

Method for processing a feedstock from a renewable source, for the production of bio-based olefins

TECHNICAL FIELD

- 5 The present invention relates to a process for treating a feedstock from a renewable source comprising triglycerides and/or fatty acids and/or esters for the selective production of naphtha, which is capable of producing olefins such as ethylene, propylene and biobased polymers for the chemical industry.

10 PRIOR ART

Numerous processes for hydrotreating feedstocks from a renewable source comprising triglycerides and/or fatty acids and/or esters have been developed in order to increase the proportion of renewable fuel in fossil fuels.

- For example, FR2917424 discloses a process for treating a feedstock from a renewable source
15 comprising a step of hydrotreatment in the presence of at least one fixed-bed catalyst, said catalyst comprising a hydro-dehydrogenating function and an amorphous support, followed by a separation, from the hydrotreated effluent from step a), of hydrogen, gases and at least one hydrocarbon-based liquid effluent consisting of at least 50% of linear n-paraffins, and steam cracking of at least part of the hydrocarbon-based liquid effluent from the separation step b).

- 20 FR3104603 discloses a process for isomerizing paraffinic feedstocks, preferably from hydrotreated vegetable and/or animal oils or from low-temperature Fischer-Tropsch synthesis, said process using a bifunctional catalyst comprising at least one metal from group VIII of the Periodic Table of the Elements, at least one matrix and at least one zeolite IZM-2. This process makes it possible to improve the selectivity toward the production of middle distillate bases by
25 limiting the production of light cracked products that cannot be incorporated into a gas oil and/or kerosene pool.

- However, it is also necessary to increase the production of biobased olefins obtained by steam cracking of feedstocks from a renewable source comprising triglycerides and/or fatty acids and/or esters in order to increase the amount of sustainable polymers produced to replace
30 polymers of fossil origin.

US2014350314 notably discloses a process comprising a step of hydrotreating a renewable feedstock to produce a hydrocarbon-based effluent, a step of hydrocracking said hydrocarbon-based effluent to produce a distribution of cracked hydrocarbons, a step of separating a heavy cut and a biobased naphtha cut, and a step of obtaining a middle distillate fraction originating from the heavy fraction.

Surprisingly, the applicant has developed an improved process that makes it possible to produce a naphtha cut from a biobased feedstock that can be co-processed in the majority of liquid steam crackers comprising a minimal number of steps.

10 SUMMARY OF THE INVENTION

The present invention relates to a process for treating a feedstock from a renewable source comprising triglycerides and/or fatty acids and/or esters, said process comprising the steps of:

a) a step of hydrotreating said feedstock in the presence of hydrogen and of at least one fixed-bed hydrotreatment catalyst, performed at a temperature of between 280°C and 410°C, and at a relative pressure of between 2.0 and 13.0 MPa, and at an hourly space velocity of between 0.3 and 5 h⁻¹, and obtaining a hydrotreated effluent;

b) a step of hydrocracking the hydrotreated effluent obtained in step a) in the presence of hydrogen and of at least one fixed-bed hydrocracking catalyst, at a temperature of between 280°C and 410°C, performed at a pressure of between 2.0 MPa and 13.0 MPa, and at an hourly space velocity of between 0.5 and 10 h⁻¹, and obtaining a hydrocracked effluent;

c) a step of separating the hydrocracked effluent obtained in step b), and obtaining at least one gaseous effluent comprising hydrogen and a hydrocarbon-based liquid effluent;

d) a step of stripping the hydrocarbon-based liquid effluent obtained in step c), and obtaining at least one off-gas cut and a stripped liquid effluent;

e) a step of fractionating the stripped liquid effluent obtained in step d), and obtaining at least one paraffin-rich naphtha cut;

f) a step of steam cracking at least part, preferably all, of the naphtha cut obtained in step e) and obtaining at least one biobased gaseous effluent comprising ethylene and propylene.

The process according to the invention makes it possible to produce ethylene, propylene and, after polymerization, biobased polymers.

Advantageously, this scheme makes it possible to only produce upgradable cuts in a liquid steam cracker accepting naphtha cuts and possibly LPG cuts.

Thus, the process according to the invention does not, preferably, produce any distillate cut.

In addition, the process is efficient because it does not require any rigorous separation of the
 5 hydrotreated effluent between step a) and step b), only a vessel generating a hydrotreated liquid effluent which is sent partly to step a) to control the exothermicity of the reaction.

In one embodiment, the hydrotreatment step a) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³.

In one embodiment, the at least one hydrotreatment catalyst comprises a support and an active
 10 phase, said active phase comprising at least one metal from group 6 and optionally one or more metals from group 9 or 10, preferably the active phase contains molybdenum only (Mo), or nickel and molybdenum (NiMo), or cobalt and molybdenum (CoMo), or nickel, cobalt and molybdenum (CoNiMo).

In one embodiment, the hydrotreatment step a) is followed by a step of separating the
 15 hydrotreated effluent at high temperature of between 150°C and 410°C, and at high pressure of between 2.0 and 13.0 MPa, and obtaining at least one gaseous effluent and one liquid effluent.

In one embodiment, part of the liquid effluent obtained in the high-temperature separation step is recycled to the hydrotreatment step a).

20 In one embodiment, the hydrocracking step b) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³.

In one embodiment, the hydrocracking step b) is performed at a minimum hydrogen partial pressure of 2.5 MPa.

In one embodiment, the at least one hydrocracking catalyst comprises a hydrogenating
 25 function and an acid function provided by supports with large surface areas having surface acidity, such as halogenated aluminas, combinations of boron and aluminum oxides, amorphous silica-aluminas and zeolites Y, beta and ZSM-5.

In one embodiment, in step b) the conversion per pass into hydrocarbon-based compounds is between 20% and 100% by weight.

30 In one embodiment, the separation step c) is followed by a step of purifying and/or washing the gaseous effluent comprising hydrogen obtained in step c) to remove the contaminants,

notably H_2S , CO and CO_2 , followed by recycling of the washed gaseous effluent into at least the hydrotreatment step a) and/or hydrocracking step b).

In one embodiment, part of the liquid effluent obtained in step c) is recycled to step a) and/or step b), preferably to step a).

- 5 In one embodiment, the off-gas cut obtained in step d) is sent to a separation step in order to recover a depropanized gaseous off-gas cut that is low in propane and butane and an LPG cut.

10 In one embodiment, the LPG cut is sent to the steam cracking step f), separately or as a mixture with the naphtha cut obtained in step e), into one or more furnaces of the steam cracking step f).

In one embodiment, in step e) of fractionating the stripped liquid effluent obtained in step d), a heavy cut comprising hydrocarbon-based compounds having boiling points greater than $150^\circ C$, preferably greater than $175^\circ C$, is also obtained.

- 15 In one embodiment, the heavy cut obtained in step e) is completely or partly recycled to the hydrotreatment step a) and/or hydrocracking step b), preferably with a recycled feedstock/fresh feedstock ratio of between 0 and 4.

BRIEF DESCRIPTION OF THE FIGURES

20 Figure 1 illustrates the implementation of the process according to a first embodiment of the invention.

Figure 2 illustrates the implementation of the process according to a second embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

- 25 According to the present invention, the expression “of between ... and ...” and “between ... and ...” are equivalent and mean that the limit values of the interval are included in the described range of values. If such is not the case and if the limit values are not included in the described range, it will be indicated as such in the present invention.

30 Within the meaning of the present invention, the various ranges of parameters for a given step, such as the pressure ranges and the temperature ranges, may be used alone or in

combination. For example, within the meaning of the present invention, a range of preferred pressure values may be combined with a range of more preferred temperature values.

Hereinafter, particular embodiments of the invention may be described. They may be implemented separately or combined together, without limitation of combinations when this is technically feasible.

In the present description, the term "Cx hydrocarbons" denotes hydrocarbon compounds comprising x carbon atoms. The term "Cx+ hydrocarbons" denotes hydrocarbon compounds having at least x carbon atoms. The term "Cx to Cy hydrocarbons" denotes hydrocarbon compounds having between x and y carbon atoms.

Throughout the present text, the groups of chemical elements are described according to the new IUPAC classification. For example, groups 9 or 10 correspond to the metals of columns 9 and 10 according to the IUPAC classification or to the last two columns of group VIIIB according to the CAS classification (CRC Handbook of Chemistry and Physics, CRC editor press, chief editor D.R. Lide, 81st edition, 2000-2001). Similarly, group 6 corresponds to the metals of column 6 according to the IUPAC classification or to the metals of columns VIB according to the CAS classification.

"Fresh feedstock" is understood to mean the feedstock to be treated entering the process in the hydrotreatment step a).

"Naphtha cut" is understood to mean a cut that may have boiling points of between that of hydrocarbon-based compounds having 5 carbon atoms per molecule up to 215°C.

"Purge" is understood to mean the cut comprising the unconverted compounds that is produced continuously or discontinuously to avoid accumulation of unwanted and non-crackable heavy molecules.

"Off-gas cut" is understood to mean the vapor cut from the stripping step.

"Depropanized off-gas cut" is understood to mean the vapor cut that is low in propane and butane. "Low in" is understood here to mean: comprising less than 2% by volume of propane and butane compounds, preferably less than 1% by volume.

"LPG cut" is understood to mean the vapor cut that is rich in propane and butane by analogy with fossil Liquefied Petroleum Gas LPG cuts comprising these compounds. "Rich in" is understood here to mean: comprising more than 95% by volume of propane and butane compounds.

“Light naphtha” is understood to mean a cut that may have boiling points of between that of hydrocarbon-based compounds having 5 carbon atoms per molecule up to 110°C.

“Paraffin-rich” is understood to mean for the naphtha of step e): comprising more than 90% by weight of desired compounds.

- 5 “Distillate” is understood to mean the cut characterized by the distillation range and having boiling points greater than 150°C and up to 560°C.

“Pyrolysis oil” is understood to mean the cut recovered at the bottom of the primary fractionating tower of the steam cracking step.

- 10 In the present text, the hydrotreatment includes the hydrotreatment reactions of impurities, notably hydrodeoxygenation, hydrodesulfurization, hydrodenitrogenation, hydrogenation of olefins, etc., using at least one catalyst in the presence of hydrogen to produce an effluent depleted of impurities.

- 15 In the present text, “hydrocracking” encompasses the processes aimed at reducing the number of carbons of the molecules using at least one catalyst in the presence of hydrogen and producing products with a distillation point lower than that of the feedstock.

In the present text, “stripping” encompasses the physical separation processes in which one or more components are removed from a liquid stream by a vapor stream or supply of heat. The “stripped” effluent is therefore the liquid effluent leaving the stripping step.

20 **Feedstock**

The process according to the present invention consists in converting a wide range of feedstocks of renewable origin, essentially composed of triglycerides and fatty acids, into paraffinic hydrocarbons.

- 25 “Essentially composed of triglycerides and fatty acids” is understood to mean a feedstock comprising at least 70% by weight of triglycerides and fatty acids, preferably at least 80% by weight. Other specific elements may be present, but only those which have no material impact on the essential features of the composition.

- 30 These feedstocks are generally characterized by a high molar mass (greater than 800 g/mol most often), and the fatty acid chains which compose them advantageously have a number of carbon atoms of between 4 and 24, and a number of unsaturations per chain generally of between 0 and 3, with higher values which can be reached on certain specific feedstocks.

Among the feedstocks that may be converted by the process according to the present invention, mention may be made of, this list not being exhaustive: vegetable oils such as rapeseed oil, jatropha oil, soybean oil, palm oil, sunflower oil, olive oil, coconut oil, camelina oil, fish oils or heterotrophic or autotrophic algal oils, or else animal fats such as beef tallow, or
 5 else residues from the paper industry (such as tall oil), or mixtures of these various feedstocks.

Preferably, the feedstocks from renewable sources are chosen from oils and fats of vegetable or animal origin, or mixtures of such feedstocks, containing triglycerides and/or free fatty acids and/or esters.

All of these feedstocks contain high contents of oxygen, that is to say typically greater than 5%
 10 by weight, preferably greater than 8% by weight, as well as, at very variable contents depending on the origin of the feedstocks, significant quantities of impurities which may contain at least one heteroatom other than oxygen and organic impurities essentially comprising nitrogen. Said feedstocks may generally comprise a content of compounds with heteroatoms other than oxygen of between 0.1 and 2500 ppm. The contents of nitrogen and of sulfur are
 15 generally less than 100 ppm by weight; they may reach up to 1% by weight on particular feedstocks.

Said feedstocks typically have a content of oxygen of at most 20% by weight, preferably at most 15% by weight, preferably of between 5% and 15% by weight, notably between 8% and 15% by weight. Said feedstocks differ from feedstocks of bio-oil type which are immiscible.

20 The feedstocks from renewable sources that are used in the process according to the invention may advantageously be unrefined, or may have undergone at least one step of refining the oil for food purposes that is known to those skilled in the art, such as for example a degumming or dephosphatation step. Said feedstocks which have undergone at least said refining step are referred to as semi-refined and at the end of this treatment still contain up to 20 ppm of
 25 phosphorus, calcium, magnesium, iron and/or zinc, in the form of phospholipids.

In one embodiment, the presence of feedstocks of fossil origin is excluded in order to produce only cuts of renewable origin for the steam cracking step.

Advantageously, said fresh feedstock is chosen from vegetable oils such as rapeseed oil, jatropha oil, soybean oil, palm oil, sunflower oil, olive oil, coconut oil, camelina oil, fish oils or
 30 heterotrophic or autotrophic algal oils, or else animal fats such as beef tallow, or else residues from the paper industry (such as tall oil), or mixtures of these various feedstocks.

Operating conditions and catalysts

Hydrotreatment step a)

The process according to the invention comprises a step a) of hydrotreating the feedstock in the presence of hydrogen and of at least one fixed-bed hydrotreatment catalyst, performed at a temperature of between 280°C and 410°C, preferably between 290°C and 320°C, and at a relative pressure of between 2.0 and 13.0 MPa, preferably between 2.5 and 9.0 MPa, and at an hourly space velocity (HSV) of between 0.3 and 5 h⁻¹, preferably between 0.7 and 3 h⁻¹, and obtaining a hydrotreated effluent.

In one embodiment, said hydrotreatment catalyst comprises a conventional hydrogenating function.

Advantageously, the hydrotreatment catalyst comprises a support and an active phase, said active phase comprising at least one metal from group 6 and optionally one or more metals from group 9 or 10, preferably the active phase contains molybdenum only (Mo), or nickel and molybdenum (NiMo), or cobalt and molybdenum (CoMo), or nickel, cobalt and molybdenum (CoNiMo).

Advantageously, use may for example be made of a catalyst comprising from 0.5% to 10% by weight of nickel (expressed as nickel oxide NiO) or from 1% to 30% by weight of molybdenum, preferably from 5% to 25% by weight of molybdenum (expressed as molybdenum oxide MoO₃) on an alumina support. The total content of oxides of metals from groups 6 and 9 or 10 in the catalyst is generally between 5% and 40% by weight and preferentially between 7% and 35% by weight. Where appropriate, the weight ratio (expressed on the basis of the metal oxides) of metal (metals) from group 6 to metal (metals) from group 9 or 10 is, in general, from around 20 to around 1, and most often from around 10 to around 2.

Advantageously, the various catalysts mentioned previously may also be stacked in successive layers. A stack may for example be the sequence of a layer comprising nickel, cobalt and molybdenum (CoNiMo), followed by a layer comprising nickel and molybdenum (NiMo), or the other way around. Another stack may for example be the sequence of a layer comprising cobalt and molybdenum (CoMo) followed by a layer comprising nickel and molybdenum (NiMo), or the other way around.

Advantageously, the hydrotreatment catalyst is supported at least partially, or even entirely, on an alumina support.

In one embodiment, the hydrotreatment step a) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³, preferably between 150 and 1000 Nm³/Sm³.

5 The hydrogen to hydrocarbon ratio is defined here as the ratio of the volume flow rate of hydrogen taken under normal temperature and pressure conditions relative to the volume flow rate of feedstock supplying step a) (in normal m³, written Nm³, of H₂ per standard m³, written Sm³, of feedstock entering step a)).

In one embodiment, the hydrotreatment step a) is performed at a minimum hydrogen partial pressure of 2.0 MPa, preferably at least 4.0 MPa.

10 This hydrotreatment step a) advantageously makes it possible to produce a cut of hydrocarbons having contents of oxygen and nitrogen compounds that are reduced.

In one embodiment, the hydrotreatment step a) is followed by an optional step of separating the hydrotreated effluent at high temperature of between 280°C and 410°C, preferably between 290°C and 320°C, and obtaining at least one gaseous effluent that is rich in hydrogen, in oxygen compounds and in light hydrocarbons and one liquid effluent. "Rich in hydrogen" is
15 understood here to mean a content of hydrogen greater than 65% by volume.

In one embodiment, part of the liquid effluent obtained in the optional high-temperature separation step is recycled to the hydrotreatment step a). This recycling advantageously makes it possible to control the increase in temperature due to the hydrotreatment reaction.

20 The non-recycled part of the liquid effluent and the gaseous effluent rich in hydrogen that are from step a) are sent into the following hydrocracking step b).

In one embodiment, the part of the liquid effluent obtained in the optional high-temperature separation step is recycled to the hydrotreatment step a) such that the mass ratio of said recycled part of the effluent to the fresh feedstock introduced into the hydrotreatment step a) is less than 3, preferably less than 1.

25 Advantageously, the configuration of the reactor capable of carrying out the reactions according to the invention is composed of a number of suitable catalyst beds. Generally, the configuration has at least 2 catalyst beds and preferentially more than 3, and in particular more than 4 beds but fewer than 20 beds, and preferentially fewer than 15 beds and in particular fewer than 10 catalyst beds. The preferred configuration comprises between 3 and 19 beds,
30 and in particular comprises between 4 and 9 catalyst beds.

The liquid effluent of step a) consists essentially of linear paraffins, that is to say that the product has a composition of at least 90% by weight of linear paraffins.

Hydrocracking step b)

The process according to the invention comprises a step b) of hydrocracking the hydrotreated effluent obtained in step a) in the presence of hydrogen and of at least one fixed-bed hydrocracking catalyst, at a temperature of between 280°C and 410°C, preferably between 290°C and 320°C, performed at a pressure of between 2.0 MPa and 13.0 MPa, preferably between 2.5 and 9.0 MPa, and at an HSV of between 0.5 and 10 h⁻¹, preferably between 1 and 4 h⁻¹, and obtaining a hydrocracked effluent.

In the process according to the invention, the hydrocracking step is performed immediately after the hydrotreatment step, with optionally an intermediate step of separation at high temperature and high pressure, such that the loss of pressure and of temperature is minimal with a minimal number of items of equipment. "High temperature" is understood to mean a temperature of between 150°C and 410°C, preferably between 200°C and 320°C. "High pressure" is understood to mean a relative pressure of between 2.0 and 13.0 MPa, preferably between 2.5 and 9.0 MPa, notably at a pressure slightly less than the pressure of step a) and slightly greater than that of step b) to take account of the pressure losses associated with the successive items of equipment.

In the embodiment where the hydrotreatment step a) is followed by a high-temperature separation step, it is the non-recycled part of the liquid effluent and the gaseous effluent rich in hydrogen that are hydrocracked in step b).

In one embodiment, the hydrocracking step b) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³, preferably between 200 and 2000 Nm³/Sm³.

Advantageously, in step b) the conversion per pass into hydrocarbon-based compounds is between 20% and 100% by weight, preferably between 45% and 80% by weight, preferably between 50% and 70% by weight. The conversion per pass is calculated relative to the feedstock entering step b) using the following operation: (the flow rate by weight of the effluent entering step b) minus the flow rate of the optional bottom cut from the fractionation of step e) by weight) divided by the flow rate by weight of effluent entering step b). Thus, the hydrocracking step b) makes it possible to advantageously produce naphtha and the amount of LPG produced is minimal.

Advantageously, the overall conversion of the fresh feedstock to naphtha is between 80% and 100%, preferably between 95% and 100%, more preferably between 99% and 100%, notably 100%. The overall conversion is calculated relative to the feedstock entering step a) using the following operation: (the flow rate by weight of the fresh feedstock entering step a) minus the

flow rate by weight of the purged part of the heavy cut in step e), described below) divided by the flow rate by weight of the fresh feedstock entering step a).

In one embodiment, the hydrocracking step b) is performed at a minimum hydrogen partial pressure of 2.5 MPa.

- 5 The operating conditions of the hydrocracking step b) are advantageously adjusted so as to maximize the production of naphtha, while ensuring good operability of the hydrocracking unit. The operating conditions used in the reaction zone(s) are generally expressed using the weighted average bed temperature (WABT). The hydrocracking temperature is advantageously determined as a function of the catalytic systems, the equipment used, and
10 the configuration thereof. For example, the weighted average bed temperature (or WABT) is calculated in the following manner:

$$\text{WABT} = (T_{\text{inlet}} + T_{\text{outlet}}) / 2$$

- where T_{inlet} : the temperature at the inlet of the catalytic bed of the hydrocracking reaction section, and T_{outlet} : the temperature of the effluent at the outlet of the catalytic bed of the
15 hydrocracking reaction section.

The hourly space velocity (HSV) is defined here as the ratio of the hourly volume flow rate of the hydrocarbon-based cut supplying step b) to volume of catalyst(s).

- Advantageously, the hydrogen used in the hydrocracking step b) may originate from a hydrogen supply and/or from recycled hydrogen in particular from the separation step c),
20 preferably after purification, and/or from a gaseous effluent rich in hydrogen originating from step a).

- The at least one hydrocracking catalyst should advantageously be a bifunctional catalyst, having a hydrogenating phase in order to be able to hydrogenate the impurities and produce the equilibrium between the saturated compounds and the corresponding olefins, and an acid
25 phase which makes it possible to promote the hydroisomerization and hydrocracking reactions. The acid function is provided by supports with large surface areas (generally 100 to 800 m².g⁻¹) having surface acidity, such as halogenated (notably chlorinated or fluorinated) aluminas, combinations of boron and aluminum oxides, amorphous silica-aluminas and zeolites Y, beta and ZSM-5. The hydrogenating function is provided either by one or more metals from columns
30 9 and 10 of the Periodic Table of the Elements, such as cobalt, nickel, rhodium, palladium, iridium and platinum, or by a combination of at least one metal from column 6 of the Periodic Table of the Elements such as molybdenum and tungsten and at least one metal from columns

9 and 10. The applicant has also developed a range of catalysts that can be used in the hydrocracking step b); these catalysts are notably described in documents FR2819430, FR2846574, FR2875417, FR2863913, FR2795341, FR2795342 and FR2984760.

Advantageously, use may for example be made of a catalyst comprising from 0.5% to 10% by weight of nickel (expressed as nickel oxide NiO) or from 1% to 30% by weight of molybdenum, preferably from 5% to 25% by weight of molybdenum (expressed as molybdenum oxide MoO₃) or from 1% to 40% by weight of tungsten (expressed as tungsten oxide WO₃) on the support in question. The total content of oxides of metals from groups 6 and 9 or 10 in the catalyst is generally between 5% and 40% by weight and preferentially between 7% and 35% by weight.

Where appropriate, the weight ratio (expressed on the basis of the metal oxides) of metal (metals) from group 6 to metal (metals) from group 9 or 10 is, in general, from around 20 to around 1, and most often from around 10 to around 2.

In one embodiment, commercial catalysts may be used, among others and depending on the features of the feedstock and the desired performance qualities, such as HDK776, HDK766, HYK732, HYK752, HYK762, HYK742, HYK 743 which are sold by the company AXENS, for example.

In the case where said catalyst comprises a zeolite, the content of zeolite in the hydrocracking catalyst(s) is advantageously between 0.1% and 80% by weight, preferably between 3% and 70% by weight, the percentages being expressed as a percentage of zeolite relative to the total weight of the catalyst.

A preferred catalyst comprises, and preferably consists of, at least one metal from column 6 and optionally at least one non-noble metal from columns 9 and 10, at least one promoter element, preferably phosphorus, at least one zeolite Y and at least one alumina binder.

An even more preferred catalyst comprises, and preferably consists of, nickel, molybdenum, phosphorus, a zeolite USY, and optionally also a zeolite beta, and alumina.

Another preferred catalyst comprises, and preferably consists of, nickel, tungsten, alumina and silica-alumina.

Another preferred catalyst comprises, and preferably consists of, nickel, tungsten, a zeolite USY, alumina and silica-alumina.

In a particular embodiment, said hydrocracking catalyst is in extruded form.

According to another aspect of the invention, the hydrocracking catalyst as described above further comprises one or more organic compounds containing oxygen and/or nitrogen and/or

sulfur. Such a catalyst is often denoted by the term "additivated catalyst". Generally, the organic compound is chosen from a compound comprising one or more chemical functions chosen from a carboxylic, alcohol, thiol, thioether, sulfone, sulfoxide, ether, aldehyde, ketone, ester, carbonate, amine, nitrile, imide, oxime, urea and amide function or also compounds including a furan ring or also sugars.

According to one embodiment, this hydrocracking step b) makes it possible to produce a cut of naphtha type which is advantageously very paraffinic, the paraffin content of which is typically greater than 90% by weight, preferably greater than 95% by weight.

Preferably, the naphtha produced in step b) consists of paraffinic compounds and any other non-paraffinic compounds contained in the feedstock.

Advantageously, the configuration of the reactor capable of carrying out the reactions according to the invention is composed of a number of suitable catalyst beds. Generally, the configuration comprises at least 2 catalyst beds and preferentially more than 3 and in particular more than 5 beds, but fewer than 20 beds and preferentially fewer than 15 beds and in particular fewer than 10 catalyst beds. The preferred configuration comprises between 2 and 19 beds and in particular between 3 and 9 catalyst beds.

Separation step c)

The process according to the invention comprises a step c) of separating the hydrocracked effluent obtained in step b), and obtaining at least one gaseous effluent comprising hydrogen and a hydrocarbon-based liquid effluent.

In one embodiment, in step c) of separating the hydrocracked effluent obtained in step b), contaminants, any light hydrocarbons, and an aqueous liquid effluent are also obtained.

The separation section of step c) is advantageously carried out in separation equipment well known to those skilled in the art (separating vessels which may be operated at various pressures and temperatures, pumps, heat exchangers, etc.).

In one embodiment, the separation step c) is followed by a step of purifying and/or washing the gaseous effluent comprising hydrogen obtained in step c) to remove the contaminants, notably H_2S , CO and CO_2 , followed by recycling of the washed gaseous effluent into at least the hydrotreatment step a) and/or hydrocracking step b). The aim of this step is to ensure the hydrogen coverage and the control of the exothermicity in step a) and/or in step b).

Typically, a small part of the gaseous effluent may optionally be purged to avoid the accumulation of oxygen compounds and light compounds toward the fuel gas network or toward a hydrogen recovery unit.

In one embodiment, part of the liquid effluent obtained in step c) is recycled to step a) and/or step b), preferably to step a). The recycling to step a) makes it possible to manage the exothermicity and to reduce the flow rate of the first recycling in the embodiment where step a) is followed by a high-temperature separation step followed by recycling of part of the liquid effluent from this separation. The recycling to step b) makes it possible to control the conversion in step b) and the overall conversion of the fresh feedstock.

10 Stripping step d)

The process according to the invention comprises a step d) of stripping the hydrocarbon-based liquid effluent obtained in step c), and obtaining at least one off-gas cut, and a stripped liquid effluent.

Step d) makes it possible in particular to remove the gases dissolved in the hydrocarbon-based liquid effluent, such as ammonia, hydrogen sulfide, CO₂, CO and light hydrocarbons having 1 to 4 carbon atoms, by producing an off-gas cut comprising these compounds.

In one embodiment, the off-gas cut is sent, after an optional washing step, completely or partly to the steam cracking step f), separately or as a mixture with the naphtha cut obtained in step e), into one or more furnaces of the steam cracking step f), making it possible to upgrade this cut into biobased olefins.

In one embodiment, the off-gas cut obtained in step d) is sent to a separation step in order to recover at least one depropanized gaseous off-gas cut that is low in propane and butane and one LPG cut. This separation step may advantageously be carried out in separation columns.

In one embodiment, the LPG cut is sent to the steam cracking step f), separately or as a mixture with the naphtha cut obtained in step e), into one or more furnaces of the steam cracking step f), making it possible to upgrade this cut into biobased olefins.

In one embodiment, the depropanized gaseous off-gas cut that is low in propane and butane is sent to the steam cracking step f), after an optional washing step, separately or as a mixture with the naphtha cut obtained in step e), into one or more furnaces of the steam cracking step f), making it possible to upgrade this cut into biobased olefins.

In another embodiment, the depropanized gaseous off-gas cut that is low in propane and butane and/or the LPG cut is sent to a steam reformer step to obtain biobased hydrogen.

According to one embodiment, step d) may be performed in a section advantageously comprising at least one stripping column equipped with a reflux circuit comprising a reflux drum. Said stripping column is advantageously supplied with the liquid effluent from step c) and with a stream of water vapor. Said column may also be reboiled by a furnace or an exchanger. The liquid effluent from step c) may optionally be heated before entering the stripping column.

Thus, the lightest compounds are entrained at the column top and into the reflux circuit comprising a reflux drum in which a gas/liquid separation takes place. The gas phase which comprises the light hydrocarbons is withdrawn from the reflux drum as a gaseous stream. The stripped hydrocarbon-based liquid effluent is advantageously stabilized and withdrawn at the stripping column bottom.

According to one embodiment, an LPG liquid cut may be recovered at the reflux drum and then stabilized in a stabilization column. The stabilized LPG liquid cut is sent into the LPG cut obtained in the step of separating the off-gas cut.

According to one embodiment, a light naphtha cut may be recovered at the reflux drum and then stabilized in a stabilization column. The stabilized light naphtha cut is sent into the naphtha cut obtained in the fractionation step f).

According to one embodiment, the stripping step d) may be performed on part of the hydrocarbon-based liquid effluent obtained in step c), the other part supplied directly to the fractionation step d), making it possible to obtain at least one off-gas cut, and a stripped liquid effluent which is sent to the fractionation step. In this embodiment, part of the stripping step d) is carried out in the fractionation step.

According to another embodiment, the stripping step d) is integrated into the fractionation step e) and those skilled in the art can, using the same fractionation section, comprising one or more columns, obtain the various streams described in these two steps.

Fractionation step e)

The process according to the invention comprises a step e) of fractionating the stripped liquid effluent obtained in step d), and obtaining at least one paraffin-rich naphtha cut.

In one embodiment, in step e) of fractionating the stripped liquid effluent obtained in step d), a heavy cut comprising hydrocarbon-based compounds having boiling points greater than 150°C, preferably greater than 175°C, is also obtained.

In a particular embodiment, the heavy cut obtained comprises compounds having boiling points greater than 215°C, preferably greater than 200°C. This makes it possible to produce a heavy naphtha cut having a boiling point of up to 215°C.

5 In one embodiment, the heavy cut is completely or partly recycled to the hydrotreatment step a) and/or hydrocracking step b), preferably with a recycled feedstock/fresh feedstock ratio of between 0 and 4. This makes it possible to control the conversion rate in the hydrocracking reactor, and achieve the overall conversion under optimal conditions in terms of investment and utility consumption.

10 Advantageously, a small part of the heavy cut is purged, continuously or intermittently, before it is sent to step a) and/or b). Those skilled in the art will adjust the amount purged to remove the compounds which cannot be cracked and which have accumulated in the reaction loop.

15 Advantageously, the amount of heavy cut recycled is adjusted such that the weight ratio of the recycled stream to the fresh feedstock supplying the overall process is less than or equal to 10, preferably less than or equal to 5, and preferentially greater than or equal to 0.001, preferably greater than or equal to 0.01, and preferably greater than or equal to 0.1. Very preferably, the amount of the recycled stream is adjusted such that the weight ratio of the recycled stream to the fresh feedstock is between 0.2 and 5, preferably between 0.3 and 2.0, even more preferably between 0.5 and 1.5.

20 Depending on the feedstocks treated, this recycling advantageously makes it possible on the one hand to dilute the impurities and on the other hand to control the temperature in the reaction step(s) a) and/or b), in which the reactions involved may be highly exothermic.

The fractionation step advantageously comprises at least one main fractionation column, making it possible to separate an overhead fraction, and a heavy fraction, said fractions comprising the various products of the units.

25 The fractionation step e) is advantageously performed at a pressure less than or equal to 1.0 MPa abs., preferably between 0.05 and 1.0 MPa abs.

In one embodiment, all of the cuts from the process are upgraded into renewable products.

The naphtha cut is sent at least partly, preferably completely, to a stream cracking unit f), making it possible to upgrade this cut into biobased olefins.

30 Advantageously, the yield of naphtha in the process according to the invention is greater than 50% by weight, notably greater than 60% by weight, preferably greater than 70% by weight, preferably between 50% and 85% by weight. The yield of naphtha is calculated relative to the

fresh feedstock entering step a) using the following operation: (the flow rate by weight of naphtha produced in step e) divided by the flow rate by weight of the effluent entering step a)).

Steam cracking step f)

5 The process according to the invention comprises a step f) of steam cracking at least part, preferably all, of the naphtha cut obtained in step e) and obtaining at least one biobased gaseous effluent comprising ethylene and propylene.

In one embodiment, the off-gas cut obtained in step d) is also treated in the steam cracking step f), separately from the naphtha cut or in co-treatment.

10 In one embodiment, the LPG cut obtained after an optional step of separating the off-gas cut obtained in step d) is also treated in the steam cracking step f), separately from the naphtha cut or in co-treatment.

In one embodiment, the depropanized gaseous off-gas cut that is low in propane and butane obtained after an optional step of separating the off-gas cut obtained in step d) is also treated in the steam cracking step f), separately from the naphtha cut or in co-treatment.

15 The steam cracking step f) advantageously consists of the non-catalytic decomposition, under the combined effect of a high temperature and a low pressure in the presence of water vapor, of saturated hydrocarbons from natural gas or naphtha in the presence of water vapor, in order to produce unsaturated aliphatic or aromatic hydrocarbon cuts. Said cuts are then used for the synthesis of a large number of products, for example polyethylene or propylene. In the case of
20 the process according to the invention, the steam cracking step f) makes it possible to produce renewable (of biobased origin) aliphatic unsaturated hydrocarbons.

Advantageously, the steam cracking step f) treats the naphtha cut and/or the LPG cut in the suitable scheme and operating conditions known to those skilled in the art.

25 Advantageously, the steam cracking unit treats the naphtha cut and/or LPG cut in the optional presence of an external feedstock of naphtha and/or LPG.

Advantageously, the residence time in the steam cracking furnace is limited in order to limit the formation of heavy products. Furthermore, quenching of the effluent is performed in order to fix the composition of the effluent at the outlet of the furnace.

30 Advantageously, the temperature at which the steam cracking furnaces are operated depends on the nature of the feedstock. Preferably, the steam cracking furnaces are suitable for treating a feedstock of naphtha type.

In the various variants of the process according to the invention, the feedstocks in the steam cracking step may comprise external feedstocks, corresponding to dedicated furnaces or furnaces in common with the furnaces treating the feedstocks produced by the steps of the process according to the invention. Said external feedstocks may be quite varied and range from light saturated hydrocarbons such as ethane, propane or also ethane-propane mixtures, to more or less heavy petroleum cuts such as petrochemical naphtha. The nature of the treated feedstocks will depend on the types of furnaces installed.

Advantageously, the steam cracking step is performed in an installation which is composed of a certain number of furnaces, quenching boilers and a fractionation train. The hydrocarbon-based feedstock enters the hot section of the unit via the convection zone A of the furnace where it is preheated, and then it is mixed with the water vapor which is also preheated in this same zone; the hydrocarbons and the water then pass through the actual radiation zone of the furnace where the rapid temperature rise and the pyrolysis reactions take place. At the outlet of the furnace, the effluents are, in order to avoid any subsequent reaction, fixed in their kinetic evolution possibilities by abrupt quenching generally performed in two stages: a first indirect quenching with water, followed by direct quenching using the heavy residue pyrolysis byproduct. The effluents are then transferred into a primary fractionating tower which separates out at the bottom a heavy residue known as "pyrolysis oil" and, by withdrawals, a steam cracking gasoline fraction and water, whereas the light pyrolysis products leave at the top in gaseous form.

After compression, washing with sodium hydroxide (intended to remove H_2S and the acidic gases) and drying, these light effluents then enter the cold section of the unit which may be designed in several ways, but which ensures the separation of the hydrogen, ethylene at 99.9% (by mass), propylene at 95% which may, completely or partly, be brought to 99.5% (by mass), a C4 cut, from the complementary fraction of the steam cracking gasoline rich in aromatic hydrocarbons (more than 50% by weight of aromatic compounds).

DESCRIPTION OF THE FIGURES

Figure 1: A vegetable oil feedstock 111 is supplied into a step a) of hydrotreatment in the presence of hydrogen 112 and of at least one fixed-bed catalyst, said catalyst comprising a conventional NiMo hydrogenating function to obtain a hydrotreated vegetable oil effluent 113, which is then sent into a step b) of hydrocracking in the presence of hydrogen 114 and in the presence of a catalyst of zeolite USY NiMo type to obtain a hydrocracked effluent 115. The hydrocracked effluent 115 is sent to a separation step c) to obtain a gaseous effluent 116 comprising hydrogen and a liquid effluent 117. The liquid effluent 117 is sent into a stripping step to recover an off-gas cut 118 and a stripped liquid effluent 119. The stripped liquid effluent 119 is then sent into a fractionation step e) to recover at least one paraffin-rich naphtha cut 121. The naphtha cut 121 is sent into a steam cracking step f) in order to produce the effluent 122 rich in ethylene, propylene and biobased light olefins. In this embodiment, the process does not produce any heavy cut comprising compounds having boiling points greater than 150°C.

Figure 2: A vegetable oil feedstock 211 is supplied into a step a) of hydrotreatment in the presence of hydrogen 212 and of at least one fixed-bed catalyst, said catalyst comprising a conventional NiMo hydrogenating function to obtain a hydrotreated vegetable oil effluent followed immediately by a high-temperature separation step in order to recover a liquid effluent and a gaseous effluent 223 rich in hydrogen, in oxygen compounds and in light hydrocarbons. Part of the liquid effluent 224 is recycled to the hydrotreatment step a) in order to control and reduce the exothermicity in the reactor during this step. The non-recycled part of the liquid effluent 213 is mixed with the gaseous effluent 223 and then is sent into a step b) of hydrocracking in the presence of hydrogen included in the gaseous effluent 223 but also in the presence of a stream 214 rich in hydrogen and in the presence of a hydrocracking catalyst of zeolite USY type, to obtain a hydrocracked effluent 215. Said hydrocracked effluent 215 is sent to a separation step c) to obtain at least one gaseous effluent 216 comprising hydrogen and one liquid effluent. The gaseous effluent 216 is optionally sent to a washing step in order to remove the contaminants and is recycled to the hydrotreatment step a) and/or to the hydrocracking step b). Part of the liquid effluent 225 may optionally be recycled to the hydrotreatment step a) and/or hydrocracking step b) in order to control and reduce the exothermicity in the reactor of these steps. The non-recycled part of the liquid effluent 217 is sent into a stripping step to recover an off-gas cut 218 and a stripped liquid effluent 219. An LPG cut 226 is separated from the gaseous effluent 218 and may optionally be sent to the

- 5 steam cracking step f). The stripped liquid effluent 219 is sent into a fractionation step e) to recover at least two liquid effluents including 221 a paraffin-rich naphtha cut and 220 a heavy cut having a boiling temperature greater than 150°C which is recycled to the hydrotreatment step a) and/or hydrocracking step b) to be converted again. The naphtha cut 221 is sent into a steam cracking step f) in order to produce the effluent 222 rich in ethylene, propylene and biobased light olefins.

EXAMPLES

Example 1: process for treating a feedstock from a renewable source according to the invention

- 10 The features of the rapeseed oil feedstock used are presented in the following table:

Table 1

Density at 15°C (kg/m ³)	923,5
Oxygen (% by weight)	11
Hydrogen (% by weight)	11,4
Sulfur (ppm by weight)	3
Nitrogen (ppm by weight)	13
Phosphorus (ppm by weight)	<1
Magnesium (ppm by weight)	<1
Calcium (ppm by weight)	<1
Sodium (ppm by weight)	<1

The operating conditions in the hydrotreatment section are presented in the following table:

Table 2

Mass flow rate of the feedstock	100 t/h
Pressure	5,5 MPa
HSV	1 h ⁻¹
Catalyst	NiMo
Temperature, °C	290
Hydrogen to hydrocarbon ratio	1000 Nm ³ /Sm ³
Mass ratio of the recycled effluent obtained after high-temperature and high-pressure separation step to the fresh feedstock	0.7
Performance	
Rate of hydrogenation of oxygen-based compounds	99.9%
Mass flow rate of hydrotreated oil	89.5 t/h
Density of hydrotreated oil (kg/m ³)	790

- 5 The operating conditions in the hydrocracking (HCK) step are presented in the following table:

Table 3

Pressure	6,0 MPa
HSV	4 h ⁻¹
Catalyst	NiMo USY
WABT	300°C
Hydrogen to hydrocarbon ratio	1000 Nm ³ /Sm ³
Conversion per pass	50% by weight
Overall conversion (HCK reactor inlet-purge) / (HCK reactor inlet)	99.9% by weight
Recycled heavy cut flow rate / fresh feedstock flow rate (by weight)	1.1

The overall outcome of the process is presented in the following table:

Table 4

	t/h
Feedstock	100.0
H ₂	4.3
Total	104.3
Products (t/h)	
Water	10.5
Off-gas (C1, C2 and impurities)	0.2
LPG cut	15.3
Naphtha	76.0
Purge	0.1
CO-CO ₂	2.2
Total	104.3

The properties of the naphtha of C5-175°C cut point are as follows:

- 5
 - Paraffinic feedstock: content of paraffins greater than 99% by weight
 - Density 677 kg/m³
 - Sulfur < 1 ppm by weight
 - Nitrogen < 1 ppm by weight
 - Content of oxygen < 0.1% by weight
- 10 These properties make it a feedstock of choice for the production of ethylene and of propylene as it is very rich in paraffins.

The biobased naphtha feedstock obtained is sent to the steam cracker at a flow rate of 76 t/h. This paraffin-rich feedstock produces high yields of ethylene and propylene of biobased origins, at least 65% of the feedstock entering the steam cracker.

The LPG cut and/or the off-gas cut may also be sent to the steam cracker.

The process according to the invention therefore makes it possible to almost exclusively produce naphtha and an LPG cut, unlike the processes according to the prior art. In addition, the process is performed in a minimum number of items of equipment, since the
5 hydrotreatment and hydrocracking steps are linked together without a separation step.

CLAIMS

1. A process for treating a feedstock from a renewable source comprising triglycerides and/or fatty acids and/or esters, said process comprising the steps of:
 - 5 a) a step of hydrotreating said feedstock in the presence of hydrogen and of at least one fixed-bed hydrotreatment catalyst, performed at a temperature of between 280°C and 410°C, and at a relative pressure of between 2.0 and 13.0 MPa, and at an hourly space velocity of between 0.3 and 5 h⁻¹, and obtaining a hydrotreated effluent;
 - b) a step of hydrocracking the hydrotreated effluent obtained in step a) in the presence of hydrogen and of at least one fixed-bed hydrocracking catalyst, at a temperature of

10 between 280°C and 410°C, performed at a pressure of between 2.0 MPa and 13.0 MPa, and at an hourly space velocity of between 0.5 and 10 h⁻¹, and obtaining a hydrocracked effluent;
 - c) a step of separating the hydrocracked effluent obtained in step b), and obtaining at

15 least one gaseous effluent comprising hydrogen and a hydrocarbon-based liquid effluent;
 - d) a step of stripping the hydrocarbon-based liquid effluent obtained in step c), and obtaining at least one off-gas cut and a stripped liquid effluent;
 - e) a step of fractionating the stripped liquid effluent obtained in step d), and obtaining at least one paraffin-rich naphtha cut;
 - 20 f) a step of steam cracking at least part, preferably all, of the naphtha cut obtained in step e) and obtaining at least one biobased gaseous effluent comprising ethylene and propylene.
2. The process as claimed in claim 1, in which the hydrotreatment step a) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³.
- 25 3. The process as claimed in either one of the preceding claims, in which the at least one hydrotreatment catalyst comprises a support and an active phase, said active phase comprising at least one metal from group 6 and optionally one or more metals from group 9 or 10, preferably the active phase contains molybdenum only (Mo), or nickel and molybdenum (NiMo), or cobalt and molybdenum (CoMo), or nickel, cobalt and

30 molybdenum (CoNiMo).

4. The process as claimed in any one of the preceding claims, in which the hydrotreatment step a) is followed by a step of separating the hydrotreated effluent at high temperature of between 280°C and 410°C, and at high pressure of between 2.0 and 13.0 MPa, and obtaining at least one gaseous effluent and one liquid effluent.
- 5 5. The process as claimed in claim 4, in which part of the liquid effluent obtained in the high-temperature separation step is recycled to the hydrotreatment step a).
6. The process as claimed in any one of the preceding claims, in which the hydrocracking step b) is performed with a hydrogen to hydrocarbon ratio of between 100 and 5000 Nm³/Sm³.
- 10 7. The process as claimed in any one of the preceding claims, in which the hydrocracking step b) is performed at a minimum hydrogen partial pressure of 2.5 MPa.
8. The process as claimed in any one of the preceding claims, in which the at least one hydrocracking catalyst comprises a hydrogenating function and an acid function provided by supports with large surface areas having surface acidity, such as
15 halogenated aluminas, combinations of boron and aluminum oxides, amorphous silica-aluminas and zeolites Y, beta and ZSM.
9. The process as claimed in any one of the preceding claims, in which in step b) the conversion per pass into hydrocarbon-based compounds is between 20% and 100% by weight.
- 20 10. The process as claimed in any one of the preceding claims, in which the separation step c) is followed by a step of purifying and/or washing the gaseous effluent comprising hydrogen obtained in step c) to remove the contaminants, notably H₂S, CO and CO₂, followed by recycling of the washed gaseous effluent into at least the hydrotreatment step a) and/or hydrocracking step b).
- 25 11. The process as claimed in any one of the preceding claims, in which part of the liquid effluent obtained in step c) is recycled to step a) and/or step b), preferably to step a).
12. The process as claimed in any one of the preceding claims, in which the off-gas cut obtained in step d) is sent to a separation step in order to recover a depropanized gaseous off-gas cut that is low in propane and butane and an LPG cut.
- 30 13. The process as claimed in claim 12, in which the LPG cut is sent to the steam cracking step f), separately or as a mixture with the naphtha cut obtained in step e), into one or more furnaces of the steam cracking step f).

14. The process as claimed in any one of the preceding claims, in which in step e) of fractionating the stripped liquid effluent obtained in step d), a heavy cut comprising hydrocarbon-based compounds having boiling points greater than 150°C, preferably greater than 175°C, is also obtained.
- 5 15. The process as claimed in claim 14, in which the heavy cut obtained in step e) is completely or partly recycled to the hydrotreatment step a) and/or hydrocracking step b), preferably with a recycled feedstock/fresh feedstock ratio of between 0 and 4.
- 10 16. The process as claimed in any one of the preceding claims, in which said feedstock is chosen from vegetable oils such as rapeseed oil, jatropha oil, soybean oil, palm oil, sunflower oil, olive oil, coconut oil, camelina oil, fish oils or heterotrophic or autotrophic algal oils, animal fats, residues from the paper industry or mixtures of these various feedstocks.