

PROCESS FOR THE PRODUCTION OF OLEFINIC COMPOUNDS AND A
HYDROCARBON FUEL OR A FRACTION THEREOF

The present invention relates to a process for the
5 production of olefinic compounds and a hydrocarbon fuel
or a fraction thereof, which comprises subjecting a
mixture of glycerides having at least one unsaturated
hydrocarbon chain to metathesis reaction and, after
separating the olefinic mixture obtained, effecting a
10 hydrodeoxygenation and subsequently hydroisomerization
process, so as to obtain the hydrocarbon fuel or a
fraction thereof.

This process advantageously allows both olefinic
compounds to be obtained, which can be used, for
15 example, as intermediates for the production of
detergents, additives, lubricants and/or plastic
materials or components which can be used in the field
of oil explorations and productions, and also a
hydrocarbon fuel, or fraction thereof, preferably
20 selected from diesel, naphtha, jet-fuel or mixtures
thereof.

Due to a decrease in fuel reserves of a fossil
origin and the negative impact on the environment
produced by anthropogenic emissions of carbon dioxide
25 (CO₂), technologies aimed at producing fuels starting
from biomasses (so-called bio-fuels), allowing, with
time, the complete transition to renewable energy
sources, are becoming increasingly more important.

Among the new sustainable energy sources, biomasses can significantly contribute to achieving these objectives. Biomasses are biodegradable vegetable or animal substances deriving from agriculture, forestry
5 and all relative industries, comprising fishing, aquaculture and waste and scraps coming from the same.

At the same time, the need for breaking free from fossil sources alone and from the legislative obligations imposed on emissions of an anthropogenic
10 origin, is also felt in the production of chemicals, indispensable for everyday life.

Consequently, the use of renewable sources such as biomasses, which are economical and sustainable from an environmental point of view, can offer an alternative
15 to the use of fossil sources for the production of chemical products useful in everyday life (biochemicals, which refers to their production starting from renewable sources).

The development of so-called "green chemistry" is
20 therefore underway, which implies a restructuring of the production chains through the use of renewable sources deriving from natural biomasses and transformation technologies with low environmental emissions, leading to the creation of so-called "bio-
25 refineries".

The process of the present invention can be advantageously effected in a bio-refinery, by integrating the production of bio-fuels with the

production of intermediates useful for the production of detergents, additives, lubricants and/or plastic materials or components that can be used in the field of oil explorations and productions (bio-chemicals),
5 starting from the same renewable raw material, i.e. a mixture of glycerides, preferably of a vegetable or animal origin or of a microbial origin.

In the present invention, the integrated production of bio-fuels and bio-chemicals is obtained through a
10 process which comprises a metathesis reaction followed by conversion of a part of the metathesis products.

At present, the production of bio-fuels from renewable sources, such as natural oils, is essentially effected through two main processes:

- 15 I. transesterification, mainly with methanol, with the production of FAME (fatty acid methyl esters), normally called bio-diesel; or
- II. through catalytic processes such as so-called "hydrotreating", with the production of
20 paraffinic cuts, mainly diesel, but also gasoline, in variable proportions according to the processes used.

In the former case, a biofuel is obtained, which however has various problems (for example,
25 unsatisfactory low-temperature performances, relating to instability in storage and distribution, etc.).

In the latter case, the starting oils are converted into hydrocarbon cuts with high performances, for

example complete miscibility with refinery cuts from fossil sources, high engine features such as cold properties and high cetane number, etc. Among the numerous hydrotreating technologies available, the
5 EcofiningTM process of ENI/UOP, can be cited, as described, for example, in patent applications WO2008/058664, EP1728844, WO2009/039347, WO2009/039335, WO2009039333, WO2009/158268 and in American patent US7915460, all in the name of ENI S.p.A. and UOP 11c,
10 wherein all the documents are incorporated herein as reference. The main product of the Ecofining technology is called Green Diesel and can be obtained with yields of up to 88% with respect to the starting oil, or renewable source. The Ecofining process, starting from
15 natural oil, typically leads to the formation (by weight) of 4-5% of propane, 1-8% of naphtha cut, 75-85% of diesel cut with about 1.5-3.8% of hydrogen consumption with respect to 100 of the starting biomass.

20 The hydrotreating process, in particular called Ecofining, is a two-step process: the first step consists in a hydrogenation/deoxygenation (hydrodeoxygenation) reaction which removes all the heteroatoms in the molecules, whereas the second step
25 is a hydroisomerization/cracking step which allows a diesel cut to be produced, having the desired characteristics. In the first step, the catalytic system effects not only a deoxygenation of the

feedstock (reduction of the esters to hydrocarbons), but also hydrogenates all the possible double bonds present in the fatty acids, whose esters form the starting oil. Consequently, the more unsaturated the starting mixture of fatty acids, the higher the specific hydrogen consumption of the catalytic hydrotreating process, will be.

Possible feeding streams for catalytic hydrotreating processes composed of completely saturated oils therefore represent particularly valuable feeds for said processes and in particular for the Ecofining process. The natural oils that can be obtained from cultivations, for example, are in fact a mixture of fatty acids in which the amount of unsaturated acids is not negligible.

More specifically, it would be desirable for these processes to have a feeding stream obtained by the selective transformation of the unsaturated components present in the starting renewable source alone, wherein the saturated components initially present have been left unaltered.

An objective of the present invention therefore relates to a process for the production of olefinic compounds and a hydrocarbon fuel or a fraction thereof, which comprises:

- (a) subjecting a mixture of glycerides having at least one unsaturated hydrocarbon chain, possibly in a mixture with free fatty acids, to a metathesis

- reaction with at least one C₂-C₆ mono-olefin in the presence of a metathesis catalyst, so as to obtain a mixture of glycerides having at least one unsaturated hydrocarbon chain with a length less than the initial length, and a mixture of C₆-C₁₈ olefins;
- 5 (b) separating the mixture of C₆-C₁₈ olefins from the mixture of glycerides obtained in step (a);
- (c) possibly subjecting the mixture of glycerides obtained in step (b) to a transesterification reaction with an alcohol selected from methanol, ethanol or mixtures thereof, so as to obtain a mixture of methyl and/or ethyl esters and glycerol;
- 10 (d) subjecting the mixture of glycerides obtained in step (b) or the mixture of methyl and/or ethyl esters obtained in step (c) to a hydrodeoxygenization process and followed by a hydroisomerization process, so as to obtain the hydrocarbon fuel or fraction thereof.
- 15 In the process described above, step (c') can be present, after step (c), wherein the glycerol is separated from the mixture of methyl and/or ethyl esters, and subsequently step (c'') wherein the methyl and/or ethyl esters having an unsaturated hydrocarbon chain are separated from the methyl and/or ethyl esters having a saturated hydrocarbon chain. The methyl and/or ethyl esters having a saturated hydrocarbon chain thus obtained are then subjected to the catalytic
- 25

hydrodeoxygenation step (d) and subsequent catalytic hydroisomerization.

In particular, the hydrocarbon fuel or fraction thereof, produced with the process of the invention, is
5 selected from: diesel, naphtha, jet-fuel, or mixtures thereof.

The mixture of C₆-C₁₈ olefins obtained from step (b) and/or the methyl and/or ethyl esters having an unsaturated hydrocarbon chain obtained from step (c")
10 are preferably intermediates that can be used for the renewable production (wherein "renewable production" refers to "production starting from renewable sources, alternative to fossil sources) of detergents, additives, lubricants and/or plastic materials or
15 components that can be used in the field of oil explorations and productions.

The glycerides having at least one unsaturated hydrocarbon chain used in the mixture in step (a) are glycerides, preferably triglycerides, of a vegetable or
20 animal origin or of a microbial origin.

As indicated in US2009/0077865 paragraph [009], the term fats and renewable oils comprises glycerides and free fatty acids, wherein the glycerides are mainly triglycerides, but monoglycerides and triglycerides can
25 also be present.

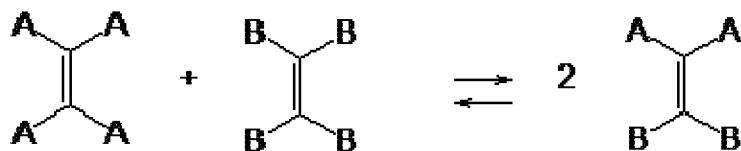
Said glycerides of a vegetable or animal origin or of a microbial origin are preferably glycerides of

fatty acids having at least one mono- or poly-unsaturated C₁₂-C₂₄ hydrocarbon chain.

The glycerides used in the process of the invention are preferably selected from: vegetable oils, such as:
 5 sunflower, rapeseed, canola, palm, soya bean, hemp, olive, linseed, mustard, peanut, castor, coconut and tall oil; recycled oils and/or fats from the food industry; lipids coming from algal cultivations; animal oils or fats, such as: lard, lard cream, tallow, milk
 10 fats; or mixtures thereof.

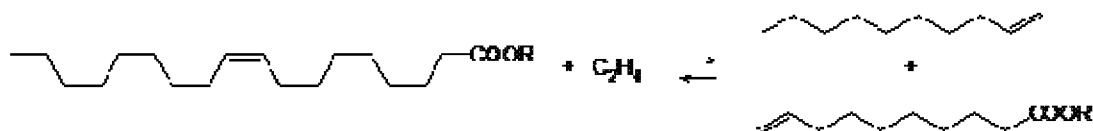
The metathesis reaction effected in step a) consists in a particular re-arrangement of the substituents present on one or more double bonds. If the reaction is attributed to the double bonds of a
 15 single olefin, this is known as homo-metathesis. If, on the other hand, it is attributed to a mixture of two or more olefins, this is called co-metathesis. The latter is of particular interest with regard to the present invention and can be schematized as follows:

20



In the case of oils, the most favourable option is their co-metathesis with a short olefin (C₂-C₆). By
 25 considering, for the sake of simplicity, only the co-metathesis of esters of oleic acid (generally the most abundant among the unsaturated compounds present in

vegetable oils) with ethylene, the reaction gives a mixture of esters of 9-decen-1-oic acid and 1-decene:



5 In practice, due to the presence in the starting oil of esters of other unsaturated acids such as linoleic and linolenic acids, the products obtained are esters of 9-decen-1-oic acid and a mixture of C₄-C₁₀ α-olefins and 1,4-pentadiene, in addition to the

10 saturated fraction to be fed to the hydrotreating process. If the co-metathesis reaction were carried out with olefins different from ethylene, the distribution of the products obtained would be considerably different. With 1-butene, for example, there would be a

15 mixture of esters of unsaturated C₁₀-C₁₃ acids, of C₄-C₁₃ olefins, terminal and internal, and olefins containing from 5 to 9 carbon atoms.

The olefin used in the metathesis process of the present invention is a C₂-C₆, preferably C₂-C₄, mono-

20 olefin, selected from: ethylene, propene, 1-butene, but-2-ene, 2-methyl-propene, or mixtures thereof.

The molar ratio between the double bonds of the mixture of glycerides having at least one unsaturated hydrocarbon chain and the double bonds of said at least

one C₂-C₆ olefin used in step a) preferably ranges from 1:0.1 to 1:20.

Furthermore, the preferred conditions for carrying out step (a) are a temperature ranging from 20 to 120 °C, for a time ranging from 0.5 to 6 hours, preferably from 20 to 80 °C and 0.5 to 3 hours.

Step (a) is preferably carried out at a pressure ranging from 1 to 30 bars and even more preferably the pressure ranges from 1 to 15 bars.

10 The metathesis reaction is catalyzed by some transition metals such as, for example, ruthenium, molybdenum, osmium, chromium, rhenium and tungsten.

 The metathesis catalyst of step (a) can be a carbene complex of a transition metal of Group 8, in particular selected from: ruthenium, molybdenum, 15 osmium, chromium, rhenium, tungsten.

 The catalysis of step a) can be either homogeneous or heterogeneous.

 The metathesis catalysts that can be used in the present invention are, for example, those described in international patent application in the name of Elevance Renewable Science Inc. publication number WO2008/046106 and in international patent application in the name of Materia Inc. WO2008/08440, both 20 incorporated herein as reference. In particular, the catalysts described in WO2008/046106, from page 15 paragraph [0061] to page 35 paragraph [106], and those 25

described in WO2008/08440, from page 20 paragraph [0068] to page 39 paragraph [0020], can be used.

Other metathesis catalysts that can be used in the present invention are, for example, those described in
5 international patent application WO2009/020667 in the name of Elevance Renewable Science Inc., incorporated herein as reference, from page 18 paragraph [0067] to page 46 paragraph [0120].

Other patent applications that describe metathesis
10 reactions, again in the name of the company Elevance Renewable Science Inc., are international patent application WO2010/062958, which describes a metathesis reaction followed by a hydrogenation of hydrocarbon cuts up to C₁₆, for obtaining jet-fuel and patent
15 application WO2011/046872 which describes the hydrogenation of the olefinic cut coming from a metathesis reaction for obtaining biofuels such as diesel, naphtha and jet-fuel.

American patent application US20120255222, again in
20 the name of Elevance Renewable Science Inc., claims the production of additives for improving the cold flow properties of fuels through a metathesis step. These additives can in fact be added to diesel for improving its properties.

25 In the present invention, the separation step (b) can be carried out by distillation.

The hydrodeoxygenation process of step (d) is preferably carried out with hydrogen in the presence of

a hydrodeoxygenation catalyst; and/or the hydroisomerization process of phase (d) is carried out with hydrogen in the presence of a hydroisomerization catalyst.

5 The hydrodeoxygenation and hydroisomerization processes effected in the present invention and the hydrodeoxygenation and hydroisomerization catalysts used are, for example, those described in patent applications WO2008/058664, EP1728844, WO2009/039347,
10 WO2009/039335, WO2009039333, WO2009/158268 and in American patent application US2009/0077865, wherein all these patent documents are in the name of ENI S.p.A. and UOP 11c, and are all incorporated herein as reference.

15 In particular, according to what is described in patent application WO2008/058664 from page 7, line 24 to page 9, line 24, all hydrogenation catalysts known in the art comprising at least one metal selected from metals of group VIII or group VIB, appropriately
20 supported, can be used as hydrodeoxygenation catalysts. Suitable carriers are, for example, one or more metal oxides, preferably selected from: alumina, silica, zirconia, titania, or mixtures thereof. Suitable metals are preferably Pd, Pt or Ni or Ni-Mo, Ni-W, Co-Mo or
25 Co-W pairs.

Some hydroisomerization catalysts that can be used in the present invention are exemplified from page 13, line 19 to page 24, line 21 of WO2008058664.

The possible transesterification reaction carried out in step c) with an alcohol selected from methanol, ethanol or mixtures thereof, so as to obtain a mixture of methyl and/or ethyl esters and glycerol, is carried out according to any of the methods known in the art. In this case, the subsequent separation of the glycerol and saturated and unsaturated esters, is effected according to any of the methods known in the art, for example by means of distillation.

10 Brief description of the figures

Figure 1: the passages of the process of the invention according to a preferred embodiment, are exemplified in a block scheme (scheme 1): effecting the metathesis step, followed by separation of the olefins with less than 18 carbon atoms, hydrolysis of the fraction comprising triglycerides by the addition of C₁-C₂ alcohols, separation of the glycerine produced and unsaturated and saturated esters formed, wherein only the latter fraction is initiated to the Ecofining process for the formation of Green diesel, jet-fuel and naphtha.

Figure 2: the passages of the process of the invention according to another preferred embodiment, are exemplified in a block scheme (scheme 2): effecting the metathesis step, followed by separation of the olefins with less than 18 carbon atoms, Ecofining process for the formation of Green diesel, naphtha and jet-fuel.

Detailed description of the figures

Figure 1

As indicated in the scheme of figure 1, in a preferred embodiment of the process of the invention, the metathesis reaction can be effected on the mixture of triglycerides which form the starting oil with C₂-C₆, preferably C₂-C₄ olefins. The olefins having a number of carbon atoms lower than C₁₈ (i.e. C₆-C₁₈), formed after the metathesis reaction, which can be used as intermediates for the production of detergents, additives, lubricants and/or plastic materials or components that can be used in the field of oil explorations and productions, are easily separated by distillation from the rest of the reaction mixture which, after separation, is still composed of triglycerides of saturated fatty acids and unsaturated fatty acids which are formed as a result of the metathesis reaction. The latter are characterized in that they have an unsaturated hydrocarbon chain having a length which is less than the starting length. A transesterification reaction is then effected on these triglycerides, thus obtaining unsaturated esters of medium-chain acids (for example, C₁₀ if the metathesis has been effected with ethylene or ester of 9-decenoic acid, C₁₀-C₁₃ if, on the other hand, the metathesis has been effected with 1-butene, etc.) and esters of saturated fatty acids, mainly C₁₆ and C₁₈, initially present in the oil and which have remained unaltered through the metathesis reaction. Again, the difference

in the boiling points allows an easy separation of the unsaturated esters from the saturated esters. The latter are sent to the hydrotreating process, or to the Ecofining process described above as a two-step
5 process, wherein the first step consists of a hydrogenation/deoxygenation reaction (hydrodeoxygenation), whereas the second step is a hydroisomerization/cracking step.

The treatment of a composition of C₁₆ and C₁₈ methyl
10 esters with respect to the treatment of lipids or glycerides (i.e. glycerine esters) minimizes the undesired formation of propane (mainly deriving from the direct hydrogenation of glycerine), obtaining a narrower distribution of the products with greater
15 applicative advantages.

The output of the metathesis section, in fact, becomes richer in the C₁₆ saturated component. The typical characteristics of the second Ecofining step (hydroisomerization, cracking), nevertheless, broadens
20 the range of products leading to the formation of jet-fuel (prevalent), naphtha and diesel having improved engine performances.

Figure 2

Analogously to what is described for figure 1, in a
25 preferred embodiment of the process of the invention, the metathesis reaction can be carried out on the mixture of triglycerides forming the starting oil with C₂-C₆, preferably C₂-C₄ olefins. The olefins having a

number of carbon atoms lower than C_{18} (i.e. C_6 - C_{18}),
formed after the metathesis reaction, which can be used
as intermediates for the renewable production of
detergents, additives, lubricants and/or plastic
5 materials or components that can be used in the field
of oil explorations and productions, are easily
separated by distillation from the rest of the reaction
mixture which, after separation, is still composed of
triglycerides of saturated fatty acids and unsaturated
10 fatty acids which are formed as a result of the
metathesis reaction. The latter are characterized in
that they have an unsaturated hydrocarbon chain having
a length which is less than the starting length.

This mixture can be sent directly to hydrocracking,
15 or to the Ecofining process described above as a two-
step process, wherein the first step consists of a
hydrogenation/deoxygenation reaction (hydro-
deoxygenation), whereas the second step is a
hydroisomerization/cracking step which, due to the
20 presence of acids having a C_{10} - C_{13} chain, again produces
not only a diesel cut but also naphtha and jet-fuel.

In view of what is described above, the process of
the present invention has the following advantages:
- a complete upgrading of the starting renewable
25 biomass, with a specific production of renewable
products to be used in the field of both intermediates
and fine chemistry, and also in refining;

- lower costs (OPEX - Operating Expenditure) in the Ecofining section, thanks to a reduction in the hydrogen consumption due to a decrease/absence of instauration on the chain of the esters sent to said process;
- improvement in the same hydrotreating section (Ecofining) as the feedstock is already pretreated and purified in the metathesis section, with a consequent reduction in investments (CAPEX - Capital Expenditure) and OPEX;
- lower production of propane in the ecofining section due to the absence of glycerine derivatives in the feedstock;
- maximization of the range of products to be used in the field of biofuels as they are component products useful in the field of naphtha, jet-fuel and diesel.

Some embodiment examples of the present invention are provided hereunder for illustrative but non-limiting purposes.

EXAMPLES

Example 1 (according to the scheme of figure 1)

1 ton of palm oil, consisting of about 49% of myristic, palmitic and stearic derivatives (saturated components) and 41% of oleic acid, 10% of linoleic acid, is sent to a metathesis section with ethylene in excess at a pressure of 10 bar (stoichiometric consumption of 41 kg of ethylene). The reaction is carried out at 60°C for about 1-1.5 hours in the

presence of 100 ppm of metathesis catalyst based on ruthenium. After separation of the catalyst, the reaction mixture is distilled according to the known techniques, so as to separate about 200 kg of 1-decene
5 and 32 kg of 1-heptene. The bottom mixture is sent to a hydrolysis section with methanol (60°C, about 2 hours of residence time, catalyst NaOMe 1% in MeOH) obtaining about 108 kg of glycerine, 330 kg of methyl ester of 9-decenoic acid, and about 470 kg of methyl esters of
10 saturated acids C₁₆-C₁₈ (85% of C₁₆ ester). The 470 kg of saturated esters are separated by distillation and sent to an Ecofining section, obtaining about 375 kg of components suitable for being used in the field of biofuels of the jet-fuel type, diesel and naphtha. The
15 components 1-decene, 1-heptene and methyl ester of 9-decenoic acid are used in the field of the production of bio-chemicals (intermediates which can be used for the production of detergents, additives, lubricants and/or plastic materials or components which can be
20 used in the field of oil explorations and productions).

CLAIMS

1. Process for producing olefinic compounds and a hydrocarbon fuel or a fraction thereof, which comprises:

5 (a) subjecting to metathesis reaction a mixture of glycerides having at least one unsaturated hydrocarbon chain, possibly in mixture with free fatty acids, with at least one monoolefin C_2-C_6 in the presence of a metathesis catalyst, so as to obtain a mixture of
10 glycerides having at least one unsaturated hydrocarbon chain with a length less than the initial one, and a mixture of olefins C_6-C_{18} ;

(b) separating the mixture of olefins C_6-C_{18} from the mixture of glycerides obtained by step (a);

15 (c) possibly subjecting the mixture of glycerides obtained by stage (b) to a transesterification reaction with an alcohol selected from methanol, ethanol or mixtures thereof, so as to obtain a mixture of methyl and/or ethyl esters and glycerol;

20 (d) subjecting the mixture of glycerides obtained by step (b) or the mixture of methyl and/or ethyl esters obtained by step (c) to a hydro-deoxygenisation process and then hydro-isomerisation, so as to obtain the hydrocarbon fuel or a fraction thereof.

25 2. Process according to claim 1, which also comprises, after step (c), step (c') of separating the glycerol from the mixture of methyl and/or ethyl esters, and then step (c'') of separating the methyl and/or ethyl esters having an unsaturated hydrocarbon

chain from the methyl and/or ethyl esters having a saturated hydrocarbon chain, and then of subjecting the methyl and/or ethyl esters having a saturated hydrocarbon chain to step (d) of catalytic hydro-
5 deoxygenisation and subsequent catalytic hydro-isomerisation.

3. Process according to claim 1 or 2, wherein the hydrocarbon fuel is selected from: diesel, naphtha, aviation petrol, or mixtures thereof.

10 4. Process according to any one of the previous claims, wherein the mixture of olefins C_6-C_{18} obtained from step (b) and/or the methyl and/or ethyl esters having an unsaturated hydrocarbon chain obtained from step (c") are intermediates usable for the production
15 of detergents, additives, lubricants and/or plastic materials or components usable in the field of oil exploration and production.

5. Process according to any one of the previous claims, wherein the glycerides having at least one
20 unsaturated hydrocarbon chain used in the mixture in step (a) are glycerides, preferably triglycerides, of vegetable or animal origin or of microbial origin.

6. Process according to claim 5, wherein the glycerides of vegetable or animal origin or of
25 microbial origin are glycerides of fatty acids having at least one hydrocarbon chain $C_{12}-C_{24}$, mono or polyunsaturated.

7. Process according to claim 5, wherein the glycerides are selected from: vegetable oils, such as:
30 sunflower, rapeseed, canola, palm, soya bean, hemp,

olive, linseed, mustard, peanut, castor, coconut and
tall oil; recycled oils and/or fats from the food
industry; lipids coming from seaweed; animal oils or
fats, such as: lard, lard cream, tallow, milk fats; or
5 mixtures thereof.

8. Process according to any one of the previous
claims, wherein said at least one monoolefin C_2-C_6 ,
preferably C_2-C_4 , is selected from: ethylene, propene,
1-butene, but-2-ene, 2-methyl-propene, or mixtures
10 thereof.

9. Process according to any one of the previous
claims, wherein, in step (a), the molar ratio between
the double bonds of the mixture of glycerides having at
least one unsaturated hydrocarbon chain and the double
15 bonds of said at least one olefin C_2-C_6 is comprised
between 1:0.1 and 1:20.

10. Process according to any one of the previous
claims, wherein stage (a) is carried out at a
temperature from 20 to 120 °C, for a period of time
20 from 0.5 to 6 hours, preferably from 20 to 80 °C and
0.5 and 3 hours.

11. Process according to any one of the previous
claims, wherein stage (a) is carried out at a pressure
of between 1 and 30 bars preferably comprised between 1
25 and 15 bars.

12. Process according to any one of the previous
claims, wherein the metathesis catalyst of step (a) is
a carbene complex of a transition metal of Group 8, in
particular selected from: ruthenium, molybdenum,
30 osmium, chromium, rhenium, tungsten.

13. Process according to any one of the previous claims, wherein step (b) of separation is carried out by distillation.

14. Process according to any one of the previous
5 claims, wherein the hydro-deoxygenisation process of step (d) is carried out with hydrogen in the presence of a hydro-deoxygenisation catalyst.

15. Process according to claim 14, wherein the hydro-deoxygenisation catalyst comprises at least one
10 metal selected from the metals of group VIII or of group VIB, preferably Pd, Pt or Ni or Ni-Mo, Ni-W, Co-Mo or Co-W pairs.

16. Process according to claim 14, wherein the hydro-deoxygenisation catalyst is supported on at least
15 one metallic oxide, preferably selected from: aluminium, silica, zirconia, titania, or mixtures thereof.

17. Process according to any one of the previous claims, wherein the hydro-isomerisation process of step
20 (d) is carried out with hydrogen in the presence of a hydro-isomerisation catalyst.

18. Process according to claim 17, wherein the hydro-isomerisation catalyst comprises at least one metal of group VIII, preferably selected from: Pt, Pd,
25 Ni and Co, possibly in mixture with at least one metal of group VIB, preferably selected from: Mo and W, and a support of the acid type.