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**Prosessi biologista alkuperää olevan materiaalin raskaiden jäännösten käsittelemiseksi ja nestemäisten polttoaineiden valmistamiseksi**

**Process för behandling av tunga rester, som härstammar från material av biologisk ursprung, och för framställning av flytande bränsle**

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The present invention relates to a process for treating heavy residue originating from material of biological origin, where said heavy residue is subjected to hydrolysis and purification treatment followed by separation of an organic phase and an aqueous phase. The invention also relates to a process for producing liquid fuels or fuel components where the obtained organic phase is further subjected to catalytic hydroprocessing.

Esillä oleva keksintö liittyy prosessiin biologista alkuperää olevasta materiaalista peräisin olevan raskaan jäännöksen käsittelemiseksi, missä mainitulle raskaalle jäännökselle suoritetaan hydrolyysi ja puhdistuskäsittely, jonka jälkeen orgaaninen faasi ja vesipitoinen faasi erotetaan. Keksintö liittyy myös prosessiin nestemäisten polttoaineiden tai polttoainekomponenttien valmistamiseksi, missä saadulle orgaaniselle faasille suoritetaan lisäksi katalyyttinen vetyprosessointi.

# PROCESS FOR TREATING HEAVY RESIDUES ORIGINATING FROM MATERIAL OF BIOLOGICAL ORIGIN AND PRODUCING LIQUID FUELS

## FIELD OF THE INVENTION

The present invention relates to a process for treating heavy residues originating from material of biological origin. The present invention also relates to a process for producing liquid fuels and fuel components from heavy residues originating from material of biological origin and feedstock comprising material of biological origin, where heavy residues originating from material of biological origin are converted to components suitable as feedstock in said process. The invention also relates to subjecting heavy residues originating from biological origin to hydrolysis, followed by purification to obtain purified components, which are subjected to hydroprocessing whereby liquid fuels may be obtained.

## BACKGROUND OF THE INVENTION

Feedstock of biological origin can be converted to liquid fuels by subjecting the feedstock to catalytic hydroprocessing with gaseous hydrogen. The resulting product stream can be further fractionated for example by distillation to obtain liquid fuels and liquid fuel components.

Feedstock of biological origin typically contains various impurities. The feedstock can be purified and/or pretreated before feeding it to the process, whereby purified feedstock and heavy residues and impurities are obtained. There are various alternative methods available for carrying out the purification and/or pretreatment of feedstock of biological origin.

An example of feedstock of biological origin is tall oil, which is a major by-product of the Kraft sulphate pulping process. In the Kraft pulping process rosin acids and fatty acids, which occur for example in pine wood as free acids or their esters, are saponified with cooking liquor (Black Liquor) to their corresponding sodium salts. These salts, or their soaps, along with some neutral components are dissolved or suspended in the spent cooking liquor. This liquor is later concentrated and the soaps and neutral components are separated as tall oil soap skimmings. Most Kraft mills which process softwood recover tall oil soap. This soap is usually acidified to produce crude tall oil (CTO).

CTO can be burned to produce heat and power, or it can be utilized further for example by tall oil refining companies. CTO may also be converted into hydrocarbons suitable as liquid fuels and the like.

Tall oil refining companies typically separate certain compound groups (e.g. free resin and fatty acids) from tall oil or CTO, leaving residual called tall oil pitch (TOP). Typical percentage of this TOP from CTO is around 30-35% in tall oil fractionation processes. TOP consists mainly of neutral components, typically in the range of 70-90 %, but usually it contains also resin acids, typically in the range of 10-20 %, and residues of fatty acids, typically in the range of 2-5 %, all percentages by weight. Neutral components consist mainly of sterols, stanols, sterol/stanol esters, polymeric acids, polymeric neutral substances, dimers, trimers and lignin derivatives. Also some resin acid esters can be found from TOP. TOP is typically burned in lime kilns or CHP-plants.

In the production of liquid fuels, CTO may be pre-processed to remove excess of metals and high boiling components (>600°C), prior to subjecting it to catalytic hydroprocessing. CTO may be subjected to depitching where CTO is evaporated. In depitching a significant amount of valuable raw material is lost as heavy residue (pitch). Said pitch is usually burned for energy production.

When evaporating CTO the amount of formed heavy residue may be at least from 5 to 15 % calculated from the feed. The removed heavy residue (pitch) still contains neutral components, such as esters of sterols and stanols, resin acids and fatty acids, and part of the acids may be chemically bound to the neutral components. The heavy residue is typically directed to burning.

To maximise the utilization of heavy residues originating from material of biological origin, such as TOP and the heavy residues and pitch fractions originating from tall oil, obtained for example during depitching, evaporation and distillation, converting particularly of neutral components contained in the heavy residues, pitch and pitch fractions, into components, such as sterols, stanols, fatty acids, resin acids, esters and alcohols would be needed.

## SUMMARY OF THE INVENTION

According to one embodiment, the present invention relates to a process for treating heavy residues originating from material of biological origin, where a mixture formed of a feedstock comprising at least one heavy residue originating from material of biological origin and an aqueous medium is subjected to hydrolysis to obtain a hydrolyzed mixture, followed by separating the hydrolyzed mixture to an organic phase and an aqueous phase, subjecting the organic phase and at least one feedstock comprising material of biological origin to at least one purification treatment to obtain a purified product.

The process of the present invention for treating heavy residues originating from material of biological origin provides purified products or components useful as starting materials in chemical processing.

According to another embodiment, the present invention relates to a process for producing liquid fuels or fuel components, where a mixture formed of a feedstock comprising at least one heavy residue originating from material of biological origin and an aqueous medium is subjected to hydrolysis to obtain a hydrolyzed mixture,, followed by separating the hydrolyzed mixture to an organic phase and an aqueous phase, subjecting the organic phase and feedstock comprising material of biological origin to at least one purification treatment to obtain a purified product and then subjecting the purified product to catalytic hydroprocessing whereby liquid fuels or components thereof are obtained.

Further, the process of the present invention for producing liquid fuels or fuel components provides bio-oils, which may be used for example as fuels and fuel components.

Thus an object of the invention is to provide a process for effectively and economically converting potential materials contained in heavy residues originating from material of biological origin, to provide useful starting materials and co-feeds for chemical processing, particularly in liquid fuel production, whereby the amount of materials which is usually discarded or burned, can be decreased.

Another object of the invention is to provide a process for the manufacture of liquid fuels and fuel components.

Still another object of the invention is to provide bio-oils based on heavy residues originating from materials of biological origin, and on renewable starting materials, for use as liquid fuels or fuel components.

## DEFINITIONS

The term “hydroprocessing” refers here to catalytic processing of organic material by all means of molecular hydrogen.

The term “neutral components” or “neutral fraction” or “neutral materials”, often also referred to as “unsaponifiables” refers here to all neutral organic components in heavy fractions or residues obtained in treating or processing material of biological origin. Examples of said materials are tall oil pitch and tall oil materials contained therein.

Examples of components contained for example in tall oil pitch include sterols, stanols, sterol and stanol esters, polymeric acids, polymeric neutral substances, dimers, trimers, lignin derivatives, resin acids and fatty acids and esters thereof.

The term “tall oil” or "crude tall oil" (CTO) refers here to a product which is mainly composed of both saturated and unsaturated oxygen-containing organic compounds such as rosins, unsaponifiables, sterols, resin acids (mainly abietic acid and its isomers), fatty acids (mainly linoleic acid, palmitic acid, oleic acid and linolenic acid), fatty alcohols, sterols, other alkyl hydrocarbon derivatives, as well as inorganic impurities (alkaline metal compounds, sulphur, silicon, phosphorus, calcium and iron compounds). Tall oil also covers soap oil.

Tall oil or CTO refers to processed mixtures of naturally-occurring compounds extracted from wood species, such as birch, pine, spruce and aspen. It is typically obtained from the acidulation of crude tall oil soap from Kraft and sulphite pulping processes used in paper making. The handling and cooking of the wood causes break down of the triglyceride structures and hence tall oil or CTO does not contain any significant amounts of triglycerides. The composition of tall oil or CTO varies depending on the specific wood species.

The term “liquid fuels” refers here to fractions or cuts or blends of hydrocarbons having distillation curves standardized for fuels, such as for diesel fuel (middle distillate from 160 to 380°C, EN 590), gasoline (150 - 210°C, EN 228), aviation fuel (160 to 300°C, ASTM D-1655 jet fuel), kerosene, naphtha, etc.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic flow diagram representing one embodiment of the process for the manufacture of liquid fuels.

Figure 2 shows distillation curves of pitch before and after processing.

## DETAILED DESCRIPTION OF THE INVENTION

The invention is based on the idea of utilizing effectively the valuable components contained in heavy residues originating from materials of biological origin Examples of such heavy residues are TOP, TOP fractions and heavy residues and/or fractions obtained in depitching, evaporation and distillation of tall oil materials, CTO, and the like. It was found that said valuable components can be converted to starting materials and co-feeds, which are suitable for chemical processing, such as catalytic hydroprocessing for providing liquid fuels or fuel components. The yields of liquid fuels or liquid fuel components can be increased and the amounts of residual materials directed to burning can be significantly decreased.

In the process of the invention heavy residues originating from materials of biological origin are subjected to hydrolysis, where particularly neutral components contained in said heavy residues are hydrolyzed to yield valuable compounds. When said heavy residue originates from tall oil materials, compounds, such as resin acids, fatty acids, sterols and stanols may be obtained. Fractions comprising valuable compounds can be separated and subsequently directed to at least one purification treatment together with feedstock comprising material of biological origin to yield purified products.

The product obtained from said purification treatment may be directed to further chemical processing. Suitably the purified product is directed to catalytic hydroprocessing for obtaining liquid fuels or fuel components.

In the case heavy residues originating from tall oil or tall oil materials are used, surprisingly high amounts of valuable compounds can be separated from said heavy residues for further processing. It was found that even up to 50 % by weight of the heavy residues, such as TOP or pitch fractions, can be converted and/or separated and suitably utilized effectively for example in the catalytic hydroprocessing. Particularly fatty acids and resin acids, which are chemically bound to the neutral components in pitch, can be released with mild hydrolysis, followed by purification, such as evaporative treatment, and then they may be further directed to catalytic hydroprocessing.

The process in accordance with the present invention, for treating heavy residues originating from material of biological origin comprises the steps of

a) subjecting a mixture formed of a feedstock comprising at least one heavy residue originating from material of biological origin and an aqueous medium to hydrolysis at a temperature from 10 to 280°C and under a pressure from 0 to 70 bar to obtain a hydrolyzed mixture,

b) separating the hydrolyzed mixture into an organic phase and an aqueous phase,

c) subjecting the organic phase and feedstock comprising at least one material of biological origin to at least one purification treatment to obtain a purified product.

Said purified product may be used as feedstock in chemical processing, such as catalytic hydroprocessing.

Suitably the heavy residue originates from tall oil material.

The process in accordance with the present invention, for producing liquid fuels or fuel components, comprises the steps a) – c) as described above and additional steps d) – f).

The process in accordance with the present invention, for producing liquid fuels or fuel components, comprises the steps of

a) subjecting a mixture formed of a feedstock comprising at least one heavy residue originating from material of biological origin and an aqueous medium to hydrolysis at a temperature from 10 to 280°C and under a pressure from 0 to 70 bar to obtain a hydrolyzed mixture,

b) separating the hydrolyzed mixture into an organic phase and an aqueous phase,

c) subjecting the organic phase and feedstock comprising at least one material of biological origin to at least one purification treatment to obtain a purified product,

d) feeding the purified product into a reactor system comprising at least one catalytically active hydroprocessing reaction phase wherein said purified product is contacted with at least one hydroprocessing catalyst,

e) treating the purified product catalytically with hydrogen in the reactor system to cause hydrodeoxygenation, hydrogenation, isomerisation and cracking of components contained in the purified product to provide a hydroprocessing product, and

f) recovering at least a fraction of the hydroprocessing product as liquid fuel or fuel component.

## Heavy residue

The heavy residue may originate from any material of biological origin, and it may be obtained from any evaporative treatment including depitching and distillation of said material. Suitably the heavy residue originates from tall oil material. Said heavy residue may be selected from TOP (tall oil pitch, which may be obtained for example from CTO), heavy residues and pitch fractions obtained from any evaporative treatment including depitching and distillation of tall oil materials, and heavy evaporation residues obtained from the purification treatment carried out as evaporative treatment in the process of the invention, and any combinations thereof.

The tall oil material comprises one or more of tall oil components, tall oil derivatives and any combinations thereof, including CTO, TOFA (tall oil fatty acids), tall oil soap etc. Tall oil material particularly refers to a by-product of Kraft pulping of wood, such as coniferous wood, birch, aspen etc. Tall oil material is typically a mixture of fatty acids, resin acids, neutral compounds and turpentine components originating from wood, such as coniferous wood. The turpentine components of tall oil are substantially composed of $C_{10}H_{16}$ terpenes.

## Hydrolysis

In accordance with the present invention heavy residues, and particularly organic compounds, such as neutral components contained therein are subjected to hydrolysis whereby phases comprising valuable compounds can be separated and subsequently directed to at least one purification treatment. In the case heavy residues originate from tall oil materials, phases comprising for example resin acids, fatty acids, sterols and stanols can be separated.

In the process of the invention, in step a) a mixture formed of a feedstock comprising at least one heavy residue originating from material of biological origin and an aqueous medium, is subjected to hydrolysis at a temperature from 10 to 280°C and under a pressure from 0 to 70 bar to obtain a hydrolyzed mixture.

The aqueous medium is selected from water, and mixtures of water with at least one alkali metal hydroxide and at least one C1-C4 alcohol.

The aqueous medium is used in the volumetric ratio with respect to the feedstock from 1:20 to 20:1.

In the case only water is used as the aqueous medium, the volumetric ratio of water to feedstock is suitably from 1:2 to 10:1. Tap water and suitably demineralized or deionized water may be used.

The alkali metal hydroxide is suitably NaOH or KOH. The amount of the alkali metal hydroxide in the mixture is from 1 to 20 %, suitably from 5 to 15 % by weight. The C1-C4 alcohol is suitably methanol, ethanol, butanol or a combination thereof. The amount of the alcohol in the mixture ranges from 50 to 96 %, suitably from 80 to 95 % by volume. The amount of alcohol needed may be estimated based on the amount of the heavy residue. Particularly suitably methanol obtained as side product from pulp manufacturing is used.

The hydrolysis may be carried out in the presence of a catalyst comprising at least one cationic amine compound. Particularly in the case where water is used as the aqueous medium the hydrolysis reaction can be enhanced with said catalysts. In case of amine catalyst is used, the volumetric ratio of water to feedstock is suitably from 1:20 to 10:5, suitably 1:15 to 1:10.

Suitable cationic amine compounds are water-soluble cationic amine soaps including primary, secondary and tertiary mono- and polyamines, such as aliphatic, including cycloaliphatic, mono- and polyamines and mixtures thereof. Said amine catalysts are used in amounts of 0.001 – 0.5 % by weight, calculated based on the feedstock, suitably 0.01 – 0.2 %.

The amine compounds may contain up to 20, suitably above 6 carbon atoms in their structural formula. For example suitable amines are isopropylamine, n-propylamine, diisopropylamine, n-butylamine, di-n-butylamine, tri-n-butylamine, triethylamine, cyclohexylamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, etc., heterocyclic N- containing mono- and polyamines, for example, morpholine, N-methyl-morpholine, 4(2-aminoethoxy) ethylmorpholine, 2-(4-morpholinylethoxy) ethanol, bis-2-(4-morpholinyl) ethyl ether, piperazine, Naminoethylpiperazine, N-hydroxy-ethyl-piperazine, pyridazine, pyrrole, pyrrolidine, pyridine, piperadine, pyrimidine, pyridazine, etc. Also long chain fatty acid amines are useful such as cocoa fatty acid primary amines, dilauryl secondary amine and N,N-dimethyl dodecyl tertiary amine.

Suitable quaternary cationic amine soaps include aliphatic and aryl amines having from 10 carbon atoms to 22 carbon atoms such as dodecyl phenol quaternary amine soaps, cetyl trimethyl ammonium bromide, cetyl trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, and nonyl trimethyl ammonium chloride.

The mixture of the feedstock comprising at least one heavy residue originating from material of biological origin and the aqueous medium may be formed using any mixing method and any mixing device, which provides vigorous mixing or agitation. Suitably the mixing is carried out with a homogenizator, with a dispersing pump, or high shear mixing device. The mixing may be carried out prior to or simultaneously with the hydrolysis.

In the case the mixing of the feedstock with the aqueous medium is carried prior to hydrolysis a, a temperature of 5 -120°C, suitably 70 - 120°C is used. In the case the aqueous medium is water a mixing temperature of 5-100°C, suitably 70-99°C is used.

The mixing/homogenizing and hydrolysis may be carried out in the same vessel, or the mixing or homogenizing is carried out in a separate mixing/homogenizer vessel or pipeline and the hydrolysis is carried out in a separate hydrolysis vessel or reactor.

If necessary the mixed/homogenized mixture may be heated prior to the hydrolysis step, suitably using heat exchangers or the like.

The hydrolysis of the mixture is carried out at the temperature of 10-280°C, suitably at 60-280°C. The hydrolysis of the mixture is carried out under a pressure from 0-70 bar, suitably from 0.1-70 bar. A hydrolyzed mixture is obtained.

When only water is used as the aqueous medium, the hydrolysis is suitably carried out at the temperature of 220-280°C. Suitably a pressure of 25-70 bar is used. The hydrolysis is suitably carried out for 30 min to 10 hours.

When an amine catalyst is used, together with water as the aqueous medium, the hydrolysis is suitably carried out at the temperature of 80-180°C, suitably 80-125°C. The pressure is from 0 to 5 bar, suitably from 0.1 to 1.5 bar. The hydrolysis is suitably carried out for 10 min to 3 hours.

When the aqueous medium comprises at least one alkali metal hydroxide and at least one alcohol the hydrolysis of the mixture is carried out at the temperature of 60-200°C, suitably 100-200°C. A pressure of 1-30 bar, suitably 1-3 bar is used. The hydrolysis is suitably carried out from 30 min to 10 hours, suitably from 45 min to 2 hours.

Suitably the pH of the hydrolyzed mixture is adjusted to the range of 2-3 with an acid selected from strong acids, such as $H_2SO_4$, $HNO_3$ etc. Suitably $H_2SO_4$ is used. When only water is used as the aqueous medium, without a catalyst, the pH of the hydrolyzed mixture is suitably adjusted to 5.8 – 6.9 if necessary.

If necessary the hydrolyzed mixture, after optional pH adjustment, may be cooled prior to the subsequent separation step, suitably using heat exchangers or the like. Suitably the hydrolyzed mixture is cooled to a temperature below 100°C, suitably to 65-95°C.

**Separation**

The hydrolyzed and optionally cooled mixture is separated at the temperature below 100°C, suitably at 65-95°C into an organic phase and an aqueous phase. The separation may be carried out by any known separation means. The organic phase comprises typically water in-soluble compounds, volatile organic compounds, free acids, alcohols and unsaponifiable components)and the aqueous phase comprises typically water-soluble compounds, alkali metal salts and the like. The aqueous phase is suitably directed to waste water treatment.

The separation may be carried out by any suitable separation means, such as hydrodynamic separation, gravimetric separation, and coalescent separation. Suitably decantation methods and devices may be used.

**Purification**

The separated organic phase and feedstock comprising at least one material of biological origin are directed to at least one purification treatment to obtain a purified product.

The material of biological origin is selected from a group consisting of

a) plant fats, plant oils, plant waxes; animal fats, animal oils, animal waxes, fish fats, fish oils, fish waxes, and

b) recycled food grade fats and oils, and fats, oils and waxes obtained by genetic engineering, and

c) fats, oils and waxes derived from algae, molds, yeasts, fungi and/or other microorganisms capable of producing said compounds; and

d) mixtures of said biological feed materials.

According to one embodiment of the present invention the material of biological origin is selected from the group consisting of fish oils such as Baltic herring oil, salmon oil, herring oil, tuna oil, anchovy oil, sardine oil, and mackerel oil; plant oils such as rapeseed oil, colza oil, canola oil, tall oil, crude tall oil, sunflower seed oil, soybean oil, corn oil, hemp oil, linen seed oil, olive oil, cottonseed oil, mustard oil, palm oil, peanut oil, castor oil, Jatropha seed oil, Pongamia pinnata seed oil, palm kernel oil, and coconut oil; and animal fats such as lard, tallow, rendered lard and rendered tallow, and waste and recycled food grade fats and oils, as well as fats, waxes and oils produced by genetic engineering; animal waxes such as bee wax, Chinese wax (insect wax), shellac wax, and lanoline (wool wax); plant waxes such as carnauba palm wax, Ouricouri palm wax, jojoba seed oil, candelilla wax, esparto wax, Japan wax, rice bran oil, terpenes, terpineols and triglycerides or mixtures thereof.

In one embodiment of the invention, the material of biological origin comprises non-edible plant oils or components thereof or derivatives thereof, for example obtained as by-products from the forest industry. In one embodiment of the invention, the material of biological origin is composed of tall oil materials. Tall oil material comprises tall oil components, tall oil derivatives and any combinations thereof, including CTO, TOFA etc.

The purification treatment is selected from bleaching, degumming, washing, ion exchange and evaporative treatments and any combinations thereof.

The purified product obtained from said purification treatment(s) may be directed to further chemical processing, suitably to catalytic hydroprocessing for obtaining liquid fuels or fuel components.

According to one embodiment degumming may be used for purification, particularly for the removal of metal complexes. Degumming may be performed by washing the organic phase and feedstock comprising at least one material of biological origin suitably at 90-105°C, 300-500 kPa, with an acid, such as $H_3PO_4$, followed by treating with a base, such as NaOH and soft water and separating the formed gums. A major amount of metal components can be removed during this degumming stage.

According to another embodiment bleaching may be used for purification. In the bleaching the organic phase and feedstock comprising at least one material of biological origin can be heated and mixed with natural or acid-activated bleaching clay. Bleaching can remove various impurity traces and reduce the oxidation tendency. Bleaching can be carried out under vacuum to minimize possible oxidation.

According to one embodiment the organic phase and feedstock comprising at least one material of biological origin may be subjected to washing with water or dilute acid solution.

According to one embodiment the organic phase and feedstock comprising at least one material of biological origin may be subjected to ion-exchange treatment.

According to one embodiment the organic phase and feedstock comprising at least one material of biological origin may be subjected to evaporative treatment. In the evaporative treatment the organic phase and feedstock comprising at least one material of biological origin are fed in an evaporation unit comprising at least three evaporators, where the organic phase and feedstock comprising material of biological origin are subjected to evaporative treatment to obtain the purified product (an effluent comprising the purified organic phase) and a heavy evaporation residue. The obtained heavy evaporation residue is recycled at least partly to the feedstock comprising heavy residue.

In the evaporative treatment, in the feed to the evaporation unit, the weight ratio of the organic phase to the material of biological origin is from 0.1:99.9 to 20:80, suitably from 0.2:99.8 to 15:85, particularly suitably from 0.2:99.8 to 10:90. Suitably, in the feed to the evaporation unit, not more than 15 % by weight of the feed is formed of the recycled heavy evaporation residue obtained the process.

By evaporation is meant here any suitable separation method for separating two or more components from each other, such as gases from liquid, which separation method is based on utilizing the differences in the vapor pressure of the components. Examples of such separation methods are evaporation, flashing and distillation. Examples of suitable evaporation methods are those using thin film evaporation technology. The evaporators can thus be selected from the group of thin film evaporator, falling film evaporator, short path evaporator, plate molecular still and any other evaporator using thin film evaporation technology. The evaporation unit can comprise one, two, three, four or more evaporators which can be either of the same type or different type and are selected independently from the suitable separation methods presented above. The evaporative treatment is carried out in an evaporation unit comprising evaporators arranged in series.

The evaporating in the process of the invention comprises three, four or more evaporation steps.

Water, metals and solids, for example lignin, compounds comprising for example metals, consisting mostly of Na, Fe, P, Si, sulfates e.g. $Na_2SO_4$ and $H_2SO_4$ are removed in the evaporative treatment.

In the embodiment where the evaporation is accomplished in three steps, i.e. the evaporation unit comprises three evaporators, water and light components are first evaporated from the feed material in the first evaporation step in order to make the following evaporation steps more efficient. In the second and third evaporation steps the residual fraction containing pitch is minimized by evaporating the liquid product of the first evaporation step. The advantage of using a three step evaporation unit is that the second evaporation step can be a small and cheap evaporator that removes light components from the material. The following third evaporation step can also be smaller and cheaper than the second step in two-step evaporation. The heavy fraction from the second evaporation step is directed to the third evaporator, from which the heavy evaporation residue containing mainly heavy polymeric components and pitch is recycled to hydrolysis and the effluent, typically containing mainly fatty acids is obtained as the purified product, which may be directed chemical processing, such as catalytic hydroprocessing.

Thus, according to one embodiment of the invention, the evaporation is performed in three steps by feeding the organic phase (obtained from hydrolysis) and feedstock comprising at least one material of biological origin to an evaporation unit comprising three evaporators. In three step evaporation, in the first step, water and light components are removed at a temperature of 50 – 250°C and a pressure of 5 - 100 mbar, suitably at a temperature of 120 – 200°C and a pressure of 10 - 55 mbar. The evaporator is suitably a thin film evaporator or a falling film evaporator. In the second step the liquid product from the first evaporation step is evaporated at a temperature of 180 - 350°C and a pressure of 0.1 - 40 mbar, suitably at a temperature of 200 - 270°C and a pressure of 0.1 - 20 mbar. The evaporator is suitably a plate molecular still or a thin film evaporator. Particularly suitably the evaporator is a thin film evaporator. The distillate of the second step is recovered as purified material and the liquid fraction is directed to third evaporation step. In the third step the liquid product from the second evaporation step is evaporated at a temperature of 200 - 450°C and a pressure of 0 - 50 mbar, suitably at a temperature of 300 - 390°C and a pressure of 0.01 - 10 mbar. The evaporator is suitably a short path evaporator or a thin film evaporator. The heavy evaporation residue from the third step is recycled to the feed to hydrolysis and the effluent (the purified material recovered from the third step) is combined with the purified material of the second step to form the purified product. The purified product may be used as feed material for catalytic hydroprocessing.

According to another embodiment of the invention, the evaporation is performed in four steps by feeding the organic phase from hydrolysis and feedstock comprising at least one material of biological origin to an evaporation unit comprising four evaporators. In four step evaporation the organic phase and feedstock comprising material of biological origin are evaporated in a first evaporator to produce a first fraction comprising water and light components, and a second fraction comprising heavy components and residues. The second fraction is evaporated in a second evaporator to produce a third fraction comprising water and low boiling light compounds and a fourth fraction comprising heavy components and residues. The fourth fraction is evaporated in a third evaporator to produce a fifth fraction comprising mainly fatty acids and a sixth fraction comprising heavy components and residues. The sixth fraction is evaporated in a fourth evaporator to produce a seventh fraction comprising mainly fatty acids and an eighth fraction comprising heavy evaporation residue, which is recycled to the feed to hydrolysis. The fifth and seventh fractions are combined and recovered as the purified product, which may be used as feed for catalytic hydroprocessing.

In the four step evaporation the first evaporator may be a falling film evaporator (falling film tube evaporator) or a plate molecular still or a thin film evaporator, suitably a falling film evaporator (FFE) or plate molecular still is used, particularly suitably a FFE is used. The feed material (organic phase and feedstock comprising material of biological origin) is evaporated in the first evaporator at the temperature from 80 to 150°C, suitably from 90 to 120°C. The evaporation is carried out under a pressure from 40 to 80 mbar, suitably from 45 to 65 mbar. A first fraction comprising water and some light components is separated and the second fraction comprising the heavier components and residues, such as fatty acids, resin acids, neutral substances etc. is directed to a second evaporator. The falling film evaporator removes effectively a major amount of water present in the feed material, typically more than 50 % by weight; the second fraction containing the remaining components is directed to the second evaporator.

The second evaporator is a thin film evaporator or a short-path evaporator or a plate molecular still, suitably a thin film evaporator is used. The second evaporator operates at a temperature from 180 to 250°C, suitably from 190 to 220°C. A pressure of 40 to 80 mbar, suitably from 45 to 65 mbar is used. A third fraction containing water and low boiling light hydrocarbon components, said fraction having boiling point of 100 – 210°C, suitably 100 – 170°C at a normal pressure, is removed and the liquid fourth fraction is directed to the third evaporator. When CTO is used as material of biological origin, Crude Sulfate Turpentine (CST) is removed in the third fraction with water. Particularly suitably the first and second evaporators are operated under the same pressure. Suitably the same pressure vessel or pressure line is used.

The liquid fraction from the second evaporator is led to a third evaporator. A thin film evaporator or plate molecular still or short path evaporator can be used, suitably the third evaporator is a short path evaporator. The third evaporator typically operates at a temperature of 200 to 350°C, suitably from 250 to 300°C. A pressure of 0.01 to 50 mbar, suitably 0.5 to 10 mbar, more suitably 1 to 5 mbar and particularly 2 to 3 mbar is used in the third evaporator. A fifth fraction (distillate) comprising typically mainly (more than 50 % by weight) fatty acids is separated and suitably fed to a reactor feed tank and the sixth fraction (liquid phase) is led to a fourth evaporator.

The fourth evaporator may be a short path evaporator or a plate molecular still, suitably a short path evaporator is used. Typical operating conditions include a temperature of 250 to 400°C, suitably from 290 to 360°C. A pressure of 0.01 to 10 mbar, suitably 0.01 to 5 mbar, more suitably 0.1 to 2 mbar is used. From the fourth evaporator, the seventh fraction (distillate) is obtained and combined with the distillate fraction obtained from the third evaporator to yield purified product, which may be used as feed for catalytic hydroprocessing and it may be fed to a hydrogenation reactor feed tank. The eighth fraction (the heavy evaporation residue, very viscous fraction), amounting typically about 5 % from the original feed, is recycled at least partly to the to the feedstock comprising heavy residue.

According to one embodiment the purification treatment is an evaporative treatment comprising three or four evaporative steps and heavy residues obtained from any of the third or fourth evaporation step are recycled to feedstock comprising at least one heavy residue originating from material of biological origin.

According to one embodiment of the invention, prior to the evaporative treatment, the organic phase from the hydrolysis and the material of biological origin may optionally be subjected to additional flashing prior to feeding to the first evaporator. Flashing may be carried out using any suitable manner, for example using heat-exchanger-expansion vessels where volatile components are released.

An advantage of purifying with a three or four or more step evaporation is that the boiling takes place in a more controlled manner because low boiling light components, i.e. components having boiling point of 150 – 210°C, suitably 150 – 170°C, in normal pressure, do not cause so much "carry over", i.e. migrating of the compounds having a boiling point range at the higher end of the above boiling point ranges as well as impurities to the vapor in the subsequent evaporation step. The light components may be, if desired, directed to hydroprocessing or refined further in another process or used further.

## Catalytic hydroprocessing

According to one embodiment of the invention the purified product from the purification treatment is directed to catalytic hydroprocessing.

Said catalytic hydroprocessing comprises the steps of

d) feeding of the purified product into a reactor system comprising at least one catalytically active hydroprocessing reaction phase wherein said purified product is contacted with at least one hydroprocessing catalyst,

e) treating the purified product catalytically with hydrogen in the reactor system to cause hydrodeoxygenation, hydrogenation, isomerisation and cracking of components contained in the purified product to provide a hydroprocessing product, and

f) recovering at least a fraction of the hydroprocessing product as liquid fuel or fuel component.

According to an embodiment of the present invention, between the purification treatment and hydroprocessing there may be optionally an additional purification. The additional purification may be realized using a guard bed, i.e. a separate pretreatment purification bed prior to the hydroprocessing. The additional purification may also be realized by a purification bed or section located in connection with the hydropocessing reactor.

The process of the present invention, for producing liquid fuels or fuel components optionally comprises treatment of the purified product in one or more guard beds. The one or more guard beds can be arranged either to separate guard bed units and/or in the hydroprocessing reactor. The guard bed has the task of acting against harmful substances in the feed. The guard bed is typically activated gamma aluminum oxide or a commercially available purifying catalyst. The guard bed material may also comprise catalyst materials that are capable of catalyzing hydroprocessing reactions. The catalyst material may comprise the same material/materials that are used in the hydroprocessing reactor. The guard bed or the guard bed units can retain both solid and solvated impurities of the feed of biological origin, such as silicon based anti-foaming agents of a tall oil process and harmful chemical elements. The guard bed and/or the guard bed units can be heated, unheated, pressurized or unpressurised, fed with hydrogen gas or without hydrogen gas. Suitably the guard bed and/or the guard bed units are heated and unpressurised.

There are basically two types of guard beds, i.e. active and inactive guard beds. The active guard beds take part in the purification of the feed and change the chemical composition of the feed and they can be placed either in separate guard bed units or inside the hydroprocessing reactor itself. In an embodiment, the active guard bed comprises only activated gamma aluminum oxide. In another embodiment, the active guard bed comprises catalyst materials capable of catalyzing hydroprocessing reactions, such as catalyst containing metals from group VI and/or VIII or mixtures or combinations thereof, which catalyst is capable of converting biological feed material to fuel components. In another embodiment, the active guard bed comprises NiW catalyst or a mixture or a combination of several thin layers or beds of NiW and NiMo catalysts on a support selected from $Al_2O_3$, zeolite, zeolite-$Al_2O_3$ and $Al_2O_3$-$SiO_2$.

The inactive guard beds merely take part in the purification of the feed. These guard beds comprise suitable passive or inert materials. The separate guard beds can be multiplied meaning there is one or several guard beds in a stand-by mode in parallel or in series with the guard bed(s) in use.

The process of the present invention comprises hydroprocessing the purified product in the presence of at least one catalyst to form a mixture of fuel components. The hydroprocessing in the present invention can be done in one, two, three or more steps.

According to one embodiment of the present invention the hydroprocessing is done in one step. The catalyst is a catalyst capable of hydrodeoxygenating, hydrogenating, isomerizing, ring opening and cracking the purified biological material to form a mixture of fuel components. In this embodiment, the catalyst is selected so, that it hydrogenates the double bonds of the purified biological material fed to the hydroprocessing. The catalyst removes heteroatoms of the feed molecules, especially oxygen, by hydrogenation. The catalyst has a capability of hydrogenating the olefinic bonds of the compounds in the feed, opening at least one of the bicyclic rings, and cracking the side chains of hydrocarbon chains. In other words, hydrocarbons are hydrogenated, isomerized and/or cracked in a single step. The cracking/isomerizing are controlled by process variables, such as pressure and/or temperature and by the properties of the catalyst, for example by controlling its acidicity. At the same time sulfur compounds are reduced to hydrogen sulfide. The catalyst contained in the hydroprocessing reactor is selected from catalysts containing metals from group VI and/or VIII of the Periodic System or mixtures or combinations thereof, which catalyst is capable of converting biological feed material to fuel components in a single step. In a suitable embodiment of the invention, the catalyst comprises NiW, typically on a support selected from $Al_2O_3$, zeolite, zeolite-$Al_2O_3$, and $Al_2O_3$-$SiO_2$. In a further suitable embodiment of the invention, the catalyst comprises NiW on an $Al_2O_3$ support.

In a still further embodiment of the invention where the hydroprocessing is carried out in one-step, the catalyst is a mixture or a combination of a NiW catalyst with a further catalyst. Said further catalyst may be selected from any catalysts containing metals from group VI and/or VIII of the Periodic System, such as Ni, Co, Mo, Pt, Pd, or mixtures or combinations thereof, such as NiMo and CoMo, typically on a support selected from $Al_2O_3$, zeolite, zeolite-$Al_2O_3$ or $Al_2O_3$-$SiO_2$. In a suitable embodiment, the further catalyst is NiMo on an $Al_2O_3$ support. In one suitable embodiment of the invention, the catalyst is a combination or a mixture or a combination of several thin layers or beds of NiMo and NiW catalysts.

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According to another embodiment, the hydroprocessing is performed in two steps. In the first step the fatty acids contained in the feed material of biological origin are converted to n-paraffins and in the second step the obtained n-paraffins are isomerised and/or cracked. In the first step a catalyst is used which has a suitable metal, such as metals from Group VIII and /or VIB of the Periodic System may be used. Suitable catalysts are supported Pt, Pd, Ni, NiMo or CoMo catalysts, on a suitable support, such as $Al_2O_3$ and/or $SiO_2$. The catalyst used in the isomerising step is for example a molecular sieve, which contains as metal component noble metals from the group VIII, such as Pt and/or Pd, or a NiW catalyst on a suitable support, such as $Al_2O_3$, zeolite, zeolite-$Al_2O_3$ or $Al_2O_3$-$SiO_2$.

In order to function and stay active the hydroprocessing catalysts used in the present invention needs organic sulfur. Therefore when the feed to the hydroprocessing does not in itself contain sulfur or its sulfur concentration is too low, additional sulfur is fed to the step of hydroprocessing. The additional sulfur can be fed to the hydroprocessing step together with the feed or it can be fed separately to the hydroprocessing step. Additional sulfur can be supplied to the process in gaseous form like hydrogen sulphide, or it can be any material that produces hydrogen sulfide in the process, like organic sulfur compounds, such as dimethyl disulfide. The amount of additional sulfur depends on the amount of sulfur contained in the feed. A person skilled in the art is able to determine the amount of needed sulfur without undue burden. Generally, the $H_2$ feed/$H_2S$ ratio is maintained over about 0.0001, suitably over about 0.001.

The catalyst material must be activated before it is effective and taken into use. The activation comprises several steps, of which one is treating the catalyst with activating sulfur compound, for example dimethyl disulfide. The procedure of activating thus comprises sulfiding of the catalyst. The activation of catalysts is common knowledge in the art and will thus not be discussed here in detail.

The catalyst contained in the reactors of the present invention can be in any suitable form. The catalyst used in the present invention can be diluted with silicon carbide, aluminum oxide, glass beads, less active catalyst and/or inert material. The catalyst used in the present invention can also be undiluted. The catalyst can be in catalyst bed and the bed can be graded by adjusting the activity, particle shape and/or size of the used catalyst. The diluting and grading of the catalyst help in controlling the exothermic balance of the reaction.

The hydroprocessing can be carried out in any kind of reactor, column, vessel, container, tube or pipe, which is suitable for hydroprocessing.

The hydroprocessing is carried out at a temperature range from about 280°C to about 500°C, suitably from about 330°C to about 430°C. The capability of opening of the fused ring structures is also a desired property of the catalyst.

The hydroprocessing is carried out at a pressure of about 20 to about 200 bar, suitably at a pressure of about 50 to about 200 bar, more suitably at about 70 to about 120 bar.

The feed is pumped to the hydroprocessing reactor at a desired speed. Feed rate WHSV (weight hourly spatial velocity) of the feed material is typically in the range of about 0.2 to about 2.5, preferably from about 0.3 to 1.5.

The amount of hydrogen gas needed is determined by the amount of feed. The suitable amount of hydrogen can be determined by a person having ordinary skills in the art. Typically, the relation $H_2$feed /feed is in the range of from about 350 to 3 000 Nl/l, preferably from about 500 to 2 500 Nl/l. (Nl = Normal litre). According to an embodiment of the present invention the gaseous compounds separated from the liquid compounds are hydrogen gas, hydrogen sulfide, light fuel gases, mainly lighter than C5 hydrocarbons.

The process of the present invention may further comprise a step for recycling a portion of the liquid hydrocarbon compounds obtained from the separation or fractionation back to the hydroprocessing.

According to an embodiment of the present invention the obtained liquid fuel or fuel components are a fraction containing gasoline and/or naphtha and a fraction containing middle distillate.

Figure 1 is a schematic diagram of a process for producing liquid fuels in accordance with one embodiment of the invention. In this embodiment, in the first step feedstock 10, comprising at least one heavy residue originating from material of biological origin, heavy evaporation residue 120 and an aqueous medium 20 are fed to vessel 100 where homogenization is carried out, the homogenized mixture 30 is directed to heat exchanger 101 for heating and then to hydrolysis reactor 200, where the mixture 30 is hydrolyzed. From the hydrolysis reactor 200 the hydrolyzed mixture 31 is directed to heat exchanger 102 for cooling, followed by directing the cooled mixture 31 to separation vessel 201, where an aqueous phase 40 (containing water soluble compounds, alkali metal salts and the like) and an organic phase 50 (containing organic compounds and water-insoluble compounds) are separated. The organic phase 50 and feedstock comprising material of biological origin 60 are directed to an evaporation unit 700, to the first evaporator 300, where water and light compounds are separated and withdrawn as stream 70 and the liquid stream 80 is directed to the second evaporator 400. The distillate 90 (comprising typically fatty acids) is directed to the hydroprocessing unit 800 and the liquid stream 110 is directed to the third evaporator 500. The heavy residue stream 120 from the evaporator 500 is recycled to the homogenization vessel 100 and the effluent 130 is combined with distillate 90 forming purified product, which is directed to the hydroprocessing unit 800, to the hydroprocessing reactor 600. The heavy residue 140 is directed to burning and the hydroprocessing product 150 is directed to further fractionation steps if desired.

The following examples are illustrative of embodiments of the present invention, as described above, and they are not meant to limit the invention in any way.

## Examples

### Example 1

A mixture was formed of 25 g of pitch (heavy residue stream obtained from evaporative treatment of CTO in three evaporators) and 100 ml of an aqueous 0.5 N KOH in ethanol (95 %) and the mixture was then hydrolyzed at approx. 80°C under NTP for 7 hours. The mixture was cooled and the pH was adjusted to 2-3 with 30 % $H_2SO_4$ (10 ml). Water (approx. 100 ml) was added to the mixture and it was extracted 3 times with diethyl ether and hexane 1:1, followed by washing with water. Distillation curves of the pitch used as starting material (highest curve) and after hydrolysis treatment as instructed above (middle curve) are presented in Figure 2, as well as of evaporated (3-step evaporation) tall oil as reference (lowest curve). (SimDis/FID, internal standard cholesterol, and sample concentration were same in all runs).

Some properties of the pitch (starting material) and treated pitch are presented in table 1 below.

Table 1

| | **Pitch** | **Treated pitch** |
|---|---|---|
| Acid number | 35.0 | 44.6 |
| β-sitosterol % (v/v) | 1.0 | 3.1 |
| β-sitostanol % (v/v) | 0.3 | 0.9 |
| Fatty acids (total) % (v/v) | 0.4 | 5.3 |
| Resin acids total % (v/v) | 5.4 | 10.1 |
| Sterols total % (v/v) | 7.6 | 20.4 |

From table 1 it can be seen that the amounts of acids and sterols were increased, whereby increased amounts of valuable starting materials were available for further chemical processing.

The present invention has been described herein with reference to specific embodiments. It is, however clear to those skilled in the art that the process(es) may be varied within the bounds of the claims.

## Claims

1. A process for treating heavy residues originating from material of biological origin, said process comprising the steps of

a) subjecting a mixture formed of a feedstock comprising heavy residue originating from material of biological origin and an aqueous medium to hydrolysis at a temperature from 10 to 280°C and under a pressure from 0 to 70 bar to obtain a hydrolyzed mixture, wherein the aqueous medium is selected from mixtures of water with at least one alkali metal hydroxide and at least one C1-C4 alcohol, and from water, and when water is used as the aqueous medium the hydrolysis is carried out in the presence of a catalyst comprising a cationic amine compound,

b) separating the hydrolyzed mixture into an organic phase and an aqueous phase,

c) subjecting the organic phase and feedstock comprising material of biological origin to at least one purification treatment to obtain a purified product.

2. The process according to claim 1, wherein the material of biological origin is selected from a group consisting of

a) plant fats, plant oils, plant waxes; animal fats, animal oils, animal waxes, fish fats, fish oils, fish waxes, and

b) recycled food grade fats and oils, and fats, oils and waxes obtained by genetic engineering, and

c) fats, oils and waxes derived from algae, molds, yeasts, fungi and/or other microorganisms capable of producing said compounds; and

d) mixtures of said materials.

3. The process according to claim 1 or 2, wherein the material of biological origin is tall oil material.

4. The process according to any one of claims 1-3, wherein the purification treatment is selected from bleaching, degumming, washing, ion exchange, evaporative treatments and any combinations thereof.

5. The process according to any one of claims 1-4, wherein the purification treatment is an evaporative treatment comprising three, four or more evaporative steps.

6. The process according to any one of claims 1-5, wherein the purification treatment is an evaporative treatment comprising three or four evaporative steps and heavy

residues obtained from any of the third or fourth evaporation step are recycled to feedstock comprising at least one heavy residue originating from material of biological origin.

7. The process according to any one of claims 1-6, wherein the heavy residue is selected from tall oil pitch, heavy residues and pitch fractions obtained from evaporative treatment of tall oil materials, and any combinations thereof.

8. The process according to any one of claims 1 - 7, wherein the hydrolysis is carried out at the temperature of 60-200°C and under a pressure from 1-30 bar, and the aqueous medium is selected from mixtures of water with at least one alkali metal hydroxide and at least one C1-C4 alcohol.

9. The process according to any one of claims 1-7, wherein the hydrolysis is carried out in the presence of a catalyst comprising a cationic amine compound, at the temperature of 80-180°C and pressure of 0-5 bar, and water is used as the aqueous medium.

10. The process according to any one of claims 1-8, wherein the pH of the hydrolyzed mixture is adjusted to the range of 2-3 with an acid.

11. The process according to any one of claims 1 – 10, wherein the evaporator is selected from thin film evaporators, falling film evaporators, short path evaporators, and plate molecular stills.

12. A process for producing liquid fuels or fuel components, comprising the steps of
a) subjecting a mixture formed of a feedstock comprising heavy residue originating from material of biological origin and an aqueous medium to hydrolysis at a temperature from 10 to 280°C and under a pressure from 0 to 70 bar to obtain a hydrolyzed mixture, wherein the aqueous medium is selected from mixtures of water with at least one alkali metal hydroxide and at least one C1-C4 alcohol, and from water and when water is used as the aqueous medium the hydrolysis is carried out in the presence of a catalyst comprising a cationic amine compound,
b) separating the hydrolyzed mixture into an organic phase and an aqueous phase,
c) subjecting the organic phase and at least one feedstock comprising material of biological origin to at least one purification treatment to obtain a purified product,

d) feeding of the purified product into a reactor system comprising at least one catalytically active hydroprocessing reaction phase wherein said purified product is contacted with at least one hydroprocessing catalyst,
e) treating the purified product catalytically with hydrogen in the reactor system to cause hydrodeoxygenation, hydrogenation, isomerisation and cracking of components contained in the purified product to provide a hydroprocessing product, and
f) recovering at least a fraction of the hydroprocessing product as liquid fuel or fuel component.

13. The process according to claim 12, wherein the material of biological origin is selected from is selected from a group consisting of
a) plant fats, plant oils, plant waxes; animal fats, animal oils, animal waxes, fish fats, fish oils, fish waxes, and
b) recycled food grade fats and oils, and fats, oils and waxes obtained by genetic engineering, and
c) fats, oils and waxes derived from algae, molds, yeasts, fungi and/or other microorganisms capable of producing said compounds; and
d) mixtures of said materials.

14. The process according to claim 12 or 13, wherein the material of biological origin is tall oil material.

15. The process according to any one of claims 12-14, wherein the purification treatment is selected from bleaching, degumming, washing, ion exchange and evaporative treatments and any combinations thereof.

16. The process according to any one of claims 12-15, wherein the purification treatment is an evaporative treatment comprising three, four or more evaporative steps.

17. The process according to any one of claims 12-16, wherein the purification treatment is an evaporative treatment comprising three or four evaporative steps and heavy residues obtained from any of the third or fourth evaporation step are recycled to feedstock comprising at least one heavy residue originating from material of biological origin.

18. The process according to any one of claims 12-17, wherein the heavy residue is selected from tall oil pitch, heavy residues or pitch fractions obtained from evaporative treatment of tall oil materials, and any combinations thereof.

19. The process according to any one of claims 12 -18, wherein the hydrolysis is carried out at the temperature of 60-200°C and under a pressure from 1-30 bar, and the aqueous medium is selected from mixtures of water with at least one alkali metal hydroxide and at least one C1-C4 alcohol.

20. The process according to any one of claims 12-18, wherein the hydrolysis is carried out in the presence of a catalyst comprising a cationic amine compound, at the temperature of 80-180°C and pressure of 0-5 bar, and water is used as the aqueous medium.

21. The process according to any one of claims 12 -19, wherein the pH of the hydrolyzed mixture is adjusted to the range of 2-3 with an acid.

22. The process according to any one of claims 12 - 21, wherein the evaporator is selected from thin film evaporators, falling film evaporators, short path evaporators, and plate molecular stills.

23. The process according to any one of claims 12-22, wherein the hydroprocessing is accomplished in a single step and the catalyst is catalyst containing metals from group VI and/or VIII or mixtures or combinations thereof, which catalyst is capable of converting biological feed material to fuel components.

24. The process according to claim 23, wherein the catalyst is NiW or a mixture or combination of NiW and NiMo catalysts on a support selected from $Al_2O_3$, zeolite, zeolite-$Al_2O_3$, and $Al_2O_3$-$SiO_2$.

25. The process according to any one of claims 12 to 24, wherein the hydroprocessing is accomplished in two steps and the catalyst in the first step is any catalyst containing metals from Group VIII and /or VIB of the Periodic System on a suitable support capable of converting hydrocarbons to n-paraffins and the catalyst in the second step is a catalyst which is selected from the group of Pt, Pd and NiW supported by $Al_2O_3$, zeolite, zeolite-$Al_2O_3$ or $Al_2O_3$-$SiO_2$.

## Vaatimukset

1. Prosessi biologista alkuperää olevasta materiaalista peräisin olevien raskaiden jäännösten käsittelemiseksi, missä mainittu prosessi käsittää vaiheet
a) suoritetaan hydrolyysi 10 - 280°C lämpötilassa ja 0 - 70 bar paineessa seokselle, joka on muodostettu syötteestä, joka käsittää biologista alkuperää olevasta materiaalista peräisin olevaa raskasta jäännöstä ja vesipitoista väliainetta, joka vesipitoinen väliaine valitaan veden seoksista, joissa on vähintään yksi alkalimetallihydroksidi ja vähintään yksi C1-C4 alkoholi, ja vedestä, jolloin saadaan hydrolysoitu seos, ja jos vettä käytetään vesipitoisena väliaineena, suoritetaan hydrolyysi kationista amiiniyhdistettä käsittävän katalyytin läsnä ollessa,
b) erotetaan hydrolysoitu seos orgaaniseksi faasiksi ja vesipitoiseksi faasiksi,
c) suoritetaan orgaaniselle faasille ja syötteelle, joka käsittää biologista alkuperää olevaa materiaalia, vähintään yksi puhdistuskäsittely, jolloin saadaan puhdistettua tuotetta.

2. Patenttivaatimuksen 1 mukainen prosessi, missä biologista alkuperää oleva materiaali valitaan joukosta, joka koostuu
a) kasvirasvoista, kasviöljyistä, kasvivahoista; eläinrasvoista, eläinöljyistä, eläinvahoista; kalarasvoista, kalaöljyistä, kalavahoista, ja
b) kierrätetyistä elintarvikelaatuisista rasvoista ja öljyistä, ja geeniteknologian avulla saaduista rasvoista, öljyistä ja vahoista, ja
c) rasvoista, öljyistä ja vahoista, jotka ovat peräisin levistä, homeista, hiivoista, sienistä ja/tai muista mikro-organismeista saaduista, jotka kykenevät tuottamaan mainittuja yhdisteitä; ja
d) mainittujen materiaalien seoksista.

3. Patenttivaatimuksen 1 tai 2 mukainen prosessi, missä biologista alkuperää oleva materiaali on mäntyöljymateriaali.

4. Jonkin patenttivaatimuksen 1-3 mukainen prosessi, missä puhdistuskäsittely valitaan valkaisun, hartsin ja pihka-aineiden poiston, pesun, ioninvaihdon, haihdutuskäsittelyjen ja näiden yhdistelmien joukosta.

5. Jonkin patenttivaatimuksen 1-4 mukainen prosessi, missä puhdistuskäsittely on haihdutuskäsittely, joka käsittää kolme, neljä tai useampia haihdutusvaiheita.

6. Jonkin patenttivaatimuksen 1-5 mukainen prosessi, missä puhdistuskäsittely on haihdutuskäsittely, joka käsittää kolme tai neljä haihdutusvaihetta, ja kolmannesta tai neljännestä vaiheesta saadut raskaat jäännökset kierrätetään syötteeseen, joka käsittää vähintään yhtä, biologista alkuperää olevasta materiaalista peräisin olevaa raskasta jäännöstä.

7. Jonkin patenttivaatimuksen 1-6 mukainen prosessi, missä raskas jäännös valitaan mäntyöljypien, mäntyöljymateriaalien haihdutuskäsittelystä saatujen raskaiden jäännöksien, pikifraktioiden, ja niiden yhdistelmien joukosta.

8. Jonkin patenttivaatimuksen 1-7 mukainen prosessi, missä hydrolyysi suoritetaan 60-200°C lämpötilassa ja 1-30 bar paineessa, ja vesipitoinen väliaine valitaan veden seoksista vähintään yhden alkalimetallihydroksidin ja vähintään yhden C1-C4 alkoholin kanssa.

9. Jonkin patenttivaatimuksen 1-7 mukainen prosessi, missä hydrolyysi suoritetaan kationista amiiniyhdistettä käsittävän katalyytin läsnä ollessa 80-180°C lämpötilassa ja 0-5 bar paineessa, ja vettä käytetään vesipitoisena väliaineena.

10. Jonkin patenttivaatimuksen 1-8 mukainen prosessi, missä hydrolysoidun seoksen pH säädetään alueelle 2-3 hapon avulla.

11. Jonkin patenttivaatimuksen 1-10 mukainen prosessi, missä haihdutin valitaan ohutkalvohaihduttimien, putoavan kalvon periaatteella toimivien haihduttimien, lyhyen tien periaatteella toimivien haihduttimien, ja levymolekyylitislainten joukosta.

12. Prosessi nestemäisten polttoaineiden tai polttoainekomponenttien valmistamiseksi, joka prosessi käsittää vaiheet

a) suoritetaan hydrolyysi 10 - 280°C lämpötilassa ja 0 - 70 bar paineessa seokselle, joka on muodostettu syötteestä, joka käsittää biologista alkuperää olevasta materiaalista peräisin olevaa raskasta jäännöstä, ja vesipitoista väliainetta, joka vesipitoinen väliaine valitaan veden seoksista, joissa on vähintään yksi alkalimetallihydroksidi ja vähintään yksi C1-C4 alkoholi, ja vedestä, jolloin saadaan hydrolysoitu seos, ja jos vettä käytetään vesipitoisena väliaineena, suoritetaan hydrolyysi kationista amiiniyhdistettä käsittävän katalyytin läsnä ollessa,

b) erotetaan hydrolysoitu seos orgaaniseksi faasiksi ja vesipitoiseksi faasiksi,

c) suoritetaan orgaaniselle faasille ja syötteelle, joka käsittää biologista alkuperää olevaa materiaalia, vähintään yksi puhdistuskäsittely, jolloin saadaan puhdistettua tuotetta,

d) syötetään puhdistettua tuotetta reaktorisysteemiin, joka käsittää vähintään yhden katalyyttisesti aktiivisen vetyprossessointireaktiovaiheen, missä mainittu puhdistettu tuote saatetaan kosketuksiin vähintään yhden vetyprosessointikatalyytin kanssa,

e) käsitellään puhdistettua tuotetta katalyyttisesti vedyllä reaktorisysteemissä, jotta aikaan saadaan puhdistetun tuotteen sisältämien komponenttien hydrodeoksygenaatio, vedytys, isomerointi ja krakkaus vetyprosessointituotteen saamiseksi, ja

f) otetaan talteen vähintään yksi vetyprosessointituotteen fraktio nestemäisenä polttoaineena tai polttoainekomponenttina.

13. Patenttivaatimuksen 12 mukainen prosessi, missä biologista alkuperää oleva materiaali valitaan joukosta, joka koostuu

a) kasvirasvoista, kasviöljyistä, kasvivahoista; eläinrasvoista, eläinöljyistä, eläinvahoista; kalarasvoista, kalaöljyistä, kalavahoista, ja

b) kierrätetyistä elintarvikelaatuisista rasvoista ja öljyistä, ja geeniteknologian avulla saaduista rasvoista, öljyistä ja vahoista, ja

c) rasvoista, öljyistä ja vahoista, jotka ovat peräisin levistä, homeista, hiivoista, sienistä ja/tai muista mikro-organismeista saaduista, jotka kykenevät tuottamaan mainittuja yhdisteitä; ja

d) mainittujen materiaalien seoksista.

14. Patenttivaatimuksen 12 tai 13 mukainen prosessi, missä biologista alkuperää oleva materiaali on mäntyöljymateriaali.

15. Jonkin patenttivaatimuksen 12 - 14 mukainen prosessi, missä puhdistuskäsittely valitaan valkaisun, hartsin ja pihka-aineiden poiston, pesun, ionivaihdon, haihdutuskäsittelyjen ja näiden yhdistelmien joukosta.

16. Jonkin patenttivaatimuksen 12 - 15 mukainen prosessi, missä puhdistuskäsittely on haihdutuskäsittely, joka käsittää kolme, neljä tai useampia haihdutusvaiheita.

17. Jonkin patenttivaatimuksen 12 - 16 mukainen prosessi, missä puhdistuskäsittely on haihdutuskäsittely, joka käsittää kolme tai neljä haihdutusvaihetta, ja kolmannesta tai neljännestä vaiheesta saadut raskaat jäännökset kierrätetään syötteeseen, joka

käsittää vähintään yhtä, biologista alkuperää olevasta materiaalista peräisin olevaa raskasta jäännöstä.

18. Jonkin patenttivaatimuksen 12 - 17 mukainen prosessi, missä raskas jäännös valitaan mäntyöljypien, mäntyöljymateriaalien haihdutuskäsittelystä saatujen raskaiden jäännöksien, pikifraktioiden ja niiden yhdistelmien joukosta.

19. Jonkin patenttivaatimuksen 12 - 18 mukainen prosessi, missä hydrolyysi suoritetaan 60-200°C lämpötilassa ja 1-30 bar paineessa, ja vesipitoinen väliaine valitaan veden seoksista vähintään yhden alkalimetallihydroksidin ja vähintään yhden C1-C4 alkoholin kanssa.

20. Jonkin patenttivaatimuksen 12 - 18 mukainen prosessi, missä hydrolyysi suoritetaan kationista amiiniyhdistettä käsittävän katalyytin läsnä ollessa 80-180°C lämpötilassa ja 0-5 bar paineessa, ja vettä käytetään vesipitoisena väliaineena.

21. Jonkin patenttivaatimuksen 12 - 19 mukainen prosessi, missä hydrolysoidun seoksen pH säädetään alueelle 2-3 hapon avulla.

22. Jonkin patenttivaatimuksen 12 - 21 mukainen prosessi, missä haihdutin valitaan ohutkalvohaihduttimien, putoavan kalvon periaatteella toimivien haihduttimien, lyhyen tien periaatteella toimivien haihduttimien, ja levymolekyylitislainten joukosta.

23. Jonkin patenttivaatimuksen 12 - 22 mukainen prosessi, missä vetyprosessointi toteutetaan yhdessä vaiheessa ja katalyytti on Ryhmän VI ja/tai VIII metallia tai niiden seosta tai yhdistelmää sisältävä katalyytti, joka kykenee konvertoimaan biologista syötemateriaalia polttoainekomponenteiksi.

24. Patenttivaatimuksen 23 mukainen prosessi, missä katalyytti on NiW-katalyytti tai NiW- ja NiMo-katalyyttien seos tai yhdistelmä, joukosta $Al_2O_3$, zeoliitti, zeoliitti-$Al_2O_3$, ja $Al_2O_3$-$SiO_2$ valitulla kantajalla.

25. Jonkin patenttivaatimuksen 12 - 24 mukainen prosessi, missä vetyprosessointi toteutetaan kahdessa vaiheessa ja ensimmäisessä vaiheessa katalyytti on jaksollisen järjestelmän Ryhmän VII ja/tai VIB metalleja sisältävä katalyytti sopivalla kantajalla, kykenevä konvertoimaan hiilivetyjä n-paraffiineiksi ja katalyytti toisessa vaiheessa on

joukosta Pt, Pd ja NiW valittu katalyytti $Al_2O_3$-, zeoliitti-, zeoliitti-$Al_2O_3$- tai $Al_2O_3$-$SiO_2$-kantajalla.

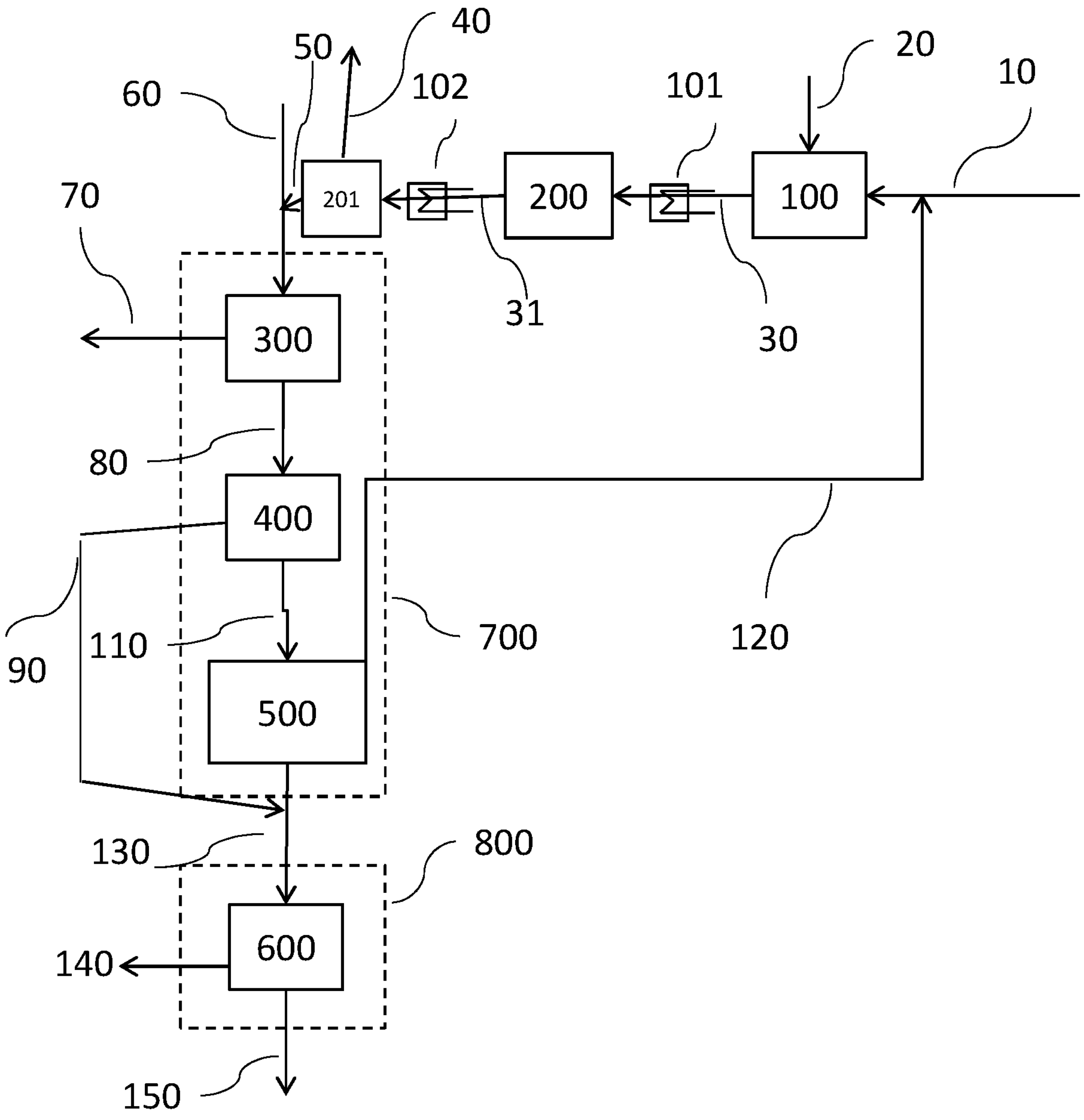
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Fig. 1

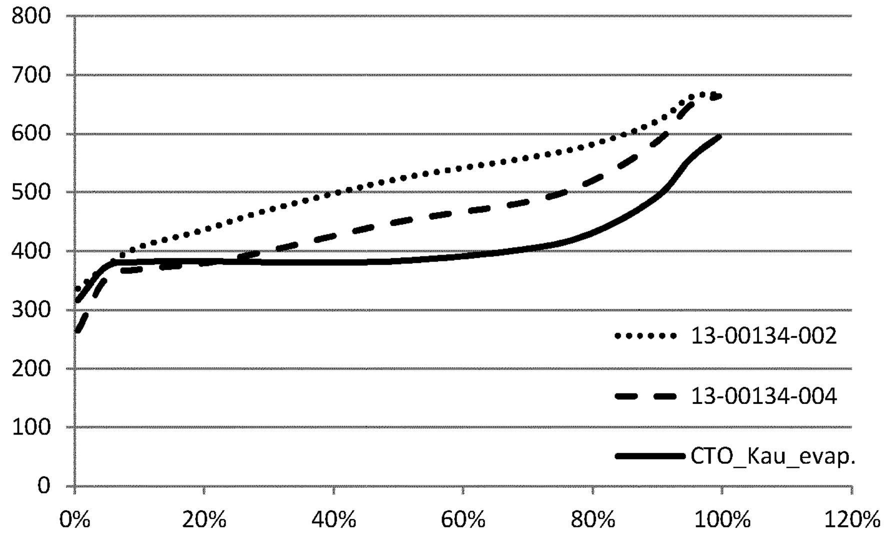
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Fig. 2