

(4) separation of the gaseous mixture G into a stream of hydrogen and a gaseous mixture of CO₂ and H₂S,

(5) separation of the gaseous mixture of CO₂ and H₂S obtained in step (4) into a stream of H₂S and a
5 stream of CO₂,

(6) feeding the stream of H₂S obtained in step (5) to the hydrodeoxygenation step (1).

In one aspect, there is provided a biorefinery containing a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by means of the hydrodeoxygenation and isomerization of said mixtures of a biological origin, wherein said biorefinery is obtained from a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, by means of the revamping method as disclosed herein and is characterized by:
10
15

- an acid gas treatment unit T1, in the unit U1 downstream of the reactor A1, containing a specific absorbent for CO₂ and H₂S;
- 20 - an acid gas treatment unit T3 downstream of the acid gas treatment unit T1 and connected to said unit T1 to separate the H₂S and obtain a concentrated H₂S stream;
- 25 - means for recycling said H₂S deriving from the unit T3 to the reactor A1 as a sulfiding agent of the catalyst of the reactor A1.

In one aspect, there is provided a process for the production of hydrocarbon fractions starting from mixtures of a biological origin containing fatty acid

esters which comprises the following steps:

(1) hydrodeoxygenation of the mixture of a biological origin;

(2) hydroisomerization of the mixture resulting from step (1), after a purification process,

wherein said production process is effected using the biorefinery as disclosed herein, and comprises recovering the mixture of CO₂ and H₂S formed during the HDO step from the absorbent of the acid gas treatment unit T1 in the unit U1 and, after separating the H₂S from the CO₂, by means of two additional absorption/regeneration steps, carried out in the acid gas treatment unit T3 downstream of the unit T1 and connected to said unit T1, recycling the resulting stream of H₂S back to the hydrodeoxygenation section.

DETAILED DESCRIPTION

A method is described for revamping a conventional refinery of mineral oils into a biorefinery, characterized by a production scheme which allows the treatment of raw materials of a biological origin (vegetable oils, animal fats, exhausted cooking oils) for the production of biofuels, prevalently high-quality biodiesel.

This method allows the re-use of existing plants, allowing, in particular, the revamping of hydrodesulfurization plants into production plants of hydrocarbon fractions which can be used as diesel fuel, or as diesel fuel components, starting from a mixture

of a biological origin containing triglycerides possibly with aliquots of free fatty acids. Together with diesel fuel, the plants deriving from the reconversion of desulfurization plants also produce
5 aliquots of naphtha and LPG, which are consequently also products deriving from mixtures of a biological origin.

Through this method, it is possible to re-use

CLAIMS

- 1) A method for revamping a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by means of their hydrodeoxygenation and isomerization, wherein each of the hydrodesulfurization units U1 and U2 comprises:
- 10 - a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
 - one or more heat exchangers between the feedstock and effluent of the reactor;
 - 15 - a heating system of the feedstock upstream of the reactor;
 - an acid gas treatment unit downstream of the reactor, containing an absorbent (B) for H₂S, T1 in the unit U1 and T2 in the unit U2,
 - 20 and wherein said method comprises:
 - installing a line L between the units U1 and U2 which connects them in series;
 - installing a recycling line of the product for the unit U1 and possibly for the unit U2,
 - 25 - substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
 - substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;
 - installing a by-pass line X of the acid gas

treatment unit T2 of the unit U2;

- substituting the absorbent (B) in the acid gas treatment unit T1 with a specific absorbent for CO₂ and H₂S.

5 2) The method according to claim 1 for the revamping of a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a HDO/ISO unit, wherein each of the hydrodesulfurization units U1 and U2 comprises:

- 10 - a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
- one or more heat exchangers between the feedstock and effluent of the reactor;
- 15 - a heating system of the feedstock upstream of the reactor;
- an acid gas treatment unit downstream of the reactor, containing an absorbent (B) for H₂S, said unit called T1 in the unit U1 and T2 in the unit
- 20 U2,

and wherein said method comprises:

- installing a line L between the units U1 and U2 which connects them in series;
- installing a recycling line of the product for the
- 25 unit U1 and possibly for the unit U2,
- substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
- substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;

- installing a by-pass line X of the acid gas treatment unit T2 of the unit U2;
 - substituting the absorbent (B) in the acid gas treatment unit T1 with a specific absorbent for CO₂ and H₂S;
 - installing an acid gas treatment unit T3 downstream of the acid gas treatment unit T1 to separate the H₂S;
 - recycling the H₂S to the reactor A1.
- 3) The method according to claim 1 or 2, wherein units U1 and U2 are used, containing hydrogen recycling lines which connect the acid gas treatment units T1 and T2 with the reactors A1 and A2.
- 4) The method according to claim 1, 2 or 3, for revamping a refinery containing a system comprising two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by their hydrodeoxygenation and isomerization, wherein each of the hydrodesulfurization units U1 and U2 comprises:
- a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
 - one or more heat exchangers between the feedstock and effluent of the reactor;
 - a heating system of the feedstock upstream of the reactor;
 - an acid gas treatment unit downstream of the

reactor, containing an absorbent (B) for H_2S , T1 in the unit U1 and T2 in the unit U2,

- a hydrogen recycling line and a compressor on said line, K1 for the unit U1 and K2 for the unit U2,

5 and wherein said method comprises:

- installing a line L between the units U1 and U2 which connects them in series;
- installing a recycling line of the product for the unit U1 and possibly for the unit U2,
- 10 - substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
- substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;
- installing a by-pass line X of the acid gas treatment unit T2 of the unit U2;
- 15 - substituting the absorbent (B) in the acid gas treatment unit T1 with a specific absorbent for CO_2 and H_2S ;
- installing an acid gas treatment unit T3 downstream of the acid gas treatment unit T1;
- 20 - installing a recycling line R3 of H_2S from the unit T3 to the compressor K1 of the hydrogen recycling line of the unit U1.

5) The method according to claim 4, wherein the acid gas treatment unit T3 contains two absorbing areas each containing a specific absorbent for CO_2 .

6) The method according to claim 1, comprising:

- connecting the unit U1 to a sulfur recovery unit containing a thermal section and a catalytic section

by the installation, from the unit T1 of U1, of a by-pass line of the thermal section of said sulfur recovery unit;

- substituting the catalyst of the first reactor of the catalytic section of the sulfur recovery unit with a cold selective redox catalyst.

7) The method according to claim 1, wherein a surge drum (S) is installed upstream of each of the reactors A1 and A2.

8) The method according to claim 1, wherein units U1 and U2 containing high-pressure separators, low-pressure separators, stripping columns and possibly driers, are used.

9) The method according to claim 1, wherein units U1 and U2 are used, containing lines for feeding make-up hydrogen, possibly after mixing with recycled hydrogen, to each of the reactors (A1) and (A2) and/or containing gas separation/washing downstream of each of the reactors (A1) and (A2).

10) The method according to claim 9, wherein said hydrogen feeding lines come from reforming units.

11) The method according to one or more of the previous claims, wherein the hydrocarbon fractions that can be obtained from the biorefinery are fuels or fuel components.

12) The method according to claim 11, wherein the fuels or fuel components that can be obtained from the biorefinery are LPG, kerosene, diesel, naphtha.

13) A biorefinery containing a production unit of

hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by means of the hydrodeoxygenation and isomerization of said mixtures of a biological origin, wherein said biorefinery is
5 obtained from a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, by means of the revamping method according to one or more of claims 1 to 12.

14) A process for the production of hydrocarbon
10 fractions starting from mixtures of a biological origin containing fatty acid esters which comprises the following steps:

(1) hydrodeoxygenation of the mixture of a biological origin;

15 (2) hydroisomerization of the mixture resulting from step (1), after a possible purification process, wherein said process is effected using the biorefinery according to claim 13.

15) A HDO/ISO process for the production of hydrocarbon
20 fractions starting from mixtures of a biological origin containing fatty acid esters, and possibly containing free fatty acids, which comprises the following steps:

(1) hydrodeoxygenation of the mixture of a biological origin;

25 (2) separation of the mixture resulting from step (1) into a hydrocarbon fraction and a gaseous mixture G comprising H_2 , CO_2 and H_2S ,

(3) hydroisomerization of the hydrocarbon fraction obtained in step (2),

(4) separation of the gaseous mixture G into a stream of hydrogen and a gaseous mixture of CO_2 and H_2S ,

(5) separation of the gaseous mixture of CO_2 and H_2S obtained in step (4) into a stream of H_2S and a
5 stream of CO_2 ,

(6) feeding the stream of H_2S obtained in step (5) to the hydrodeoxygenation step (1).

16) The process according to claim 14 or 15, wherein the hydrocarbon fractions produced are fuels or fuel
10 components.

17) The process according to claim 14, wherein the fuels or fuel components are LPG, kerosene, diesel, naphtha.

15

CLAIMS

1) A method for revamping a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by means of their hydrodeoxygenation and isomerization, wherein each of the hydrodesulfurization units U1 and U2 comprises:

- a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
- one or more heat exchangers between the feedstock and effluent of the reactor;
- a heating system of the feedstock upstream of the reactor;
- an acid gas treatment unit downstream of the reactor, containing an absorbent (B) for H_2S , T1 in the unit U1 and T2 in the unit U2,

and wherein said method comprises:

- installing a line L between the units U1 and U2 which connects them in series;
- installing a recycling line of the product for the unit U1 and possibly for the unit U2,
- substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
- substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;
- installing a by-pass line X of the acid gas treatment unit T2 of the unit U2;

- substituting the absorbent (B) in the acid gas treatment unit T1 with a specific absorbent for CO₂ and H₂S.

2) The method according to claim 1 for the revamping of a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a HDO/ISO unit, wherein each of the hydrodesulfurization units U1 and U2 comprises:

- a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
- one or more heat exchangers between the feedstock and effluent of the reactor;
- a heating system of the feedstock upstream of the reactor;
- an acid gas treatment unit downstream of the reactor, containing an absorbent (B) for H₂S, said unit called T1 in the unit U1 and T2 in the unit U2,

and wherein said method comprises:

- installing a line L between the units U1 and U2 which connects them in series;
- installing a recycling line of the product for the unit U1 and possibly for the unit U2,
- substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
- substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;
- installing a by-pass line X of the acid gas treatment unit T2 of the unit U2;
- substituting the absorbent (B) in the acid gas

- treatment unit T1 with a specific absorbent for CO₂ and H₂S;
- installing an acid gas treatment unit T3 downstream of the acid gas treatment unit T1 to separate the H₂S;
 - recycling the H₂S to the reactor A1.
- 3) The method according to claim 1 or 2, wherein units U1 and U2 are used, containing hydrogen recycling lines which connect the acid gas treatment units T1 and T2 with the reactors A1 and A2.
- 4) The method according to claim 1, 2 or 3, for revamping a refinery containing a system comprising two hydrodesulfurization units, U1 and U2, into a biorefinery comprising a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by their hydrodeoxygenation and isomerization, wherein each of the hydrodesulfurization units U1 and U2 comprises:
- a hydrodesulfurization reactor, (A1) for the unit U1 and (A2) for the unit U2, wherein said reactor contains a hydrodesulfurization catalyst;
 - one or more heat exchangers between the feedstock and effluent of the reactor;
 - a heating system of the feedstock upstream of the reactor;
 - an acid gas treatment unit downstream of the reactor, containing an absorbent (B) for H₂S, T1 in the unit U1 and T2 in the unit U2,
 - a hydrogen recycling line and a compressor on said line, K1 for the unit U1 and K2 for the unit U2,
- and wherein said method comprises:

- installing a line L between the units U1 and U2 which connects them in series;
 - installing a recycling line of the product for the unit U1 and possibly for the unit U2,
 - substituting the hydrodesulfurization catalyst in the reactor A1 with a hydrodeoxygenation catalyst;
 - substituting the hydrodesulfurization catalyst in the reactor A2 with an isomerization catalyst;
 - installing a by-pass line X of the acid gas treatment unit T2 of the unit U2;
 - substituting the absorbent (B) in the acid gas treatment unit T1 with a specific absorbent for CO₂ and H₂S;
 - installing an acid gas treatment unit T3 downstream of the acid gas treatment unit T1;
 - installing a recycling line R3 of H₂S from the unit T3 to the compressor K1 of the hydrogen recycling line of the unit U1.
- 5) The method according to claim 4, wherein the acid gas treatment unit T3 contains two absorbing areas each containing a specific absorbent for CO₂.
- 6) The method according to claim 1, comprising:
- connecting the unit U1 to a sulfur recovery unit containing a thermal section and a catalytic section by the installation, from the unit T1 of U1, of a by-pass line of the thermal section of said sulfur recovery unit;
 - substituting the catalyst of the first reactor of the catalytic section of the sulfur recovery unit with a cold selective redox catalyst.

- 7) The method according to claim 1, wherein a surge drum (S) is installed upstream of each of the reactors A1 and A2.
- 8) The method according to claim 1, wherein units U1 and U2 containing high-pressure separators, low-pressure separators, stripping columns and possibly driers, are used.
- 9) The method according to claim 1, wherein units U1 and U2 are used, containing lines for feeding make-up hydrogen, possibly after mixing with recycled hydrogen, to each of the reactors (A1) and (A2) and/or containing gas separation/washing downstream of each of the reactors (A1) and (A2).
- 10) The method according to claim 9, wherein said hydrogen feeding lines come from reforming units.
- 11) The method according to one or more of the previous claims, wherein the hydrocarbon fractions that can be obtained from the biorefinery are fuels or fuel components.
- 12) The method according to claim 11, wherein the fuels or fuel components that can be obtained from the biorefinery are LPG, kerosene, diesel, naphtha.
- 13) A biorefinery containing a production unit of hydrocarbon fractions from mixtures of a biological origin containing fatty acid esters by means of the hydrodeoxygenation and isomerization of said mixtures of a biological origin, wherein said biorefinery is obtained from a refinery comprising a system containing two hydrodesulfurization units, U1 and U2, by means of the revamping method according to one or more of claims 1 to 12 and is characterized by:

- an acid gas treatment unit T1, in the unit U1 downstream of the reactor A1, containing a specific absorbent for CO₂ and H₂S;
 - an acid gas treatment unit T3 downstream of the acid gas treatment unit T1 and connected to said unit T1 to separate the H₂S and obtain a concentrated H₂S stream;
 - means for recycling said H₂S deriving from the unit T3 to the reactor A1 as a sulfiding agent of the catalyst of the reactor A1.
- 14) Biorefinery according to claim 13, wherein the recycling of said H₂S is realized by means of a recycling line between the unit T3 and the hydrodeoxygenation HDO unit.
 - 15) Biorefinery according to claim 14, wherein the recycling line is installed between the unit T3 and the compressor K1 of the hydrogen recycling line of the unit U1.
 - 16) Biorefinery according to claim 13 or 14, wherein the gas treatment unit T3 contains two absorbing areas each containing a specific absorbent for CO₂.
 - 17) A process for the production of hydrocarbon fractions starting from mixtures of a biological origin containing fatty acid esters which comprises the following steps:
 - (1) hydrodeoxygenation of the mixture of a biological origin;
 - (2) hydroisomerization of the mixture resulting from step (1), after a purification process,
 wherein said production process is effected using the biorefinery according to any one of claims 13 to 16, and comprises recovering the mixture of CO₂ and H₂S formed during the HDO step from the absorbent of the acid gas

treatment unit T1 in the unit U1 and, after separating the H_2S from the CO_2 , by means of two additional absorption/regeneration steps, carried out in the acid gas treatment unit T3 downstream of the unit T1 and connected to said unit T1, recycling the resulting stream of H_2S back to the hydrodeoxygenation section.

- 18) A HDO/ISO process for the production of hydrocarbon fractions starting from mixtures of a biological origin containing fatty acid esters, and possibly containing free fatty acids, which comprises the following steps:

- (1) hydrodeoxygenation of the mixture of a biological origin;
- (2) separation of the mixture resulting from step (1) into a hydrocarbon fraction and a gaseous mixture G comprising H_2 , CO_2 and H_2S ,
- (3) hydroisomerization of the hydrocarbon fraction obtained in step (2),
- (4) separation of the gaseous mixture G into a stream of hydrogen and a gaseous mixture of CO_2 and H_2S ,
- (5) separation of the gaseous mixture of CO_2 and H_2S obtained in step (4) into a stream of H_2S and a stream of CO_2 ,
- (6) feeding the stream of H_2S obtained in step (5) to the hydrodeoxygenation step (1).

- 19) The process according to claim 17 or 18, wherein the hydrocarbon fractions produced are fuels or fuel components.

- 20) The process according to claim 19, wherein the fuels or fuel components are LPG, kerosene, diesel, naphtha.