(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 March 2015 (05.03.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/028677 A1

(51) International Patent Classification:
B01J 23/755 (2006.01) *C10G 1/00* (2006.01)
B01J 37/02 (2006.01) *C10G 3/00* (2006.01)

(21) International Application Number:
PCT/EP2014/068563

(22) International Filing Date:
2 September 2014 (02.09.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13182675.2 2 September 2013 (02.09.2013) EP

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(71) Applicant *(for US only)*: **SHELL OIL COMPANY** [US/US]; PO Box 2463, One Shell Plaza, Houston, Texas 77252-2463 (US).

(72) Inventors: **AZGHAY, Ali**; Grasweg 31, NL-1031 HW Amsterdam (NL). **ESPINOSA ALONSO, Leticia**; Egeskovvej 265, Postbox 106, DK 7000 Fredericia (DK). **FRANSSEN, Nicole Maria Gerarda**; Grasweg 31, NL-1031 HW Amsterdam (NL). **RIGUTTO, Marcello Stefano**; Grasweg 31, NL-1031 HW Amsterdam (NL). **SCHAVERIEN, Colin John**; Grasweg 31, NL-1031 HW Amsterdam (NL).

(74) Agent: **MATTHEZING, Robert Maarten**; P.O. Box 384, NL-2501 CJ The Hague (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2015/028677 A1

(54) **Title**: PROCESS FOR PREPARING A CATALYST, CATALYST OBTAINED BY SUCH PROCESS, AND USE OF SUCH CATALYST

(57) **Abstract**: Process for converting a biomass-derived pyrolysis oil comprising the following steps: i) preparing a catalyst, preferably containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, by a method including - mixing one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture; and - subjecting the metal-containing aqueous mixture to precipitation conditions; and ii) contacting a feed containing the biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 350°C in the presence of the catalyst.

PROCESS FOR PREPARING A CATALYST, CATALYST OBTAINED BY SUCH PROCESS, AND USE OF SUCH CATALYST

Technical field of the invention

The present invention relates to a process for preparing a catalyst, a catalyst obtainable or obtained by such a process, and the use of such a catalyst. More specifically the present invention relates to the preparation of a catalyst, a catalyst and a process for converting a biomass-derived pyrolysis oil.

Background to the invention

With the diminishing supply of crude petroleum oil, use of renewable biomass as an energy source is becoming increasingly important for the production of liquid fuels and/or chemicals. The use of renewable biomass as an energy source may also allow for a more sustainable production of liquid fuels and more sustainable CO_2 emissions that may help meet global CO_2 emissions standards under the Kyoto protocol.

The fuels and/or chemicals from renewable biomass are often referred to as biofuels and/or biochemicals. Biofuels and/or biochemicals derived from non-edible biomass materials, such as cellulosic materials, are preferred as these do not compete with food production. These biofuels and/or biochemicals are also referred to as second generation or advanced biofuels and/or biochemicals. Most of these non-edible biomass materials, however, are solid materials that are cumbersome to convert into liquid fuels.

A well-known process to convert solid biomass material into a liquid is pyrolysis. By means of such pyrolysis of a solid biomass material a biomass-derived pyrolysis oil can be obtained. The energy density of the obtained pyrolysis oil is higher than that of the original solid biomass material. This has logistic advantages as it makes the pyrolysis oil more

attractive for transport and/or storage than the original solid biomass material. Pyrolysis oils, however, can be less stable than conventional petroleum oils during storage and transport. Some of the compounds within the pyrolysis oil can react with each other during transport and/or storage and an undesired sludge may form. In order to improve the quality of biomass-derived pyrolysis oil, several manners of hydroprocessing have been suggested.

WO2011064172 describes a process including pyrolysis of biomass to obtain a pyrolysis oil and hydro-deoxygenation of this pyrolysis oil at a temperature in the range from 200 to 400°C with a catalyst that may for example comprise metals of Group VIII and/or Group VIB of the Periodic Table of Elements. In passing it is mentioned that the catalyst may possibly comprise nickel , copper and/or alloys or mixtures thereof, such as Ni-Cu on a catalyst carrier. Examples of carriers mentioned include alumna, amorphous silica-alumina, titania, silica and zirconia. As an example of suitable catalysts Ni-Cu/ZrO2 is mentioned.

WO2012/030215 describes a process for the hydrotreatment of vegetal biomass. It mentions that fast pyrolysis may be an attractive technology to transform difficult-to-handle biomass into a clean and uniform liquid, called pyrolysis oil. It further mentions that several processes have been proposed for upgrading the pyrolysis oil including hydrogenation under hydrogen pressure, catalytic cracking and high pressure thermal treatment. WO2012/030215 subsequently mentions that a problem with the catalysts known from the conventional refinery processes, such as nickel/molybdenum or cobalt/molybdenum on alumina supports, is that they are not meant to handle high water contents, whilst high water contents are common in pyrolysis oils. WO2012/030215 alleges that known catalysts will decay under reaction conditions,

where a large amount of water is present and rather high temperatures are applied; and that the formation of coke may cause parts of the porous catalysts, prepared by impregnation of active metals on a porous support, to become inaccessible to the reactant, leading to quick catalyst inactivation as the catalyst support disintegrates, leaching of active components into the water and clogging of catalyst pores and or clogging of the reactor. According to WO2012/030215, there is a need for an improved catalyst and process for treating biomasses. A specific catalyst is claimed which is prepared by mixing hydrated metal oxides and a NH_3 aqueous solvent, adding a solution of a C_1- C_6 alkyl silicate in a C_1 to C_6 alkyl alcohol; impregnating with $ZrO(NO_3)_2.2H_2O$ and $La(NO_3)_3.6H_2O$ in water; drying the obtained product; and calcining the product at a temperature in the range from 350°C to 900°C. WO2012/030215 states that the catalysts described therein are more effective in the hydrogenation of pyrolysis biomasses.

The catalyst proposed in WO2012/030215, however, is too expensive to be used in a scaled up - commercial scale - conversion plant. Preparation of the catalyst as described in WO2012/030215 would require too large volumes of tetraalkylorthosilicates (in WO2012/030215 referred to as C_1-C_6 alkylsilicates, e.g. ethylsilicate), making the catalyst and process uneconomical.

In addition the presence of C1-C6-alkyl alkanols, such as ethanol, during the preparation of a catalyst as proposed in WO2012/030215 is undesirable. Ethanol is volatile, flammable, toxic and potentially carcinogenic and for all these reasons difficult to handle in a catalyst manufacturing environment.

It would therefore be an advancement in the art to provide a catalyst and process for converting a biomass-derived pyrolysis oil that would be more economical whilst

still maintaining a good catalyst activity and avoiding any safety risks.

Summary of the invention

It has now unexpectedly been found that a safe and cheaper but still sufficiently active and stable catalyst for the above mentioned conversion of a biomass-derived pyrolysis oil can be provided, when the catalyst is produced on an waterborne basis.

Accordingly, the present invention provides a process for converting a biomass-derived pyrolysis oil comprising the following steps:

i) preparing a catalyst, preferably containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, by a method including

- mixing one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture; and
- subjecting the metal-containing aqueous mixture to precipitation conditions; and

ii) contacting a feed containing the biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 350°C in the presence of the catalyst.

The process according to the invention may conveniently result in a stabilized biomass-derived pyrolysis oil. The biomass-derived pyrolysis oil may further have a reduced oxygen content. The catalyst, however, advantageously does not have the disadvantages as mentioned above. The hydroprocessed biomass-derived pyrolysis oil may optionally be dewatered and further converted via one or more

hydrocarbon conversion processes into one or more fuel components and/or one or more chemical components. The one or more fuel components and/or one or more chemical components may be blended with one or more other components to produce a biofuel and/or biochemical.

In addition, the present invention provides a method for preparing a catalyst containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, comprising the steps of

- mixing a sufficient amount of one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture;
- subjecting the metal-containing aqueous mixture to precipitation conditions to prepare a catalyst powder or catalyst; and
- optionally calcining the catalyst powder or catalyst to prepare a calcined catalyst.

The catalyst obtained pursuant to such a method is believed to be also novel and inventive in itself and hence the present invention also provides a catalyst obtainable by a method as described above. Such a catalyst may for example be a precipitated catalyst comprising one or more Group VIII metals or metal components; a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof, which precipitated catalyst comprises in the range from equal to or more than 30wt% of the one or more Group VIII metal(s) based on the total weight of the catalyst.

Detailed description of the invention

By a biomass-derived pyrolysis oil is herein understood a pyrolysis oil obtained or obtainable by pyrolysis of a biomass material. In a preferred embodiment the process according to the invention may comprise an additional step of providing such a biomass-derived pyrolysis oil. Such a step may comprise pyrolyzing of a biomass material to produce a biomass-derived pyrolysis oil. By biomass material is herein understood a composition of matter of biological origin as opposed to a composition of matter obtained or derived from petroleum, natural gas or coal. Without wishing to be bound by any kind of theory it is believed that such biomass material may contain carbon-14 isotope in an abundance of about 0.0000000001 %, based on total moles of carbon.

The biomass material may suitably comprise animal fat, tallow and/or solid biomass material.

Preferably the biomass material is a solid biomass material. More preferably the biomass material is material containing cellulose and/or lignocellulose. Such a material containing "cellulose" respectively "lignocellulose" is herein also referred to as a "cellulosic", respectively "lignocellulosic" material. By a cellulosic material is herein understood a material containing cellulose and optionally also lignin and/or hemicellulose. By a lignocellulosic material is herein understood a material containing cellulose and lignin and optionally hemicellulose.

Examples of biomass materials include aquatic plants and algae, agricultural waste and/or forestry waste and/or paper waste and/or plant material obtained from domestic waste.

Examples of cellulosic or lignocellulosic material include for example agricultural wastes such as corn stover, soybean stover, corn cobs, rice straw, rice hulls, oat hulls, corn fibre, cereal straws such as wheat, barley, rye and oat straw; grasses; forestry products and/or forestry residues

such as wood and wood-related materials such as sawdust and bark; waste paper; sugar processing residues such as bagasse and beet pulp; or mixtures thereof.

More preferably the solid biomass material comprises or consists of a cellulosic or lignocellulosic material selected from the Group consisting of wood, sawdust, bark, straw, hay, grasses, bagasse, corn stover and/or mixtures thereof. The wood may include soft wood and/or hard wood.

When the biomass material is a solid biomass material such as for example a lignocellulosic material, it may suitably be washed, steam exploded, dried, roasted, torrefied and/or reduced in particle size before being pyrolyzed. In addition, if the biomass material is a cellulosic or lignocellulosic material it may preferably be demineralized before being pyrolyzed. During such a demineralization amongst others chloride may be removed.

By pyrolysis or pyrolyzing is herein understood the decomposition of the biomass material, in the presence or in the essential absence of a catalyst, at a temperature of equal to or more than 380°C.

Preferably pyrolysis is carried out in an oxygen-poor, preferably an oxygen-free, atmosphere. By an oxygen-poor atmosphere is understood an atmosphere containing equal to or less than 10 vol.% oxygen, preferably equal to or less than 5 vol.% oxygen and more preferably equal to or less than 1 vol.% oxygen. By an oxygen-free atmosphere is understood an atmosphere where oxygen is essentially absent. More preferably pyrolysis is carried out in an atmosphere containing equal to or less than 2 vol.% oxygen, more preferably equal to or less than 0.1 vol. % oxygen and most preferably equal to or less than 0.05 vol.% oxygen. In a most preferred embodiment pyrolysis is carried out in the essential absence of oxygen.

The biomass material is preferably pyrolyzed at a pyrolysis temperature of equal to or more than 400°C, more preferably equal to or more than 450°C, even more preferably equal to or more than 500°C and most preferably equal to or more than 550°C. The pyrolysis temperature is further preferably equal to or less than 800°C, more preferably equal to or less than 700°C and most preferably equal to or less than 650°C.

The pyrolysis pressure may vary widely. For practical purposes a pressure in the range from 0.01 to 0.5 MPa (MegaPascal), more preferably in the range from 0.1 to 0.2 MPa is preferred. Most preferred is an atmospheric pressure (about 0.1 MPa).

In one embodiment the pyrolysis does not include an externally added catalyst. In another embodiment the pyrolysis is a so-called catalytic pyrolysis wherein a catalyst is used. Examples of suitable catalysts in such a catalytic pyrolysis include mesoporous zeolites. By a mesoporous zeolite is herein preferably understood a zeolite containing pores with a pore diameter in the range from 2 - 50 nanometer, in line with IUPAC notation (see for example Rouquerol *et al.* (1994). "Recommendations for the characterization of porous solids (Technical Report)" *Pure & Appl. Chem* 66 (8): 1739-1758). Especially preferred catalysts for such a catalytic pyrolysis include ZSM-5 type zeolites, such as for example Zeolyst 5524G and 8014 and Albemarle UPV-2.

In certain embodiments, chemicals may be employed for a pretreatment of the biomass material, or catalysts may be added to the pyrolysis mixture, cf. for example, H Wang cs., "Effect of acid, alkali, and steam explosion pretreatment on characteristics of bio-oil produced from pinewood", Energy Fuels (2011) 25, p. 3758 - 3764.

In a preferred pyrolysis process, generally referred to as a flash pyrolysis process, the biomass is rapidly heated (for example within 3 seconds) in the essential absence of oxygen to a temperature in the range of from 400 °C to 600 °C and kept at that temperature for a short period of time (for example equal to or less than 3 seconds). Such flash pyrolysis processes are known, for example from A. Oasmaa et al, "Fast pyrolysis of Forestry Residue 1. Effect of extractives on phase separation of pyrolysis liquids", Energy & Fuels, volume 17, number 1, 2003, pages 1-12; and A. Oasmaa et al, Fast pyrolysis bio-oils from wood and agricultural residues, Energy & Fuels, 2010, vol. 24, pages 1380-1388; US4876108; US5961786; and US5395455.

In another preferred pyrolysis process a solid heating medium is used, such as for example silica or sand. The solid heating medium may for example be a fluidized solid heating medium provided in for example a fluidized bed or a riser reactor. In such a pyrolysis process the biomass material may be fluidized within the fluidized solid heating medium and subsequently the biomass material may be pyrolysed with the heat provided by such fluidized solid heating medium. Hereafter any residual coke formed on the solid heating medium may be burned off to regenerate the solid heating medium. The coke that is burned off may conveniently supply the heat needed to prehead the solid heating medium.

During such pyrolysis of the biomass material a biomass-derived pyrolysis oil is produced. The biomass-derived pyrolysis oil used in the process according to the invention may comprise or consist of part of the product of such pyrolysis of the biomass material. The biomass-derived pyrolysis oil may for example be separated from the remainder of the pyrolysis product (including gases and solids) by any

manner known to be suitable for such purpose by one skilled in the art, including for example filtration, flashing etc.

The biomass-derived pyrolysis oil may include for example one or more hydrocarbons (compounds comprising or consisting of hydrogen and carbon), carbohydrates, olefins, paraffins, oxygenates and residual water. By an oxygenate is herein understood a compound containing carbon, hydrogen and oxygen. The oxygenates may for example include aldehydes, carboxylic acids, ethers, esters, alkanols, phenols and ketones.

The biomass-derived pyrolysis oil may suitably further still comprise water therein. Such water may for example be present in a dispersed and/or emulsified form. For example, the biomass-derived pyrolysis oil may suitably comprise water in an amount equal to or more than 0.1 wt%, preferably equal to or more than 1wt%, more preferably equal to or more than 2 wt%, even more preferably equal to or more than 5 wt%, still more preferably equal to or more than 10 wt% and most preferably equal to or more than 15wt% water and preferably equal to or less than 55 wt%, more preferably equal to or less than 45 wt%, and still more preferably equal to or less than 35 wt%, still more preferably equal to or less than 30 wt%, most preferably equal to or less than 25 wt% water, based on the total weight of the biomass-derived pyrolysis oil. In practice, the biomass-derived pyrolysis oil may suitable comprise in the range from 1 to 55 wt% water, more suitably in the range from 10 to 45 wt% water, most suitably in the range from 15 to 35 wt% water, based on the total weight of the biomass-derived pyrolysis oil.

As used herein, water content is as measured by ASTM E203. Such water may preferably be removed before or after carrying out the hydroprocessing as described herein below.

In step i) of the process according to the invention a catalyst is prepared, preferably containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, by a method including

- mixing one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture; and
- subjecting the metal-containing aqueous mixture to precipitation conditions.

As indicated above, some of these methods are considered novel and inventive in itself and therefore the invention also provides a method for preparing a catalyst containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, comprising the steps of

- mixing a sufficient amount of one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture;
- subjecting the metal-containing aqueous mixture to precipitation conditions to prepare a catalyst powder; and
- optionally calcining the catalyst powder to prepare the catalyst.

By a Group VIII metal is herein understood a metal from Group VIII of the Periodic System of Elements pursuant to the Chemical Abstracts Service (CAS) notation. Examples of such Group VIII metals include metals from Groups 8, 9 and 10

pursuant to the IUPAC notation. Preferably the one or more Group VIII metal components include one or more Group VIII metals chosen from the Group consisting of Iron, Cobalt, nickel, Ruthenium, Rhodium, Palladium, Iridium and Platinum. More preferably the one or more Group VIII metals are non-noble Group VIII metals, such as Iron, Cobalt and/or nickel. Most preferably the Group VIII metal is nickel and most preferably the Group VIII metal component comprises a nickel component.

In addition, the presence of one or more Group IB metals in the catalyst may be advantageous. Such one or more Group IB metals may act as a promoter. Hence, in a preferred embodiment the above process step i) and/or the above method may include mixing one or more Group VIII metal components; one or more Group IB metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture.

By a Group IB metal is herein understood a metal from Group IB of the Periodic System of Elements pursuant to the Chemical Abstracts Service (CAS) notation. Examples of such Group IB metals include metals from Group 11 pursuant to the IUPAC notation. Preferably the one or more Group IB metal components include one or more Group IB metals chosen from the Group consisting of copper, Silver and Gold. Most preferably the Group IB metal is copper and most preferably the Group IB metal component comprises a copper component.

Preferably the catalyst comprises essentially no Group VIB metal(s). By a Group VIB metal is herein understood a metal from Group VIB of the Periodic System of Elements pursuant to the Chemical Abstracts Service (CAS) notation.

Examples of such Group VIB metals include metals from Group 6 pursuant to the IUPAC notation. For example Group VIB metals include molybdenum and tungsten. Most preferably the above process step i) and/or the above method is/are carried out in the essential absence of a Group VIB metal. Hence, preferably the aqueous solution does not comprise any Group VIB metal components. Group VIB metals such as molybdenum and tungsten may require a sulfide form to be sufficiently active. Due to the high oxygen content of the pyrolysis oil, however, such a sulfide form of any Group VIB metal may be converted to the oxide form. This may lead to inactivation and/or destabilization of the catalyst.

The above mentioned metal components, such as the Group VIII metal component(s) and/or Group IB metal component(s) may be provided in any manner known to be suitable by the person skilled in the art. For example, each of the metal component(s) may independently be a metal oxide, a metal salt or elemental metal. By an elemental metal is herein understood a metal present in its elemental form. By a metal oxide is herein understood a metal in its oxidized form, such as for example a nickel-oxide or copper-oxide. By a metal salt is herein understood a salt of a metal. Examples include metal carbonates, metal silicates, metal phosphates, metal acetates, metal citrates, metal hydroxides, metal nitrates, metal sulfates, metal formiates and mixtures thereof. Metal carbonates are especially preferred. Preferably each metal component mentioned above independently is a metal oxide or a metal salt.

Preferably the one or more Group VIIIB metal component(s) is/are selected from the Group consisting of nickel carbonate, nickel oxide, nickel hydroxide, nickel phosphate, nickel formiate, nickel sulfate, nickel nitrate, nickel citrate, nickel acetate, or a mixture of two or more thereof. Most

preferably the above process step i) and/or the above method comprise mixing a nickel carbonate.

Preferably the one or more Group IB metal component(s) is/are selected from the Group consisting of copper carbonate, copper oxide, copper hydroxide, copper phosphate, copper formiate, copper sulfate, copper nitrate, copper citrate, copper acetate or a mixture of two or more thereof. Most preferably the above process step i) and/or the above method comprise mixing a copper carbonate.

The above process step i) and the above method include mixing of the above one or more metal components and a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof.

More preferably the waterborne refractory oxide component comprises one or more refractory oxide(s) selected from the Group consisting of zirconia, silica and mixtures thereof. Zirconia-silica is especially preferred as it may render the catalyst more acid-resistant and/or corrosion-resistant.

Preferably the waterborne refractory oxide component and/or the refractory oxide contain essentially no alumina. More preferably the catalyst as a whole contains essentially no alumina. That is, the catalyst is preferably an alumina-free catalyst. Without wishing to be bound by any kind of theory it is believed that a refractory oxide and/or catalyst without alumina may advantageously be more resistant to acidic and/or corrosive components that may be present in a bio-mass derived pryrolysis oil. In addition a refractory oxide and/or catalyst without alumina may be less prone to deactivation and/or disintegration in the presence of any water that may be contained in a biomass-derived pyrolysis oil. Hence, a catalyst which does not include alumina, may advantageously be more stable and/or deactivate less quickly

than an alumina containing catalyst when used in hydroprocessing a biomass-derived pyrolysis oil.

By a waterborne refractory oxide component is herein understood a component comprising or consisting of one or more refractory oxide(s) provided or present in admixture with water. Such a waterborne refractory oxide component therefore advantageously comprises essentially no alkanols.

The waterborne refractory oxide component may for example be a slurry, dispersion and/or suspension of one or more refractory oxide(s) in water. Examples of such a slurry, dispersion or suspension of one or more refractory oxide(s) in water include slurries, dispersions and/or suspensions of titania, zirconia, silica and/or mixtures thereof in water.

The waterborne refractory oxide component may be made in-situ during process step i) and/or the method according to the invention. It is for example possible to use a precipitated or pyrolytic refractory oxide (such as a precipitated or pyrolytic silica) and add this refractory oxide (for example such silica) to the mixture, whereafter the refractory oxide becomes waterborne.

Preferably the waterborne refractory oxide is provided to the mixture in an aqueous form, that is, in a form where it is already admixed with water.

In one preferred embodiment the waterborne refractory oxide component comprises or consists of an aqueous titania and/or zirconia dispersion. Such titania and/or zirconia could advantageously provide additional acidity resistance and/or corrosion resistance to the catalyst. The waterborne refractory oxide component may for example comprise or consist of an aqueous colloidal dispersion of titania and/or zirconia, also referred to as a waterborne colloidal dispersion of titania and/or zirconia.

In another preferred embodiment the waterborne refractory oxide component comprises or consists of an aqueous dispersion of silica. Any type of silica may be used, preferably however a colloidal silica is used. For example the waterborne refractory oxide component may comprise or consist of an aqueous colloidal dispersion of silica, also sometimes referred to as a waterborne colloidal silica dispersion. Preferably the silica is an amorphous silica. More preferably the waterborne refractory oxide component comprises or consists of an aqueous colloidal dispersion of amorphous silica. The later is sometimes also referred to as a waterborne colloidal amorphous silica dispersion. Still more preferably the waterborne refractory oxide component comprises or consists of an aqueous silicasol, also referred to as a waterborne silicasol. As indicated above such waterborne colloidal dispersion of, preferably amorphous, silica or such waterborne silicasol would advantageously comprise essentially no alkanols. Without wishing to be bound by any kind of theory it is believed that the use of such waterborne colloidal amorphous silica or such waterborne silicasol may advantageously lead to a higher thermal resistance and/or acidity resistance, making the prepared catalyst more suitable for use in a process for hydroprocessing of a biomass-derived pyrolysis oil.

Preferably the refractory oxide has a BET surface area in the range from equal to or more than 10 m^2/gram to equal to or less than 1000 m^2/gram, more preferably in the range from equal to or more than 50 m^2/gram to equal to or less than 400 m^2/gram.

Preferably the refractory oxide has a particle size distribution with a mean particle size in the range from equal to or more than 0.2 nanometer to equal to or less than

1000 nanometer, more preferably in the range from equal to or more than 2 nanometer to equal to or less than 150 nanometer.

The pH of the waterborne refractory oxide component may vary widely. For example, the pH of the waterborne refractory oxide component may lie in the range from equal to or more than 2.0 to equal to or less than 11.0. More preferably, the waterborne refractory oxide component may have a pH equal to or more than 7.0, still more preferably in the range from equal to or more than 7.0 to equal to or less than 11.0, still more preferably in the range from equal to or more than 8.0 to equal to or less than 11.0.

The refractory oxide may be stabilized for example by sodium or ammonia. More preferably the refractory oxide may be stabilized by ammonia. Preferably the refractory oxide is a sodium-free refractory oxide. In a preferred embodiment the refractory oxide component may comprise or consist of an aqueous dispersion of ammonia stabilized colloidal silica. As indicated before, the silica is preferably an amorphous silica or silicasol.

Examples of preferred waterborne refractory oxide components include aqueous mixtures of colloidal amorphous silica such as LEVASIL and BINDZIL (LEVASIL and BINDZIL are trademarks) as supplied by AKZO NOBEL; or aqueous suspensions of amorphous silicas such as LUDOX AS-30 or LUDOX AS-40 (LUDOX is a trademark) as supplied by Grace Davison. LEVASIL 300/30 is especially preferred.

Process step i) and the method as mentioned above further include mixing of a water-soluble base. The water-soluble base may preferably be chosen from the Group consisting of ammonia, ammonium hydroxide, sodium hydroxide, ammonium silicate, ammonium carbonate, sodium carbonate and/or mixtures thereof. More preferably such water-soluble base is a base that will generate ammonia and/or ammonium ions. For

example the water-soluble base may preferably be chosen from the Group consisting of ammonia, ammonium hydroxide, ammonium silicate, ammonium acetate, ammonium nitrate, ammonium sulphate, ammonium carbonate and/or mixtures thereof. Most preferably the water-soluble base comprises or consists of ammonia.

The above described components and the water-soluble base are mixed in an aqueous solvent to prepare a metal-containing aqueous mixture.

Preferably the aqueous solvent in process step i) and the method according to the invention is water.

The one or more metal component(s) may or may not be completely dissolved in the aqueous solvent. It is possible for the one or more metal component(s) to be partly in the solid state and partly in the dissolved state in the metal-containing aqueous mixture. The metal-containing aqueous mixture may therefore in part be a dispersion and in part be a solution. Higher concentrations of the water-soluble base may lead to higher dissolutions of the one or more metal component(s).

The one or more Group VIII metal components; optional one or more Group IB metal components; waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and the water-soluble base may be mixed in any order desired. It is possible for all components and the water-soluble base to be added to or into the aqueous solvent at the same time or sequentially. For example the waterborne refractory oxide component and the water-soluble base may be added simultaneously (for example as an aqueous ammonium-stabilized refractory oxide or as a dispersion of the refractory oxide in an aqueous ammonia solution) to a dispersion and/or solution of the metal components in an

aqueous solvent. But it is also possible for one or more of the metal components and the waterborne refractory oxide component to be present as a dispersion and/or solution within the aqueous solvent (for example water) and for the water-soluble base to be added to such a dispersion and/or solution.

Preferably process step i) and/or the method according to the invention comprise mixing the one or more Group VIII metal components (such as for example nickel carbonate), optionally the one or more Group IB metal components (such as for example copper carbonate) and the water-soluble base (such as for example an aqueous ammonia solution) to prepare an aqueous dispersion and/or solution; and subsequently adding the waterborne refractory oxide component (such as for example a waterborne colloidal amorphous silica) to such aqueous dispersion and/or solution to prepare the metal-containing aqueous mixture.

More preferably process step i) and/or the method according to the invention comprise mixing the one or more Group VIII metal components (such as for example nickel carbonate), optionally the one or more Group IB metal components (such as for example copper carbonate) and the water-soluble base (such as for example an aqueous ammonia solution) to prepare an aqueous dispersion and/or solution; stirring such aqueous dispersion and/or solution; subsequently adding the waterborne refractory oxide component (such as for example a waterborne colloidal amorphous silica) to such aqueous dispersion and/or solution; and stirring again to prepare the metal-containing aqueous mixture.

Mixing may conveniently be carried out in a so-called Ultra Turrax blender.

Preferably the mol amount of water-soluble base, such as for example ammonia, is at least 0.2 mol and at most 20 mol

per mol of the total moles of metals, on an elemental metal basis. That is, preferably the mol ratio of moles of water-soluble base to the total moles of both Group VIII metal(s) and optionally Group IB metal(s), on an elemental metal basis, lies preferably in the range from equal to or more than 0.2:1 to equal to or less than 20:1. More preferably, the mol ratio of moles of water-soluble base to total moles of both Group VIII metal(s) and optionally Group IB metal(s), on an elemental metal basis, lies in the range from equal to or more than 0.5:1 to equal to or less than 10:1.

As indicated above, one or more Group IB metal(s) may advantageously act as a promoter to the one or more Group VIII metal(s). If any one or more Group IB metal(s) are present, they are preferably present in a weight ratio of the one or more Group VIII metals to the one or more Group IB metals in the range from equal to or less than 10:1 to equal to or more than 2:1.

Preferably process step i) and/or the method for preparation of the catalyst are carried out in a manner suitably to prepare a catalyst containing the one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, more preferably in an amount in the range from equal to or more than 30wt% to equal to or less than 80wt%, still more preferably in the range from equal to or more than 40wt% to equal to or less than 65wt%, based on the total weight of the catalyst. Based on the desired amount of Group VIII metal(s) and the type of Group VIII metal component used, a person skilled in the art may calculate the amount of Group VIII metal component(s) required.

Preferably step (i) and/or the method according to the invention are carried out in the essential absence of any alkanols. Preferably the metal-containing aqueous mixture

prepared, and/or the catalyst prepared comprise essentially no alkanols.

The metal-containing aqueous mixture may conveniently comprise both dissolved as well as non-dissolved components and may also be referred to as a metal-containing aqueous slurry, metal-containing aqueous dispersion and/or metal-containing aqueous suspension.

The mixing may be carried out at any temperature or temperature profile known by the person skilled in the art to be suitable for such a mixing step. Pressures applied during the mixing are preferably equal to or less than 0.5 MegaPascal (corresponding to equal to or less than about 5 bar). More preferably the mixing is carried out at ambient pressure (corresponding to a pressure of about 0.1 MegaPascal, i.e. about 1 bar).

Preferably the mixing step is carried out at a temperature below the boiling temperature of water at the pressure applied. For example, process step i) and/or the method according to the invention may include heating the metal-containing aqueous mixture, preferably whilst stirring, to a temperature in the range from equal to or more than 30°C to equal to or less than 100 °C to prepare a heated metal-containing aqueous mixture. More preferably process step i) and/or the method according to the invention may include heating the metal-containing aqueous mixture, preferably whilst stirring, to a temperature in the range from equal to or more than 50°C to equal to or less than 95 °C to prepare a heated metal-containing aqueous mixture.

The metal-containing aqueous mixture may conveniently be held, preferably whilst stirring, at ambient temperature and pressure (i.e. at about 20°C and about 0.1 MegaPascal) or at elevated temperature (for example at about 0.1 MegaPascal and a temperature in the range from equal to or more than 30°C to

equal to or less than 100°C) for a certain period of time - often also referred to as ageing. For example, process step i) and/or the method according to the invention may include heating the metal-containing aqueous mixture, preferably whilst stirring, to a temperature in the range from equal to or more than 30°C to equal to or less than 100 °C to prepare a heated metal-containing aqueous mixture and maintaining the heated metal-containing aqueous mixture, preferably whilst stirring, at such temperature (also referred to as ageing temperature) during a period of time in the range from equal to or more than 10 minutes to equal to or less than 10 hours, more preferably during a period of time in the range from equal to or more than 30 minutes to equal to or less than 7 hours. More preferably the ageing temperature may lie in the range from equal to or more than 50°C to equal to or less than 95 °C.

During the mixing the pH of the aqueous solvent and/or metal-containing aqueous mixture may preferably be kept at a pH value equal to or more than 7.0.

Without wishing to be bound by any kind of theory it is believed that during mixing one or more of the components and/or the water-soluble base may at least partially dissolve and/or reprecipitate. This advantageously allows for an intimate mixture of the one or more metal components and the waterborne refractory oxide component to be formed.

process step i) and/or the method according to the invention further comprise subjecting the metal-containing aqueous mixture to precipitation conditions to prepare a catalyst powder. By precipitation conditions is herein preferably understood conditions causing one or more dissolved compounds present in the aqueous solvent to precipitate. Such one or more dissolved compounds may include for example one or more Group VIII metal components, one or

more Group VIII metals, one or more Group IB metal components, one or more Group IB metals, one or more refractory oxide components, one or more refractory oxide(s) and/or a water-soluble base.

The process step i) and/or the method according to the invention may comprise the (co-)precipitation of one, two or more metal components and/or metals.

During process step i) and/or the method according to the invention mixing, dissolution and/or precipitation may be carried out simultaneously. Preferably process step i) and/or the method according to the invention comprise simultaneous dissolution and reprecipitation. The dissolution and reprecipitation may be slowly at lower temperatures, such as for example 20°C, and quicker at higher temperatures, such as for example 80°C.

In addition, further precipitation can be induced or forced by subjecting the metal-containing aqueous mixture to precipitation conditions, for example by varying temperature, pH and/or pressure of the metal-containing aqueous mixture. Such precipitation conditions may for example include cooling, lowering the pH, lowering the pressure, filtration, evaporation and/or drying. Suitably the precipitation conditions may comprise or consist of conditions for the removal of water and/or other liquids. Water and/or other liquids may for example be removed from the metal-containing aqueous mixture by evaporation, spray drying, flash drying evaporation and/or vacuum distillation.

More preferably the subjecting of the metal-containing aqueous mixture to precipitation conditions comprises or consists of drying the metal-containing aqueous mixture, preferably including spray drying the metal-containing aqueous mixture, to obtain the catalyst powder or catalyst.

Possible drying conditions can include a drying

temperature in the range of from equal to or more than 50°C to equal to or less than 200°C, more preferably from equal to or more than 80°C to equal to or less than 150°C; and can include a drying period of time in the range from equal to or more than 10 minutes to equal to or less than 10 hours, more preferably in the range from equal to or more than 30 minutes to equal to or less than 6 hours.

Still more preferably the subjecting of the metal-containing aqueous mixture to precipitation conditions comprises or consists of evaporation (for example with help of a nitrogen flow) of at least part of the liquid, for example water, present in the metal-containing aqueous mixture to prepare a caked powder; and subsequently drying the caked powder, preferably at a temperature in the range from equal to or more than 60°C to equal to or less than 160°C, more preferably at a temperature in the range from equal to or more than 80°C to equal to or less than 140°C, for a certain period of time, preferably in the range from equal to or more than 10 minutes to equal to or less than 10 hours, more preferably in the range from equal to or more than 30 minutes to equal to or less than 6 hours, to prepare a catalyst powder or catalyst.

The catalyst or catalyst powder may optionally be calcined to prepare a calcined catalyst. Such calcining preferably comprises or consists of heating the catalyst powder to a temperature in the range from more than 160°C to equal to or less than 600°C and maintaining the catalyst powder within that temperature range for a period of time in the range from equal to or more than 30 minutes to equal to or less than 6 hours.

In addition to the above, process step i) and/or the method according to the invention may preferably comprise shaping, preferably by extrusion, of the catalyst powder or

catalyst to prepare a shaped catalyst. For example the catalyst or catalyst powder may be shaped, optionally together with any fillers or binders, into balls, rings, trilobes and/or otherwise shaped extrudates.

The catalyst may be calcined, before and/or after shaping or extrusion.

In addition to the above, the process step i) and/or the method for preparing the catalyst may optionally comprise one or more additional steps wherein supplementary materials such as fillers and/or binders are added to the catalyst to prepare a catalyst-containing composition. Such fillers and/or binders may for example be added before or during any shaping or extrusion of any catalyst powder or catalyst.

Preferably the catalyst or catalyst powder prepared according to process step i) or the method according to the invention is shaped (preferably extudated), without the use of any fillers and/or binders, to prepare a shaped catalyst and subsequently the shaped catalyst is calcined to produce a shaped and calcined catalyst.

The catalyst obtained pursuant to the catalyst preparation method as described herein is believed to be also novel and inventive in itself and hence the present invention also provides a catalyst obtainable by a method as described above.

Such a catalyst may for example comprise or consist of a precipitated or co-precipitated catalyst comprising

- one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of catalyst; and
- a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof.

The catalyst preferably comprises in the range from equal to or more than 30wt% to equal to or less than 80wt%, more preferably in the range from equal to or more than 40wt% to

equal to or less than 65wt% of the one or more Group VIII metal(s), calculated as elemental metal based on the total weight of the catalyst. The one or more Group VIII metal(s) is/are preferably chosen from the Group consisting of Iron, Cobalt, nickel, Ruthenium, Rhodium, Palladium, Iridium and Platinum. Most preferably the Group VIII metal is nickel.

Preferably the catalyst in addition comprises one or more Group IB metals. The one or more Group IB metal(s) is/are preferably chosen from the Group consisting of copper, Silver and Gold. Most preferably the Group IB metal is copper. The one or more Group IB metal(s) may advantageously act as a promoter to the one or more Group VIII metal(s). Preferably the weight ratio of the one or more Group VIII metals to the one or more Group IB metals in the catalyst lies in the range from equal to or less than 10:1 to equal to or more than 2:1. Preferably the catalyst contains essentially no Group VIB metals, such as molybdenum or tungsten.

Preferences for the refractory oxide are as described herein above for the method of preparing the catalyst. Preferably the refractory oxide comprises at least a colloidal amorphous silica. More preferably the catalyst comprises a zirconia-silica mixture as a refractory oxide. The catalyst preferably comprises in the range from equal to or more than 5 wt% to equal to or less than 60 wt%, more preferably in the range from equal to or more than 7wt% to equal to or less than 40wt% of the one or more refractory oxides, based on the total weight of the catalyst.

The catalyst according to the invention may advantageously be used in hydroprocessing of a biomass-derived pyrolysis oil. In contrast to some of the prior art catalysts comprising molybdenum or tungsten the catalyst according to this invention advantageously does not require any activation by means of a sulfidation step. Hence, any

contacting with any sulfidation agent such as hydrogen sulfide is not needed. Advantageously the catalyst according to this invention may be activated by the mere reduction with hydrogen. This allows the catalyst to be activated by its mere use. That is, the catalyst may for example be activated in-situ by reduction with hydrogen during any hydroprocessing of a biomass-derived pyrolysis oil. The present invention therefore also provides the use of a catalyst as described above for the hydroprocessing of any biomass-derived pyrolysis oil. Preferences for such hydroprocessing are as described below

In process step ii) a feed containing the biomass-derived pyrolysis oil is contacted with hydrogen at a temperature in the range from 50°C to 350°C in the presence of the catalyst.

In step ii) the biomass-derived pyrolysis oil is converted to a converted biomass-derived pyrolysis oil. This step may also be referred to as a hydroprocessing step. The converted biomass-derived pyrolysis oil may suitably also be referred to as a hydroprocessed biomass-derived pyrolysis oil. Process step ii) may advantageously result in stabilizing and/or hydrodeoxygenation of the biomass-derived pyrolysis oil. This is explained in more detail below.

Process step ii) may comprise one or more hydroprocessing stages.

In one preferred embodiment, process step ii) comprises merely one stage, wherein a biomass-derived pyrolysis oil is stabilized by contacting it with hydrogen at a temperature in the range from 50°C to 250°C in the presence of the catalyst. This may allow one to prepare a so-called stabilized biomass-derived pyrolysis oil, which may be more suitable for transport and/or storage.

In another preferred embodiment, process step ii) comprises two or more sequential stages, wherein each

subsequent stage is carried out at a higher temperature than its preceding stage.

More preferably process step ii) comprises a first hydroprocessing stage comprising contacting a feed containing the biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 250°C in the presence of the catalyst to prepare a partially hydroprocessed biomass-derived pyrolysis oil; and a second hydroprocessing stage comprising contacting the partially hydroprocessed biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 150°C to 350°C in the presence of the catalyst to prepare a further hydroprocessed biomass-derived pyrolysis oil, where preferably the second hydroprocessing stage is carried out at a higher temperature than the first hydroprocessing stage. Such first hydroprocessing stage may advantageously allow the biomass-derived pyrolysis oil to be stabilized, whereas the second hydroprocessing stage may advantageously allow for a reduction of oxygen content of the biomass-derived pyrolysis oil.

Most preferably process step ii) comprises a stabilizing stage comprising contacting a feed containing the biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 250°C in the presence of the catalyst to prepare a stabilized biomass-derived pyrolysis oil; and a hydrodeoxygenation stage comprising contacting the stabilized biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 150°C to 350°C in the presence of the catalyst to prepare an at least partially hydrodeoxygenated biomass-derived pyrolysis oil, where preferably the hydrodeoxygenation stage is carried out at a higher temperature than the stabilizing stage.

The stabilized biomass-derived pyrolysis oil may conveniently be stored and/or transported before being

forwarded to the hydrodeoxygenation stage. Alternatively it is also possible for both the stabilizing stage as well as the hydrodeoxygenation stage to be carried out sequentially in time, in the same reactor or reactor(s).

Preferably the stabilized biomass-derived pyrolysis oil is at least partly hydrodeoxygenated in the hydrodeoxygenation stage. By at least partially hydrodeoxygenating is herein preferably understood that part or the whole of the oxygen-containing hydrocarbon compounds (also referred to as oxygenates) present in the biomass-derived pyrolysis oil are hydrodeoxygenated. That is, if a feed containing biomass-derived pyrolysis oil is partly hydrodeoxygenated some oxygenates will remain within the biomass-derived pyrolysis oil after the hydrodeoxygenation reaction. If a feed containing biomass-derived pyrolysis oil is wholly hydrodeoxygenated essentially no oxygenates will remain within the biomass-derived pyrolysis oil after the hydrodeoxygenation reaction.

Process step ii) may be carried out in any one or more reactor(s) known by the person skilled in the art to be suitable for such hydroprocessing reaction(s), for example a stirred autoclave, a reactor with one or more fixed catalyst beds, one or more reactors comprising a moving catalyst bed, one or more slurry reactors or one or more reactors comprising an ebullating catalyst bed or combinations of any one or more of such reactors.

Process step ii) is preferably carried out at a total pressure in the range from equal to or more than 0.1 MegaPascal (about 1 bar) to equal to or less than 40 MegaPascal (about 400 bar). More preferably process step ii) is carried out at a total pressure in the range from equal to or more than 0.2 MegaPascal (about 2 bar) to equal to or less than 12 MegaPascal (about 120 bar).

Preferably step ii) of the process according to the invention is carried out such, that the converted biomass-derived pyrolysis oil obtained in the process according to the invention may advantageously have an oxygen content (on a dry basis) in the range from 5 wt% to 30 wt%, based on the total weight of the converted biomass-derived pyrolysis oil. The oxygen content may suitably be determined by elemental analysis calculating the oxygen content as weight difference after determination and subtraction of carbon and hydrogen content.

In one embodiment the feed containing the biomass-derived pyrolysis oil used in step ii) of the process according to the invention may further comprise a petroleum-derived hydrocarbon composition. In such an embodiment, the petroleum-derived hydrocarbon composition may be co-processed alongside the biomass-derived pyrolysis oil. The presence of the petroleum-derived hydrocarbon composition may be advantageous as it may stabilize the biomass-derived pyrolysis oil during hydroprocessing in step ii).

When step ii) comprises a stabilizing stage and a hydrodeoxygenation stage, the petroleum derived hydrocarbon composition may be co-fed before the stabilizing stage; or after the stabilizing stage and before the hydrodeoxygenation stage.

The petroleum-derived hydrocarbon composition may comprise one or more hydrocarbon compounds and preferably comprises two or more hydrocarbon compounds. By a hydrocarbon compound is herein understood a compound containing hydrogen and carbon. Such hydrocarbon compound may further contain heteroatoms such as oxygen, sulphur and/or nitrogen. The petroleum-derived hydrocarbon composition may also comprise hydrocarbon compounds consisting of only hydrogen and carbon.

In a preferred embodiment, the C7-asphaltenes content of the petroleum-derived hydrocarbon composition may be equal to or more than 0.2 %wt (percent by weight), more preferably equal to or more than 0.7 %wt, still more preferably equal to or more than 2.0 %wt, even more preferably in the range of from 0.8 to 30 %wt, still even more preferably in the range of from 2.0 %wt to 30 %wt, based on the total weight of the petroleum-derived hydrocarbon composition. Most preferably the C7-asphaltenes content is in the range of from 0.9 to 15 %wt or in the range of from 2.0 to 15 %wt based on the total weight of the petroleum-derived hydrocarbon composition. As used herein, asphaltenes content or C7-asphaltenes content is as determined by IP143, using n-heptane as a solvent.

Suitable the petroleum-derived hydrocarbon composition has an initial atmospheric boiling point of equal to or more than 130 °C. Preferably, the initial atmospheric boiling point of the petroleum-derived hydrocarbon composition is equal to or more than 150 °C, more preferably equal to or more than 180 °C. In preferred embodiments, the atmospheric boiling point range of the petroleum-derived hydrocarbon composition may be from 220 °C to 800 °C, more preferably from 300 °C to 700 °C. In preferred embodiments, the hydrogen to carbon weight ratio (H/C ratio) of the petroleum-derived hydrocarbon composition may be at most 0.15 w/w, more preferably in the range of from 0.1 to 0.14 w/w, even more preferably in the range of from 0.11 to 0.13 w/w.

As used herein, boiling point is the atmospheric boiling point, unless indicated otherwise, with the atmospheric boiling point being the boiling point as determined at a pressure of 100 kiloPascal (i.e. 0.1 MegaPascal). As used herein, initial boiling point and boiling point range of the high boiling hydrocarbon mixtures are as determined by ASTM D2887. As used herein, pressure is absolute pressure. As used

herein, H/C ratio is as determined by ASTM D5291. As used herein, asphaltenes content or C7-asphaltenes content is as determined by IP143, using n-heptane as a solvent.

In a preferred embodiment the petroleum-derived hydrocarbon composition comprises shale oil, oil derived from oil sands, bitumen, a straight run (atmospheric) gas oil, a flashed distillate, a vacuum gas oil (VGO), a coker (heavy) gas oil, a diesel, a gasoline, a kerosene, a naphtha, a liquefied petroleum gas, an atmospheric residue ("long residue"), a vacuum residue ("short residue") and/or mixtures thereof. Most preferably the petroleum-derived hydrocarbon composition comprises an atmospheric residue or a vacuum residue. The petroleum-derived hydrocarbon composition may suitably also be derived from an unconventional oil resource such as oil shale or oil sands. For example the petroleum-derived hydrocarbon composition may comprise a pyrolysis oil derived from oil shale or oil sands.

In a preferred embodiment the petroleum-derived hydrocarbon composition may be mixed in a weight ratio of biomass-derived pyrolysis oil to petroleum-derived hydrocarbon composition (grams biomass-derived pyrolysis oil/grams petroleum-derived hydrocarbon composition) in the range from 1/99 to 30/70, more preferably in the range from 5/95 to 25/75, most preferably in the range from 10/90 to 20/80.

If so desired the biomass-derived pyrolysis oil obtained may suitably be dewatered before or after conversion in step ii) of the process according to the invention. Dewatering may for example be carried out by evaporating of the water; membrane separation; phase separation; absorption or adsorption of the water; and/or any combination thereof.

When the biomass-derived pyrolysis oil is dewatered before conversion in step ii) of the process according to the

invention, it may be convenient to carry out such dewatering in the presence of a petroleum derived hydrocarbon composition as described above. Further preferences for such a dewatering process may be found in WO2013064563, herein incorporated by reference.

The converted biomass-derived pyrolysis oil prepared in step ii) of the process according to the invention may be converted further via one or more hydrocarbon conversion processes into one or more fuel components and/or one or more chemical components.

The one or more hydrocarbon conversion processes may for example include a fluid catalytic cracking process, a hydrocracking process, a thermal cracking process, a hydro-isomerization process, a hydro-desulphurization process or any combination thereof.

In a preferred embodiment the reaction product or part thereof of any of the hydrocarbon conversion processes can subsequently be fractionated to produce one or more product fractions, for example a product fraction boiling in the gasoline range (for example from about 35°C to about 210°C); a product fraction boiling in the diesel range (for example from about 210°C to about 370°C); a product fraction boiling in the vacuum gas oil range (for example from about 370°C to about 540°C); and a short residue product fraction (for example boiling above 540°C).

Any one or more product fractions obtained by fractionation may or may not be further hydrotreated or hydroisomerized to obtain a hydrotreated or hydroisomerized product fraction.

The, optionally hydrotreated or hydroisomerized, product fraction(s) may be used as biofuel and/or biochemical component(s).

In a preferred embodiment the, optionally hydrotreated or hydroisomerized, one or more product fractions produced in the fractionation can be blended as a biofuel component and/or a biochemical component with one or more other components to produce a biofuel and/or a biochemical. By a biofuel respectively a biochemical is herein understood a fuel or a chemical that is at least party derived from a renewable energy source.

Examples of one or more other components with which the, optionally hydrotreated or hydroisomerized, one or more product fractions may be blended include anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components, but also conventional petroleum derived gasoline, diesel and/or kerosene fractions.

Herein below the invention is further illustrated by the following non-limiting examples:

Examples:

Example 1: Preparation of a co-precipitated catalyst with 50.5wt% nickel (Ni), 9.2wt% copper (Cu) and 24.1wt% silica (SiO_2)

To a mixture of 250 milliliter water and 62.5 grams ammonia (29wt%) in a covered beaker were added 26 grams basic copper carbonate and 200 grams nickel carbonate, and the resulting slurry was stirred overnight at room temperature (i.e. about 20°C). Next, 10 grams ammonia (29wt%) was added, and after 1 hour of further stirring, 126.8 grams silica sol (LEVASIL 300N, 30wt% SiO_2). The obtained mixture was heated to 80°C with stirring and without cover for 4-5 hour until a viscous mixture was formed. A nitrogen flow was carried over mixture while stirring overnight resulting in a superficially dry, caked powder which was dried in a stove at 120°C for 4 hour,

shaped by extrusion, and finally dried (2 hour at 120°C) and calcined (5°C/minute to 400°C, and 2 hour dwell)

Example 2: Preparation of a co-precipitated catalyst with 46.4wt% nickel (Ni), 5wt% copper (Cu) and 7.9wt% zirconia-silica (Zr-SiO_2)

To a mixture of 206 millilitre water and 52 grams ammonia (29wt%) in a covered beaker were added 52.6 grams zirconium carbonate, 13 grams basic copper carbonate and 200 grams nickel carbonate, and the resulting slurry was stirred overnight at room temperature (i.e. about 20°C). Next, 10 grams ammonia (29wt%) was added, and after 1 hour of further stirring, 117 grams silica sol (LEVASIL 300N, 30wt% SiO_2). The obtained mixture was heated to 80°C with stirring and without cover for 4-5 hour until a viscous mixture was formed. A nitrogen flow was carried over mixture while stirring overnight resulting in a superficially dry, caked powder which was dried in a stove at 120°C for 4 hour, shaped by extrusion, and finally dried (2 hour at 120°C) and calcined (5°C/minute to 400°C, and 2 hour dwell).

Example 3: larger scale production of catalysts of Example 1 and 2

Catalysts of Example 1 and 2 were produced on larger scale using the following recipe:

- Feeding soda/water/waterglas solution,
- Increasing temperature to 60°C,
- Precipitation by feeding of the metal nitrate solution (Ni/Cu),
- Aging at 60°C,
- Filtration, washing (sodium content < 0.3%),
- Drying, calcinations, grinding
- Extrusion or tablet forming,
- Reduction/passivation (temperature depends on the TPR measurement).

The compositions and surface areas of the catalysts obtained in Example 3 are:

Catalyst	Composition (wt%)								BET area (m^2/g)
	Ni	Cu	P	TiO_2	SiO_2	ZrO_2	La_2O_3	Ni:Cu	
A	10.3		2.31		82				52
B	6.3	0.8		87.6	3.4			7.8	160
C	52.6	9.3			21			5.7	243
D	49.5	5			19	9.3		9.9	265
E	18.4	2		74				9.2	30

CLAIMS

1. Process for converting a biomass-derived pyrolysis oil comprising the following steps:

i) preparing a catalyst, preferably containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, by a method including

- mixing one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; and a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture; and

- subjecting the metal-containing aqueous mixture to precipitation conditions; and

ii) contacting a feed containing the biomass-derived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 350°C in the presence of the catalyst.

2. The process according to claim 1, wherein the method in step i) further comprises mixing one or more Group IB metal components into the metal-containing aqueous mixture.

3. The process according to anyone of claims 1 and 2, wherein the waterborne refractory oxide component is an aqueous zirconia-silica dispersion.

4. The process according to anyone of claims 1 and 2, wherein the waterborne refractory oxide component is a waterborne colloidal amorphous silicasol.

5. The process according to anyone of claims 1 to 4, wherein the waterborne refractory oxide component comprises essentially no alkanols.

6. The process according to anyone of claims 1 to 5, wherein step ii) comprises two or more sequential stages, wherein each subsequent stage is carried out at a higher temperature than its preceding stage.

7. The process according to anyone of claims 1 to 6, wherein a converted biomass-derived pyrolysis oil is prepared, which converted biomass-derived pyrolysis oil is converted further via one or more hydrocarbon conversion processes into one or more fuel components and/or one or more chemical components.

8. A method for preparing a catalyst containing one or more Group VIII metals in an amount of equal to or more than 30wt%, based on the total weight of the catalyst, comprising the steps of

- mixing a sufficient amount of one or more Group VIII metal components; a waterborne refractory oxide component comprising a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof; a water-soluble base; in an aqueous solvent to prepare an metal-containing aqueous mixture;
- subjecting the metal-containing aqueous mixture to precipitation conditions to prepare a catalyst powder or catalyst; and
- optionally calcining the catalyst powder or catalyst to prepare a calcined catalyst.

9. The method according to claim 8, wherein such method further comprises mixing one or more Group IB metal components.

10. The method according to anyone of claims 8 and 9, wherein the waterborne refractory oxide component is a waterborne colloidal amorphous silicasol.

11. The method according to anyone of claims 8 and 9, wherein the waterborne refractory oxide component is an aqueous zirconia-silica dispersion.

12. The method according to anyone of claims 8 to 11, wherein the waterborne refractory oxide component comprises essentially no alkanols.

13. A catalyst obtainable or obtained by anyone of claims 8 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/068563

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/755 B01J37/02 C10G1/00 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)
B01J C10G

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	WO 2012/030215 A1 (BTG BIOMASS TECHNOLOGY GROUP B V [NL]; VENDERBOSCH ROBERTUS HENDRIKUS) 8 March 2012 (2012-03-08) cited in the application claims; examples -----	1-13
A	A.R. ARDIYANTI ET AL: "Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports", APPLIED CATALYSIS A: GENERAL, vol. 449, 1 December 2012 (2012-12-01), pages 121-130, XP055088423, ISSN: 0926-860X, DOI: 10.1016/j.apcata.2012.09.016 the whole document -----	1-13
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 November 2014	12/11/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schoofs, Bart

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/068563

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/064172 A1 (SHELL INT RESEARCH [NL]; HOGENDOORN JOHANNES ANTONIUS [NL]; KERSTEN SA) 3 June 2011 (2011-06-03) cited in the application the whole document	1-13
A	WO 2012/166402 A2 (UOP LLC [US]; TRAYNOR THOMAS [US]; BRANDVOLD TIMOTHY A [US]; ABRAHAMIA) 6 December 2012 (2012-12-06) the whole document	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/068563

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012030215 A1	08-03-2012	CA 2812976 A1	08-03-2012
		CN 103080275 A	01-05-2013
		EP 2611883 A1	10-07-2013
		US 2013219774 A1	29-08-2013
		WO 2012030215 A1	08-03-2012
WO 2011064172 A1	03-06-2011	CA 2780575 A1	03-06-2011
		CN 102630247 A	08-08-2012
		EP 2504412 A1	03-10-2012
		US 2011119994 A1	26-05-2011
		WO 2011064172 A1	03-06-2011
WO 2012166402 A2	06-12-2012	AU 2012262781 A1	10-10-2013
		CA 2829432 A1	06-12-2012
		CN 103502395 A	08-01-2014
		EP 2714850 A2	09-04-2014
		US 2012305836 A1	06-12-2012
		WO 2012166402 A2	06-12-2012