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

(57) **Abstract:** A process for converting a biomass-derived pyrolysis oil comprising contacting a feed containing the biomass-de-
rived pyrolysis oil with hydrogen at a temperature in the range from 50°C to 350°C in the presence of a catalyst, wherein the catalyst
comprises - equal to or more than 5wt% of one or more Group VIII metals, calculated on an elemental metal basis, based on the total
weight of the catalyst; - one or more Group V elements; and - a refractory oxide selected from the Group consisting of titania, zir-
conia, silica and mixtures thereof.



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

Technical field of the invention

5 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
10 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
15 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 CO₂ emissions that may help
meet global CO₂ emissions standards under the Kyoto protocol.

The fuels and/or chemicals from renewable biomass are
20 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
25 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
30 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
5 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
10 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
15 possibly comprise nickel, copper and/or alloys or mixtures thereof, such as Ni-Cu on a catalyst carrier. Examples of carriers mentioned include alumina, 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
20 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
25 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
30 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,

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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 $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 C_1 - C_6 -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
5 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 by means of impregnation.

Accordingly, the present invention provides a process for
10 converting a biomass-derived pyrolysis oil comprising 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 a catalyst, wherein the catalyst comprises

- 15 - equal to or more than 5wt% of one or more Group VIII metals, calculated on an elemental metal basis, based on the total weight of the catalyst;
- one or more Group V elements; and
- a refractory oxide selected from the Group consisting of
20 titania, zirconia, silica and mixtures thereof.

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
25 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
30 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.

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
5 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
10 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
15 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
20 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
25 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
30 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 preheat 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

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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 suitably 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 the process according to the invention a catalyst is used comprising

- equal to or more than 5wt% of one or more Group VIII metals, calculated on an elemental metal basis, based on the total weight of the catalyst;
- one or more Group V elements; and
- a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof.

Such a catalyst may conveniently be prepared by a method including

- preparing an acid metal-containing aqueous solution with a pH of equal to or less than 7.0, by mixing one or more Group VIII metal components and a water-soluble acid in an aqueous solvent;
- impregnating a refractory oxide, selected from the group consisting of titania, zirconia, silica and mixtures thereof, with the acid metal-containing aqueous solution;
- drying the impregnated refractory oxide to prepare a catalyst powder or catalyst; and
- optionally calcining the catalyst powder or catalyst to prepare a calcined catalyst.

One or more Group V elements, such as for example phosphorus, may be added at any step during this preparation method. For example such Group V element may be included via the acid metal-containing aqueous solution, or it may be included via the refractory oxide. That is, preferably the above method includes:

- preparing an acid metal-containing aqueous solution with a pH of equal to or less than 7.0, by mixing one or more Group VIII metal components, one or more phosphorus components and a water-soluble acid in an aqueous solvent; and/or
- impregnating a phosphorus-containing refractory oxide, selected from the group consisting of phosphorus-containing titania, phosphorus-containing zirconia, phosphorus-containing

silica and mixtures thereof, with the acid metal-containing aqueous solution.

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 method may include preparing an acid metal-containing aqueous solution with a pH of equal to or less than 7.0, by mixing one or more Group VIII metal components, one or more Group IB metal components and a water-soluble acid in an aqueous solvent.

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.

5 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 method is carried out in the essential absence of a Group VIB metal. Hence, preferably the above acid metal-containing
10 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
15 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
20 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
25 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 citrates, metal silicates, metal phosphates, metal acetates, metal hydroxides, metal nitrates, metal sulfates, metal formates and mixtures thereof. Metal
30 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 method comprises mixing a nickel nitrate.

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 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 citrate, copper formiate, copper sulfate, copper nitrate, copper acetate or a mixture of two or more thereof. Most preferably the above method comprises mixing a copper nitrate.

Preferably the Group V element is phosphorus. During mixing, phosphorus may be added as such or as a phosphorus compound. Examples of phosphorus compounds that may be included during mixing include phosphoric acid, ammonium phosphate, metal phosphates or organic phosphates.

The method as mentioned above further includes mixing of a water-soluble acid. The water-soluble acid may preferably be chosen from the group consisting of phosphoric acid, nitric acid and/or mixtures thereof.

The above described metal components, the water-soluble acid, and optionally the phosphorus or phosphorus compound are mixed in an aqueous solvent to prepare the acid metal-containing aqueous solution. Preferably the aqueous solvent in the method is water.

Suitably the water-soluble acid is mixed in the aqueous solvent in such an amount to ensure that an acid metal-containing aqueous solution with a pH of equal to or less than 7.0 is formed. Preferably the mol amount of water-soluble acid, such as for example nitric acid or phosphoric acid, 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 acid 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 acid 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.

More preferably an acid metal-containing aqueous solution with a pH of equal to or less than 6.5 or equal to or less than 6.0 is prepared. Possibly the pH of the prepared acid metal-containing aqueous solution may be equal to or more than 1.0, preferably equal to or more than 1.5.

The one or more metal component(s), the water-soluble acid and optionally the phosphorus or phosphorus compound are preferably completely dissolved in the aqueous solvent.

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, the method may include mixing at a temperature in the range from equal to or more than 15°C

to equal to or less than 100 °C, more preferably equal to or less than 80°C. More preferably mixing is carried out at ambient temperature, i.e. in the range from equal to more than about 18°C to equal to or less than 30°C. Most
5 preferably mixing is carried out at room temperature (about 20°C).

The above method includes impregnating a refractory oxide, selected from the group consisting of titania, zirconia, silica and mixtures thereof, with the acid metal-
10 containing aqueous solution to prepare an impregnated refractory oxide. In a preferred embodiment such refractory oxide is a refractory oxide, for example selected from the group consisting of phosphorus-containing titania, phosphorus-containing zirconia, phosphorus-containing silica
15 and mixtures thereof. Preferences as listed below for the refractory oxide conveniently also may apply to such phosphorus-containing refractory oxides.

More preferably the refractory oxide comprises one or more refractory oxide(s) selected from the group consisting
20 of titania, zirconia, silica, zirconia-silica and titania-silica. Titania and/or zirconia is/are especially preferred as it may render the catalyst more acid-resistant and/or corrosion-resistant.

Preferably the refractory oxide contains essentially no
25 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
30 to acidic and/or corrosive components that may be present in a bio-mass derived pyrolysis 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
5 hydroprocessing a biomass-derived pyrolysis oil.

The refractory oxide advantageously comprises essentially no alkanols.

The refractory oxide may be provided in any shape known to be suitable for the purpose of impregnation by the person
10 skilled in the art. Preferably the refractory oxide is shaped into a shaped refractory oxide before impregnation with the acid metal-containing aqueous solution. Hence preferably the method includes a step of shaping a refractory oxide selected from the group consisting of titania, zirconia, silica and
15 mixtures thereof, to form a shaped refractory oxide; and impregnating the shaped refractory oxide with the acid metal-containing aqueous solution to prepare an impregnated refractory oxide. The refractory oxide is preferably shaped by extrusion. A shaped refractory oxide formed by extrusion
20 may herein also be referred to as an extruded refractory oxide or refractory oxide extrudates. Preferably the refractory oxide comprises or consists of refractory oxide extrudates.

To form the shaped refractory oxide or refractory oxide
25 extrudates, the refractory oxide, which preferably is in powder form, is preferably mixed with water and, if desired or needed, a peptizing agent and/or a binder to form a mixture that can be shaped into an agglomerate. It is desirable for the mixture to be in the form of an extrudable
30 paste suitable for extrusion into extrudate particles. The extrudate particles (also referred herein to as refractory oxide extrudates) may have various shapes, including for example cylinders, balls, tubes and/or trilobes. The shaped

refractory oxide or refractory oxide extrudates may suitably be dried under standard drying conditions that 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
5 equal to or more than 80°C to equal to or less than 150°C. After drying the shaped refractory oxide or refractory oxide extrudates are preferably calcined under standard calcination conditions that can include a calcination temperature in the range of from equal to or more than 250°C to equal to or less
10 than 900°C, more preferably from equal to or more than 300°C to equal to or less than 800°C.

Preferably the, optionally shaped or extruded, refractory oxide has a BET surface area in the range from equal to or more than 10 m²/gram to equal to or less than 1000 m²/gram,
15 more preferably in the range from equal to or more than 50 m²/gram to equal to or less than 450 m²/gram.

The mean pore diameter in angstroms (Å) of any calcined refractory oxide extrudates preferably lies in the range of from equal to or more than 50 to equal to or less than 200,
20 more preferably from equal to or more than 70 to equal to or less than 150. The pore volume of any calcined refractory oxide extrudates preferably lies in the range of from equal to or more than 0.5 cc/gram to equal to or less than 1.1 cc/gram. The references herein to the pore size distribution
25 and pore volume of any calcined refractory oxide extrudates are to those properties as determined by mercury intrusion porosimetry, ASTM test method D4284.

After optional shaping, extruding, drying and/or calcining, the refractory oxide is impregnated with the acid
30 metal-containing aqueous solution to prepare an impregnated refractory oxide.

The impregnation may be carried by any impregnation method known to be suitable therefore by the person skilled

in the art. Preferably impregnation is carried out by means of an so-called incipient wetness or a so-called pore volume impregnation.

Preferably, the (optionally shaped, extruded, dried
5 and/or calcined) refractory oxide is impregnated in one or more impregnation steps with the acid metal-containing aqueous solution.

Preferably the concentration of the one or more metal components in the acid metal-containing aqueous solution is
10 selected so as to provide the desired metal content in the final catalyst, taking into consideration the pore volume of the refractory oxide into which the solution is to be impregnated.

Further, preferably the method for preparation of the
15 catalyst is 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 5 wt%, based on the total weight of the catalyst, more preferably in an amount in the range from equal to or more than 5wt% to equal to or less
20 than 80wt%, still more preferably in the range from equal to or more than 6wt% 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
25 amount of Group VIII metal component(s) required.

The method for preparing the catalyst may further include drying the impregnated refractory oxide to prepare a catalyst powder or catalyst.

During such drying, water and/or other liquids may be
30 removed from the impregnated refractory oxide by for example evaporation, spray drying and/or flash drying.

The impregnated refractory oxide may suitably be dried under standard drying conditions that 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 that can include a drying period of time in the range from equal
5 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 the catalyst powder or catalyst.

The catalyst or catalyst powder may optionally be
10 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
15 the range from equal to or more than 30 minutes to equal to or less than 6 hours.

In addition to the above, the method for preparing the catalyst may optionally comprise one or more additional steps wherein supplementary materials such as fillers and/or
20 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. It is further also possible to add any fillers and/or binders after calcining of the
25 catalyst or catalyst powder to prepare a catalyst-containing composition.

With the method as described above suitably a catalyst may be prepared that is advantageous in the process according to the invention.

30 Such a catalyst may for example comprise or consist of an impregnated catalyst comprising

- 20 -

- equal to or more than 5wt% of one or more Group VIII metals, calculated on an elemental metal basis, based on the total weight of the catalyst;

- one or more Group V elements, preferably phosphorus; and

5 - 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 5wt% to equal to or less than 80wt%, more preferably in the range from equal to or more than 6wt% to

10 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
15 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
20 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.

25 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 silica. More

30 preferably the catalyst comprises silica extrudates. The catalyst preferably comprises in the range from equal to or more than 5 wt% to equal to or less than 95 wt%, more preferably in the range from equal to or more than 20 wt% to

equal to or less than 94wt% 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 the process according to the invention 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 the process according to the invention, 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. The process according to the invention may advantageously result in stabilizing and/or hydrodeoxygenation of the biomass-derived pyrolysis oil. This is explained in more detail below.

The process according to the invention may comprise one or more hydroprocessing stages.

In one preferred embodiment, the process according to the invention comprises merely one stage, wherein a biomass-
5 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.

10 In another preferred embodiment, the process according to the invention comprises two or more sequential stages, wherein each subsequent stage is carried out at a higher temperature than its preceding stage.

More preferably the process according to the invention
15 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
20 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
25 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
30 reduction of oxygen content of the biomass-derived pyrolysis oil.

Most preferably the process according to the invention 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

5 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

10 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

15 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

20 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

25 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

30 hydrodeoxygenation reaction.

The process according to the invention 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
5 combinations of any one or more of such reactors.

The process according to the invention 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 the
10 process according to the invention 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 the process according to the invention is
15 carried out such, that the converted biomass-derived pyrolysis oil obtained in the process 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
20 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 the process according to the invention
25 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
30 stabilize the biomass-derived pyrolysis oil during hydroprocessing.

When the process 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
5 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
10 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
15 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
20 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, asphaltene content or C7-asphaltenes content is as determined by IP143, using n-heptane as a solvent.

25 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
30 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.

5 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
10 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.

15 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
20 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
25 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
30 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
5 may suitably be dewatered before or after conversion (i.e. before or after hydroprocessing). 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.

10 When the biomass-derived pyrolysis oil is dewatered before conversion in the hydroprocessing, 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
15 found in WO2013064563, herein incorporated by reference.

The converted biomass-derived pyrolysis oil prepared in 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
20 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
25 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
30 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 partly 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 $\text{Ni}_2\text{P}/\text{SiO}_2$ with 10wt% Ni

A clear solution with a molar ratio of moles nickel to moles phosphorus (Ni/P) of 2 mol/mol and a nickel concentration to reach 10wt% Ni on the final catalyst was prepared from $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, demineralized water and HNO_3 to adjust the pH to 2-3. The solution was impregnated onto

silica extrudates, dried for 2 hours at 120 °C, and calcined in air at 540 °C for 3 hours. The catalyst was subsequently reduced in flowing hydrogen, first heating with 5°C/minutes to 400°C and maintaining it there for 1 hour, and next
5 heating with 2°C/minutes to 500°C and maintaining it there for 3 hour. Subsequently, the product was cooled to ambient temperature under flowing hydrogen and was passivated for 1 hour under flowing 1vol% O₂/N₂.

CLAIMS

1. A process for converting a biomass-derived pyrolysis oil comprising contacting a feed containing the biomass-derived
5 pyrolysis oil with hydrogen at a temperature in the range from 50°C to 350°C in the presence of a catalyst, wherein the catalyst comprises
- equal to or more than 5wt% of one or more Group VIII metals, calculated on an elemental metal basis, based on the
10 total weight of the catalyst;
 - one or more Group V elements; and
 - a refractory oxide selected from the Group consisting of titania, zirconia, silica and mixtures thereof.
- 15 2. The process according to claim 1, wherein the Group V element is phosphorus.
3. The process according to claim 1 or 2, wherein the catalyst is prepared by a method including
- 20 - preparing an acid metal-containing aqueous solution with a pH of equal to or less than 7.0, by mixing one or more Group VIII metal components and a water-soluble acid in an aqueous solvent;
- impregnating a refractory oxide, selected from the group
25 consisting of titania, zirconia, silica and mixtures thereof, with the acid metal-containing aqueous solution;
 - drying the impregnated refractory oxide to prepare a catalyst powder or catalyst; and
 - optionally calcining the catalyst powder or catalyst to
30 prepare a calcined catalyst.
4. The process according to claim 3, wherein the method includes:

- preparing an acid metal-containing aqueous solution with a pH of equal to or less than 7.0, by mixing one or more Group VIII metal components, one or more phosphorus components and a water-soluble acid in an aqueous solvent; and/or

5 - impregnating a phosphorus-containing refractory oxide, selected from the group consisting of phosphorus-containing titania, phosphorus-containing zirconia, phosphorus-containing silica and mixtures thereof, with the acid metal-containing aqueous solution.

10

5. The process according to anyone of claims 1 to 4, wherein the water-soluble acid comprises phosphoric acid and/or nitric acid.

15 6. The process according to anyone of claims 1 to 5, wherein the refractory oxide comprises or consists of refractory oxide extrudates.

20 7. The process according to anyone of claims 1 to 6, wherein the refractory oxide comprises phosphorus.

8. The process according to anyone of claims 1 to 7, wherein the refractory oxide advantageously comprises essentially no alkanols.

25

9. The process according to anyone of claims 1 to 8, 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
30 more fuel components and/or one or more chemical components.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/068580

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 <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>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</td> <td>1-9</td> </tr> <tr> <td>A</td> <td> 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 ----- -/-- </td> <td>1-9</td> </tr> </tbody> </table>			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	1-9	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 ----- -/--	1-9
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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	1-9									
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 ----- -/--	1-9									
☒ 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		Date of mailing of the international search report									
6 November 2014		12/11/2014									
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 Schoofs, Bart									

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/068580

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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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 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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