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(71) Applicant: UPM-KYMMENE CORPORATION
[FI/FI]; Eteläesplanadi 2, FI-00130 Helsinki (FI).

(72) Inventors: GUTIERREZ, Andrea; Rajakatu 2 F 12, FI-53200 Lappeenranta (FI). NOUSIAINEN, Jaakko; Variksenmarjantie 7, FI-53500 Lappeenranta (FI). JOKELA, Pekka; Katri Valan tie 15, FI-02660 Espoo (FI).

(74) Agent: BOCO IP OY AB; Itämerenkatu 5, FI-00180 Helsinki (FI).

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(54) Title: PROCESS FOR CONVERTING BIOMASS TO LIQUID FUELS

(57) Abstract: The present invention relates to a process for converting biomass, comprising the stages where, in the first stage starting material comprising biomass is subjected to pyrolysis under pyrolysis conditions to yield pyrolysis oil, in the second stage the pyrolysis oil is subjected to non-catalytic high pressure high temperature treatment, followed by separation of an aqueous phase and HTHP treated pyrolysis oil, and in the third stage the HTHP treated pyrolysis oil is subjected to hydroprocessing in the presence of at least one hydroprocessing catalyst and hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range is obtained. The invention also relates to hydrocarbon components useful as transportation fuel or as a blending component in transportation fuel, obtainable by said process.



5 **PROCESS FOR CONVERTING BIOMASS TO LIQUID FUELS**

FIELD OF THE INVENTION

The present invention relates to the converting of biomass, whereby liquid fuels, fine
10 chemicals, solvents and building-block chemicals may be obtained, and particularly
the present invention relates to a process for converting of biomass to liquid fuels,
where biomass is subjected to pyrolysis and the obtained pyrolysis oil is subjected to
non-catalytic high temperature high pressure treatment, followed by hydroprocessing.
The invention also relates to liquid fuels, fine chemicals, solvents and building-block
15 chemicals obtainable by said process.

BACKGROUND OF THE INVENTION

There is an increasing need for biofuels, suitable as liquid fuels as such, and
particularly as transportation fuels, or compatible with said fuels. Pyrolysis oils
20 obtainable by conversion of biomass have become an object of growing interest as an
alternative source of liquid fuels.

Pyrolysis is generally understood as the chemical decomposition of organic materials
by heating in the absence or with limited supply of oxidizing agent such as air or
oxygen. Pyrolysis can be used for converting biomass to pyrolysis oil which is
25 sometimes referred to as bio-oil.

Commercial pyrolysis applications are typically either focused on the production of
charcoal (slow pyrolysis) or production of liquid products (fast pyrolysis), the pyrolysis
oil. Both the slow pyrolysis and the fast pyrolysis processes may be used for the
manufacture of pyrolysis oil, which is potentially interesting for a substitute for fuel oil
30 and as a feedstock for the production of synthetic fuels, such as gasoline, kerosene,
jet fuel and diesel fuel.

During pyrolysis of biomass, for example of lignocellulosic material, carried out at
temperatures in the range 400-700°C, most of the cellulose and hemicellulose, and
part of lignin typically disintegrate to form smaller and lighter molecules which are
35 vapors at the pyrolysis temperatures. During cooling some of the vapors condense to
form a liquid product, called pyrolysis oil. The remaining part of the biomass, in this
example mainly parts of lignin, is left as a solid i.e. the charcoal.

Several methods have been proposed for the manufacture of pyrolysis oils by the
conversion of biomass and waste liquids, for producing renewable liquid fuels suitable

5 for use in boilers, gas turbines and diesel engines, as well as for gasoline, kerosene and jet fuel use.

In fast pyrolysis the biomass is rapidly heated and it decomposes to yield vapors, aerosols, and some charcoal-like char. The vapors and aerosols are condensed to form pyrolysis oil that has a heating value that is about half of that of conventional
10 fuel oil.

Depending on the feedstock, fast pyrolysis produces about 60-75 wt% of liquid pyrolysis oil, 15-25 wt% of solid char and 10-20 wt% of non-condensable gases. Slow pyrolysis, carried out at about 500 °C for 5 to 30 minutes, produces about 30 wt% of pyrolysis liquid, about 35 wt% of non-condensable gases and about 35 wt% of char.

15 Pyrolysis oil is a chemically complex mixture of compounds, typically comprising water, light volatiles and non-volatiles. Pyrolysis oil is highly acidic, which may lead to corrosion problems, it has substantial water content of approximately 15 to 30 w%, variable viscosity and high oxygen content of around 45 w%. High concentration of oxygenates (oxygen containing compounds) and water have negative impact if
20 pyrolysis oil is used as fuel.

Pyrolysis oil contains insignificant amounts of sulfur if any, but due to its instability pyrolysis oil is often difficult to use as such. It can be used to replace heavy heating oil in, for example, industrial boilers, but in order to be able to use it as transportation fuel it needs to be upgraded or processed further. Therefore several processes for
25 additional processing of pyrolysis oil have been suggested in the art.

Pyrolysis oil is typically upgraded with catalytic hydrodeoxygenation at high hydrogen pressures and temperatures, in the presence of supported sulphided catalysts such as Al₂O₃ supported NiMo and CoMo. These catalysts are sensible to water present and/or
30 generated during the process, and also to alkali metals, and their use requires the addition of sulphur containing compounds to the feed.

US 2011/0119994 relates to catalytic hydrotreatment of pyrolysis oil where feed comprising pyrolysis oil is subjected to a hydrodeoxygenation step in the presence of
35 a catalyst. Patent US 7,578,927 discloses diesel production from pyrolytic lignin where pyrolytic lignin is hydrotreated in a hydrocracking unit in the presence of a catalyst. In US 4,795,841 pyrolysate oil is exposed to hydrogen gas and a suitable catalyst at a temperature in the range of 250 °C to 300 °C.

- 5 A process for converting pyrolysis oil by alcoholysis of pyrolysis oil, followed by hydrotreatment to transportation fuel is presented in US 2012/003540.

Despite of the ongoing research and development of processes for the manufacture and upgrading of pyrolysis oil, there is still a need to provide an improved process for
10 converting biomass to pyrolysis oil and further to liquid fuels or blending stocks for liquid fuels. There is also an increasing need for fine chemicals, solvents and building-block chemicals, originating partly or completely from biomass.

SUMMARY OF THE INVENTION

- 15 The present invention relates a process for converting of biomass whereby liquid fuels, solvents, fine chemicals and building-block chemicals may be obtained. Particularly the present invention relates to a process for the manufacture of liquid fuels. Said liquid fuels may suitably be used as transportation fuels or as blending stocks or components in said fuels. Particularly a process is provided where biomass
20 is converted to pyrolysis oil, which is subjected to non-catalytic high temperature high pressure (HTHP) treatment followed by hydroprocessing.

The process for converting of biomass comprises the stages where, in the first stage starting material comprising biomass is subjected to pyrolysis under pyrolysis
25 conditions to yield pyrolysis oil,
in the second stage the pyrolysis oil is subjected to high pressure high temperature treatment, followed by separation of an aqueous phase and organic phase (HTHP treated pyrolysis oil),
in the third stage the organic phase (HTHP treated pyrolysis oil) is subjected to
30 hydroprocessing in the presence of at least one hydroprocessing catalyst and hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range is obtained.

Further, the invention provides a process for producing transportation fuels, such as
35 gasoline, kerosene, jet fuel, diesel oil, or blending components useful in transportation fuels, as well as a process for producing heating oil, solvents, fine chemicals and building-block chemicals.

The present invention also relates to products obtainable by said process.

Thus an object of the invention is to provide a process for effectively and economically converting feed comprising biomass to more valuable components, particularly to provide liquid fuels, suitably transportation fuels and blending components for said fuels, as well as heating oil, solvents, fine chemicals and building-block chemicals.

Another object of the invention is to provide an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range, which may be separated to fractions boiling in the transportation fuel range, in the heating oil range, in the solvent range, and to fractions which may be processed further to other valuable components.

Another object of the invention is to provide thermally stable and fungible liquid fuels based at least partly or totally on renewable starting materials, whereby said fuels are CO₂ neutral and contain only very low amounts of bonded sulfur and nitrogen, if any.

Another object of the invention is to provide thermally stable and fungible solvents, fine chemicals and building-block chemicals based at least partly or totally on renewable starting materials, whereby said components are CO₂ neutral and contain only very low amounts of bonded sulfur and nitrogen, if any.

DEFINITIONS

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

The term "hydrotreatment" refers here to a catalytic process, which removes oxygen from organic oxygen compounds as water (hydrodeoxygenation, HDO), sulphur from organic sulphur compounds as dihydrogen sulphide (hydrodesulphurisation, HDS), nitrogen from organic nitrogen compounds as ammonia (hydrodenitrogenation, HDN) and halogens, for example chlorine from organic chloride compounds as hydrochloric acid (hydrodechlorination, HDCl), typically under the influence of sulphided NiMo or sulphided CoMo catalysts.

The term "deoxygenation" refers here to the removal of oxygen from organic molecules, such as carboxylic acid derivatives, alcohols, ketones, aldehydes or ethers.

5 The term “decarboxylation” and/or “decarbonylation” refers here to the removal of carboxyl oxygen as CO₂ (decarboxylation) or as CO (decarbonylation) with or without the influence of molecular hydrogen.

The term “hydrocracking” refers here to catalytic decomposition of organic hydrocarbon materials using molecular hydrogen at high pressures.

The term “hydrodewaxing” (HDW) refers here to catalytic treatment of organic hydrocarbon materials using molecular hydrogen at high pressures alter the structure of high molecular weight hydrocarbons by hydroisomerization, hydrodeoxygenation, hydrodearomatization and/or hydrocracking.

The term “hydrogenation” means here saturation of carbon-carbon double bonds by means of molecular hydrogen under the influence of a catalyst.

20 The term “building-block chemicals” refers here to chemical compounds useful as starting materials and intermediates for the manufacture of chemical and pharmaceutical products. Examples of such chemical building-blocks are fumaric acid, furfural, glycerol, citric acid, treonin, propanic acid etc.

25 The term “aqueous media” refers here to water, waste water streams, recirculated aqueous streams from the process of the invention or from another processes, aqueous solutions and aqueous emulsions. Said aqueous media is suitably free of metals, alkali metals and solid particles.

30 Transportation fuels refer here to fractions or cuts or blends of hydrocarbons having distillation curves standardized for fuels, such as for diesel fuel (middle distillate from 180 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.

35 **BRIEF DESCRIPTION OF THE DRAWINGS**

Fig 1 is a schematic flow diagram representing one embodiment of the process for converting biomass where biomass is subjected to pyrolysis, followed by HTHP treatment and hydroprocessing.

5 Fig 2 is a schematic flow diagram representing another embodiment of the process for converting biomass where the HTHP treated pyrolysis oil is subjected to prehydrogenation prior to the hydroprocessing stage.

Fig 3 is a schematic flow diagram representing another embodiment of the process for
10 converting biomass where the HTHP treated pyrolysis oil is subjected to prehydrogenation comprising two steps, prior to the hydroprocessing stage.

Fig 4 is a schematic flow diagram representing another embodiment of the process for
converting biomass where pyrolysis oil is pretreated with an aqueous media prior to
15 the HTHP stage, the HTHP treated pyrolysis oil is subjected to prehydrogenation comprising two steps, prior to the hydroprocessing stage where crude tall oil is co-processed with the prehydrogenated, HTHP treated pyrolysis oil.

Fig 5 illustrates water content of pyrolysis oil before and after treatment with an
20 aqueous media.

Fig 6 illustrates densities of pyrolysis oil before and after treatment with an aqueous media.

25 Fig 7 illustrates the results from viscosity measurements of pyrolysis oil before and after treatment with an aqueous media.

DETAILED DESCRIPTION OF THE INVENTION

It was surprisingly found out that a process where starting material comprising
30 biomass is subjected to pyrolysis to yield pyrolysis oil, followed by subjecting the obtained pyrolysis oil to non-catalytic high pressure high temperature (HTHP) treatment prior to the hydroprocessing stage, provides several advantages in view of the state of the art. The proposed process is more effective, economic and enables to convert compounds comprised in biomass to more valuable components with
35 improved yields.

The process for converting biomass comprises the stages where, in the first stage starting material comprising biomass is subjected to pyrolysis under pyrolysis conditions to yield pyrolysis oil,

5 in the second stage the pyrolysis oil is subjected to non-catalytic high temperature high pressure treatment, followed by separation of water phase and organic phase (HTHP treated pyrolysis oil),
in the third stage the organic phase (HTHP treated pyrolysis oil) is subjected to hydroprocessing in the presence of at least one hydroprocessing catalyst and
10 hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range is obtained.

First stage

Pyrolysis conditions refer here conditions used in pyrolysis, particularly in a slow
15 pyrolysis or fast pyrolysis process, suitably fast pyrolysis is used. The starting material is subjected to heating at a temperature from 300 to 1000°C, suitably from 350 to 900°C, for 0.1 s to 30 days in the absence or with limited supply of an oxidizing agent such as air or oxygen. In slow pyrolysis suitably a residence time of 4 min – 30 days is used. Fast pyrolysis (flash pyrolysis) is suitably carried out at a
20 temperature from 350 to 900°C, suitably at a temperature from 400 to 800°C, particularly suitably from 460 to 520°C. Suitably a short residence time from 0.1 to 400 s, particularly suitably from 0.1 to 100 s is used. Fast pyrolysis is suitably carried out under oxygen free atmosphere or with limited supply of oxygen, containing 1-7 vol% of oxygen. Oxygen free atmosphere refers here to gas atmosphere comprising
25 inert gas, such as N₂, CO₂, CO, H₂, and recirculated non-condensable gases from the pyrolysis stage of the process, and any combinations thereof. Suitably preheated gas, heat exchangers or heat transfer materials, such as heated sand may be used for heating. The heating rate in slow pyrolysis is suitably 5-80°/min and in fast pyrolysis 500 - 10000 °C/s. Reactors suitable for the pyrolysis stage are any types of reactors
30 used in the art for pyrolysis processes. Several variations and reactors have been proposed for carrying out fast pyrolysis, however, the basic principles are the same in each of them. Suitably fluidized bed reactors may be used for fast pyrolysis.

The pyrolysis vapor formed in the pyrolysis stage is condensed at a temperature
35 below 300°C, suitably below 150°C and more suitably at a temperature of 40-60°C to yield pyrolysis oil. Prior to condensation the pyrolysis vapor may be subjected to hot-filtering or hot-gas-filtering. The obtained pyrolysis oil is then subjected to the second stage of the process. The solid component (char) is removed from the pyrolysis reactor and the non-condensable gaseous component comprising hydrogen (H₂),
40 carbon monoxide (CO), carbon dioxide (CO₂) and light hydrocarbons (CH₄), is

- 5 separated for further use or alternatively recirculated with optional heating to the pyrolysis stage, suitably for use as fluidizing gas.

The starting material used in the first stage comprises biomass, which may typically comprise any virgin and waste materials of plant origin, animal origin, fish origin or
10 microbiological origin, or any combinations thereof. Examples of said materials comprise virgin wood, wood residues, forest residues, waste, municipal waste, industrial waste or by-products, agricultural waste or by-products (including also dung and manure), residues or by-products of the wood-processing industry, waste or by-products of the food industry, solid or semi-solid organic residues of anaerobic or
15 aerobic digestion, such as residues from bio-gas production from lignocellulosic and/or municipal waste material, or residues from bio-ethanol production process, and any combinations thereof. Biomass may include the groups of the following four categories: wood and wood residues, including sawmill and paper mill discards, municipal paper waste, agricultural residues, including corn stover (stalks and straw)
20 and sugarcane bagasse, and dedicated energy crops, which are mostly composed of tall, woody grasses. The starting material comprising biomass may optionally additionally comprise any other organic matter, such as synthetic polymeric and/or plastic waste originating from other sources.

25 Suitably biomass selected from non-edible sources such as non-edible wastes and non-edible plant materials is used for fuel production. Particularly suitably said biomass comprises virgin wood, wood waste and residues, and by-products of the wood-processing industry such as slash, urban wood waste, lumber waste, wood chips, wood waste, sawdust, straw, firewood, wood materials, paper, by-products of
30 the papermaking or timber processes, where the biomass (plant biomass) is composed of cellulose and hemicellulose, and lignin.

The starting material comprising biomass may optionally be dried before subjecting it to pyrolysis, using any drying methods known in the art.

35

The pyrolysis oil, also called bio-oil, obtained in the first stage, refers here to a complex mixture of oxygen containing compounds (oxygenates), comprising typically water, light volatiles and non-volatiles. Pyrolysis oil is acidic, with a pH of 1.5-3.8, wood based pyrolysis oil typically has pH between 2 and 3. The exact composition of
40 pyrolysis oil depends on the biomass source and processing conditions. Typically pyrolysis oil comprises 20-30 % of water, 22-36 % of suspended solids and pyrolitic

5 lignin (including low molecular mass lignin and high molecular mass lignin), 8-12 % of hydroxyacetaldehyde, 3-8 % of levoglucosan, 4-8 % of acetic acid, 3-6 % of acetol, 1-2 % of cellubiosan, 1-2 % of glyoxal, 3-4 % of formaldehyde, and 3-6 % of formic acid by weight. Pyrolysis oil may also comprise other ketones, aldehydes, alcohols, furans, pyranes, sugars, organic acids, lignin fragments, phenolics, extractives and
10 small amounts of inorganics. Pyrolysis oil may contain sugar compounds even 35 % by weight. The density of pyrolysis oil is approximately 1.2-1.3 kg/l and usually the water molecules which are split during pyrolysis stay bound within the complex pyrolysis liquid as an emulsion. The pyrolysis oil as such is immiscible in mineral oil and mineral oil derived products and it cannot be blended with solvents or oils having
15 too low polarity.

Second stage

In the second stage of the process the pyrolysis oil is subjected to high temperature high pressure (HTHP) treatment. Optionally the pyrolysis oil may be subjected to one
20 or more pretreatment steps selected from treatment with aqueous media, filtering, and extraction prior to the HTHP treatment; thus the pyrolysis oil used as feed (starting material) in the HTHP stage refers also to pyrolysis oil subjected to one or more of said pretreatments. The high temperature high pressure treatment is a non-catalytic treatment comprising at least two steps where in the first step (a) of HTHP
25 pyrolysis oil is heated in the absence of added catalyst at 100 to 200 °C temperature and 50 to 250 bar pressure to yield product of the first step, and in the second step (b) of HTHP the product of the first step is heated in the absence of added catalyst at 200 to 400 °C temperature and 50 to 250 bar pressure, whereby a liquid product is obtained. The liquid product is subjected to separation of an aqueous phase and an
30 organic phase. The organic phase (HTHP treated pyrolysis oil) is used as feed in the third stage. The aqueous phase may be directed to further processing for converting to more valuable products, such as reforming etc. or it may be recirculated to the optional pretreatment with an aqueous media.

35 The term "non-catalytic" refers to a process where no heterogeneous or homogeneous catalyst is added to the process and where the reaction(s) take place in the absence of an added catalyst. Typically this means in practice that the reaction(s) take place, only between the materials fed into the reactor(s) and the reagents formed during the reaction(s), without a catalyst.

5 The temperature of the first step (a) of HTHP is adjusted to a temperature from 100 to 200 °C, suitably from 100 to 150 °C, including the temperature being between two of the following temperatures; 100 °C, 105 °C, 110 °C, 120 °C, 125 °C, 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 190 °C and 200 °C for the heating of the pyrolysis oil. At the same time the pressure is adjusted to a pressure from 50 to 250 bar, suitably
10 from 150 to 200 bar, including the pressure being between two of the following pressures; 50 bar, 60 bar, 70 bar, 80 bar, 90 bar, 100 bar, 110 bar, 120 bar, 130 bar, 140 bar, 150 bar, 160 bar, 170 bar, 180 bar, 190 bar, 200 bar, 210 bar, 220 bar, 230 bar, 240 bar and 250 bar.

15 The temperature of a second later step (b) HTHP is adjusted to a temperature from 200 to 400 °C, suitably from 300 to 350 °C, including the temperature being between two of the following temperatures; 200 °C, 210 °C, 220 °C, 230 °C, 240 °C, 250 °C, 260 °C, 270 °C, 280 °C, 290 °C, 300 °C, 310 °C, 320 °C, 330 °C, 340 °C, 350 °C, 360 °C, 370 °C, 380 °C, 390 °C and 400 °C for the heating of the product of the first step (step
20 a). At the same time the pressure is adjusted to a pressure of 50 to 250 bar, suitably 150 to 200 bar, including the pressure being between two of the following pressures; 50 bar, 60 bar, 70 bar, 80 bar, 90 bar, 100 bar, 110 bar, 120 bar, 130 bar, 140 bar, 150 bar, 160 bar, 170 bar, 180 bar, 190 bar, 200 bar, 210 bar, 220 bar, 230 bar, 240 bar and 250 bar.

25

Typically the most reactive compounds react during the first step (a), but due to the low temperature during the first step there will be no significant coke formation. In the first step typically oxygenates are hydrogenated. In the second step (b) the more resistant compounds react whereby oxygen is removed for example from lignin
30 and/or lignin derived phenolics.

The heating rate of the first and second heating is typically between two of the following rates; 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 °C /min. The heating time of the first and second step depends on the heating rate and varies between two
35 of the following periods of time; 20, 25, 30, 45, 60, 90, 120, 150 and 180 minutes. Heating is carried out using direct heat, heat exchangers etc.

The HTHP may optionally be carried out under reducing conditions whereby a gas atmosphere comprising at least one of carbon monoxide, hydrogen, nitrogen or
40 mixtures thereof are used. Accordingly at least one of the process steps a) or b) is performed under said a gas atmosphere. The use of CO typically causes

5 decarbonylation and decarboxylation and eventually some hydrogenation and thermal cracking, and acid functionality breaks. Adding H₂ typically leads to the formation of methane and a larger amount of water; also hydrogenation reactions and thermal cracking, carbonylation, and decarboxylation takes place. The use of an inert N₂ atmosphere typically leads to less water being separated and causes thermal cracking
10 and some hydrogenation and eventually decarboxylation and decarbonylation. Although H₂ is not added, the pyrolysis oil itself comprises enough hydrogen donors for enabling the reactions to take place.

The HTHP may optionally be carried out under alkaline conditions in the presence of
15 at least one alkali metal hydroxide compound such as NaOH. The alkali metal compound is added to the feed to the HTHP treatment in an amount of 5 – 55 w%, suitably 10-40 w%, based on the organic material in the feed. This improves the depolymerization of lignin compounds, enhances the yields of the product and minimizes solids formation.

20 **Third stage**

In the third stage the HTHP treated pyrolysis oil (organic phase obtained in the second stage), or optionally the HTHP treated pyrolysis oil subjected to prehydrogenation, is subjected to hydroprocessing in the presence of at least one
25 hydroprocessing catalyst and hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range is obtained. In the hydroprocessing stage mainly hydrosimerization, removal of heteroatoms, hydrodearomatization and/or hydrocracking is carried out.

30 The hydroprocessing catalyst may be arranged in at least one catalyst bed and/or in at least one reaction zone. The catalyst or catalysts may also be arranged in two or more catalyst beds and/or in two or more reaction zones, arranged in the same reactor or different reactors, or alternatively, the catalysts may be mixed or combined and arranged in at least one catalyst bed and/or in at least one reaction zone. The
35 temperatures in each catalyst bed and each reaction zone may be adjusted separately.

The hydroprocessing catalyst is selected from HDO catalysts and HDW catalysts and combinations thereof.

5 The HDO catalyst can be any hydroprocessing catalyst known in the art for the removal of hetero atoms (O, S, N) from organic compounds. Suitably the HDO catalyst is a supported catalysts comprising at least one metal of Group VIB or Group VIII of the Periodic table of elements. Suitably said metal is selected from cobalt (Co), molybdenum (Mo), nickel (Ni), tungsten (W), chromium (Cr), manganese (Mn),
10 rhenium (Re), iron (Fe), osmium (Os), rhodium (Rh), ruthenium (Ru), copper impregnated chromium oxide (Cu/Cr), cobalt molybdenum (CoMo), nickel molybdenum (NiMo), nickel molybdenum tungsten (NiMoW), nickel copper (NiCu). The support is suitably metal oxide, metal carbide or carbon, such as Al_2O_3 , Ti_2O_3 , CeO_2 , ZrO_2 , $\text{CeO}_2\text{-ZrO}_2$, and any combinations thereof. In an embodiment, the HDO
15 catalyst is selected from a group consisting of NiMo, CoMo, and a mixture of Ni, Mo and Co. The support for the HDO catalyst can be an oxide which is typically used in the art as support for HDO catalysts, suitably the support is selected from Al_2O_3 , SiO_2 , ZrO_2 , and mixtures thereof. In one embodiment, solid particles of NiMo/ Al_2O_3 are used as HDO catalyst. The HDO catalyst is suitably sulphided prior to start up. Adequate
20 sulphidation during operation is usually provided by adding sulphur in the feed material, however if crude tall oil (CTO) is used as co-feed, the feed itself may contain sufficient sulphur whereby no additional sulphur is needed.

The HDW catalyst may comprise any HDW catalyst known in the art, as well as
25 catalysts used for isomerizing paraffinic hydrocarbons. Suitably the HDW catalyst comprises Group VIB metals, oxides and sulfides, and/or one or more Group VIII metal components and combinations thereof, on a support. Said support may comprise an intimate mixture of a porous refractory oxide and a crystalline silica molecular sieve essentially free of aluminum and other Group IIIA metals of the
30 Periodic table of elements. Examples of suitable catalysts are catalysts comprising a molecular sieve or zeolite and/or a metal from Group VII and/or a carrier, such as SAPO-11 or SAPO41 or ZSM-22 or ZSM-23 or zeolite-beta or Y-zeolite or ferrierite and Pt, Pd or Ni and Al_2O_3 or SiO_2 . Examples of noble metal catalysts are Pt/SAPO-11/ Al_2O_3 , Pt/ZSM-22/ Al_2O_3 , Pt/ZSM-23/ Al_2O_3 and Pt/SAPO-11/ SiO_2 , the use of which
35 require the removal of sulphur compounds from the feed prior to contacting it with the catalyst and they suitably are arranged separated from NiMo and CoMo catalysts requiring sulphidation. Also catalysts based on Ni, W and molecular sieves may be used and they require sulphidization. NiW has excellent isomerising and dearomatising properties and it also has the capacity of performing the
40 hydrodeoxygenation and other hydroprocessing reactions of feed materials. The molecular sieves, such as porous refractory oxides comprise alumina, silica, beryllia,

5 chromia, zirconia, titania, magnesia and thoria, also combinations of these refractory oxides such as silica-alumina and silica-titania are suitable support materials, optionally combined with zeolites. Group IIIA metal-free crystalline silica molecular sieve (silicalite) which may form a portion of the support, may also be used. Another catalyst which can be used as the HDW catalyst is somewhat similar to the catalyst
10 described above except that a crystalline aluminosilicate of the ZSM-5 type, preferably in an acidic form, is substituted in the support for the crystalline silica molecular sieve essentially free of Group IIIA metals. The crystalline aluminosilicate zeolite may be ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and the like. Such zeolites are preferably utilized in the acid form by replacing at least some of the
15 ion-exchanged metal cations in the zeolite with hydrogen ions.

The support materials in the HDW catalysts may be the same as or different from those of the HDO catalyst. The support for the HDW catalyst is suitably selected from Al_2O_3 , SiO_2 , ZrO_2 , a zeolite, silica/alumina, and mixtures thereof. Suitably the HDW
20 catalyst is selected from $\text{NiW}/\text{Al}_2\text{O}_3$ and $\text{NiW}/\text{zeolite}/\text{Al}_2\text{O}_3$. These HDW catalysts are well suited for mixing with the HDO catalyst since they also require sulphiding for proper catalytic activity. Thus hydrogenation, hydroisomerization, hydrodeoxygenation, dearomatization and hydrocracking may take place simultaneously.

25

In one embodiment, a catalyst bed may comprise a mixture of sulphided HDO and HDW catalysts, wherein the HDO catalyst is $\text{NiMo}/\text{Al}_2\text{O}_3$ and the HDW catalyst is $\text{NiW}/\text{zeolite}/\text{Al}_2\text{O}_3$. The $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst mainly serves the purpose of hydrogenation, hydrodeoxygenation, hydrodesulphurization and hydrodenitrification.
30 The $\text{NiW}/\text{zeolite}/\text{Al}_2\text{O}_3$ catalyst mainly serves the purpose of hydroisomerization, hydrogenation, dearomatization and hydrocracking. NiW has also capacity for some hydrodeoxygenation, hydrodesulphurisation and hydrodenitrification.

The proportions of the catalysts may vary in the reactor e.g. in such a way that the
35 proportion of the HDW catalyst grows towards the outlet end of the reactor/reactors. Some catalyst beds of the reactor may comprise only one or the other of the catalyst types, i.e. they comprise either HDO or HDW catalyst.

The catalysts may also be arranged in several reactors, arranged in consecutively in
40 series.

5 Optionally one or more catalytically active guard-beds or a guard-bed reactors may be used upstream of the reactors for effecting the removal of metals, such as Al, Na and sulphur and/or phosphorus from the feed. The purpose of the guard bed/beds is to protect the catalyst(s) in the reactor/reactors from poisoning and fouling. The hydroprocessing conditions refer here to a pressure from 5 to 350 bar and a
10 temperature from 100 to 450°C.

If only a HDO catalyst is used or a combination of HDW and HDO catalysts is used the reactions conditions suitably include a temperature in the range from 250° to 450°C, suitably from 250° to 380°C. The pressure (total pressure) is in the range from 10 to
15 250 bar, suitably from 50 to 100 bar. The liquid hourly space velocity (LHSV) is suitably in the range from 0.1 to 10 hr⁻¹. The hydrogen flow rate through the reactor is generally between 250 and 4000 NI/I of feed-stock, suitably the range is 500-2500 NI/I feed-stock.

20 In order to retain the metal component of the catalysts in the sulphided form instead of converting back into the metal oxide form it is preferred that the feedstock is contacted with the catalyst composition in the presence of sulphur components such as hydrogen sulphide (H₂S) or a precursor thereof, such that said hydrogen sulphide is present in the hydrogen gas in an amount between 10 ppm and 10000 ppm,
25 suitably between 10 ppm and 1000 ppm. This can be achieved for example by adding an organic sulphur compound to the feed, suitably DMDS (dimethyldisulfide) in amounts of 1 to 2 % by weight. If the feed comprises organic sulphur compounds, there may be no need to add sulphur to the feedstock. The sulphur component may also originate from light gaseous components separated from the process. Suitably
30 the content of sulfur compounds in the feed is determined prior to the reaction, for calculating the amount of possibly required additional sulfur compound in the feed.

Depending on the HDW catalyst and the catalyst arrangement it may be necessary to remove sulfur from the reaction mixture or effluent or product from the previous
35 process step before subjecting to HDW, for example by stripping with water vapor or suitable gas such as light hydrocarbon, nitrogen or hydrogen.

If crude tall oil is used as co-feed in the hydroprocessing stage, at least one HDW catalyst is necessary.

5 If only HDW catalyst is used, or a combination of HDW and HDO catalyst is used, the reaction conditions suitably include the temperature in the range between 200°C and 450°C, suitably between 250°C and 390°C. The pressure in the reactor will normally be between about 10 to about 150 bar, suitably between 20 to 110 bar. The rate at which the feedstock is passed through the hydroprocessing reactor in contact with the catalyst particles is typically set at a LHSV (liquid hourly space velocity) between
10 about 0.1 and about 10 hr⁻¹. The feed rate WHSV (weight hourly spatial velocity) of the feed material varies between 0.1 and 5, and is suitably in the range of 0.2 – 0.7. The hydrogen flow rate is generally between 600 and 4000 NI/I, suitably in the range of 1300-2500 NI/I, particularly suitably the range is 500-2500 NI/I feed-stock.

15

If desired, recirculation of at least a portion of the product stream and/or effluent gas provides an efficient means for constraining the exothermic reaction whereby the recycled streams act as media for lowering the temperature of the catalyst beds in a controlled manner.

20

A gaseous stream containing hydrogen from the third stage, may be cooled and then carbon monoxide, carbon dioxide, nitrogen, phosphorus and sulphur compounds, other impurities and gaseous light can be removed therefrom. After compressing, purified or recycled hydrogen can be returned the process steps needing hydrogen.

25 Water removed from the condensed liquid may be used in the optional pretreatment with aqueous media.

The liquid product (effluent from the third stage) may suitably be cooled and directed to a separator. In the separator, water and light gases containing hydrogen, light
30 hydrocarbons, H₂S, CO and CO₂ are separated from the product. Water and gases may also be separated by other means which are well known to those skilled in the art.

The light gases are suitably directed to an amine scrubber, which removes H₂S and
35 CO₂ from the gaseous products. Scrubbed gases, comprising mainly hydrogen and some impurities, are recycled to the process as feed hydrogen and quench gas. Light hydrocarbons may be directed to further processing to obtain gasoline etc.

The reaction products i.e. the hydrocarbon mixture from the separator, is suitably
40 directed to fractionation, suitably to a fractionation column where different fuel grade hydrocarbon fractions may be recovered. From the fractionation column, the heavier

5 hydrocarbons may be recycled back to into the feed of the process if desired. Any suitable fractionation methods, such as distillation etc. may be used.

A middle distillate, suitable as diesel fuel may be separated and lighter hydrocarbons may be directed to a stabilizer, where a naphtha fraction can be recovered. The
10 middle distillate fraction comprises gas oil, i.e. a hydrocarbon fraction boiling in the diesel range. The boiling range is from 160 °C to 380 °C, meeting the specification of EN 590 diesel. The diesel product is fed to a diesel storage tank. Also hydrocarbon fractions distilling at temperatures ranging from 40 °C to 210 °C and at a temperature of about 370 °C can be recovered. These fractions are useful as high quality gasoline
15 fuel and/or naphtha fuel, or as blending components for these fuels. The hydrocarbon mixture obtained from the reactor system includes fuel grade hydrocarbons having a boiling point of at most 380 °C according to ISO EN 3405. Additionally, fraction suitable as solvents, aviation fuels, kerosene etc may be obtained. The obtained fractions may also be used without limitations as blending components, suitably in
20 fuels derived from crude oil, mineral oil or renewable sources.

Optional co-processing in third stage with crude tall oil

Optionally crude tall oil (CTO) may be added as co-feed to the third stage and it is co-processed with the HTHP treated pyrolysis oil (organic phase from the second stage)
25 which is optionally subjected to prehydrogenation.

Crude tall oil (CTO) refers 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
30 (mainly linoleic acid, oleic acid and linolenic acid), fatty alcohols, sterols and other alkyl hydrocarbon derivatives. The handling and cooking of the wood causes break down of the triglyceride structures and hence CTO does not contain any significant amounts of triglycerides. Typically, CTO contains minor amounts of impurities such as sulphur compounds, residual metals such as Na, K, Ca and phosphorus. The
35 composition of the CTO varies depending on the specific wood species. CTO is derived from pulping of coniferous wood.

CTO is understood to refer here also to tall oil, tall oil components such as tall oil fatty acids (TOFA), tall oil derivatives such as tall oil resin acids, tall oil pitch and tall oil
40 neutral substances, as well as any mixtures thereof. The fatty acids of tall oil include mainly palmitic acid, oleic acid and linoleic acid. Fractional distillation of tall oil

- 5 provides rosin acids and further reduction of the rosin content provides tall oil fatty acids (TOFA) which consists mostly of oleic acid.

CTO may be purified using any methods, suitably using evaporative methods, where the purification process conditions are controlled in such a way that as much as
10 possible of the neutral components of the tall oil are recovered. The evaporation may be carried out by using a heater and evaporator combination, where CTO is first heated up to a temperature of 150 to 230 °C at a pressure of 40 to 80 mbar. The gas phase containing CST (Crude Sulfate Turpentine) and water is separated and liquid phase is directed to an evaporator for further purification.

15

The purification of said liquid phase may be performed by using two or three evaporators in the purification where the first evaporator is a thin film evaporator that operates at a temperature of 150 to 200°C, and a pressure of 10 mbar. The gas phase containing CST and water is separated and led to water separation and CST
20 purification.

In a purification using two evaporators, the liquid fraction from the first evaporator is led to a second evaporator. A thin film evaporator or plate molecular still can be used as the second evaporator. The second evaporator operates at a temperature of 300 to
25 390°C and a pressure of 0.01 - 15 mbar. The distillate, i.e. purified CTO may be fed to the reactor system for catalytic treatment.

In a purification using three evaporators, the liquid fraction from the first evaporator is led to a second evaporator, which is a thin film evaporator or a plate molecular still
30 operating at a temperature of 200 – 280°C and a pressure of 5 mbar, and further to a third evaporator, which is a short path evaporator operating at a temperature of 250 – 300°C and a pressure of 0.1 mbar. From the last evaporator, the distillate, i.e. purified CTO may be fed to the reactor system.

35 The content of harmful substances, such as metal ions, sulphur, phosphorus and lignin residues, is typically reduced by the purification. However, the sulphur content of CTO remains typically from 1000 to 5000 ppm after the purification. Light components, such as crude sulphate turpentine, and heavy components such as tall oil pitch are removed and may be directed to another process for utilization. Said
40 purified CTO material is particularly suitable for being subjected to catalytic treatment with hydrogen.

5

The HTHP treated pyrolysis oil (from the second stage, optionally prehydrogenated) and the crude tall oil may be fed in the third stage of the process of the invention to the hydroprocessing reactor using one feed inlet, or alternatively the HTHP treated pyrolysis oil and crude tall oil are fed to the reactor using separate feed inlets, each inlet for the HTHP treated pyrolysis oil and for the crude tall oil.

10

15

The hydroprocessing of the HTHP treated pyrolysis oil and crude tall oil (the co-processing) is carried out under a pressure from 5 to 300 bar and at a temperature from 100 to 450°C. Suitably a temperature between 250 and 380°C is used. Suitably the pressure ranges from 10 to 150 bar, suitably between 50 to 100 bar. Suitably a catalyst selected from HDW catalysts and combinations of HDO and HDW catalysts may be used.

20

HTHP treated pyrolysis oil obtained from the second stage may be co-processed with crude tall oil in an amount from 5 to 95 wt% of HTHP treated pyrolysis oil and from 95 to 5 wt% of crude tall oil, suitably the amount of HTHP treated pyrolysis oil may range from 5 to 75 wt% and from 95 to 25 wt% of crude tall oil, including the amount of the HTHP treated pyrolysis oil being between two of the following; 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 and 95 wt%; and the amount of CTO being between two of the following; 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90 and 95 wt%.

25

30

In the process crude tall oil may be co-processed with the product from the second stage originating from pyrolysis oil even though they differ significantly with respect to their chemical composition and in practice they are immiscible. Pyrolysis oils and components comprised therein generally have a high tendency to coke formation in hydroprocessing. Therefore catalysts having high activity for coke gasification reactions are used, and thus higher volumes of the HTHP treated pyrolysis oil can be co-processed with crude tall oil. Further, as the HTHP treated pyrolysis oil is practically sulfur free it is necessary to add a sulfiding agent to the feed for maintaining the catalyst active. Since crude tall oil comprises sulphur compounds, these sulphur compounds can act as a sulfiding agent in co-processing.

35

40

Co-processing of the HTHP treated pyrolysis oil with crude tall oil reduces coking in the reactor.

5 Unstable molecules comprising oxygen are removed in the third stage from the HTHP treated pyrolysis oil. The lignin fragment of pyrolysis oil, mainly comprising oxygen containing aromatics may be converted to a product comprising cyclic hydrocarbons. Oxygen may be completely removed at higher temperatures of 300 to 350°C and aromatic compounds are obtained. At lower temperatures the hydrogen consumption
10 is higher, but the light hydrocarbons present in the feed act as hydrogen donors at said conditions, thus reducing the consumption of external hydrogen.

Optional pretreatment of pyrolysis oil

Optionally the pyrolysis oil obtained in the first process stage may be subjected to
15 one or more pretreatment steps prior to the second stage of the process (HTHP). Said pretreatment steps may be selected from treatment with aqueous media, filtering, extraction and any combinations thereof. In the pretreatment steps at least part of the impurities, such as solid materials and alkali metals may be removed conveniently.

20

The pyrolysis oil obtained in the first stage may be contacted with an aqueous media whereby a mixture is formed. The aqueous media is suitably selected from water, waste water streams, recirculated aqueous streams, aqueous solutions and aqueous emulsions. The recirculated aqueous streams, aqueous solutions and aqueous
25 emulsions may originate from the process of the invention, or from other processes or sources. The amount of the aqueous media is from 1 to 80 vol-%, suitably from 10 to 75 vol-%, particularly suitably from 30 to 60 vol-% and the amount of pyrolysis oil is from 20 to 99 vol-%, suitably from 25 to 90 vol-%, particularly suitably from 40 to 70 vol-%. The pyrolysis oil refers here to the product obtained from the pyrolysis of
30 biomass and it typically contains water. The obtained mixture, suitably having a temperature from 10 to 70°C, particularly suitably from 15 to 50°C, is agitated, suitably for 5 to 60 min and then it is allowed to settle whereby phases are formed. The organic (less polar) phase and the aqueous (more polar) phase are separated. In this step the amount of water in the original pyrolysis oil (prior to the second stage) is
35 reduced, i.e. the pyrolysis oil is dried. The water content of the organic phase (Aq-treated pyrolysis oil) is lower than that of the pyrolysis oil used as feed in this step. For example, when the water content of original pyrolysis oil was 30 wt%, after this step it was 14 wt%. In the aqueous phase water soluble and water miscible organic compounds and inorganic compounds, salts are removed, particularly sugars such as
40 glucose, xylose, arabinose, mannose, and galactose, organic acids, including glucuronic acid and galacturonic acid, aldehydes, ketones and some substituted

5 phenols and cyclopentanones. The aqueous phase may be directed to further processing for converting the compounds therein to more valuable products, such as building block chemicals, fine chemicals, fuels, or alternatively, it may at least partly be directed to recirculation to the optional pretreatment with aqueous media for use as the aqueous media.

10

The pyrolysis oil treated with an aqueous media (the organic phase), containing organic compounds insoluble or immiscible in water, such as highly aromatic compounds, phenolic compounds, fragments of lignin, furfurals, toluene, substituted phenols, benzene derivatives, etc is directed to the second (HTHP) stage of the process.

15

In the treatment with aqueous media the selected ratio of the aqueous media to pyrolysis oil provides removal of desired amount of water and impurities. If too much of the aqueous media is used the organic phase is almost solid and the handling of it becomes difficult. If too little of the aqueous media is used the organic phase becomes very viscose, additionally the water soluble and water miscible compounds and impurities are not removed very effectively. The selected ratio achieves suitable removal of water, water soluble and water miscible organic compounds and impurities. Reduced water content and reduced levels of impurities are also particularly important for the subsequent hydroprocessing stage, where the hydroprocessing catalyst can thus be maintained active for longer periods of time. Naturally the original water content in the pyrolysis oil is taken into account when adding the aqueous media.

20

25

30 Filtering and extraction pretreatment methods generally known in the art may also be used for pretreating the pyrolysis oil.

Water bound within the complex pyrolysis oil is separated very efficiently and to desired degree during the process. The separated water phase contains water-miscible and water-soluble compounds, for example formic acids, hydroxyl acids, alcohols, aldehydes, ketones and sugars, which would interfere in the subsequent hydroprocessing stage. Such compounds are now removed and they can be further processed to more valuable compounds.

35

40 The hydroprocessing catalysts stay active for longer periods of time and the process is more stable and easier to control.

- 5 During the process also light hydrocarbons such as methane, ethane and propane are removed as gases.

Optional prehydrogenation of the HTHP treated pyrolysis oil prior to the hydroprocessing stage

- 10 Optionally the HTHP treated pyrolysis oil, obtained from the second stage may be subjected to prehydrogenation prior to the hydroprocessing stage. Said prehydrogenation may comprise one step or alternatively said prehydrogenation may comprise at least two steps.
- 15 The prehydrogenation of the HTHP treated pyrolysis oil may be carried out in one step or in at least two steps in the presence of at least one hydrogenation catalyst and hydrogen, the first step under milder conditions and the second step under more severe conditions, whereby a prehydrogenated product from the HTHP stage (effluent) is obtained. Said prehydrogenation may be carried out in a separate
- 20 pressure vessel or in the same pressure vessel as the hydroprocessing stage. In the case the prehydrogenation comprises more than one steps, each step may if desired, be carried out in separate pressure vessels.

- In the case the prehydrogenation of the organic phase is carried out in one step, it
- 25 may be carried out under a pressure 10 to 300 bar and at a temperature from 50 to 350°C.

- If the prehydrogenation is carried out as a two-step hydrogenation, the first step is carried out under a pressure from 10 to 300 bar and at a temperature from 100 to
- 30 250°C, and the second step under a pressure from 100 to 300 bar and at a temperature from 200 to 350°C.

- The catalyst may contain metals from Group VIII and/or VIB of the Periodic System. Suitably the catalyst is a supported catalyst comprising nickel (Ni), NiMo, CoMo noble metal, such as platinum (Pt), palladium (Pd), or rhodium (Rh), ruthenium (Ru), is
- 35 used, the support being suitably alumina and/or silica.

- Suitably a catalyst based on CoMo or NiMo on a support selected from Al_2O_3 , SiO_2 , ZrO_2 , and mixtures thereof is used in the first step. A catalyst based on noble or transition metals, such as Pt/SAPO-11/ Al_2O_3 , Pt/ZSM-22/ Al_2O_3 , Pt/ZSM-23/ Al_2O_3 and
- 40 Pt/SAPO-11/ SiO_2 can be used for the second step. These catalyst don't tolerate sulfur but at this point the feed is sulfur free. However, HDO catalysts and HDW catalysts

5 such as NiW as defined above in connection with the hydroprocessing stage may also be used.

In the prehydrogenation, particularly the lignin fragment in the organic phase originating from pyrolysis oil, mainly comprising oxygen containing aromatics, may be converted to a product comprising cyclic hydrocarbons, suitably when using moderate
10 temperatures in the range of 100 to 250°C whereby aromatic compounds are completely hydrogenated. An aqueous fraction is obtained and it may be recirculated at least partly to the second stage for use as the aqueous media, or it may be directed to further processing to other components. Also a gaseous fraction is
15 obtained, comprising hydrogen, CO, CO₂ and light hydrocarbons.

The prehydrogenated product from HTHP stage may be directed to the third stage for hydroprocessing as such, or for co-processing with crude tall oil.

20 The process of the invention may additionally comprise one or more conventional steps, such as separation of gases, washing, cooling, filtering, hot-filtering, extraction, recovering of intermediates and products, recycling of products, intermediates, aqueous phases and gases, mixing of obtained products with mineral oil or transportation fuel originating from renewable sources or from crude oil or other
25 sources or any blends thereof; refining and/or fractionation of effluent. These embodiments can be used in combination with all the different embodiments of the invention.

The process of the invention may be batch-type or semi-batch-type or continuous.

30

The process of the invention as described above has several advantages. It provides a convenient and efficient means for processing starting material comprising biomass to valuable products, such as transportation fuels, solvents, fine chemicals and chemical building-blocks.

35

The HTHP treatment reduces the amount of water and sugar compounds. HTHP is performed to improve the quality (physical and chemical stability) of the oil and this is achieved by removing (partially or completely) oxygen. Oxygen is usually removed in the form of water therefore H₂ is needed. In the case an inert atmosphere is used
40 (N₂) the molecules present in pyrolysis oil can generate H₂ at the conditions used in HTHP. Carboxylic acids in pyrolysis oil are the ones that at the reaction conditions

- 5 give H₂ that can react with oxygen in pyrolysis oil to form water that is separated later.

Oxygen removal is proportional to the amount of H₂ that is generated in the reactor or the H₂ added. By controlling the amount of H₂ one can in principle control the
10 degree of deoxygenation of pyrolysis oil. This also improves the hydroprocessing stage because reactive compounds are removed. Thus the aqueous phase(s) obtained from any of stages of the process may be recirculated or directed for use as starting materials in chemical manufacture.

- 15 Water bound within the complex pyrolysis oil, obtained from biomass, is separated very efficiently and to desired degree during the process, particularly in the optional step where pyrolysis oil is treated with the aqueous media (dried). The separated aqueous phase contains water-miscible and water-soluble compounds, for example formic acids, hydroxyl acids, alcohols, aldehydes, ketones and sugars, which would
20 interfere in the subsequent stages. Such compounds are now removed and they can be further processed to more valuable compounds.

In the hydroprocessing stage the catalysts stay active for longer periods of time and the process is more stable and easier to control. The process tolerates well variations
25 in the starting materials.

Suitably the product (organic phase) obtained from the second (HTHP) stage is subjected to one or more pretreatment steps prior to the hydroprocessing stage whereby light acids, aldehydes, sugars and water is removed at least partly. This
30 reduces polymerization and fouling of the reactor in the hydroprocessing stage. The consumption of hydrogen in the hydroprocessing stage may also be reduced with said pretreating steps.

When co-processing with CTO is carried out, lower temperatures and pressures can
35 be used, which results in reduced consumption of hydrogen, more easily controllable reaction and lower content of aromatic compounds in the product. Thus amount of aromatic compounds in the product may be controlled with the amount of CTO in the hydroprocessing stage.

- 40 During the process of the invention also light hydrocarbons such as methane, ethane and propane are removed as gases and they may be directed to further use.

5

Products, such as transportation fuels and blending components for said fuels, as well as heating oil, solvents, fine chemicals and chemical building-blocks, at least partly or even totally based on renewable starting materials may be obtained.

10 In the embodiments where the aqueous phases obtained in the process stages, are recycled, less water is needed and several valuable compounds get concentrated in the aqueous phase, such as sugars, acids, etc. This aqueous phase with high concentration of chemical compounds has more process alternatives that are more interesting from the economical point of view than diluted solution, for example
15 higher product yields are obtained.

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. The invention is illustrated also with reference to the drawings.

20

Figure 1 presents in the schematic diagram one embodiment of the process for converting biomass. Starting material comprising biomass 10 is fed to pyrolysis reactor 100 where pyrolysis is carried out, and pyrolysis oil 30 is formed, non-condensable gases 20 and solids 21 are separated. Pyrolysis oil 30 is passed to HTHP reactor 200 where it is treated non-catalytically under high temperature and high pressure, optionally in the presence of one or more gases 40 selected from hydrogen, nitrogen and carbon monoxide. An aqueous phase 50 and light gaseous component 60 are passed to purification and recirculation (not shown in the figure) and the HTHP-treated effluent (HTHP treated pyrolysis oil) 70 is passed to hydroprocessing reactor 300 comprising at least one catalyst bed (not shown) where the HTHP treated pyrolysis oil is hydroprocessed with hydrogen 80 in the presence of at least one catalyst and added sulphur compound 81 at hydroprocessing conditions. An aqueous phase 90 and light gaseous component 110 are passed to purification and recirculation (not shown in the figure) and the hydroprocessed effluent (liquid product) 120 comprising hydrocarbons boiling in the liquid fuel range is passed
35 through one or more separation/fractionation devices 400 for separation and fractionation of components to obtain transportation fuels 130. Any reactor types or configurations and devices used in the art may be used.

40 Figure 2 presents in the schematic diagram another embodiment of the process for converting biomass. Starting material comprising biomass 10 is fed to pyrolysis

5 reactor 100 where pyrolysis is carried out, and pyrolysis oil 30 is formed, non-condensable gases 20 and solids 21 are separated. Pyrolysis oil 30 is passed to HTHP reactor 200 where it is treated non-catalytically under high temperature and high pressure, optionally in the presence of one or more gases 40 selected from hydrogen, nitrogen and carbon monoxide. An aqueous phase 50 and light gaseous component
10 60 are passed to purification and recirculation (not shown in the figure) and the HTHP-treated effluent (HTHP treated pyrolysis oil) 70 is passed to prehydrogenation reactor 500 comprising at least one hydrogenation catalyst bed (not shown) where the HTHP treated pyrolysis oil 70 is hydrogenated with hydrogen 80 in the presence of at least one hydrogenation catalyst at hydrogenation conditions. An aqueous phase
15 140 and light gaseous component 150 are passed to purification and recirculation (not shown in the figure) and prehydrogenated effluent (HTHP treated and prehydrogenated pyrolysis oil) 160 is passed to hydroprocessing reactor 300 comprising at least one catalyst bed (not shown). The HTHP treated and prehydrogenated pyrolysis oil 160 is co-processed with crude tall oil 170 at
20 hydroprocessing conditions with hydrogen 80 in the presence of at least one hydroprocessing catalyst. An aqueous phase 90 and light gaseous component 110 are passed to purification and recirculation (not shown in the figure) and the hydroprocessed effluent 120 (liquid product) comprising hydrocarbons boiling in the liquid fuel range is passed through one or more separation/fractionation devices 400
25 for separation and fractionation of components to obtain transportation fuels 130. Any reactor types or configurations and devices used in the art may be used.

Figure 3 presents in the schematic diagram another embodiment of the process for converting biomass. Starting material comprising biomass 10 is fed to pyrolysis
30 reactor 100 where pyrolysis is carried out, and pyrolysis oil 30 is formed, non-condensable gases 20 and solids 21 are separated. Pyrolysis oil 30 is passed to HTHP reactor 200 where it is treated non-catalytically under high temperature and high pressure, optionally in the presence of one or more gases 40 selected from hydrogen, nitrogen and carbon monoxide. An aqueous phase 50 and light gaseous component
35 60 are passed to purification and recirculation (not shown in the figure) and the HTHP-treated effluent (HTHP treated pyrolysis oil) 70 is passed to mild (first) prehydrogenation reactor 600 comprising at least one hydrogenation catalyst bed (not shown) where the HTHP treated pyrolysis oil 70 is hydrogenated with hydrogen 80 in the presence of at least one hydrogenation catalyst at mild
40 hydrogenation conditions. An aqueous phase 170 and light gaseous component 180 are passed to purification and recirculation (not shown in the figure) and the effluent

5 (the HTHP treated and mildly prehydrogenated pyrolysis oil) 190 is passed to second prehydrogenation reactor 500 comprising at least one hydrogenation catalyst bed (not shown) where the HTHP treated and mildly prehydrogenated pyrolysis oil 190 is hydrogenated with hydrogen 80 in the presence of at least one hydrogenation catalyst at hydrogenation conditions. An aqueous phase 140 and light gaseous component 150
10 are passed to purification and recirculation (not shown in the figure) and prehydrogenated effluent (HTHP treated and prehydrogenated pyrolysis oil) 160 is passed to hydroprocessing reactor 300 comprising at least one catalyst bed (not shown). The HTHP treated and prehydrogenated pyrolysis oil 160 is subjected to hydroprocessing at hydroprocessing conditions with hydrogen 80 in the presence of at
15 least one hydroprocessing catalyst and added sulphur compound 81. An aqueous phase 90 and light gaseous component 110 are passed to purification and recirculation (not shown in the figure) and the hydroprocessed effluent 120 comprising hydrocarbons boiling in the liquid fuel range is passed through one or more separation/fractionation devices 400 for separation and fractionation of
20 components to obtain transportation fuels 130. Any reactor types or configurations and devices used in the art may be used.

Figure 4 presents in the schematic diagram another embodiment of the process for converting biomass. Starting material comprising biomass 10 is fed to pyrolysis reactor 100 where pyrolysis is carried out, and pyrolysis oil 30 is formed, non-
25 condensable gases 20 and solids 21 are separated. Pyrolysis oil 30 and an aqueous media 210 are passed to reactor 700 to form a mixture which is then agitated, and phases are allowed to form. The pyrolysis oil treated with aqueous media (formed organic phase) 230 and aqueous phase 220 are separated, the aqueous phase 220 is
30 at least partly recirculated to the aqueous media 210, partly to further processing and/or refining (not shown in the figure). The pyrolysis oil treated with aqueous media 230 is passed to HTHP reactor 200 where it is treated non-catalytically under high temperature and high pressure, optionally in the presence of one or more gases 40 selected from hydrogen, nitrogen and carbon monoxide. An aqueous phase 50 and
35 light gaseous component 60 are passed to purification and recirculation (not shown in the figure) and the HTHP-treated effluent (HTHP treated pyrolysis oil) 70 is passed to passed to mild (first) prehydrogenation reactor 600 comprising at least one hydrogenation catalyst bed (not shown) where the HTHP treated pyrolysis oil 70 is hydrogenated with hydrogen 80 in the presence of at least one hydrogenation catalyst
40 at mild hydrogenation conditions. An aqueous phase 170 and light gaseous component 180 are passed to purification and recirculation (not shown in the figure)

5 and the effluent (the HTHP treated and mildly prehydrogenated pyrolysis oil) 190 is passed to second prehydrogenation reactor 500 comprising at least one hydrogenation catalyst bed (not shown) where the HTHP treated and mildly prehydrogenated pyrolysis oil 190 is hydrogenated with hydrogen 80 in the presence of at least one hydrogenation catalyst at hydrogenation conditions. An aqueous phase 140 and light gaseous component 150 are passed to purification and recirculation (not shown in the figure) and prehydrogenated effluent (HTHP treated and prehydrogenated pyrolysis oil) 160 is passed to hydroprocessing reactor 300 comprising at least one catalyst bed (not shown). The HTHP treated and prehydrogenated pyrolysis oil 160 is co-processed with crude tall oil 170 at 15 hydroprocessing conditions with hydrogen 80 in the presence of at least one hydroprocessing catalyst. An aqueous phase 90 and light gaseous component 110 are passed to purification and recirculation (not shown in the figure) and the hydroprocessed effluent 120 comprising hydrocarbons boiling in the liquid fuel range is passed through one or more separation/fractionation devices 400 for separation and fractionation of components to obtain transportation fuels 130. Any reactor types or configurations and devices used in the art may be used.

Example 1 HTHP pre-treatment of pyrolysis oil

25 PO (pyrolysis oil) was pre-treated at high temperatures and high pressure. The procedure was performed in two steps. The reactor was packed with the PO and pressurised to 70 bar with N₂ or CO. In some tests also NaOH was mixed with PO in the reactor and the reactor was pressurised to 70 bar with either N₂ or CO. The different tests performed are presented in Table 1.

30

In the first step of the treatment the target temperature was 150 °C, at this temperature the pressure was expected to be 100 bar. These conditions were kept for 30 minutes and after this the temperature was increased further to target temperature of 300 °C and the expected pressure was 170 bar.

35

5 Table 1. Experimental conditions in HTHP pre-treatment.

	PO + N ₂	PO+CO	PO+NaOH+N ₂	PO+NaOH+CO
Reactor	1L	1L	1L	1L
Pyrolysis oil (g)	400	400	400	400
T1	151	149	148	151
P1	103	96	98	88
T2	301	313	300	303
P2	186	165	169	188
NaOH (%)	-	-	10	10

After the treatment, the reactor was cooled down and gas, liquid, and solid samples were taken. The gas sample was sent for GC analysis.

10 The solid, liquid, and gas yields (Eq. 1) obtained are presented in Table 2.

$$\text{Yield (\%)} = \frac{\text{mass of solid, liquid or gas (g)}}{\text{mass of PO (g)}} 100 \quad (\text{Eq. 1})$$

Table 2. Gas phase composition and product yields in HTHP pre-treatment of PO

15

	PO+N ₂	PO+NaOH+N ₂	PO+NaOH+CO
Gas composition (%)			
H ₂	18,3	6,3	3,4
C1	-	0,0	0,1
C2	0,2	0,0	0
C2=	0,1	0,1	0
C5+	9,3	7,6	5,6
CO ₂	72,2	85,9	87,3
CO	-	-	3,6
Product yields (%)			
Solid	35	41	22
Liquid	29	31	35
Gas	6	6	6
Mass balance (%)	70	79	64

- 5 It was not possible to recover all the solids formed during the reactions and some wet solids were left in the reactor thus the mass balance closure is not 100%.

Similar liquid yields are obtained when the PO is pre-treated using N₂ or CO. However, the pre-treatment performed with NaOH addition and in the CO atmosphere
10 gives higher liquid yield product and the less formation of solids.

Example 2

The effect the treatment of pyrolysis oil with an aqueous media in the process is demonstrated in this example. Pyrolysis oil was obtained by fast pyrolysis from
15 lignocellulosic material.

The treatment (drying of pyrolysis oil (PO)) was performed by adding different amounts of an aqueous media (water) to PO. The solutions prepared are presented in Table 3. The samples were mixed for 15 minutes and then they were allowed to settle
20 overnight. The phases (aqueous and organic) were separated and analysed. For the organic phase the following determinations were performed:

- pH
- density
- 25 - viscosity
- GCMS (identify the compounds present)
- Karl-Fisher titration (to determine the water content).
- Elemental composition (CHNS/O)

- 30 In all cases the results for the organic phase were compared with the result for PO.

For the water phase the following determinations were performed:

- pH
- 35 - GCMS (identify the compounds present)
- Analysis of sugars (quali- and quantitative)

5 Table 3. Treatment of PO with water at room temperature and 50 °C.

Sample N°	PO (vol-%)	PO (ml)	Water (ml)	Temperature
1	2			room
2	10			room
3	40	80	120	room
4	50	100	100	room
5	60	120	80	room
6	80	160	40	room
7	40	80	120	50
8	50	100	100	50
9	70	140	60	50
10	90	180	20	50

Adding large amounts of water to PO (2% PO and 10% PO in water) yield a large water phase, and a solid organic phase. The organic phase was mainly composed of lignin and all other chemical compounds such as acids, ketones, aldehydes, sugars, etc. were in the water phase. Considering the entire industrial process, drying PO completely is not desired as the organic phase is not fluid or requires high temperatures to be in a fluid form and significant amount of valuable chemicals are discarded in the water phase when the phases are separated.

Adding small amount of water like in the case of sample 10 where the concentration of water was only 20% yield only one phase and no phase separation occurred. The water added dissolved in the PO. This is not desired either as more water than the originally present in PO is introduced in the process damaging catalysts in downstream steps and reducing the product yields.

The chemical composition of the organic and aqueous phase was analysed with GCMS, yielding qualitative results. Oxygen containing compounds are present in both phases. In the organic phase substituted phenols, furfurals, some ketones and aldehydes (benzaldehyde), and alcohols like benzenediols can be found. These compounds are generated during the pyrolysis process (thermal degradation of lignin). The water phase has some acids like butanoic acid, ketones like cyclopentanone, some phenols and substituted phenols (smaller molecules than the ones present in the organic phase), and sugars like levoglucosan.

- 5 The water content of pyrolysis oil before and after treatment with an aqueous media is presented in Figure 5. The water content of the organic phase after the treatment (drying) was lower than that of PO. The water content of PO was 30% while for the organic phases obtained in samples 3 to 9 the water content was between 15-20%.
- 10 Densities are compared in Figure 6. The density of the dried organic phase increase as this fraction gets richer in large molecular weight compounds. Light molecular weight compounds are present in the water phase.

The results from viscosity measurements are presented in Figure 7. The viscosity of
15 PO decreases with temperature as expected. However, at temperatures higher than 70 °C the viscosity of PO increases thus the chemical compounds present in PO react at these temperature giving high molecular weight compounds and therefore the viscosities increases. This behaviour is not detected in the dried organic phases. For these samples the viscosity decreases with temperature in the range tested (room
20 temperature to 80 °C. The dried samples have significantly higher viscosity than PO as the concentration of higher molecular weight compounds, mainly lignin, is higher than that of PO.

Based on the results presented above for content, density, and viscosity it can be
25 concluded that the drying temperature doesn't affect the process significantly and for the industrial process the selected temperature for the drying of PO will be room temperature.

Elemental composition of the organic phases is shown in Table 4. Although the
30 elemental compositions for the organic phases are similar, lower oxygen content is achieved when large amounts of water are used (Sample 3 and 4). Based on the results temperatures close to room temperature are suitable as at higher temperatures there is evaporation of light compounds reducing the carbon content of the organic phase.

5 Table 4. Elemental composition of the organic phase.

Sample number	PO	3	4	5	6	7	8	9
Volume of PO and water (ml)		80 PO + 120 water	100 PO + 100 water	120 PO + 80 water	160 PO + 40 water	80 PO + 120 water	100 PO + 100 water	140 PO + 60 water
Phase		Organic	Organic	Organic	Organic	Organic	Organic	Organic
Temperature (°C)		room	room	room	room	50	50	50
Carbon (wt%)	41.53	58.59	56.28	55.48	52.85	56.70	54.28	53.81
Hydrogen (wt%)	5.92	6.93	6.92	7.08	7.06	6.85	6.79	6.90
Nitrogen (wt%)	0.19	0.26	0.26	0.25	0.24	0.26	0.25	0.24
Sulphur (wt%)	0.00							
Oxygen (wt%)	34.68	30.16	32.46	32.80	31.71	31.98	31.95	30.09
Water content (wt%)	30.8	15.1	14.7	17.1	19.6	14.4	15.9	18.4

10 The pH of pyrolysis oil before the addition of water was 2.5. The organic phase samples have higher pH than PO suggesting that the concentration of acidic compounds is less. However, the pH of the aqueous phase samples was between 2.7 and 2.8, thus large concentrations of organic acids in the aqueous phase are expected. The amount of metals was reduced in the organic phase after the treatment with an aqueous phase. The use of higher content of the aqueous phase resulted in more efficient removal of metals and phosphorus, which were enriched in the aqueous phase.

15 In following Table 5 the content of sugar components in the aqueous phase after treatment of PO with and aqueous media at RT and 50°C is presented.

5 Table 5.

Sample number		3	4	5	7	8	9
Volume of PO and water (ml)		PO 80 + water 120	PO 100 + water 100	PO 120 + water 80	PO 80 + water 120	PO 100 + water 100	PO 140 + water 60
Phase		Water	Water	Water	Water	Water	Water
Temperature (°C)		room	room	room	50	50	50
Galactose, Methanolysis+ GC	mg/l	27,3	33,8	27,7	34,8	43,1	30,3
Glucose, Methanolysis+ GC	mg/l	528	681	525	637	801	587
Mannose, Methanolysis+ GC	mg/l	45,6	57,5	45,6	55,2	68,9	49,1
Arabinose, Methanolysis+ GC	mg/l	31,8	40,5	30,2	36,3	45,9	33,3
Xylose, Methanolysis+ GC	mg/l	86,3	109	84,5	104	131	95
Glucuronic acid, Methanolysis+ GC	mg/l	5,1	4,5	5,4	7,1	7,8	5,3
Galacturonic acid, Methanolysis+ GC	mg/l	34,8	39,6	34,1	43,5	52,3	36,2
Carbohydrates, total, Methanolysis+ GC	mg/l	759	966	753	918	1150	836
Galactose, monomeric, GC	mg/l	4,8	4,2	3,6	4,9	5,5	5,3
Glucose, monomeric, GC	mg/l	6	7	4,4	6,3	8,1	5,6
Mannose, monomeric, GC	mg/l	6,1	8,1	4,2	6,7	8,1	7
Arabinose, monomeric, GC	mg/l	32	35	25,3	32,7	38,6	27,9
Xylose, monomeric, GC	mg/l	29,3	33,4	23,2	30,6	37,1	27,8
Glucuronic acid, monomeric, GC	mg/l	9	9,8	6	10,3	11	7,9
Galacturonic acid, monomeric, GC	mg/l	5,1	4,9	3,9	11,9	14,5	9,8
Carbohydrates, monomeric total, GC	mg/l	92,3	102	70,6	103	123	91,3

It was demonstrated that the aqueous treatment (drying) of pyrolysis oil can be achieved by adding water and causing the separation into organic and water phase. The water phase comprises valuable compounds that can be process further e.g. reformed or converted into gasoline or diesel in the upgrading, or in the production of hydroxymethylfurfural which can be utilize as intermediate in gasoline production.

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(s) may be varied within the bounds of the claims.

5 Claims

1. A process for converting biomass, comprising the stages where, in the first stage starting material comprising biomass is subjected to pyrolysis under pyrolysis conditions to yield pyrolysis oil,
10 in the second stage the pyrolysis oil is subjected to non-catalytic high temperature high pressure HTHP treatment comprising at least two steps, followed by separation of an aqueous phase and HTHP treated pyrolysis oil, and
15 in the third stage the HTHP treated pyrolysis oil is subjected to hydroprocessing in the presence of at least one hydroprocessing catalyst and hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in the liquid fuel hydrocarbon range is obtained.
2. The process according to claim 1, wherein the pyrolysis is fast pyrolysis.
20
3. The process according to claim 1 or 2, wherein the starting material comprising biomass comprises virgin and waste materials of plant origin, animal origin, fish origin, microbiological origin, or any combinations thereof.
- 25 4. The process according to any one of claims 1-3, wherein the starting material comprises additionally polymeric material.
5. The process according to any one of claims 1-4, wherein the starting material comprises virgin wood, wood residues, forest residues, wood waste, residues
30 and by-products of the wood-processing industry.
6. The process according to any one of claims 1-5, wherein in the HTHP treatment, in the first step (a) the pyrolysis oil is heated in the absence of added catalyst at 100 to 200 °C temperature and 50 to 250 bar pressure to
35 yield a product of the first step, and in the second step (b) the product of the first step is heated in the absence of added catalyst at 200 to 400 °C temperature and 50 to 250 bar pressure.
7. The process according to any one of claims 1-6, wherein the high temperature
40 high pressure HTHP treatment is carried out in the presence of at least one alkali metal hydroxide.

- 5 8. The process according to any one of claims 1-7, wherein the hydroprocessing is carried out under a pressure from 5 to 350 bar and at a temperature from 100 to 450°C.
- 10 9. The process according to any one of claims 1-8, wherein crude tall oil is used as co-feed in the hydroprocessing stage.
10. The process according to claim 9, wherein the hydroprocessing is carried out under a pressure from 10 to 150 bar, preferably between 50 to 100 bar.
- 15 11. The process according to claim 9 or 10, wherein the hydroprocessing is carried out at a temperature from 100 to 450°C, preferably 250 °C and 380 °C.
- 20 12. The process according to any one of claims 9-11, wherein a catalyst selected from HDW catalysts and combinations of HDO and HDW catalysts is used in the hydroprocessing stage.
- 25 13. The process according to any one of claims 1-12, wherein the pyrolysis oil is pretreated prior to the second stage and the pretreatment is selected from treatment with aqueous media, filtering, extraction and any combinations thereof.
- 30 14. The process according to claim 13, where in the treatment with aqueous media, 1 – 80 vol% of the aqueous media is added to 20 – 99 vol% of pyrolysis oil.
- 35 15. The process according to any one of claims 1-14, wherein the HTHP treated pyrolysis oil is subjected to prehydrogenation prior to the hydroprocessing stage, said prehydrogenation comprising one step or at least two steps.
- 40 16. The process according to any one of claims 1-15, wherein the effluent is subjected to fractionation to yield hydrocarbon fractions boiling in the transportation fuel ranges.
17. The process according to claim 16, wherein the hydrocarbon fractions comprise fractions boiling in the ranges of gasoline, kerosene, jet fuel, diesel oil, naphtha, blending components for transportation fuels, heating oil and solvents.
- 45 18. A product obtainable by the process according to any one of claims 1-17.

- 5 19. The product of claim 18, said product being selected from hydrocarbon fractions boiling in the ranges of gasoline, kerosene, jet fuel, diesel oil, naphtha, blending components for transportation fuels, heating oil and solvents, and fine chemicals and building-block chemicals.
- 10 20. A process for the manufacture of liquid fuels, said process comprising the stages where, in the first stage starting material comprising biomass is subjected to pyrolysis under pyrolysis conditions to yield pyrolysis oil, in the second stage the pyrolysis oil is subjected to non-catalytic high temperature high pressure HTHP treatment comprising at least two steps,
- 15 followed by separation of an aqueous phase and HTHP treated pyrolysis oil, and in the third stage the HTHP treated pyrolysis oil is subjected to hydroprocessing in the presence of at least one hydroprocessing catalyst and hydrogen, whereby an effluent comprising one or more hydrocarbons boiling in
- 20 the liquid fuel hydrocarbon range is obtained.
21. The process according to claim 20, wherein the pyrolysis is fast pyrolysis.
22. The process according to claim 20 or 21, wherein the starting material
- 25 comprising biomass comprises virgin and waste materials of plant origin, animal origin, fish origin, microbiological origin, or any combinations thereof.
23. The process according to any one of claims 20-22, wherein the starting material comprises additionally polymeric material.
- 30 24. The process according to any one of claims 20-23, wherein the starting material comprises virgin wood, wood residues, forest residues, wood waste, residues and by-products of the wood-processing industry.
- 35 25. The process according to any one of claims 20-24, wherein in the HTHP treatment, in the first step (a) the pyrolysis oil is heated in the absence of added catalyst at 100 to 200 °C temperature and 50 to 250 bar pressure to yield a product of the first step, and in the second step (b) the product of the first step is heated in the absence of added catalyst at 200 to 400 °C
- 40 temperature and 50 to 250 bar pressure.

- 5 26. The process according to any one of claims 20-25, wherein the high temperature high pressure HTHP treatment is carried out in the presence of at least one alkali metal hydroxide.
- 10 27. The process according to any one of claims 20-26, wherein the hydroprocessing is carried out under a pressure from 5 to 350 bar and at a temperature from 100 to 450°C.
- 15 28. The process according to any one of claims 20-27, wherein crude tall oil is used as co-feed in the hydroprocessing stage.
- 20 29. The process according to claim 28, wherein the hydroprocessing is carried out under a pressure from 10 to 150 bar, preferably between 50 to 100 bar.
- 25 30. The process according to claim 28 or 29, wherein the hydroprocessing is carried out at a temperature from 100 to 450°C, preferably 250°C and 380°C.
- 30 31. The process according to any one of claims 28-30, wherein a catalyst selected from HDW catalysts and combinations of HDO and HDW catalysts is used in the hydroprocessing stage.
- 35 32. The process according to any one of claims 20-31, wherein the pyrolysis oil is pretreated prior to the second stage and the pretreatment is selected from treatment with aqueous media, filtering, extraction and any combinations thereof.
- 40 33. The process according to claim 32, where in the treatment with aqueous media, 1 – 80 vol% of the aqueous media is added to 20 – 99 vol% of pyrolysis oil.
34. The process according to any one of claims 20-33, wherein the HTHP treated pyrolysis oil is subjected to prehydrogenation prior to the hydroprocessing stage, said prehydrogenation comprising one step or at least two steps.
35. The process according to any one of claims 20-34, wherein the effluent is subjected to fractionation to yield hydrocarbon fractions boiling in the transportation fuel ranges.
36. The process according to claim 35, wherein the hydrocarbon fractions comprise fractions boiling in the ranges of gasoline, kerosene, jet fuel, diesel oil,

- 5 naphtha, blending components for transportation fuels, heating oil and solvents.

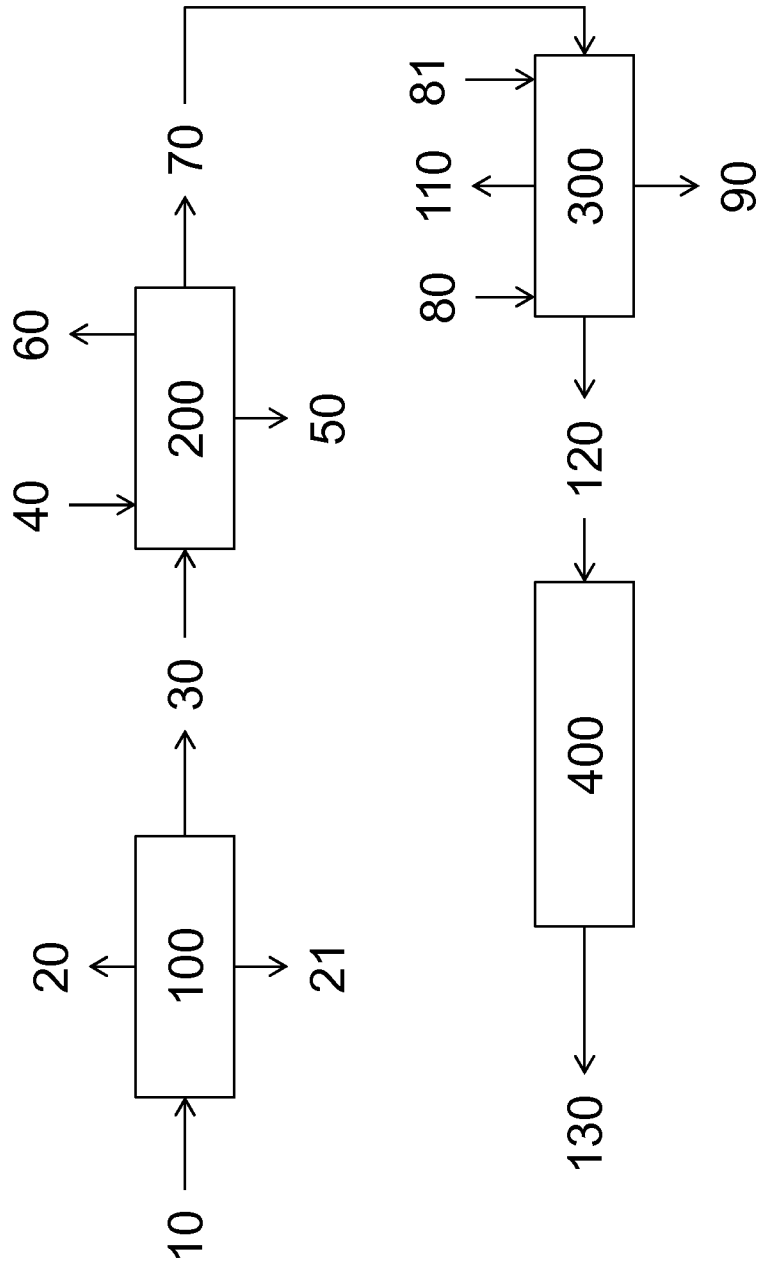


Fig. 1

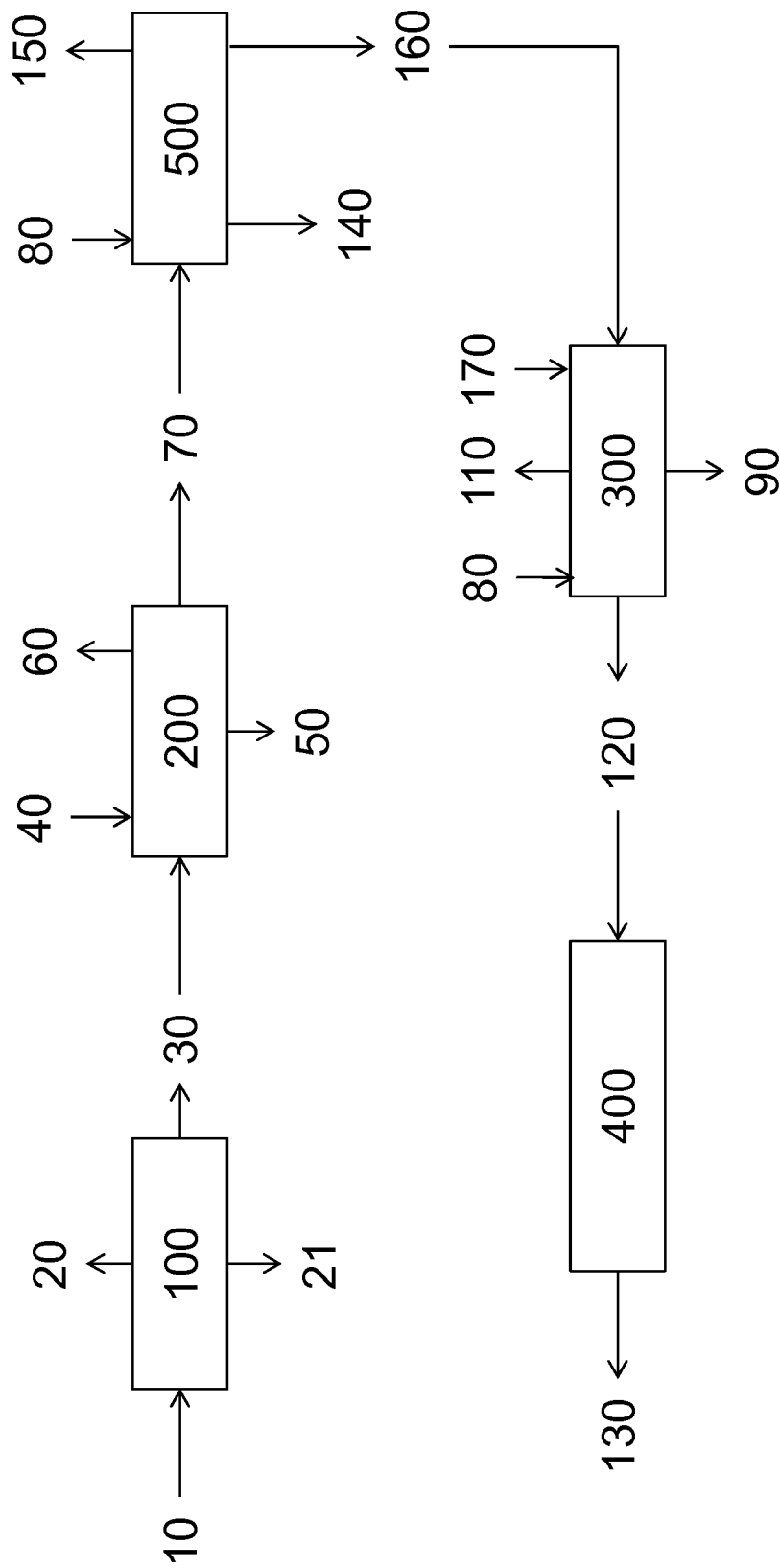


Fig. 2

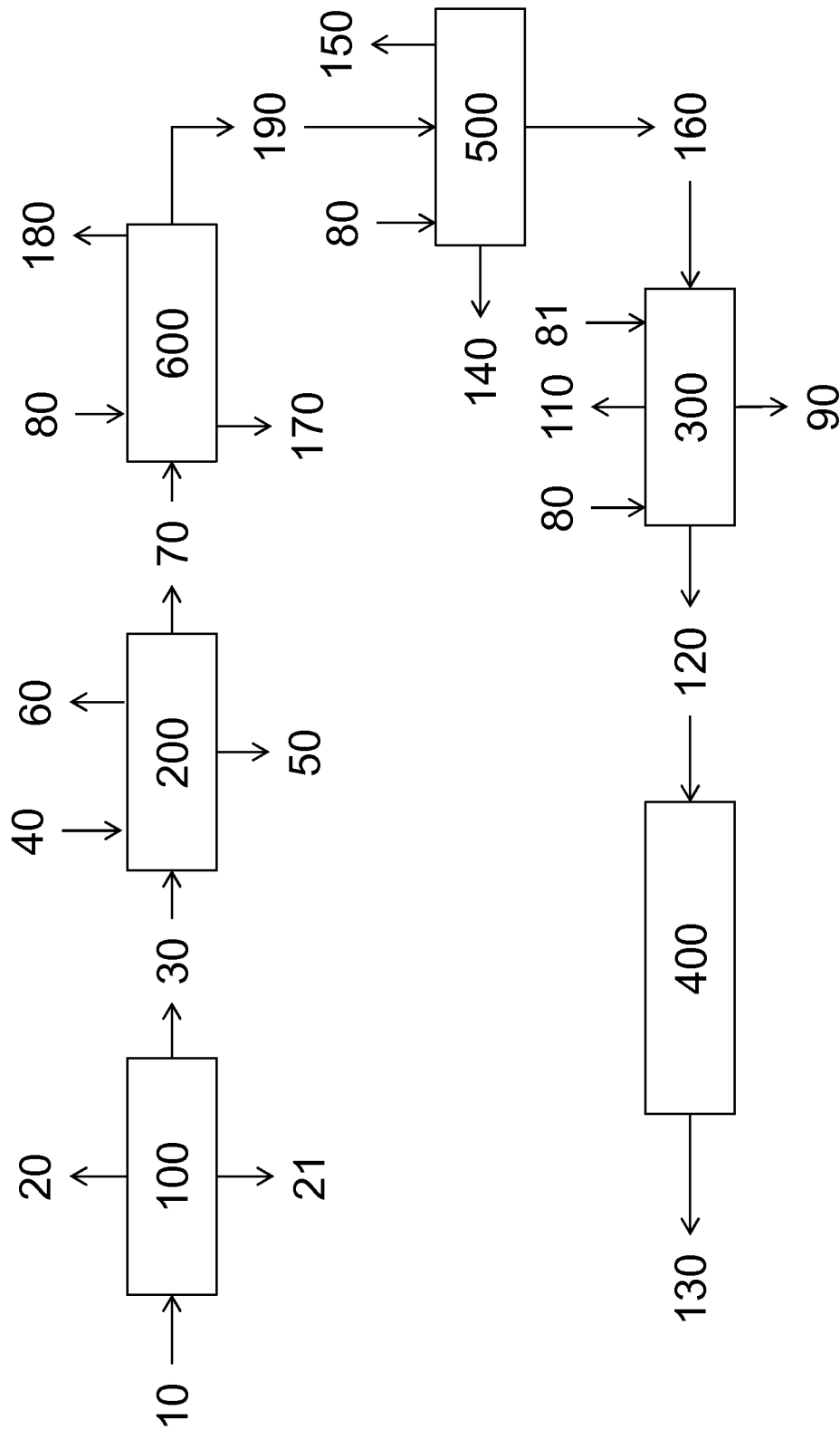


Fig. 3

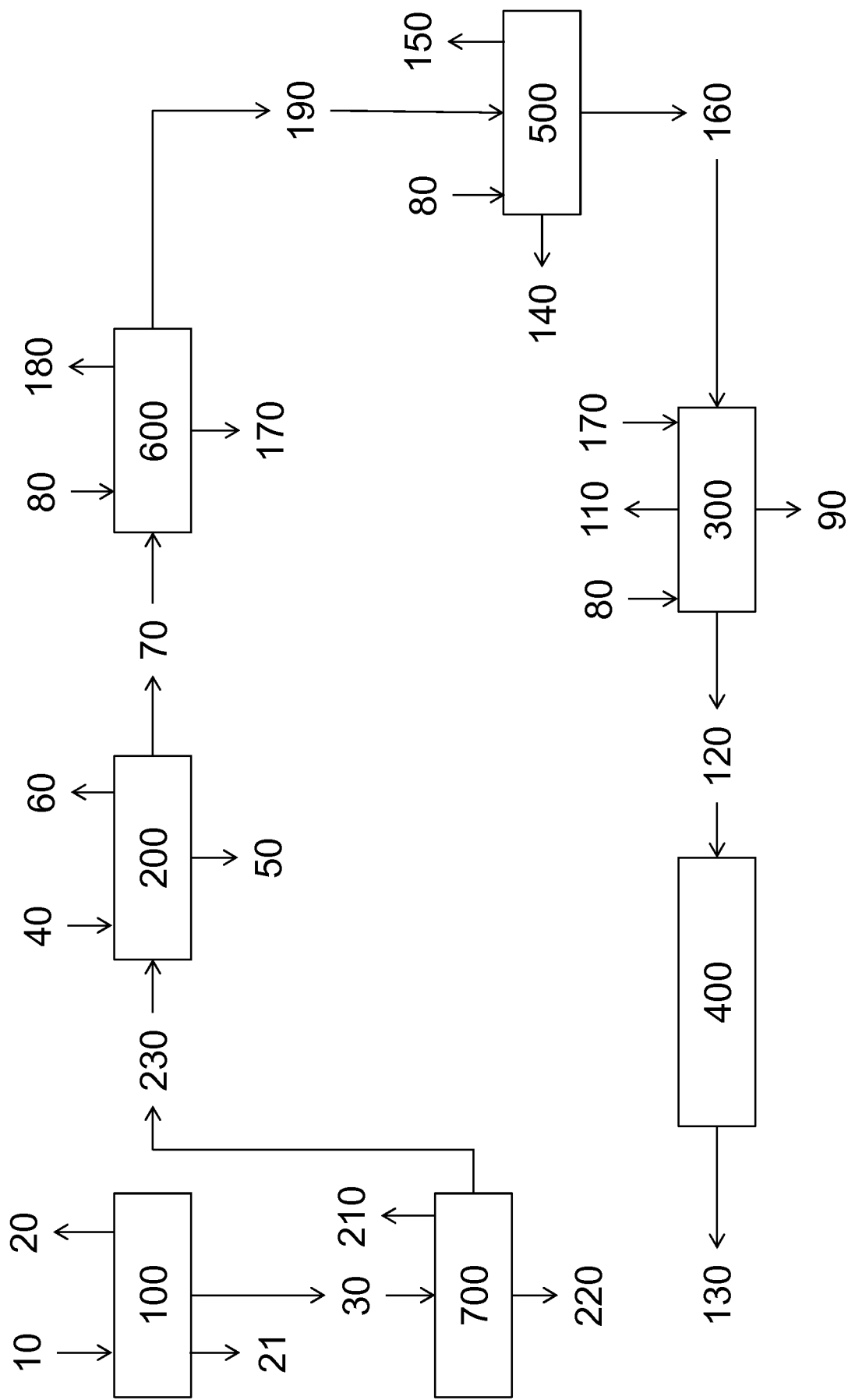


Fig. 4

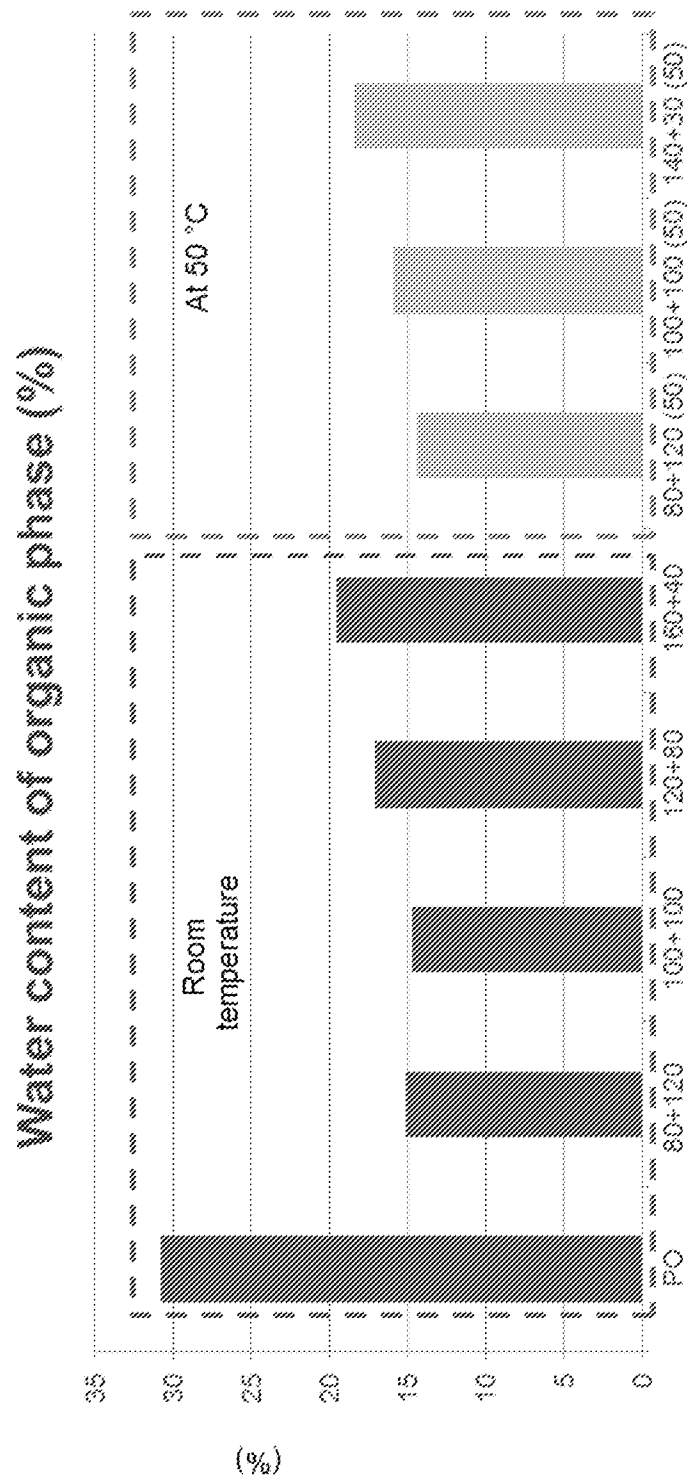


Fig. 5

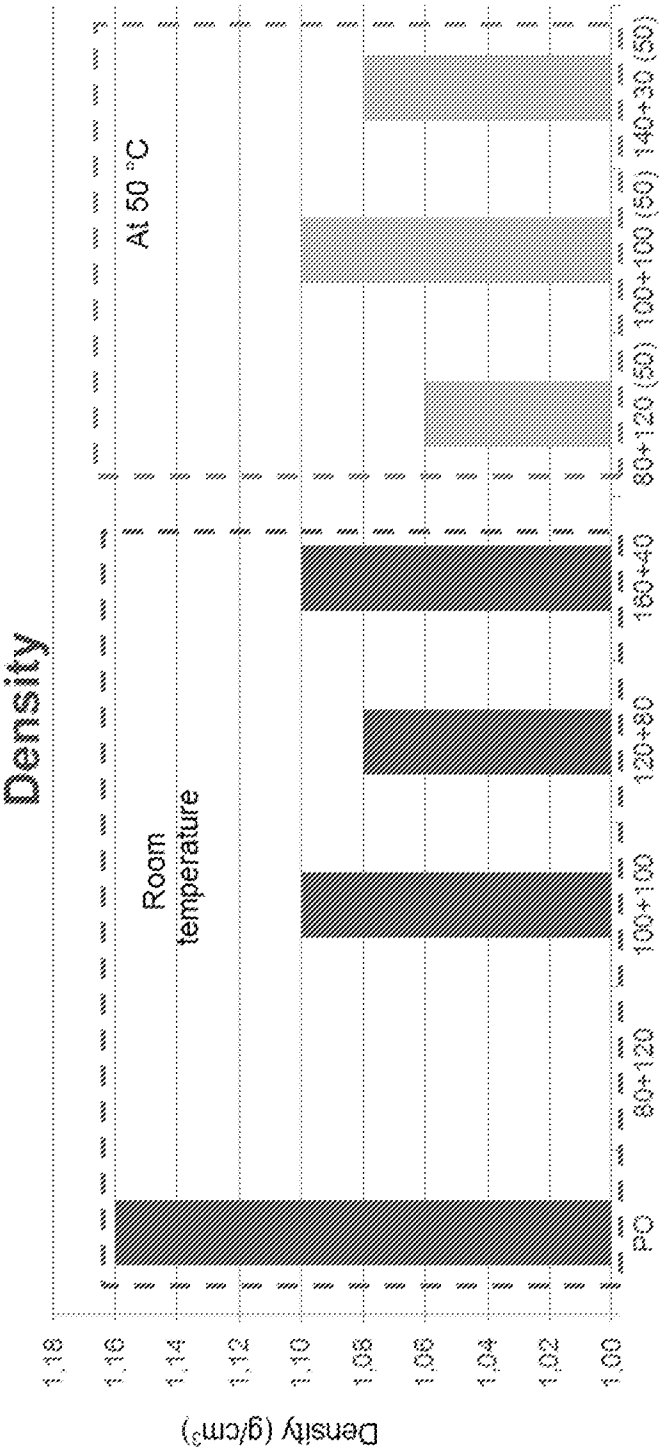


Fig. 6

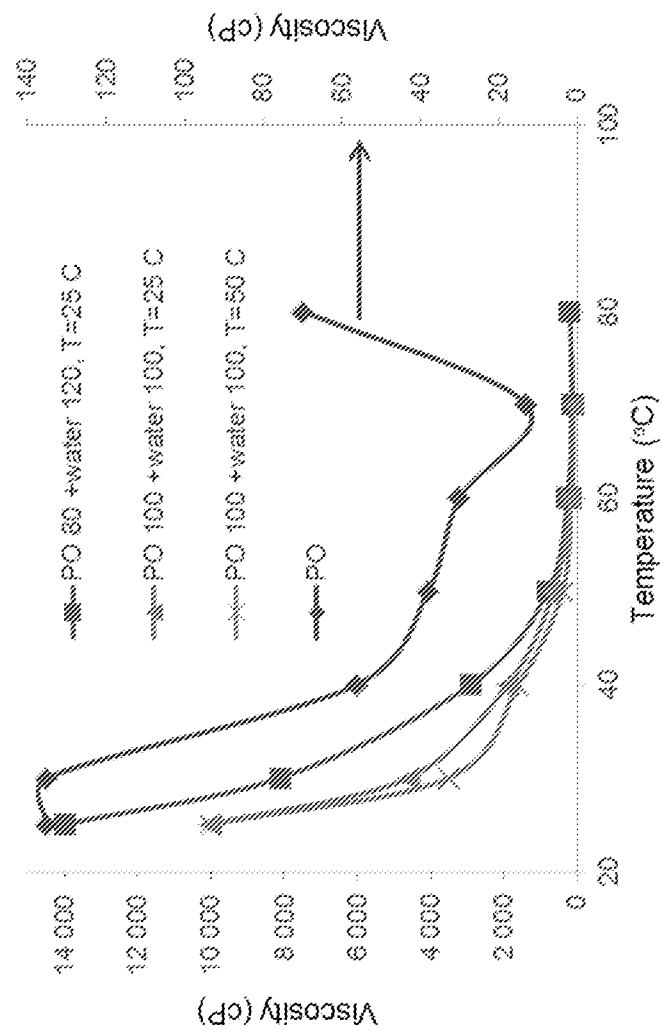


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No

PCT/FI2013/050692

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G1/00 C10B53/02 C10G1/10 C10G3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/035404 A1 (ALEGRIA EDGAR LOTERO [US] ET AL) 9 February 2012 (2012-02-09) figure 1 paragraph [0046] - paragraph [0059] -----	1-36
A	WO 2012/071005 A1 (WEIHONG YANG [SE]; WLODZIMIERZ BLASIAK [SE]; GUPTA ASHWANI KUMAR [US]) 31 May 2012 (2012-05-31) page 6, line 30 - line 31 page 13 - page 16; example 1 -----	1-36
A	WO 2011/159768 A2 (VIRESCO ENERGY [US]; RAJU ARUN [US]) 22 December 2011 (2011-12-22) figures 1-2 -----	1-36
A	US 2011/160505 A1 (MCCALL MICHAEL J [US]) 30 June 2011 (2011-06-30) paragraph [0012] -----	1-36



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

7 October 2013

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bernet, Olivier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2013/050692

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