

PRODUCING HYDROCARBONS FROM ORGANIC MATERIAL OF BIOLOGICAL ORIGIN

FIELD OF THE INVENTION

The present invention relates to a process of producing hydrocarbons from organic material of biological origin, in particular organic material of biological origin comprising a high amount of impurities, such as nitrogen, silicon, chloride and phosphorus containing compounds, as well as metals. The presented process is particularly suitable for challenging feedstock, which would typically not be introduced to a hydrogenation process using sensitive catalysts.

BACKGROUND OF THE INVENTION

Various oils and fats have been used as feedstock in production of middle distillate components suitable as fuels especially for diesel engines. The purpose of using renewable and recycled organic material of biological origin in production of fuel components is mainly to reduce the use of fossil based feedstock and thereby to tackle global warming and other environmental issues. Hydrogenated vegetable oil (HVO) is a promising alternative to fossil based middle distillate fuels. Although HVO is mainly produced from vegetable oils, also other sources such as animal fats and algae oils can be used. There is still a need for alternative non-fossil based sources and processes to produce especially middle distillate fuels.

Many sources containing organic material that could be used to produce hydrocarbon components, contain high amounts of impurities such as nitrogen, silicon, chloride and phosphorus containing compounds and metals. These and other impurities weaken the possibility of many organic materials to be used as feedstock or lowers the quality of the products.

Many previous methods have suggested various pre-treatment and purification processes for feedstock containing high amounts of impurities. There is also a need for new overall processes to handle feedstock with high amounts of impurities, as well as other feedstock.

BRIEF DESCRIPTION OF THE INVENTION

An object of the present invention is thus to provide a method or process, which is particularly suitable for challenging feedstocks that typically contain high amounts of impurities. With challenging feedstock is meant herein low-quality feedstock containing e.g. phosphorus and metal impurities, which are difficult to

remove by regular pretreatment methods, such as degumming or bleaching, and which cause problems for catalysts, such as deactivation, when used in the subsequent hydrotreatment processes. Moreover, challenging feedstock may include chemically challenging materials like resin acids and unsaponifiable matter included in e.g. crude tall oil. Low-quality or challenging feedstock would typically not be introduced to a hydrogenation process, which uses sensitive catalysts.

The objects of the invention are achieved by a method or process characterized by what is stated in the independent claims. The preferred embodiments of the invention are disclosed in the dependent claims.

10 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for producing middle distillate composition from a feedstock comprising organic material of biological origin. The middle distillate composition obtained by the process herein described can be used as diesel fuel, diesel fuel component and/or jet fuel component.

15 As used herein the term “organic material of biological origin” refers to organic material, i.e. material containing carbon. The organic material is of biological origin, i.e. from natural resources such as but not limited to plants, trees, algae, microbes but also animal sources are possible. Organic material of biological origin is here meant to exclude fossil based organic material. Organic material of biological origin as herein used can also be renewable material. The organic material suitable for the present process typically contains organic compounds such as fatty acids, resin and rosin acids and other lipophilic compounds but also other organic compounds.

25 Waste and residues containing organic material may further be used as feedstock, while containing compounds and/or impurities that are not allowed or just spoiling the usability thereof for e.g. food or feed or cosmetics applications.

The renewable character of carbon-containing compositions, such as feedstocks and products of biological origin i.e. renewable feedstock and products, can be determined by comparing the ^{14}C -isotope content of the feedstock to the ^{14}C -isotope content in the air in 1950. The ^{14}C -isotope content can be used as evidence of the renewable origin of the feedstock or product. Carbon atoms of renewable material comprise a higher number of unstable radiocarbon (^{14}C) atoms compared to carbon atoms of fossil origin. Therefore, it is possible to distinguish between carbon compounds derived from biological sources, and carbon compounds derived from fossil sources by analyzing the ratio of ^{12}C and ^{14}C isotopes. Thus, a

particular ratio of said isotopes can be used to identify and quantify renewable carbon compounds and differentiate those from non-renewable i.e. fossil carbon compounds. The isotope ratio does not change in the course of chemical reactions. Examples of a suitable method for analyzing the content of carbon from biological sources is ASTM D6866 (2020). An example of how to apply ASTM D6866 to determine the renewable content in fuels is provided in the article of Dijs et al., Radio-carbon, 48(3), 2006, pp 315-323. For the purpose of the present invention, a carbon-containing material, such as a feedstock or product is considered to be of renewable origin if it contains 90% or more modern carbon, such as 100% modern carbon, as measured using ASTM D6866.

Particular examples of the feedstock comprising organic material of biological origin of the present invention include, but are not limited to, animal based fats and oils, such as suet, tallow, blubber, lard, train oil, milk fat, fish oil, poultry oil, and poultry fat; plant based fats and oils, such as sludge palm oil, rape-seed oil, canola oil, colza oil, sunflower oil, soybean oil, hemp oil, olive oil, linseed oil, cottonseed oil, mustard oil, palm oil, arachis oil, castor oil, coconut oil, lignocellulosic pyrolysis liquid (LPL), HTL biocrude, crude tall oil (CTO), tall oil pitch (TOP), crude fatty acid (CFA), tall oil fatty acid (TOFA) and distilled tall oil (DTO); microbial oils; algal oils; recycled fats or various waste streams of the food industry, such as used cooking oil, yellow and brown greases; free fatty acids, any lipids containing phosphorous and/or metals, oils originating from yeast or mold products, recycled alimentary fats; starting materials produced by genetic engineering, and any mixtures of said feedstocks.

In one embodiment of the current invention the feedstock comprising organic material of biological origin comprise pitch containing crude tall oil (CTO), residue and waste oils from palm oil production and/or recycled fats and oils.

In an embodiment of the present invention organic material of biological origin used as feedstock is selected from a group consisting of crude tall oil (CTO), tall oil pitch (TOP), tall oil fatty acid (TOFA), crude fatty acid (CFA), and distilled tall oil (DTO); more particularly the organic material of biological origin is crude tall oil (CTO) or tall oil pitch (TOP).

In addition, or as an alternative the organic material of biological origin can also be selected from acid oils, such as acidulated soapstock (ASK), technical corn oil (TCO), plant oil from plants of the family Brassicaceae (carinata oil), palm effluent sludge (PES), also known as palm mill effluent (POME), used cooking oil (UCO), gutter oil and brown grease (BG).

As defined herein crude tall oil (CTO, CAS Registry Number 8002-26-4) is most frequently obtained as a by-product of either Kraft or Sulphite pulping processes and tall oil pitch (TOP, CAS number of 8016-81-7) is the residual bottom fraction from crude tall oil distillation processes.

5 Crude tall oil (CTO) comprises resin acids, fatty acids, and unsaponifiables. Resin acids are a mixture of organic acids derived from oxidation and polymerization reactions of terpenes. The main resin acid in crude tall oil is abietic acid but abietic derivatives and other acids, such as pimaric acid are also found. Fatty acids are long chain monocarboxylic acids and are found in hardwoods and
10 softwoods. The main fatty acids in crude tall oil are oleic, linoleic and palmitic acids. Unsaponifiables cannot be turned into soaps as they are neutral compounds which do not react with sodium hydroxide to form salts. They include sterols, higher alcohols and hydrocarbons. Sterols are steroids derivatives which also include a hydroxyl group. Typically, CTO feeds contain 48 wt.% fatty acids (e.g. oleic acid),
15 29wt.% resin acids (e.g. abietic acid) and 23wt.% neutrals (e.g. sterols).

 Tall oil pitch (TOP) can be considered to be a UVCB substance (Substances of Unknown or Variable composition, Complex reaction product or Biological materials) under the REACH definition (ECHA; Guidance in a Nutshell, Identification and naming of substances under REACH and CLP; Version 2.0, April 2017).
20 Composition of TOP according to Holmbom (1978) is presented in Table 1, wherein A, B, C, D denote ordinary grades of tall oil pitch received from three plants in Finland and E and F denote US grades investigated.

 Tall oil pitch typically comprises from 34 to 51 wt.% free acids, from 23 to 37 wt.% esterified acids, and from 25 to 34 wt.% unsaponifiable neutral compounds of the total weight of the tall oil pitch. The free acids are typically selected
25 from a group consisting of dehydroabietic acid, abietic and other resin acids. The esterified acids are typically selected from a group consisting of oleic and linoleic acids. The unsaponifiables neutral compounds are typically selected from a group consisting of diterpene sterols, fatty alcohols, sterols, and dehydrated sterols.

30 The term "crude fatty acid (CFA)" refers to fatty acid-containing materials obtainable by purification (e.g., distillation under reduced pressure, extraction, and/or crystallization) of CTO. The term "tall oil fatty acid (TOFA)" refers to fatty acid rich fraction of crude tall oil (CTO) distillation processes. TOFA typically comprises mainly fatty acids, typically at least 80 wt.% of the total weight of the
35 TOFA. Typically, TOFA comprises less than 10 wt.% rosin acids.

Table 1. Component Group Composition of Tall Oil Pitch (wt.% of pitch)^a

Constituents	A	B	C	D	E	F
Free acids, total	39.3	52.6	48.6	44.6	46.7	34.6
Fatty acids	1.4	1.8	1.3	0.8	1.3	2.4
Resin acids	10.6	12.5	9.7	6.1	3.3	6.5
Other acids	27.3	37.3	37.3	37.7	42.1	25.7
Esterified acids, total	30.6	23.2	23.3	26.8	27.9	37.8
Fatty acids	8.2	12.9	13.3	15.2	13.8	12.4
Resin acids	1.7	0.9	1.2	0.9	1.6	1.9
Other acids	20.7	9.4	8.8	10.7	12.5	23.5
Equiv. weight for free acids	648	591	716	642	873	719

a) Holmbom B, and Erä V, 1978. Composition of Tall oil pitch, Journal of the American oil chemistry society, 55, pp. 342-344.

5 The term “distilled tall oil (DTO)” refers to resin acid rich fraction of crude tall oil (CTO) distillation processes. DTO typically comprises mainly fatty acids, typically from 55 to 90 wt.%, and rosin acids, typically from 10 to 40 wt.% rosin acids, of the total weight of the DTO. Typically, DTO comprises less than 10 wt.% unsaponifiable neutral compounds of the total weight of the distilled tall oil.

10 Acid oils refers to by-products of alkali or physical refining of crude oils and fats. One example of acid oils are oils obtained by acidulation of soapstock (ASK), which contains free fatty acids, acylglycerols and other lipophilic compounds.

15 The term “technical corn oil” TCO refers to corn oil extracted through a dry milling process. In the dry milling process, corn grains are cleaned and ground directly to obtain a fine corn flour. This flour is then mixed with water, enzymes and other ingredients (cooking and liquefaction) to convert starch into simple sugars, then into glucose (saccharification). This glucose is fermented to produce ethanol, which is then removed by distillation and purified by dehydration. The remaining stillage (called distillers grain) is then processed further to expel technical
20 corn oil (generally called “distillers corn oil” in the United States) through centrifugation. De-emulsifiers can be used to enhance separation of the TCO from the rest of the stillage.

The organic material can also comprise plant oil originating from a plant of the family Brassicaceae (carinata oil). The plant of the family Brassicaceae is selected from *Brassica juncea* (brown mustard), *Brassica carinata* (Ethiopian mustard), *Brassica nigra* (black mustard), *Brassica rapa*, *Brassica rapa* subsp. *oleifera* (field mustard), *Brassica elongate* (elongated mustard), *Brassica nariosa* (broad-baked mustard), *Brassica rupestris* (brown mustard), *Brassica tournefortii* (Asian mustard), *Brassica napus*, *Brassica napus* el, *Sinapis hirta* (mustard), *Sinapis alba* (white mustard), *Sinapis arvensis*, *Nasturtium floridanum*, *Nasturtium gambelium*, *Nasturtium gronlandicum*, *Nasturtium microfullum*, *nasturtium officinale*, *Nasturtium sordidum* and combinations thereof. Preferably the plant is *Brassica carinata*.

The term "palm effluent sludge" (PES), also commonly referred to, as palm oil mill effluent (POME) here refers to the voluminous liquid waste that comes from the sterilisation and clarification processes in milling oil palm. The raw effluent contains 90-95% water and includes residual oil, soil particles and suspended solids.

The term "used cooking oil" (UCO) refers to oils and fats that have been used for cooking or frying in the food processing industry, restaurants, fast foods and at consumer level, in households.

Gutter oil is a general term for oil that has been recycled. It can be used to describe the practice of restaurants re-using cooking oil that has already been fried before.

Brown grease (BG) means an emulsion of fat, oil, grease, solids, and water separated from wastewater in a grease interceptor (grease trap) and collected for use as feedstock.

In one embodiment the organic material of biological origin comprises crude tall oil (CTO) optionally including tall oil pitch (TOP), tall oil pitch (TOP), brown grease (BG), acidulated soapstock (ASK), technical corn oil (TCO), low quality animal fat (AF), *Brassica carinata* (BC), palm effluent sludge (PES) or any combination thereof, wherein these materials typically contain difficult to remove heavy molecular weight compounds, metal or phosphorus containing impurities.

In one embodiment the feedstock comprises crude tall oil (CTO), tall oil pitch (TOP), brown grease (BG), acidulated soapstock (ASK) and/or palm effluent sludge (PES).

In one embodiment the feedstock comprising organic material of biological origin comprises crude tall oil (CTO) and/or tall oil pitch (TOP). In one embodiment the feedstock comprising organic material of biological origin comprises resin acids from 10 wt.% to 30 wt.%, based on the total feedstock.

5 The process of the present invention further comprises a step of pre-treating the feedstock in one or more pre-treatment stages. The pre-treatment stages vary and are selected based on the feedstock and especially on the amount and type of impurities in the feedstock. The pre-treatment stages can be selected from heat treatment optionally followed by evaporation of volatiles; heat treat-
10 ment with adsorbent (HTA) optionally followed by flash evaporation; degumming; bleaching or any combination thereof. The pre-treatment also typically comprises a step of removing impurities from the feedstock, including any suitable removal of solids from a liquid, including filtration, centrifugation and sedimentation; and removing volatiles from liquid, e.g. by evaporation. In the pre-treatment the feed-
15 stock comprising organic material of biological origin, as previously defined, is purified and a purified feedstock is obtained. With purification is meant herein that the amount of at least one impurity, such as metal impurity, phosphorus and silicon, is decreased in the feedstock as a result of the pre-treatment.

 In one embodiment the pre-treatment is selected from heat treatment
20 optionally followed by evaporation of volatiles, whereby the feedstock is heated at a temperature of from 80 °C to 325 °C, preferably 180 °C to 300 °C, more preferably 200 °C to 280 °C, in a residence time from 1 to 300 min. The heat treatment can be followed by an evaporation step, where especially silicon and phosphorus contain-
25 ing organic material can be found in WO 2020/016405. Heat treatment can also be followed by filtration as an addition or an alternative to evaporation. When the feedstock comprises brown grease or acidulated soapstock the pre-treatment comprising heat treatment with or without filter-aid (adsorbent) followed by filtration and possible bleaching.

30 In one embodiment the pre-treatment is selected from heat treatment with adsorbent (HTA) optionally followed by flash evaporation. HTA as pre-treatment is especially suitable when the feedstock comprises CTO and/or TOP, but also for other feedstock. Heat treatment with adsorbent (HTA) can be performed in a temperature from 180 °C to 325 °C, preferably from 200 °C to 300 °C, more prefer-
35 ably from 240 °C to 280 °C, optionally in the presence of an acid. The adsorbent can be selected from alumina silicate, silica gel and mixtures thereof and is typically

added in an amount of 0.1 wt.% to 10 wt.%, such as 0.5 wt.%. An example of HTA can be found in WO 2020/016410.

In one embodiment the pre-treatment is selected from bleaching. Bleaching can be conducted by acid addition in an amount of from 500 to 5000 ppm based on feed. The bleaching treatment can be performed in a temperature from 60 °C to 90 °C and including a drying step in 110 °C to 130 °C. The bleaching is finished by a filtration step to remove formed solids and possible filter aids. In one example bleaching includes the following sequence

- (1) acid addition 1000-4000 ppm citric acid (50% water) 85 °C, 10 min;
- (2) adsorbent/filter aid addition 0.1-1 wt.%, 85 °C, 800 mbar, 20 min;
- (3) drying 120 °C, 80 mbar, 25 min
- (4) filtering 120 °C, 2.5bar.

Both heat treatment (HT) and heat treatment with adsorbent (HTA) can be performed under pressure, the pressure can be 500 to 5000 kPa. Also water can be added before or during HT and HTA to a level of up to 5 wt.%, such as 1 wt.% - 3 wt.%. The evaporation, e.g. performed by flashing can be performed after HT or HTA or any other pre-treatment stage and can be performed at about 160 °C, such as from 150 °C to 225 °C, in a pressure of 10 to 100 mbar (1 to 10 kPa).

For a feedstock comprising palm oil effluent sludge (PES) the pre-treatment can comprise acid degumming followed by solid removal from the liquid, using filtration or centrifugation. The degumming process can further be followed by a bleaching step.

In one embodiment of the invention the pre-treatment, comprises heat treatment (HT) and bleaching.

In one embodiment of the invention the pre-treatment, comprises heat treatment (HT) with alkali addition and bleaching.

In one embodiment of the invention the pre-treatment, comprises heat treatment with adsorption (HTA) followed by flash (removal of light components comprising Si components etc. by evaporation) and bleaching.

In addition, the pre-treatment may or may not include additional steps such as removal of solids (using technologies such as centrifugation or filtration) before and/or after HT or HTA, water washing, degumming, hydrolysis, distillation, strong acid treatment, 2nd bleaching or any combination of the mentioned methods.

The level and type of impurities vary with the organic material, but can also vary from one feedstock to another depending on source and how the organic

material has been treated. Typical impurity levels of the most significant impurities are listed in Table 2 below.

Table 2. Typical impurities and ranges in different organic materials

	P (ppm)	N (ppm)	Si (ppm)	Tot Cl (ppm)	metals* (ppm)
CTO	1-100	100-500	1-100	1-10	10-1000
TOP	1-200	100-1500	1-500	1-20	30-1500
PES	5-100	30-500	0-100	1-50	20-1200
UCO	0-500	1-600	0-50	1-300	1-1000
BG	5-3500	50-5000	0-50	1-300	10-20000
TCO	0-100	20-100	0-20	1-20	1-200
BC	0-50	30-100	0-1	0-5	1-100
AF	0-700	1-3000	0-30	1-100	0-600

5 Metals = Ca, Mg, Na, Fe; in total

Different organic materials can be blended in the final feedstock to avoid unwanted reactions. For example, if the feed Cl content is over 100 ppm and simultaneously N content is over 1000 ppm it is possible that ammonium chloride
 10 NH_4Cl precipitation reaction takes place in pre-hydrotreatment step. In order to avoid this, organic material like BG, having a high Cl content and a high N content, are blended with organic material having a low Cl and/or N content, such as PES.

In one embodiment of the present invention the feedstock of the invention comprises an impurity level of

- 15 - nitrogen compounds from more than 30 ppm, preferably more than 50 ppm or 100 ppm, such as up to 5000 ppm;
- silicon compounds from more than 1 ppm, preferably more than 5 ppm or more than 10 ppm or 30 ppm, up to 500 ppm;
- phosphorous compounds from more than 5 ppm, preferably more than 10 ppm or 50 ppm, up to 3500 ppm;
- 20 - chloride from more than 1 ppm, preferably more than 5 ppm or 10 ppm, up to 300 ppm; and/or
- metals from more than 10 ppm, preferably more than 30 ppm or 50 ppm, up to 20000 ppm.

25 The amount of metals are given as the total sum of at least Ca, Mg, Na and Fe.

In one embodiment of the present invention at least one impurity selected from nitrogen, silicon, phosphorous, chloride and metals, is present in the feedstock prior to pre-treatment in high amount, such as for nitrogen over 1000 ppm, silicon over 100 ppm, phosphorous over 700 ppm, chloride over 60 ppm or metals over 4000 ppm.

The process of the present invention further comprises a step of subjecting the purified feedstock to pre-hydrotreatment to obtain a stream of partly hydrotreated feed. The pre-hydrotreatment can also be called pre-hydrodeoxygenation or pre-HDO. The aim of the pre-hydrotreatment is to prepare the purified feed to the subsequent processes and also partly to function as a further purification step for the purified feedstock.

In one embodiment of the present invention, the pre-hydrotreatment is performed in conditions selected from:

- a temperature range of 300 °C to 380 °C, preferably of 320 °C to 360 °C;
- a pressure range of 40 to 100 bar, preferably 40 to 80 bar, more preferably 50 to 70 bar;
- a weight hourly space velocity (WHSV) of 0.2 1/h to 10 1/h, preferably 0.25 1/h to 10 1/h, more preferably 0.3 1/h to 8 1/h; and
- a H₂/oil feed of 800 dm³/dm³ to 1200 dm³/dm³, preferably of 900 dm³/dm³ to 1100 dm³/dm³.

The catalyst used in the pre-hydrotreatment step is a typical hydrotreating catalyst such as Ni, Co, Mo, W or any combination thereof on a carrier such as alumina. Alternatively or in addition the catalyst in pre-hydrotreatment can also be a typically hydrocracking catalyst such as NiW on acidic supports (ASA, Zeolites). In one embodiment the catalyst in the pre-hydrotreatment is NiMo on alumina carrier. The pre-hydrotreatment step is typically carried out in a reactor with one or more catalyst beds. In an embodiment, the pre-hydrotreatment reactor is a fixed bed reactor. The extent of the pre-hydrotreatment depends on the organic material and level of impurities. The aim of the pre-treatment is to prepare the feed, e.g. to remove heteroatoms and other impurities, to such a level that the hydrotreatment can remove the rest of the heteroatoms and impurities prior to the isomerization. The feed to the hydrotreatment essentially contains only a minor amount of heteroatoms and other impurities compared to the feed to the pre-hydrotreatment.

As the purified feedstock subjected to the pre-hydrotreatment typically

still, after pretreatment, contains heteroatoms, such as oxygen and nitrogen, the decrease of the amount of oxygen and/or nitrogen in the heteroatom containing feed compounds, such as triglycerides, may be depicted by using the term oxygen conversion. In this disclosure the term "oxygen conversion" is taken to mean the depletion, by a deoxygenation reaction, of the amount of oxygen contained in or bound to oxygen-containing feed compounds wherein the oxygen is depleted or removed from said feed compound. For example, oxygen contained in fatty acid is reacted with hydrogen (hydrodeoxygenation) to form water, which can be removed as a gaseous by-product and the corresponding oxygen depleted or oxygen-free hydrocarbon, thus formed at a 100% oxygen conversion.

In an embodiment, the oxygen conversion of the purified feedstock in the pre-hydrotreatment step, is adjusted to at least 60 %, preferably at least 70 %, more preferably at least 80 %, such as at least 90 % or even at least 95 %. The maximum oxygen conversion in pre-hydrotreatment step is 99 %. This is the conversion of oxygen containing compounds to oxygen-free compounds. The aim is to remove most of the oxygen already in the pre-hydrotreatment to allow optimal removal conditions for other heteroatoms, such as nitrogen, in the hydrotreatment step.

In an embodiment the nitrogen conversion of the purified feedstock in the pre-hydrotreatment step is lower than the oxygen conversion, such as 4 percentage points or 10 percentage points lower than the oxygen conversion. In one embodiment the nitrogen conversion of the purified feedstock in the pre-hydrotreatment step, is adjusted to at least 55 %, preferably at least 65 %, more preferably at least 75 %, such as at least 90 %. The maximum nitrogen conversion in pre-hydrotreatment step is 95 %. The term "nitrogen conversion" is applied similarly to oxygen conversion and is herein taken to mean the conversion of nitrogen containing compounds to nitrogen-free compounds. Nitrogen in the nitrogen containing compounds also react with hydrogen and forms e.g. NH_3 , which can be removed as a gaseous by-product.

In an embodiment, the conditions for pre-hydrotreatment and hydrotreatment are different from each other, particularly the temperature of hydrotreatment is at least 10°C higher than in the pre-hydrotreatment.

Hydrodenitrogenation (HDN) of nitrogen containing compounds is typically more difficult than the hydrodeoxygenation (HDO) of oxygen containing compounds. The amount of HDN and HDO can be controlled by adjusting the hy-

drotreatment conditions, such as temperature, pressure, weight hourly space velocity (WHSV) and/or catalyst.

The pre-hydrotreatment step is meant to remove a major part of the heteroatoms and those other impurities, such as metals and phosphorus, still left after the pre-treatment. In one embodiment of the present invention the pre-hydrotreatment is carried out such that the amount of nitrogen is removed by at least 80 wt.% and oxygen by at least 90 wt.% in the partly hydrotreated feed as compared to the purified feedstock entering the pre-hydrotreatment step.

In an embodiment overall hydrotreatment (including pre-hydrotreatment and hydrotreatment) is adjusted such that at least 80 %, preferably at least 90 %, more preferably at least 95 %, of the total oxygen conversion is conducted in the pre-hydrotreatment step.

In an embodiment overall hydrotreatment (including pre-hydrotreatment and hydrotreatment) is adjusted such that at least 60 %, preferably at least 70 %, more preferably at least 80 %, of the total nitrogen conversion is conducted in the pre-hydrotreatment step.

These high levels of removal of heteroatoms and impurities shows that major part of the removal of heteroatoms as well as impurities takes place in pre-hydrotreatment compared to the hydrotreatment step. Thereby, more adverse effect, such as formation of water and ammonia and catalyst de-activation, takes place in the pre-hydrotreatment step. The catalyst in the pre-hydrotreatment can be changed frequently, while the catalyst in the hydrotreatment step stays fresh. This arrangement enables one to avoid a total shut down due to a catalyst change and still be able to continue production using either the mere hydrotreatment catalyst, or a combination of a spare pre-hydrotreatment unit together with the hydrotreatment unit. Moreover, the influence of corrosion due to acidic feeds may be mitigated. Also, fresh hydrogen can be introduced to the hydrotreatment step, which enables highly efficient conversion. Since major part of the conversion takes place in pre-hydrotreatment, the hydrotreatment step can be controlled such that the hydrotreated product is of high quality.

In the pre-hydrotreatment the partly hydrotreated feed withdrawn from the reactor, can be recycled in a relatively high ratio. The ratio of recycled partly hydrotreated feed to fresh purified feedstock in the pre-hydrotreatment step can be from 1:1 to 15:1, preferably 1:1 to 10:1 and more preferably 1:1 to 5:1.

One aim of the present method or process hereby disclosed is therefore

to lower the amount of heteroatoms and impurities by a combination of pre-treatment and pre-hydrotreatment. Examples of levels of impurities before pre-treatment is given in Table 3, which also shows typical amounts of impurities still left in the feedstock prior to the pre-hydrotreatment (pre-HDO) step.

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Table 3. Examples of levels of impurities before pre-treatment and before pre-hydrotreatment (pre-HDO)

Impurity	Unit	Typical impurity levels	
		Pre-treatment	Pre-HDO
Water	wt.%	< 2	No free water
Chloride	ppm	< 100	< 100
Metals (Ca, Mg, Na, Fe), Total	ppm	< 1000	< 1.5
Phosphorus, Total	ppm	< 500	<1.5
Nitrogen, Total	ppm	< 600	< 500
Silicon, Total	ppm	< 100	< 2.0
Solids	wt.%	< 1	To min.

It should be noted that ppm (part per million) corresponds to mg/kg.

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The process of the present invention further comprises distilling the stream of partly hydrotreated feed to obtain at least two fractions. The two fractions are a first heavy bottom fraction and a second middle fraction. The first heavy bottom fraction is typically removed from the present process and the middle fraction is collected and subjected to further treatments. The first heavy bottom fraction can be characterized such that at least 90% of the components (compounds) of the first heavy bottom fraction have a boiling point of 360 °C or above. The second middle fraction can be characterized such that at least 90 % of the components (compounds) of the second middle fraction have a boiling point of from 180 °C to 360 °C. All boiling points are given in atmospheric pressure. The first heavy bottom fraction can be used as a product as such or subjected to other processes (not disclosed here). Separating the middle fraction by distillation reduces the volume of the stream to be subsequently hydrotreated. The hydrotreatment can be optimised for removal of remaining impurities from the middle fraction. For example, high

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molecular weight (HMW) compounds are directed to the heavy bottom fraction for alternative further processing. Moreover, as the volume of the stream directed to hydrotreatment is decreased, the size of the required equipment decreases respectively.

5 In one embodiment of the present invention the distillation is performed using the following conditions: a cut point target of 340 °C to 360 °C, vacuum set point of 2 mbar, top column temperature of 180 °C, nitrogen feed rate of 2 l/h and feed rate of 0.24 l/h. These conditions are to be regarded as examples and a skilled person is able to operate the distillation such that the target fractions are
10 obtained.

The process of the present invention further comprises subjecting the collected middle fraction to hydrotreatment to obtain a stream of hydrocarbons and subjecting the stream of hydrocarbons to isomerization to obtain an isomerized stream of hydrocarbons.

15 In one embodiment of the present invention, the hydrotreatment is performed in conditions selected from:

- a temperature range of 300 °C to 380 °C, preferably of 320 °C to 360 °C;
- a pressure range of 40 to 80 bar, preferably 50 to 70 bar;
- 20 - a weight hourly space velocity (WHSV) of 0.25 1/h to 1.5 1/h, preferably 0.3 1/h to 1 1/h; and
- a H₂/oil feed of 800 dm³/dm³ to 1200 dm³/dm³, preferably of 900 dm³/dm³ to 1100 dm³/dm³.

The catalyst used in the hydrotreatment step is a typical hydrotreating
25 catalyst such as Ni, Co, Mo, W or any combination thereof on a carrier such as alumina. Alternatively or in addition, the catalyst in the hydrotreatment can also be a typically hydrocracking catalyst such as NiW on acidic supports (ASA, Zeolites). In one embodiment the catalyst in the hydrotreatment is NiMo on alumina carrier. The treatment step is typically carried out in a reactor with one or more catalyst
30 beds.

In the hydrotreatment step there is typically no recycling of the stream of hydrocarbon withdrawn from the reactor. If there is any recycling in the hydrotreatment step a maximum of 10 wt.% of the stream of hydrocarbons is recycled back to hydrotreatment. In one embodiment the hydrotreatment step does
35 not contain any recycling.

The aim of the hydrotreatment step is to essentially remove all impurities and heteroatoms from the feed, and the stream of hydrocarbons should therefore essentially only contain hydrocarbons.

In one embodiment of the current invention, the isomerization of the stream of hydrocarbons to obtain a stream of isomerized hydrocarbons is performed in conditions selected from:

- a temperature range of 300 °C to 360 °C, preferably 310 °C to 345 °C;
- a pressure range of 35 bar to 60 bar, preferably 40 bar to 50 bar;
- a weight hourly space velocity (WHSV) of 1 1/h to 1.5 1/h.

The catalyst used in the isomerization of the stream of hydrocarbons is any typical isomerization catalyst, such as Pt or Pd on a suitable support, preferably the isomerization catalyst is Pt-SAPO11.

In one embodiment of the present invention the process further comprises a stripping step to remove gaseous compounds from a stream of the process. The stripping step can be performed after the pre-treatment step, the pre-hydrotreatment step, the hydrotreatment step, the isomerization step or any combination thereof. In one embodiment the stripping is performed after the pre-hydrotreatment step to remove gaseous compounds before the distillation step. Gaseous compounds which can be removed in a stripping step include sulphide (H₂S), ammonia (NH₃) and water. The stripping step can also be called a flash step or flash evaporation or flash distillation.

In one embodiment of the present invention the process further comprises a second distillation after the isomerisation. The second distillation is performed such that a fraction boiling up to 300°C from the initial boiling point (iBP) is obtained. This fraction is useful as a jet fuel component.

In the process of the present invention said feedstock comprising organic material of biological origin has prior to the pre-treatment step preferably not been distilled or evaporated, such that the gaseous fraction is collected for further processing steps and residue or liquid fraction is discarded.

The current invention also provides a middle distillate fuel composition obtained or obtainable by any process herein described. In one embodiment, the middle distillate of the invention fulfils the paraffinic diesel (EN15940) specification, which means the middle distillate have properties that make it useable as paraffinic diesel as is specified in EN15940. In one embodiment, the middle distillate composition is obtained from a feedstock comprising crude tall oil (CTO) and/or

tall oil pitch (TOP).

In one embodiment, the middle distillate composition has an oxidation stability fulfilling the requirements of EN15940, preferably the oxidation stability of the middle distillate composition is more than 70 min, such as more than 80 min or more preferably more than 90 min. The oxidation stability is measured according to EN16091.

The middle distillate composition according to the invention can be used as diesel fuel, diesel fuel component or jet fuel component. The middle distillate composition can be used as a jet fuel blend component. The current invention thereby also provides a blend fulfilling requirement of ASTM D7566-19 comprising a middle distillate composition according to the current invention, preferably the middle distillate composition is obtained from a feedstock comprising crude tall oil (CTO) and/or tall oil pitch (TOP). As a second or subsequent component, the blend can comprise a fossil or petroleum based jet fuel component, such as kerosene, e.g. Jet A1.

The middle distillate composition according to the invention can be blended with other fuel components to form a final fuel, e.g. the middle distillate fuel composition of the invention can be blended with fatty acid methyl esters (FAME), fatty acid ethyl esters (FAEE), FCC gasoil, steam cracker gasoil, hydrocracked gasoil, and/or straight-run diesel.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

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EXAMPLES

Example 1

30 A product (middle distillate composition) was prepared in a process according to the invention and certain properties of the product thus obtained were measured.

A feed containing a mixture of 30 wt.% crude tall oil (CTO) and 70 wt.% animal fat (AF) was prepared. The CTO contained 48 wt.% fatty acids (e.g. oleic acid), 29 wt.% resin acids (e.g. abietic acid) and 23 wt.% neutrals (e.g. sterols). The

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feed was purified by bleaching in a pre-treatment stage. The purified feed was subjected to a pre-hydrotreatment step using a NiMo catalyst. The conditions of the pre-treatment step were as follows: a temperature of 350 °C, a pressure of 60 bar (6000 kPa) and WHSV 0.5 1/h. Thus obtained partly hydrotreated stream was subjected to a distillation step, using a cut point of 320 °C. The heavy bottom fraction (boiling above 320 °C) was removed and the middle fraction (boiling up to 320 °C) was collected and subjected to a hydrotreatment step.

The hydrotreatment of the collected middle fraction was performed in the following conditions: a temperature of 335 °C, a pressure of 50 bar (5000 kPa) and WHSV of 0.5 1/h. The catalyst used was a NiMo catalyst.

After the hydrotreatment step the hydrotreated feed was subjected to an isomerisation step. The isomerisation was conducted in the following conditions: a fixed bed reactor containing platinum oxide on porous silica-alumina support as the isomerisation catalyst, WHSV was fixed at 1.5, and pressure at 40 bar (4000 kPa). Runs were performed at 300 normal liter/liter H₂ to oil ratio, and at temperature of about 338 °C.

The product obtained by distillation was collected starting from iBP 286.2 °C onwards (after a jet fuel range component was removed) and its properties were analysed. The summary of the properties and test methods can be seen in Table 4 below

The analysis of the product properties shows that the product produced in a process according to the invention (30 CTO:70AF) meet the paraffinic diesel specification EN15940. The sample according to the invention however has a higher oxidation stability as measured according to EN16091 compared to typical reference values (around from 60 to below 70 min). The EN 16091 method includes pressurizing a sample (5ml) with oxygen (700kPa) at 140 °C. The break-point as measured in minutes is when the oxygen pressure collapses. A higher value therefore indicates a better oxidation stability. The cetane number is improved when CTO is added to the feed.

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Table 4; Diesel properties of the middle distillate product produced with the method according to the invention (30CTO:70AF) compared to the requirements of the paraffinic diesel specification EN 15940, Class A and to diesel fuel specification EN590

Property	30CTO:70 AF	Standard
Density; ENISO12185; kg/m ³	788.5	765 – 800 EN 15940
Cloud point; ASTM5773; C	-19	
Cetane-IQT; EN15195	81.4	min. 70 EN 15940
Oxidation Stability; EN16091; Min	104	min. 60* EN 590
Distillation temperature, ENISO3405;C		
T10	296.2	
T50	296.6	
T90	298.1	
FBP	304.1	

- 5 The standard require that at 180°C maximum 10% is recovered and at 340°C a minimum of 95% is recovered.

Example 2

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Another set of samples were prepared with 30 % CTO and 70 % CTO and the balance being animal fat (30CTO:70AF and 60CTO:40AF). The samples were subjected to a hydrotreatment process according to the invention, see example 1 for details.

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The isomerisation of the two samples were performed in two different temperatures; 310 – 314 °C for summer grade middle distillate and 328 °C for winter grade middle distillate.

The product properties of the summer and winter grade middle distillates for the two samples were analysed and are summarised in table 5 below.

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Table 5; properties of the summer and winter grade samples

Property	Summer 30CTO:70AF	Summer 60CTO:40AF	Winter 30CTO:70AF	Winter 60CTO:40AF
Density; ENISO12185; kg/m ³	782.4	784.2	782.5	784.2
Cloud point; ASTM5773; C	-13	-12	-32	-30
Cetane-IQT; EN15195	87	89	80	80
Viscosity 40C; ENISO3104; mm ² /s	3.287	3.366	3.215	3.301
Aromatics; EN12916; wt%	<0.2	<0.2	<0.1	<0.1
Dist. ENISO3405; C				
iBP	269.2	269.4	262.8	267.3
T10	279.9	281.9	275.2	277.5
T50	288.2	286.7	282.7	284.8
T90	294.8	295.4	291.2	292.2
FBP	299.6	299.4	296.2	296.7

As can be seen from the results presented in table 5, both summer and winter grade middle distillates, meeting the requirements of the paraffinic diesel (EN15940) specification, can be produced with the process according to the invention. A winter grade middle distillate could also be produced when the CTO content was increased to 60 wt.% of the total amount.

The chemical content of the samples (summer and winter grade and 30wt.% CTO and 60 wt.% CTO) was also analysed using GC-GC-MS. As expected, the content of naphthenes increased with increased amount of CTO in the feed. The total amount of naphthenes in products with 60 wt.% CTO in feed were 3.9 wt.% for summer grade and 3.8 wt.% for winter grade.

Example 3

A set of samples were prepared, using a feed containing 100 % CTO. The samples were subjected to a hydrotreatment process as described in example 1. However, this time a cut point of 340 °C was used in the distillation step of the partly hydrotreated stream. The heavy bottom fraction (boiling above 340 °C) was removed and the middle fraction (boiling up to 340 °C) was collected and subjected to the hydrotreatment step as in Example 1. The isomerisation was performed as

in Example 1, at about 331 °C.

The 100% CTO isomerisation product was heavier compared to products originating from animal fat, containing mostly components boiling in the >300 °C region. Hence, to avoid unnecessary loss of valuable material and reduction of the jet fuel component yield, the 100% CTO jet fuel component was distilled and collected as iBP to 300 °C fraction, i.e. without removing the light end. Properties of the collected jet fuel component were analysed and are reported in Table 6.

Additionally two jet fuel blends were prepared containing 35 vol-% or 40 vol-% of the jet component and 65 vol-% or 60 vol-% of a conventional fossil Jet A1. Properties of the jet fuel blends were analysed and compared to the jet fuel standard (ASTM D7566-19, Table 1). The summary of the properties and test methods can be seen in Table 6 below.

Table 6. Properties of the jet fuel blends

	Jet fuel compo- nent	Jet fuel blend	Jet fuel blend	Jet fuel standard
Property	100% CTO	35 vol-% jet component + 65 vol-% Jet A1	40 vol-% jet component + 60 vol-% Jet A1	ASTM D7566-19, Table 1
Density; ENISO12185; kg/m ³	792	797	796	775-840
Flash point; ASTM D7236; °C	50,5*	47	-	Min. 38
Freezing point; IP529; °C	-59.2	-61.4	-	Max. -47
Viscosity -20 °C; ENISO3104; mm ² /s	13	5.3	5.7	Max. 8.0
Viscosity -40 °C; ENISO3104; mm ² /s	38	11	12	Max. 12**
Distillation ENISO3405, °C				
T10	201.1	175.2	175.6	Max. 205
T50	274.7	210.2	215.3	Report
T90	286.4	272.7	274.7	Report
FBP	290.5	275.5	277.0	Max. 300
T50-T10 (difference)	73.6	35.0	39.7	Min 15**
T90-T10 (difference)	85.3	97.5	99.1	Min 40**

* by ENISO13736; ** Part 2 - Extended Requirements

As can be seen from the results presented in table 6, a jet fuel component having excellent freezing point, flash point and distillation characteristics is obtainable with the process according to the invention. Surprisingly, good results were obtained even when using 100% CTO as the renewable feedstock.

Due to the elevated content of naphthenes in the 100% CTO-derived jet fuel component, it had somewhat higher density than an animal fat derived jet fuel component (data not shown). However, despite the elevated density, the produced jet fuel component had an excellent freezing point (-59.2 °C). When blended with conventional fossil Jet A1, a further improvement in the freezing point was observed. The obtained jet fuel component could be blended even in high shares with the conventional fossil jet fuel component, without any troubles meeting the ASTM D7566 Table 1 basic requirements, and even meeting the extended requirements. As the flash point of the 100% CTO jet fuel component is naturally high, no material was lost in the light end. Additionally, the higher than usual flash point is foreseen to provide further benefits in the aviation fuel supply chain, especially in fuel blending and transportation. This is because the jet component would also meet flash point requirements tighter than those of ASTM D7566-19 specification, as is sometimes encountered in the aviation fuel supply chain.

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CLAIMS

1. A process for producing middle distillate composition from a feedstock comprising organic material of biological origin, the process comprising
- 5 a) providing a feedstock comprising organic material of biological origin,
- b) pre-treating the feedstock in one or more pre-treatment stages to obtain a purified feedstock,
- c) subjecting said purified feedstock to pre-hydrotreatment to obtain a stream of partly hydrotreated feed,
- 10 d) distilling the stream of partly hydrotreated feed to obtain at least two fractions, a first heavy bottom fraction, which is removed from the process and a second middle fraction, which is collected for further treatment,
- e) subjecting the collected middle fraction to hydrotreatment to obtain a stream of hydrocarbons, and
- 15 f) subjecting the stream of hydrocarbons to isomerization to obtain an isomerised stream of hydrocarbons.
2. The process of claim 1, wherein the feedstock comprises crude tall oil (CTO), tall oil pitch (TOP), tall oil fatty acid (TOFA), crude fatty acid (CFA), distilled tall oil (DTO), acid oils, such as acidulated soapstock (ASK), technical corn oil (TCO),
- 20 plant oil from plants of the family Brassicaceae (carinata oil), palm effluent sludge (PES), used cooking oil (UCO), gutter oil, brown grease (BG) or any combination thereof.
3. The process of claim 1 or 2, wherein the feedstock comprising organic material of biological origin comprises crude tall oil (CTO) and/or tall oil pitch (TOP).
- 25 4. The process of claims 1 – 3, wherein the feedstock comprising organic material of biological origin comprises resin acids from 10 wt.% to 30 wt.%, based on the total weight of the feedstock.
5. The process of any claim 1 – 4, wherein the feedstock comprising organic material of biological origin comprises an impurity level of nitrogen compounds from more than 30 ppm, such as up to 5000 ppm; silicon compounds from more than 1 ppm or 5 ppm, up to 500 ppm; phosphorous compounds from more than 5 ppm, up to 3500 ppm; chloride from more than 1 ppm or 5 ppm, up to 300 ppm and/or metals from more than 10 ppm or 30 ppm, up to 20000 ppm.
- 30 6. The process of any preceding claim, wherein the pre-treatment stages of step b) comprises heat treatment (HT) optionally followed by evaporation of
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volatiles; heat treatment with adsorbent (HTA) optionally followed by evaporation; degumming; bleaching or any combination thereof.

7. The process of any preceding claim, wherein the pre-hydrotreatment of step c) is carried out at a temperature of 300 °C to 380 °C, a pressure of 40 bar to 100 bar, a WHSV of 0.2 1/h to 10 1/h and in the presence of a hydrotreatment or hydrocracking catalyst, preferably selected from Ni, Co, Mo and/or W, on a carrier such as alumina.

8. The process of any preceding claim, wherein the distilling of the stream partly hydrotreated of step d) is carried out such that at least 90% of the first heavy bottom fraction have a boiling point of 360 °C or above, and of the second middle fraction at least 90 % have a boiling point of from 180 °C to 360 °C.

9. The process of any preceding claim, wherein the hydrotreatment of the collected middle fraction of step e) is carried out at a temperature of 300 °C to 380 °C, a pressure of 40 bar to 80 bar, a WHSV of 0.25 1/h to 1.5 1/h and in the presence of a hydrotreatment and/or hydrocracking catalyst, preferably selected from Ni, Co, Mo and/or W, on carrier such as alumina.

10. The process of any preceding claim, wherein the isomerization of the stream of hydrocarbons of step f) is carried out at a temperature of 300 °C to 360 °C, preferably 310 °C to 345 °C, a pressure of 35 bar to 60 bar, WHSV of 1.0 1/h to 1.5 1/h and in the presence of an isomerising catalyst selected from supported Pt or Pd catalyst, preferably a Pt-SAPO11 catalyst.

11. The process of any preceding claims, wherein the pre-hydrotreatment is carried out such that at least 80 wt.% of nitrogen and at least 90 wt.% of oxygen is removed from the feedstock comprising organic material of biological origin.

12. The process of any preceding claim, wherein the process further comprises a stripping step to remove gaseous compounds from a stream of the process, preferably the stripping step is performed after pre-treatment step b), after hydrotreatment step e), after isomerisation step f) or any combination thereof.

13. The process of any preceding claim, wherein the process further comprises a second distillation step after the isomerisation step, preferably the second distillation step obtains a fraction boiling up to 300 °C.

14. A middle distillate composition obtained by a process according to any of claims 1 to 13.

15. The middle distillate composition of claim 14, fulfilling requirements of paraffinic diesel (EN15940) specification.

16. The middle distillate composition according to claim 15, wherein the feedstock comprises crude tall oil (CTO) and/or tall oil pitch (TOP).

17. The middle distillate composition according to claim 14, wherein the composition has an oxidation stability fulfilling the requirements of EN15940, preferably the oxidation stability is more than 70 min, as measured according to EN16091.

- 5 18. A blend fulfilling the requirements of ASTM D7566-19 specification comprising the middle distillate composition obtained according to claim 3.