METHOD AND APPARATUS FOR SEPARATING COMPONENTS FROM FUEL RAW MATERIAL

Abstract: The invention relates to a method for separating components from fuel raw material, where tall oil feedstock is introduced to a continuous process comprising a catalytic hydrodeoxygenation step to convert unsaturated fatty acids to fuel components. A light fraction comprising the unsaturated fatty acids is separated from a heavier fraction of the feedstock, and the light fraction is introduced separately to the hydrodeoxygenation step and taken out as fuel component product stream, and the heavier fraction comprising the sterols is left untreated in the hydrodeoxygenation step and is taken out as residual stream. The separation step and the hydrodeoxygenation step take place in the same reactor. The invention also relates to an apparatus for separating components from fuel raw material.
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Method and apparatus for separating components from fuel raw material

Field of the invention

The present invention relates to a method for separating components from fuel raw material which is of the type set forth in the preamble portion of claim 1. The invention also relates to an apparatus for performing the method, the apparatus being of the type set forth in the preamble portion of claim 9.

Background of the invention

Raw materials of natural origin are potential sources of various fuels or fuel components. For example, tall oil, a by-product of the kraft pulping of coniferous trees, has been used as raw material for hydrocarbon fuel components. US patent 5,705,722 describes converting unsaturated fatty acids of tall oil to cetane improvers for diesel fuels. According to this patent, a feedstock consisting of tall oil is fed through a catalytic reactor by contacting it simultaneously with gaseous hydrogen. The resulting product is drawn off the reaction as one product stream which is further fractionated by distillation, from which cetane stream is drawn off as middle distillate.

In the above-mentioned US patent 5,705,722, all components of the tall oil feedstock undergo the catalytic treatment and the distillates obtained in the subsequent distillation step are all used as various fuels or fuel additives for different combustion processes.

In the above-mentioned process, depitched tall oil is used as raw material feedstock. According to the document, depitched tall oil is obtained by evaporating crude tall oil, for example by thin-film evaporator, to remove unsaponifiables and ash in the tall oil, which is followed by possible further distillation stages for the fractionation of fatty acids, diterpenic acids etc. The depitching (thermal evaporation) reduces both unsaponifiables and ash in the tall oil.
Crude tall oil contains, in addition to fatty acids, many other components which may be valuable in other uses than as fuel. The main components of the crude tall oil are free fatty acids, part of which are unsaturated, rosin acids and so-called pitch, which contains various sterols. The depitched tall oil used in the process of US patent 5,705,722 contains still about 5-20 wt % unsaponifiable components.

Still one process using biological raw materials is described in European patent 1396531, where raw materials containing fatty acids and/or fatty acid esters, including tall oil, are converted to hydrocarbon components in catalytic hydrodeoxygenation and isomerization steps.

Crude tall oil (CTO) is a promising candidate as raw material for manufacturing various fuel components. In the solutions of prior art expensive distillation steps are used to produce tall oil fatty acid fractions from crude tall oil. These fatty acid fractions are then processed e.g. by catalytic HDO (hydrodeoxygenation) and isomerization to desired fuel components while the fuel potential of other fractions left out is lost.

On the other hand, if all organic carbon compounds of the tall oil are passed through catalytic conversion steps, some of them may have molecule size and structure that requires additional processing such as cracking to make them suitable as fuel fractions.

Summary of the invention

It is the purpose of the invention to use various components of the crude tall oil or any other tall-oil based feedstock more effectively by retaining the native form of the components despite the conversion of its fatty acid components to fuel or fuel additives. This purpose is attained by a method which is characterized by the features in the characterizing portion of claim 1. The separation step and the hydrodeoxygenation step take place in the same reactor. In the separation step, light components are separated from the heavier components of the tall oil feedstock, and the heavier components form a fraction of their own, which is not introduced to the hydrogenation step. The apparatus according to the invention comprises a hydrogenation
reactor, which is used at the same time as a separator for separating the heavier components from the feedstock before it is introduced to the hydrogenation treatment.

The structure of the heavier components in the separated heavier fraction that bypasses the hydrogenation treatment remains unaltered and, consequently, their useful native structure can be used in many applications. One important group in this fraction are sterols, especially β-sitosterol. In normal hydrogenation treatment of all components of the crude tall oil, this substance would be converted to a stigmastane of practically no value other than a potential fuel component, which would require cracking so that it would be suitable for that purpose.

Known commercial desulphurization catalysts can be used in the hydrogenation step of the lighter components, which is optionally followed by an isomerization step for producing diesel oil components.

Sterol components, for example β-sitosterol, can be separated from the unaltered heavier fraction by extraction or other suitable separation methods. Other potential components can also be separated from this fraction by a suitable method.

**Brief description of the drawings**

The invention will be described in the following with reference to the enclosed drawing, which shows schematically an apparatus which performs the process according to the invention.

**Detailed description of the preferred embodiments**

In the present specification and claims, the following terms have the meanings defined below.

The term "catalytic HDO" or "catalytic hydrodeoxygenation" refers to a catalytic treatment of the feedstock with hydrogen under catalytic conditions, wherein the following reactions take place: deoxygenation by removal of
carboxyl oxygen as water by the means of hydrogen under the influence of catalyst and hydrogenation by saturation of carbon-carbon double bonds by means of hydrogen under the influence of a catalyst. According to a preferred embodiment, the catalytic HDO has also a ring opening character. The preferred HDO of the invention also removes non-desired impurities such as sulphur as hydrogen sulphide and nitrogen as ammonia.

The term "HDO product" and related terms refer to the products of the above-mentioned catalytic HDO.

The terms "decarboxylation" and "decarbonylation" refer to removal of carboxyl oxygen as CO₂ (decarboxylation) or as CO (decarbonylation) with or without the influence of hydrogen.

The term "isomerization" refers to catalytic and hydrogen assisted introduction of short chain (typically methyl) branches into n-paraffinic hydrocarbons.

The term "cracking" refers to catalytic decomposition of organic hydrocarbon materials using hydrogen.

The term "n-paraffins" refer to normal alkanes or linear alkanes that do not contain side chains.

The term "isoparaffins" mean alkanes having one or more C₁ - C₉ , typically C₁ - C₂ alkyl side chains, typically mono-, di-, tri- or tetramethylalkanes.

The term "crude tall oil" refers to a byproduct of the Kraft process of wood pulp manufacture. Crude tall oil contains generally both saturated and unsaturated oxygen-containing organic compounds such as rosins, unsaponifiables, sterols, rosin acids (mainly abietic acid and its isomers), fatty acids (mainly linoleic acid, oleic acid and linolenic acid), fatty alcohols, and other alkyl hydrocarbon derivatives, as well as inorganic impurities (alkaline metal (Na, K) compounds, sulphur, silicon, phosphorus, calcium and iron compounds).
The term "tall oil feedstock" refers to a tall-oil based feedstock used as raw material of the product, which may be crude tall oil or purified crude tall oil, where various impurities are absent depending on the extent of purification treatment, but which contain sterols which have not been removed by the purification treatment.

The term "separation step" refers to a process by which the tall oil feedstock can be divided into two fractions whose components have different molecule sizes. The separation of the components takes place according to the boiling points of the components by means of temperature and pressure.

Light components refer to the components that are separated in the separation step and form a light fraction of the tall oil feedstock that is subjected to catalytic HDO. Heavier components refer to the the components that are separated in the separation step and form a heavier fraction of the tall oil feedstock that bypasses the catalytic HDO. Without wishing to restrict the concept of light fraction and heavier fraction and consequently light components and heavier components too narrowly, it can be said that the heavier fraction contains preferably components of the tall oil feedstock that contain more than 21 carbon atoms. Consequently, the light fraction contains components having 21 carbon atoms at the most, and on the basis of known components of tall oil, the light fraction contains components having less than 21 carbon atoms.

The apparatus comprises a reactor 1, a feedstock inlet 1a connected to the lower part of the reactor 1, a hydrogen inlet 1b connected to the lower part of the reactor, a HDO product stream outlet 1c connected to the upper part of the reactor, and a residual stream outlet 1d connected to the lower part of the reactor.

The HDO product stream outlet 1c is connected through a conduit 3 to an isomerisation reactor 2, which comprises a gaseous stream outlet 2a and a fuel product outlet 2b for lights and diesel components, respectively.

The reactor 1 is divided in two sections, a separation section S, which forms the lower part of the reactor, and a catalytic HDO section H, which forms the
upper part of the reactor. Both sections are inside a common pressure-
resistant reactor housing. The catalytic HDO section H contains catalyst, which may be any known catalyst, selected according to the conversion process for converting the unsaturated fatty acids in the tall oil feedstock to useful aliphatic fuel components. The catalyst in the hydrogenation section is a HDO catalyst. In case of fatty acids of tall oil, the HDO catalyst catalyzes deoxygenation where oxygen atoms are removed from carboxyl groups and replaced with hydrogen, this conversion being called hydrodeoxygenation (HDO). This may be combined with simultaneous decarboxylation and decarbonylation where the carbon of the carboxyl group is also eliminated. These reactions are well known and they are not described in more detail.

The HDO catalyst is preferably sulphur resistant, because the tall oil feedstock supplied to the catalytic HDO section H may contain residual organic sulphur compounds which are not removed in the possible previous treatment steps. As catalyst for these reactions a known commercial desulphurization catalysts, for example based on nickel and/or molybdenum, can be used. The catalyst can be a supported NiMo or CoMo catalyst for example on alumina and/or silica support. These catalysts are well known and they are not described in more detail.

Through these reactions, the unsaturated fatty acids linoleic, oleic and linolenic acid are converted to octadecane (HDO) or heptadecane (HDO + decarboxylation and/or decarbonylation). Abietinic acid, a representative of rosin acids, is converted to abietane through HDO.

For the catalytic HDO section H, hydrogen is fed in excess of the theoretical hydrogen consumption. The pressure may be between 50 and 100 bar and the temperature between 280°C and 340°C.

The catalyst used in the catalytic HDO section H has preferably also ring-opening properties, in which case it can function as a combined HDO and ring-opening catalyst. When the above-mentioned NiMo or CoMo catalysts are used in the HDO section H, no ring compounds originally present in the rosin acids of the tall oil feedstock or corresponding hydrogenated ring compounds (such as the above-mentioned abietane) are detected in the
product stream. Consequently, the catalytic HDO section H is a combined HDO/ring-opening section. The native rosin acids have undesirable pour point and cloud point raising effect in diesel fuel, and they have a very poor cetane number. By ring-opening treatment the pour point and cloud point can be lowered and cetane number improved.

Tall oil feedstock is fed through the feedstock inlet 1a to the separation section S while gaseous hydrogen is fed through the hydrogen inlet 1b to the separation section S, below the feedstock inlet 1a. The tall oil feedstock can be crude tall oil feedstock or purified crude tall oil feedstock, where various impurities are absent depending on the extent of purification treatment. According to a preferred embodiment, the purified crude tall oil feedstock contains at least part of the heavier components originally present in the crude tall oil, such as sterols or polymers, as a rule compounds with the boiling point above 350 °C. These components will not enter the catalytic HDO section but will be separated in their original form from the feedstock and they remain in liquid phase in the separation.

In the reactor shown in the drawing, the hydrogen inlet 1b is arranged to the bottom of the reactor 1. The temperature of the separation section S is kept at around 350 °C. In the separation section S, the feedstock flows counter currently to the hydrogen stream bubbling through the feedstock upwards towards the catalytic HDO section H. The hydrogen gas stream bubbling through the separation section S enhances the separation of the components of the light fraction. In this way, a light fraction is separated from the heavier fraction of the feedstock that flows towards the residual stream outlet 1d that is arranged to the bottom of the reactor 1. The hydrogen flows cocurrently with the light fraction in the catalytic HDO section H. The light fraction contains light components that include free fatty acids. Unsaturated fatty acids and rosin acids are converted to n-paraffins and acyclic hydrocarbons, respectively, by the HDO catalyst, and the conversion products leave the reactor through the HDO product stream outlet 1c at the top of the reactor 1.

The separation section S has preferably a system that keeps the level of the liquid phase at constant height therein. The light components separated in the separation section S enter as gaseous components the HDO section H.
where they will undergo the catalytic HDO treatment. According to one
embodiment, the hydrogen passing through the HDO section H is circulated
and the catalytic HDO section H is operated at lower pressure than usually.
In this way the hydrogen excess can be kept at sufficient level for the
catalytic HDO treatment. If the circulated hydrogen is cooled, it can be used
at the same time as coolant for the catalytic HDO section H. In this case the
hydrogen bypasses the separation section S which is kept at a higher
temperature.

Since components which would result in hydrocarbons having more than 21
atoms in the HDO are left in the heavier fraction that is removed from the
reactor 1 and does not enter the HDO treatment, the HDO products leaving
the HDO section H have suitable carbon chain lengths to be used as fuel
components after isomerization, and they do not need cracking.

The choice of the temperature in the separation section S is dependent on
the desired division of various components between the light fraction and
heavier fraction, depending on the boiling points of the components to be
separated. The temperature of about 350°C is sufficient for separating
unsaturated fatty acids and rosin acids important as fuel component
precursors from the tall oil feedstock as gaseous components and to keep
them in gas phase till the HDO section H. The heavier fraction leaving the
reactor 1 through the residual stream outlet 1d without being treated in the
HDO step stays in liquid phase. The temperature can also be some degrees
above or below the above-mentioned value.

The product stream can further be isomerized in the isomerization reactor 2
to convert n-paraffins to branched hydrocarbons, which leave the reactor 2
through the fuel product outlet 2b at the bottom of the reactor. The
isomerization reactor 2 contains non-cracking isomerization catalyst capable
of converting straight carbon backbones of n-paraffins (linear alkanes) to
branched backbones of isoparaffins (branched alkanes). The n-paraffins are
isomerized moderately so that the cold flow properties of the diesel fuel will
be improved but the cetane number will not decrease too much. The
isomerization is also dependent on whether the diesel fuel is for winter use or
summer use.
The fuel product stream taken from the fuel product outlet 2b of the isomerization reactor 2 can be used as diesel fuel or as a diesel fuel component which raises the cetane number and lowers the cloud point of the fuel. The fuel product of the isomerization reactor 2 is preferably EN 590 quality diesel.

The lights leaving the isomerization reactor 2 through the gaseous stream outlet 2a contain mainly hydrogen and hydrogen sulphide, and, as result of decarboxylation and decarbonylation in the HDO reactions, carbon monoxide and carbon dioxide.

The isomerisation reactor 2 may contain commonly known catalyst. The isomerization catalyst can contain Pt or Pd and SAPO or ZSM. Examples are Pt/SAPO-11 or Pt/ZSM-23. Hydrogen gas is supplied to the lower part of the reactor 2 through a conduit branched off the hydrogen conduit leading to the reactor 1 (not shown), and it flows countercurrently to the diesel fraction through the catalyst bed in the isomerization reactor 2. In the isomerization reactor 2, the pressure may be 30-100 bar and the temperature may be 280-400 °C.

It is also possible to perform the catalytic HDO and catalytic isomerization simultaneously in the HDO section H by suitable choice of catalyst, in which case the reactor 2 for the isomerization is not needed and only a separation step for separating the lights (hydrogen, hydrogen sulphide, carbon dioxide and carbon monoxide) from the fuel components of the fuel product stream is needed. Examples of dual-functional catalysts for such a single-step hydrodeoxygenation/hydroisomerization step are disclosed e.g. in international publication WO 2006/1 00584, and they have a metal component Pt or Pd (Pt being preferred) and an acidic component comprising an acidic function in a porous solid support, SAPO-11 being the preferred acidic component.

The heavier fraction separated in the separation section S in the reactor 1 bypasses, that is, does not enter the catalytic HDO treatment, and its many components thus retain their original form, for example sterols. The heavier
fraction drawn off through the residual stream outlet 1d can be treated further in a separation step where useful components are separated. For example β-sitosterol can be separated by extraction from the heavier fraction.

Additionally to sterols, the heavier fraction separated from the light fraction contains other substances, for example polymers and esters. Although β-sitosterol is one example of a valuable substance that can be separated from the heavier fraction, the invention is not limited to the separation of that substance known, but it can be utilized for recovering any other substances that may be useful due to the fact that they have not undergone the HDO treatment.

If crude tall oil is used as the feedstock to the reactor 1, the heavier fraction contains also non-volatile impurities harmful to the function of catalysts, such as metals, phosphorus and polymeric compounds that usually must be separated in a purification step. The separation section S serves in this case also as a purification section, and a separate pretreatment of the crude tall oil feedstock before the reactor 1 is not needed.
Claims:

1. Method for separating components from fuel raw material, where tall oil feedstock comprising unsaturated fatty acids, rosin acids and sterols is introduced to a continuous process comprising a catalytic hydrodeoxygenation (HDO) step to convert unsaturated fatty acids to fuel components, the process also comprising a separation step to separate different fractions, characterized in that the separation step and the hydrodeoxygenation step take place in the same reactor, and the separation step where a light fraction comprising the unsaturated fatty acids and rosin acids is separated from a heavier fraction of the feedstock is before the hydrodeoxygenation step, and only the light fraction is introduced to the hydrodeoxygenation step and taken out as HDO product stream, while the heavier fraction is led out as residual stream.

2. Method as claimed in claim 1, characterized in that the heavier fraction comprises components having more than 21 carbon atoms, including sterols.

3. Method as claimed in claim 1 or 2, characterized in that the separation step and hydrodeoxygenation step are performed as successive steps in such a way that the components of the light fraction rise in gaseous form upwards in the separation step and enter the hydrogenation step and the components of the heavier fraction flow downwards in the separation step and leave the separation step in the residual stream.

4. Method as claimed in any of the preceding claims, characterized in that hydrogen is fed towards the hydrodeoxygenation step countercurrently to the heavier fraction.

5. Method as claimed in any of the preceding claims, characterized in that the HDO product stream from the hydrodeoxygenation step is introduced to an isomerization step.

6. Method as claimed in any of the preceding claims 1 to 4, characterized in that the hydrodeoxygenation step comprises also an isomerization step.
7. Method as claimed in any of the preceding claims 2 to 6, characterized in that the sterols comprise \( \beta \)-sitosterol.

8. Method as claimed in claim 7, characterized in that \( \beta \)-sitosterol is separated from the residual stream by extraction.

9. Apparatus for separating components from fuel raw material, comprising
   - a reactor \((1)\) containing a hydrodeoxygenation (HDO) catalyst,
   - a feedstock inlet \((1a)\) to the reactor \((1)\) for introducing tall oil feedstock to the reactor \((1)\),
   - at least one hydrogen inlet \((1b)\) to the reactor \((1)\),
   - a HDO product stream outlet \((1c)\) for taking out a HDO product stream from the reactor \((1)\),

characterized in that the reactor \((1)\) comprises a separation section \((S)\) and a hydrodeoxygenation section \((H)\), which contains said catalyst, and the feedstock inlet \((1a)\) is connected to the separation section \((S)\), which is arranged to separate a light fraction comprising unsaturated fatty acids and rosin acids from a heavier fraction of the feedstock the reactor \((1)\) further comprising
   - a flow connection from the separation section \((S)\) to the hydrodeoxygenation section \((H)\) for introducing the light fraction to the hydrogenation section \((H)\), as well as
   - a residual stream outlet \((1d)\) from the separation section \((S)\) for taking out a residual stream comprising the heavier fraction without flow connection to the hydrogenation section \((H)\).

10. Apparatus as claimed in claim 9, characterized in that the heavier fraction comprises components having more than 21 carbon atoms, including sterols.

11. Apparatus as claimed in claim 9 or 10, characterized in that the separation section \((S)\) is placed below the hydrodeoxygenation section \((H)\) in a common reactor housing and the light fraction separated in the separation section \((S)\) is arranged to rise upwards to the hydrodeoxygenation section \((H)\) in the reaction housing.
12. Apparatus as claimed in claim 9, 10 or 11, characterized in that it further comprises an isomerization reactor (2) connected to the HDO product stream outlet (1c) of the reactor (1).

13. Apparatus as claimed in any of the claims 9 to 12, characterized in that the catalyst is Ni and/or Mo based desulphurization catalyst.

14. Apparatus as claimed in any of the claims 9 to 13, characterized in that the hydrodeoxygenation section (H) contains catalyst capable of catalysing hydrodeoxygenation (HDO) of unsaturated fatty acids.

15. Apparatus as claimed in any of the claims 9 to 14, characterized in that the hydrogen inlet (1c) is arranged to the separation section (S) below the feedstock inlet (1a).

16. Apparatus as claimed in claim 15, characterized in that the hydrogen inlet (1c) is arranged to the bottom of the reactor (1).