization in the unit, with Isane supplemented with 3% by weight of dimethyl disulfide, under a total pressure of 5.1 MPa, a hydrogen/supplemented Isane ratio of 700 Nm³ per m³. The volume of supplemented Isane per volume of catalyst and per hour is set at 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 first hydroconversion step 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 Nm³ of hydrogen/m³ 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 first hydroconversion reactor, the reaction effluent is sent to a gas-liquid separation step performed using a first flash vessel operated at a pressure comparable to that of the first 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 first stripper for stabilizing this first hydroconverted 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 from the first hydroconversion is weighed separately, topped off at 120°C to remove the naphtha fraction, and the 120°C⁺ liquid effluent is then reweighed and analysed, notably by measuring

the cold filter plugging point (CFPP) (NF EN 116) targeting gas oil in the first hydroconversion step.

Temperature steady stages in the range 250 to 400°C were applied so as to adjust the severity of the first hydroconversion. The measurement (typically daily) of the cold filter plugging point (operation of the first hydroconversion step targeting gas oil) of the first hydroconverted liquid effluent at 120°C⁺ allows the evolution of the catalyst's performance to be monitored at each temperature steady stage. For each temperature, the test duration is extended until, on the one hand, a stable cold filter plugging point is obtained (operation of the first step of hydroconversion targeting gas oil) and, on the other hand, a sufficient amount of 120°C⁺ liquid effluent is produced to feed it as the feedstock for the second hydroconversion step.

Once the cold filter plugging point is stable, the yield of 120°C⁺ cut (gas oil) at the boundaries of the first hydroconversion step is determined by means of the following calculation:

120°C⁺ (gas oil) yield of step 1 = [(mass of 120°C⁺ liquid effluent) / (mass of feedstock)] × 100, where the feedstock here corresponds to the hydrocarbon effluent obtained from Example 5.

The mass of 120°C⁺ liquid effluent corresponds to the amount of 120°C⁺ 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 first hydroconversion reactor over the same period of time.

The temperature adjustment was performed so as to achieve the target cold properties for a summer gas oil fuel and a winter gas oil fuel (target for the first hydroconversion step). For each gas oil target, the characteristics obtained for the stabilized 120°C⁺ cut from the first hydroconversion step according to the compliant Example 6, along with the operating conditions and associated 120°C⁺ yields (at the boundaries of step 1), are shown in Summary Table 3.

Second hydroconversion step with catalyst (C3)

In a second reactor, temperature-controlled so as to ensure isothermal operation and containing a fixed bed charged with 50 ml of hydroconversion catalyst C3—the catalyst having been previously activated by reduction—the hydroconversion of the stabilized and topped 120°C⁺ cut (gas oil) from the first hydroconversion step according to the compliant Example 6 is performed. 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).

After reduction, the unit's operating conditions are adjusted so as to perform the second hydroconversion step on the stabilized and topped 120°C⁺ gas oil cut from the first hydroconversion step within 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 Nm³ of hydrogen/m³ 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 second hydroconversion reactor, the reaction effluent is sent to a gas-liquid separation step performed using a second flash vessel operated at a pressure comparable to that of the second 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 second stripper for stabilizing this second hydroconverted 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 from the second hydroconversion is weighed separately, topped off at 120°C to remove the naphtha fraction, and the 120°C⁺ liquid effluent is then reweighed and analysed, notably by measuring the crystal disappearance point (ASTM D5972) targeting kerosene in the second hydroconversion step.

Steady temperature stages in the range from 250 and 400°C were applied so as to adjust the severity of the second hydroconversion step. The measurement (typically daily) of the crystal disappearance point (operation of the second hydroconversion step targeting kerosene) of the second hydroconverted 120°C⁺ liquid effluent allows the evolution of the catalyst's performance to be monitored at each temperature steady stage. For each temperature, the test time is prolonged until a stable point of disappearance of the crystals is obtained.

Once the crystal disappearance point is stable, the yield of 120°C⁺ cut (kerosene) at the boundaries of the second hydroconversion step is determined by means of the following calculation:

120°C⁺ (kerosene) yield for step 2 = [(mass of 120°C⁺ liquid effluent) / (mass of feedstock)] × 100, where the feedstock here corresponds to the 120°C⁺ feedstock produced by the first hydroconversion step and fed into the second hydroconversion step according to Example 6.

The mass of 120°C⁺ liquid effluent corresponds to the amount of 120°C⁺ 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 second hydroconversion reactor over the same period of time.

The yield of 120°C⁺ cut (kerosene) at the boundaries of the compliant process according to the invention is determined by means of the following calculation:

120°C⁺ (kerosene) yield of the compliant process = [(mass of 120°C⁺ liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 5.

The mass of 120°C⁺ liquid effluent corresponds to the amount of 120°C⁺ 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 first hydroconversion reactor over the same period of time.

The temperature adjustment was performed so as to achieve the target cold properties for a kerosene fuel (the target for this second hydroconversion step). The features obtained for the stabilized 120°C⁺ cut obtained from the second hydroconversion step according to compliant Example 6, along with the operating conditions and associated 120°C⁺ yields (at the boundaries of step 2 and at the boundaries of the compliant process) are shown in Summary Table 3.

The reference temperature, referred to as “Tbase” in Summary Table 3, is the temperature required to achieve the kerosene target in the 120°C⁺ cut produced via the non-compliant process according to Example 8 (crystal disappearance point of -50°C), the non-compliant process comprising a single hydroconversion step.

The compliant process according to Example 6 was evaluated according to two variants, respectively named “Case 1” and “Case 2”. Each case features a degree of hydroconversion

of the hydrocarbon liquid effluent from Example 5 that varies within the first hydroconversion step.

In “Case 1”, the degree of conversion for the first hydroconversion step (catalyst C2) is adjusted so as to achieve a cold filter plugging point (CFPP) of 0°C on the 120°C⁺ cut produced, representative of a “summer gas oil” fuel target. The degree of conversion of the second hydroconversion step (catalyst C3) is adjusted so as to achieve the kerosene target on the 120°C⁺ cut produced via the compliant process (crystal disappearance point of -50°C).

In “Case 2”, the degree of conversion for the first hydroconversion step (catalyst C2) is adjusted so as to achieve a cold filter plugging point (CFPP) of -15°C for the 120°C⁺ cut produced, representative of a “winter gas oil” fuel target. The degree of conversion of the second hydroconversion step (catalyst C3) is adjusted so as to achieve the kerosene target on the 120°C⁺ cut produced via the compliant process (crystal disappearance point of -50°C).

The compliant process in accordance with Example 6 allows the temperature used in the first hydroconversion step to be reduced; the reduction is 20°C for “Case 1” and 12°C for “Case 2”.

The compliant process according to Example 6, using a specific catalyst C3 in the second hydroconversion step, enables the production of a kerosene cut at a lower temperature than that used according to the non-compliant Example 8. The reduction is 11°C for “Case 1” and 12°C for “Case 2”.

The compliant process according to Example 6, using a specific catalyst C3 in the second hydroconversion step, allows the production of a kerosene cut with a more favourable overall 120°C⁺ yield for the process than the one obtained according to the non-compliant Example 8. The gain amounts to 17.7 points for “Case 1” and 14.3 points for “Case 2”.

The use of the process in accordance with the invention, performed by means of two hydroconversion steps and using a specific catalyst C3 in the second hydroconversion step, thus allows a significant improvement in the temperatures used within said process and also a significant improvement in the overall selectivity of the process for the 120°C⁺ kerosene cut of interest for said process.

Table 3

	Compliant Example 6		Compliant Example 7		Non-compliant Example 8
	Case 1	Case 2	Case 1	Case 2	
Operating conditions of the first hydroconversion step					
Catalyst	C2	C2	C2	C2	C2

Total pressure	(MPa)	5.1	5.1	5.1	5.1	5.1
HSV	(h ⁻¹)	0.5	0.5	0.5	0.5	0.5
H2/HC ratio	(Nm ³ /m ³)	350	350	350	350	350
Temperature	°C	Tbase - 20	Tbase - 12	Tbase - 20	Tbase - 12	Tbase
Operating conditions of the second hydroconversion step						
Catalyst		C3	C3	C4	C4	Not applicable
Total pressure	(MPa)	5.1	5.1	5.1	5.1	
HSV	(h ⁻¹)	0.5	0.5	0.5	0.5	
H2/HC ratio	(Nm ³ /m ³)	350	350	350	350	
Temperature	°C	Tbase - 11	Tbase - 12	Tbase - 19	Tbase - 20	
Yields and product qualities at the boundaries of the first hydroconversion step						
C1-C4 (gas) yield	(% by wt.)	1.17	1.72	1.17	1.72	Not applicable
C5-120°C (naphtha) yield	(% by wt.)	4.70	8.26	4.70	8.26	
120°C+ (gas oil) yield	(% by wt.)	94.3	90.3	94.3	90.3	
Cold filter plugging point	(°C)	0	-15	0	-15	
Density at 15°C	(g/cm ³)	0.7808	0.7752	0.7808	0.7752	
Cetane number	(°C)	> 60	> 60	> 60	> 60	
Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10	
Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1	
Yields and product qualities at the boundaries of the second hydroconversion step						
C1-C4 (gas) yield	(% by wt.)	6.30	5.50	6.10	5.10	Not applicable
C5-120°C (naphtha) yield	(% by wt.)	9.70	10.5	10.1	11.2	
120°C+ (kerosene) yield	(% by wt.)	84.2	84.2	84.0	83.9	
Crystal disappearance point	(°C)	-50	-50	-50	-50	
Density at 15°C	(g/cm ³)	0.7721	0.7707	0.7714	0.7698	
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	
Yields and qualities at the process boundaries						
C1-C4 (gas) yield	(% by wt.)	7.11	6.69	6.92	6.32	7.18
C5-120°C (naphtha) yield	(% by wt.)	13.8	17.7	14.2	18.4	32.0
120°C+ (kerosene) yield	(% by wt.)	79.4	76.0	79.2	75.7	61.7
Crystal disappearance point	(°C)	-50	-50	-50	-50	-50
Density at 15°C	(g/cm ³)	0.7721	0.7707	0.7714	0.7698	0.7523
Smoke point	(°C)	> 25	> 25	> 25	> 25	> 25
Sulfur content	(ppm by weight of S)	< 10	< 10	< 10	< 10	< 10
Nitrogen content	(ppm by weight of N)	< 1	< 1	< 1	< 1	< 1
Final point ASTM D86	(°C)	< 300	< 300	< 300	< 300	< 300

Table 3: Operating conditions, yields and properties of the cuts obtained for the various examples of the invention

Example 7 in accordance with the invention: Two-step hydroconversion of the hydrocarbon liquid effluent obtained from Example 5 in accordance with a compliant

process, using catalyst (C2) in the first hydroconversion step and catalyst (C4) in the second hydroconversion step

The hydroconversion catalysts C2 and C4 were 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 mimics the industrial implementation of the process according to the invention, are identical in every respect to those described in Example 6 in accordance with the invention; the only difference lies in the use of catalyst (C4) instead of catalyst (C3).

The reference temperature, referred to as “Tbase” in Summary Table 3, is the temperature required to achieve the kerosene target in the 120°C⁺ cut produced via the non-compliant process according to Example 8 (crystal disappearance point of -50°C), the non-compliant process comprising a single hydroconversion step.

The compliant process according to Example 7 was evaluated according to two variants, respectively named “Case 1” and “Case 2”. Each case features a degree of hydroconversion of the hydrocarbon liquid effluent from Example 5 that varies within the first hydroconversion step.

In “Case 1”, the degree of conversion for the first hydroconversion step (catalyst C2) is adjusted so as to achieve a cold filter plugging point (CFPP) of 0°C on the 120°C⁺ cut produced, representative of a “summer gas oil” fuel target. The degree of conversion of the second hydroconversion step (catalyst C4) is adjusted so as to achieve the kerosene target on the 120°C⁺ cut produced via the compliant process (crystal disappearance point of -50°C).

In “Case 2”, the degree of conversion for the first hydroconversion step (catalyst C2) is adjusted so as to achieve a cold filter plugging point (CFPP) of -15°C for the 120°C⁺ cut produced, representative of a “winter gas oil” fuel target. The degree of conversion of the second hydroconversion step (catalyst C4) is adjusted so as to achieve the kerosene target on the 120°C⁺ cut produced via the compliant process (crystal disappearance point of -50°C).

The process in accordance with Example 7 allows the temperature used in the first hydroconversion step to be reduced; the reduction is 20°C for “Case 1” and 12°C for “Case 2”.

The compliant process according to Example 7, using a specific catalyst C4 in the second hydroconversion step, enables the production of a kerosene cut at a lower temperature than that used according to the non-compliant Example 8. The reduction is 19°C for “Case 1” and 20°C for “Case 2”.

The compliant process according to Example 7, using a specific catalyst C4 in the second hydroconversion step, allows the production of a kerosene cut with a more favourable overall 120°C⁺ yield for the process than the one obtained according to the non-compliant Example 8. The gain amounts to 17.5 points for “Case 1” and 14.0 points for “Case 2”.

The use of the process in accordance with the invention, performed by means of two hydroconversion steps and using a specific catalyst C4 in the second hydroconversion step, thus allows a significant improvement in the temperatures used within said process and also a significant improvement in the overall selectivity of the process for the 120°C⁺ kerosene cut of interest for said process.

Example 8 not in accordance with the invention: One-step hydroconversion of the hydrocarbon liquid effluent obtained from Example 5 using catalyst (C2)

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 not in accordance with the invention. The various steps and unit operations of the pilot plant, which mimics the industrial implementation of the non-compliant process according to the invention, are described hereinbelow.

The hydroconversion of the hydrocarbon liquid effluent obtained from Example 5 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 sulfurization. Given the nature of the catalyst C2 (sulfide form), sulfur in the form of dialkyl pentasulfide is first introduced into said hydrocarbon liquid effluent, so as to obtain a total sulfur content of 25 ppm by weight.

The catalyst C2 undergoes a step of *in situ* sulfurization in the unit, with Isane supplemented with 3% by weight of dimethyl disulfide, under a total pressure of 5.1 MPa, a hydrogen/supplemented Isane ratio of 700 Nm³ per m³. The volume of supplemented Isane per volume of catalyst and per hour is set at 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 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 Nm³ of hydrogen/m³ 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 hydroconverted 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 obtained is weighed separately, topped off at 120°C to remove the naphtha fraction, and the 120°C⁺ liquid effluent is then reweighed and analysed, notably by measuring the crystal disappearance point (non-compliant process operation targeting kerosene).

Temperature steady stages in the range 250 to 400°C were applied so as to adjust the severity of the sole hydroconversion step. The measurement (typically daily) of the crystal disappearance point (non-compliant process operation targeting kerosene) of the 120°C⁺ liquid effluent allows the evolution of the catalyst's performance to be monitored at each temperature steady stage. For each temperature, the test duration is extended until a stable crystal disappearance point is obtained (non-compliant process operation targeting kerosene).

Once the crystal disappearance point is stable, the yield of 120°C⁺ cut (kerosene) at the boundaries of the non-compliant process is determined by means of the following calculation:

120°C⁺ (kerosene) yield = [(mass of 120°C⁺ liquid effluent) / (mass of feedstock)] × 100, where the feedstock corresponds here to the hydrocarbon effluent obtained from Example 5.

The mass of 120°C⁺ liquid effluent corresponds to the amount of 120°C⁺ 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 step over the same period of time.

The temperature adjustment was performed so as to achieve the cold property targets for a kerosene fuel (target for the non-compliant process). The characteristics obtained for the

stabilized 120°C⁺ cut according to the non-compliant Example 8, and also the associated operating conditions and 120°C⁺ yields, are shown in Summary Table 3.

CLAIMS

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

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,

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 first 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 containing at least one metal from group VIII and/or at least one metal from group VIB of the Periodic Table, an acidic support comprising a silica-alumina or one or more zeolites and optionally at least one binder, said first 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,

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,

e) a step of fractionating the hydrocarbon liquid effluent obtained from step d) into at least one light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and a heavy cut with an initial boiling point of between 250 and 300°C, or a step of stabilizing the hydrocarbon liquid effluent obtained from step d) to enable the separation of at least a light gaseous fraction, a naphtha hydrocarbon cut and a heavy cut with an initial boiling point of between 100 and 180°C,

f) a second step of hydroconversion, separate from step c), of all or part of the heavy cut with an initial boiling point of between 250 and 300°C obtained from step e) in the case where step e) is a fractionation step, or of all or part of the heavy cut with an initial boiling point of between 100 and 180°C obtained from step e) in the case where step e) is a stabilization step, said second hydroconversion step being performed in a fixed bed in the presence of a difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum, and a support comprising a silica-alumina, or a difunctional hydroconversion catalyst comprising at least one noble metal, said noble metal being platinum and a support comprising a zeolite chosen from zeolites of structure codes MTW and IZM-2, alone or as a mixture, said hydroconversion step being performed at a temperature of between 250 and 500°C, at a pressure of between 1 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 total feedstock processed in said step f), to produce a hydroconverted effluent,

g) a step of separating at least a portion of the hydroconverted effluent obtained from step f) making it possible to separate at least a gaseous fraction and at least a hydrocarbon liquid effluent,

h) a step of fractionating the hydrocarbon liquid effluent obtained from step g) into at least one light gaseous fraction, a naphtha hydrocarbon cut, a kerosene cut with an initial boiling point of between 100 and 180°C, and a heavy cut with an initial boiling point of between 250 and 300°C, or a step of stabilizing the hydrocarbon liquid effluent obtained from step g) to separate at least one light gaseous fraction, a naphtha hydrocarbon cut and a kerosene cut with an initial boiling point of between 100 and 180°C, said steps d) and g) and e) and h) being possibly performed in the same equipment or in separate equipment.

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 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 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 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 of 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 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 a catalyst used in the first hydroconversion step c) comprises at least one Group VIII metal, preferably nickel, and at least one Group VIB metal, preferably tungsten, preferably active in their sulfide form.
7. Process according to one of Claims 1 to 5, in which a catalyst used in the first hydroconversion step c) comprises at least one Group VIII metal, preferably a Group VIII noble metal chosen from platinum and palladium and preferably, the Group VIII metal of the catalyst used in step c) is platinum, preferably active in its reduced form.

8. Process according to one of Claims 1 to 7, in which, in the case where the acidic support of the catalyst used in the first hydroconversion step c) is one or more zeolites, said zeolites are chosen from zeolites of structure types FAU, *BEA, ISV, IWR, IWW, MEI and UWY, taken alone or as a mixture, preferably chosen from zeolites of structure types FAU and *BEA, taken alone or as a mixture; preferably, the zeolite is chosen from zeolite Y and beta zeolite, taken alone or as a mixture, and very preferably, the zeolite is zeolite Y and, even more preferably, de-aluminated USY zeolite.

9. Process according to one of Claims 1 to 8, in which a hydroconversion catalyst used in the first hydroconversion step c) includes nickel and tungsten, and a silica-alumina as support, without any other binder.

10. Process according to one of Claims 1 to 9, in which a second external paraffinic feedstock is sent into said second hydroconversion step f).

11. Process according to one of Claims 1 to 10, in which a catalyst used in the second hydroconversion step f) comprises, and is preferably composed of, platinum, and a support comprising, and preferably composed of, a zeolite of structure code MTW, preferably ZSM-12, and an alumina binder.

12. Process according to one of Claims 1 to 10, in which a catalyst used in the second hydroconversion step f) comprises, and is preferably composed of, platinum, and a support comprising, and preferably composed of, an IZM-2 zeolite and an alumina binder.

13. Process according to one of Claims 1 to 12, in which said second hydroconversion step f) and also steps g) and h) may be performed at the same site as the preceding steps a) to e) of said process or at a different site, in a dedicated hydroconversion unit not belonging to said process.