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(54) PYROLYSIS OIL PURIFICATION

(57) The present invention provides a process for the purification of a crude pyrolysis oil, the process comprising the steps of a) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, b) hydrogenating the crude pyrolysis oil in the presence of an organic hydrogen donor and a supported Pd catalyst in a reactor to obtain a hydrogenated crude pyrolysis oil, the hydrogenated crude pyrolysis oil comprising the hydrocarbons and hydrogenated impurities, wherein the organic hydrogen donor comprises a compound containing a formate group.

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Description

[0001] The present invention relates to a process for purifying a crude pyrolysis oil, such as a crude pyrolysis oil originating at least partially from the pyrolysis of plastic waste, to obtain a purified pyrolysis oil. The invention is further directed to a method for producing a cracker feedstock, particularly a steam cracker feedstock, comprising the purified pyrolysis oil.

[0002] Pyrolysis is an important technique for chemically recycling e.g. plastic waste. The pyrolysis is generally a thermal degradation of feedstock in an inert atmosphere and yields value added products such as pyrolysis gas, liquid pyrolysis oil and char (residue), wherein pyrolysis oil is the major product.

[0003] Dependent on the type and quality of feedstock used for the preparation of pyrolysis oil, a broad range of impurities can typically be found in the pyrolysis oil. Typical feedstock for the preparation of pyrolysis oil is plastic waste, but also biomass may be used. Pyrolysis oil produced from plastic waste contains more and other contaminants than fossil feedstock whereas plastics are used for a wide variety of applications and therefore contains a wide variety of different additives. Such impurities found in the pyrolysis oil are for example inorganic compounds, such as metal-containing compounds and complexes, and organic compounds containing heteroatoms, such as nitrogen, oxygen, sulfur, silicon, and halogens, particularly chlorine. The pyrolysis oil also generally has a much higher content of unsaturated hydrocarbon compounds, such as olefins, particularly diolefins, than fossil feedstock. Low concentrations of these impurities, particularly chlorine-containing compounds and diolefins, is for instance of high importance for avoiding problems during storage and processing of the pyrolysis oil, including for use as (steam) cracker feedstock in base chemical production such as ethylene and propylene. Otherwise, the impurities can lead to problems in the further processing or use of the pyrolysis oil, such as sedimentation and gum formation, deactivation/poisoning of catalysts, formation of deposits and corrosion of lines and reactors. Steam cracking of untreated plastic waste pyrolysis oils is for example discussed by Kusenberg et al, "Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation", Waste Management, vol 141, pages 104-114 (2022), where the authors conclude that purification of the pyrolysis oil prior to steam cracking is a prerequisite to avoid operational issues resulting from increased coke formation and fouling.

[0004] In accordance with Kusenberg et al, "Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oil as steam cracker feedstocks: To decontaminate or not to decontaminate?", Waste Management, vol 148, pages 83-115 (2022), a typical steam cracker feedstock for base chemical production may include not more than 3 ppm chlorine, not more than 100 ppm nitrogen, and not more than 100 ppm oxygen.

[0005] For being able to meet the high purity standards that are required for the use of these pyrolysis oils, for example as steam cracker feedstock for base chemical production, typically dilution with fossil naphtha and/or upgrading of the pyrolysis oil is required. Purification of crude pyrolysis oil can for example be done by a costly hydrotreatment, treatment of the oil with adsorbents, reduction agents or simply by a washing step, i.e., by extracting the impurities with a solvent that is immiscible with the oil such as water or alcohols.

[0006] Generally, pyrolysis oil at least partially originating from the pyrolysis of plastic waste requires dehalogenation (particularly dechlorination), denitrogenation and desulfurization to reduce the concentrations of these impurities and allow use in cracker feedstock, such steam cracker feedstock.

[0007] It is an object of the present invention to provide a process for purifying a crude pyrolysis oil originating from the pyrolysis of a feedstock, in particular purifying a crude pyrolysis oil having various impurities.

[0008] It is a further object of the present invention to provide a process for purifying a crude pyrolysis oil originating from the pyrolysis of a feedstock, particularly crude pyrolysis oil at least partially originating from the pyrolysis of plastic waste, which process reduces the content of polar and non-polar impurities from the crude pyrolysis oil.

[0009] It is still a further object of the present invention to provide a process for purifying a crude pyrolysis oil originating from the pyrolysis of a feedstock having an improved removal efficiency for impurities present in the crude pyrolysis oil.

[0010] It is a further object of the present invention to provide a purified pyrolysis oil, which meets the standards for use as cracker feedstock (alone or diluted with fossil naphtha) in base chemical production. As used herein, "cracker feedstock" refers to a feedstock suitable for steam cracking, hydrocracking or catalytic cracking. More particularly, an object of the invention is to obtain a cracker feedstock that meets the requirements for use as feedstock (alone or diluted with fossil naphtha) in a steam cracker.

[0011] To solve all the above objects, the present invention provides in a first aspect a process for purifying a crude pyrolysis oil according to claim 1.

[0012] In a first aspect, a process for the purification of a crude pyrolysis oil is provided, the process comprising the steps of

a) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil preferably at least partially originating from pyrolysis of plastic waste,

b) hydrogenating the crude pyrolysis oil in the presence of an organic hydrogen donor and a supported Pd catalyst in a reactor to obtain a hydrogenated crude pyrolysis oil, the hydrogenated crude pyrolysis oil comprising the hydrocarbons and hydrogenated impurities,

wherein the organic hydrogen donor comprises a compound containing a formate group.

[0013] Particularly, the present invention provides a process for purifying a crude pyrolysis oil by dehalogenation (particularly dechlorination) and denitrogenation of the crude pyrolysis oil, thereby reducing the concentrations of halogens and nitrogen in the crude pyrolysis oil.

[0014] More particularly, the present invention provides a process for purifying a crude pyrolysis oil by dehalogenation (particularly dechlorination), denitrogenation and desulfurization of the crude pyrolysis oil, thereby reducing the concentrations of halogens, nitrogen and sulfur in the crude pyrolysis oil.

[0015] The present invention provides a purified pyrolysis oil having reduced nitrogen and halogen content in relation to the crude pyrolysis oil, particularly a purified pyrolysis oil having reduced nitrogen, halogen, and sulfur contents in relation to the crude pyrolysis oil. A further advantage of the present invention is that the provided purified pyrolysis oil may have reduced content of olefins in relation to the crude pyrolysis oil.

[0016] It is a still further advantage of the present invention that the removal of the different impurities provides a positive effect on the lifetime of catalysts, reduced formation of deposits and reduced corrosion in the down-stream processing of the oil, such as distillation and steam cracking of the oil.

[0017] In step a) of the process, a crude pyrolysis oil is provided. The crude pyrolysis oil comprises hydrocarbons and impurities. Preferably, the crude pyrolysis oil at least partially originates from pyrolysis of plastic waste. More particularly, the crude pyrolysis oil is a crude plastic waste pyrolysis oil.

[0018] As used herein, the term "olefins" refers to unsaturated open-chain (linear) hydrocarbons.

[0019] As used herein, the term "hydrocarbon" refers to organic compounds consisting of carbon and hydrogen.

[0020] Preferably, the impurities comprise inorganic compounds, the inorganic compounds preferably comprising metals or metal ions, the metals preferably being heavy metals and the metal ions being preferably heavy metal ions, and/or organic compounds containing heteroatoms, the heteroatoms preferably being oxygen, nitrogen, sulfur, silicon and/or a halogen.

[0021] In the present invention, the term "pyrolysis" relates to a thermal decomposition or degradation of end of life plastics under inert conditions and results in a gas, a liquid and a solid char fraction. During the pyrolysis, the plastics are converted into a great variety of chemicals including gases such as H_2, C1 -C4-alkanes, C2-C4-alkenes, acetylene, propyne, 1-butyne, pyrolysis oil having a boiling temperature of 25 to 500°C and char.

[0022] The term "pyrolysis" includes slow pyrolysis, fast pyrolysis, flash catalysis and catalytic pyrolysis. These types of pyrolysis differ in the process temperature, heating rate, residence time, feed particle size, etc. resulting in different product quality. Sharuddin et al, "A review of pyrolysis of plastic waste", Energy Conversion and Management, vol 115, pages 308-326 (May 2016) describes typical process conditions for pyrolysis of plastic waste.

[0023] In the context of the present invention, the term "crude pyrolysis oil" is understood to mean any oil originating from the pyrolysis of a feedstock, preferably an oil at least partially originating from the pyrolysis of plastic waste, including (i) any crude pyrolysis oil fully originating from the pyrolysis of plastic waste (herein referred to as "crude plastic waste pyrolysis oil"), (ii) any crude pyrolysis oil originating from the pyrolysis of a mixture of plastic waste and biomass, or (iii) any crude pyrolysis oil comprising a mixture of crude plastic waste pyrolysis oil and crude biomass pyrolysis oil.

[0024] As used herein, "crude plastic waste pyrolysis oil" means pyrolysis oil derived from pyrolysis of a feedstock consisting of plastic waste.

[0025] As used herein, "crude biomass pyrolysis oil" means pyrolysis oil derived from pyrolysis of a feedstock consisting of biomass.

[0026] The crude pyrolysis oil typically is a liquid at 15 °C. The term "liquid at 15°C" means that the crude pyrolysis oil has a dynamic viscosity in the range of from 0.1 to 100 mPa • s as determined by ASTM D7042, for example using Viscometer SVM3000.

[0027] Depending on the waste plastic material subjected to the pyrolysis, the crude pyrolysis oil may have varying contents of sulfur, nitrogen, halogen, oxygen and, if present, heavy metal. There are very many different qualities of crude pyrolysis oil derived from varying compositions of plastic waste which means that the content and types of impurities may vary significantly.

[0028] The crude pyrolysis oil generally contains saturated hydrocarbon compounds, unsaturated hydrocarbon compounds (olefins) and organic or inorganic compounds comprising at least one heteroatom selected from oxygen, sulfur, nitrogen and halogens, particularly organic or inorganic compounds comprising two or more heteroatoms selected from oxygen, sulfur, nitrogen and halogens. The crude pyrolysis oil typically contains sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds and halogen-containing compounds.

[0029] In a specific embodiment, the crude pyrolysis oil is a nitrogen-containing and halogen-containing crude plastic waste pyrolysis oil, particularly a nitrogen-containing, halogen-containing and sulfur-containing crude plastic waste pyrolysis oil, and more particularly a nitrogen-containing, halogen-containing, oxygen-containing and sulfur-containing crude plastic waste pyrolysis oil.

[0030] In one embodiment, the crude pyrolysis oil has a sulfur content of 10 mg/l or more, such as 50 mg/l or more, or 100 mg/l or more; or 500 mg/l or more, relative to the total volume of the crude pyrolysis oil. In another embodiment, the crude pyrolysis oil has a sulfur content of 100 to 5000 mg/l, often 500 to 4000 mg/l, relative to the total volume of the crude pyrolysis oil.

[0031] In another embodiment, the crude pyrolysis oil has a sulfur content of at least 10 mg/l but not more than 100 mg/ml, such as within the range of from 10 mg/ml to 50 mg/ml, or from 10 mg/ml to 30 mg/ml, relative to the total volume of the crude pyrolysis oil.

[0032] In one embodiment, the crude pyrolysis oil has a nitrogen content of 50 mg/l or more, such as 100 mg/l or more; or 500 mg/l or more; or 2 000 mg/l or more, relative to the total volume of the crude pyrolysis oil. In another embodiment, the crude pyrolysis oil has a nitrogen content of 800 to 4 000 mg/l, often 900 to 3 000 mg/l, relative to the total volume of the crude pyrolysis oil.

[0033] In one embodiment, the crude pyrolysis oil has a halogen content of 10 mg/l or more, such as 20 mg/ml or more; 80 mg/l or more; or 120 mg/l or more; or 400 mg/l or more; or 600 mg/l or more, relative to the total volume of the crude pyrolysis oil. In another embodiment, the crude pyrolysis oil has a halogen content of 100 to 1 000 mg/l, often 120 to 900 mg/l, relative to the total volume of the crude pyrolysis oil.

[0034] When the density of the pyrolysis oil is about 1 g/ml (1 000 kg/m^3), the above concentrations given in mg/l equals the same concentrations in ppm, i.e. 1 mg/l then equals 1 ppm.

[0035] Organofluorine, organochlorine, organobromine and/or organoiodine compounds typically are the source for the halogen content in the crude pyrolysis oil. Specifically, the halogen content is a bromine and chlorine content to 90% or more, such as 95% or more or even 100%. More specifically, the halogen content is to 90% or more, such as 95% or more or even 100% a chlorine content. Thus, the crude pyrolysis oil may have a chlorine content of 5 mg/ml or more, 10 mg/ml or more, such as within the range of from 10 to 30 mg/ml.

[0036] In one embodiment, the crude pyrolysis oil has an oxygen content of 40 mg/l or more, such as 80 mg/l or more; or 120 mg/l or more; or 400 mg/l or more; or 600 mg/l or more, relative to the total volume of the crude pyrolysis oil. In another embodiment, the crude pyrolysis oil has an oxygen content of 100 to 5 000 mg/l, often 120 to 2 000 mg/l, relative to the total volume of the crude pyrolysis oil.

[0037] In case that the crude pyrolysis oil also has a heavy metal content, the heavy metal content is at least 1 mg/l, relative to the total volume of the crude pyrolysis oil. In one embodiment, the crude pyrolysis oil has a heavy content of 1 mg/l to 3 mg/l, or 1 to 4 mg/l relative to the total volume of the crude pyrolysis oil.

[0038] As used herein, the term "heavy metal" refers to a metal or metalloid having a density >4.51 g/cm^3 (at 20°C). Examples of heavy metals include arsenic, antimony, bismuth, selenium, tin, cadmium, chromium, copper, mercury, nickel and lead.

[0039] Two or more of the above described embodiments of the crude pyrolysis oil as regards its sulfur, nitrogen, halogen, oxygen, and heavy metal content can be combined in any manner. For example, the crude pyrolysis oil may preferably have a nitrogen content as described above, a halogen content as described above and a sulfur content as described above.

[0040] In an embodiment, the crude pyrolysis oil has a sulfur content of 10 mg/l or more, a nitrogen content of 50 mg/l or more, such as 200 mg/l or more, and a chlorine content of 10 mg/l or more. More particularly, the crude pyrolysis oil has a sulfur content within the range of from 10 mg/ml to 50 mg/ml (for example, within the range of from 10 mg/ml to 30 mg/ml), a nitrogen content of 200 mg/l or more, and a chlorine content of 10 mg/l or more.

[0041] In another embodiment, the crude pyrolysis oil has an oxygen content of 40 mg/l or more, a sulfur content of 10 mg/l or more, a nitrogen content of 50 mg/l or more, and a chlorine content of 10 mg/l or more.

[0042] In still another embodiment, the crude pyrolysis oil has an oxygen content of 40 mg/l or more, a sulfur content of 10 mg/l or more, a nitrogen content of 50 mg/l or more, a chlorine content of 10 mg/l or more and an olefin content of 30 wt.% or more based on the total weight of the crude pyrolysis oil.

[0043] The process according to the invention may provide purified pyrolysis oil having the nitrogen content reduced by more than 20%, such as by more than 30%, particularly within the range of from 30% to 50%, relative to the nitrogen content of the crude pyrolysis oil.

[0044] The process according to the invention may provide purified pyrolysis oil having the chlorine content reduced by more than 20%, such as by more than 30%, particularly within the range of from 30% to 50%, relative to the chlorine content of the crude pyrolysis oil.

[0045] The process according to the invention may provide purified pyrolysis oil having the sulfur content reduced by more than 20%, relative to the sulfur content of the crude pyrolysis oil.

[0046] Preferably, the pyrolysis oil comprises paraffins, preferably n-paraffins and/or i-paraffins, olefins, naphthenes and/or aromatics. The crude pyrolysis oil is further characterized by a boiling point in the range of from 30 to 600 °C as determined by ASTM D2887, and/or

a dynamic viscosity in the range of from 0.1 to 100 mPa • s as determined by ASTM D7042, for example using Viscometer SVM3000, and/or

a paraffin content in the range of from 5 to 80 wt.%, or 15 to 70 wt.%, or 20 to 65 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

a n-paraffin content in the range of from 20 to 80 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

an i-paraffin content in the range of from 2 to 80 wt.%, or 5 to 60 wt.%, or 10 to 45 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

an olefin content in the range of from 0 to 70 wt.%, or 15 to 65 wt.%, or 20 to 60 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

a naphthene content in the range of from 0 to 50 wt.%, or 5 to 45 wt.%, or 10 to 40 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

an aromatic content in the range of from 0 to 50 wt.%, or 5 to 30 wt.%, or 10 to 25 wt.%, based on the total weight of the crude pyrolysis oil, as determined by GC×GC-FID/MS or GC-MS and GC-FID, and/or

a density in the range from 600 kg/m^3 to 1 200 kg/m^3, at 15°C and 1013 mbar, as determined according to DIN EN ISO 12185.

[0047] The above further characteristics or properties of the crude pyrolysis oil originating from plastic waste can be combined with each other in any way or they can be combined in any way with other characteristics or properties of the crude pyrolysis oil originating from plastic waste disclosed herein.

[0048] The feedstock for the pyrolysis is typically plastic waste or plastic waste combined with biomass.

[0049] As used herein, the term "plastic waste" refers to any plastic material discarded after use, i.e. the plastic material has reached the end of its useful life. The plastic waste can be pure polymeric plastic waste, mixed plastic waste or film waste, including soiling, adhesive materials, fillers, residues etc. The plastic waste has a nitrogen content, sulfur content, halogen content, oxygen content, silicone and optionally also a heavy metal content. The plastic waste can originate from any plastic material containing source. Accordingly, the term "plastic waste" includes industrial and domestic plastic waste including used tires and agricultural and horticultural plastic material. The term "plastic waste" also includes used petroleum-based hydrocarbon material such as used motor oil, machine oil, greases, waxes, etc.

[0050] Typically, plastic waste is a mixture of different plastic material, including hydrocarbon plastics, e.g., polyolefins such as polyethylene (HDPE, LDPE) and polypropylene, polystyrene and copolymers thereof, etc., and polymers composed of carbon, hydrogen and other elements such as chlorine, fluorine, oxygen, nitrogen, sulfur, silicone, etc., for example chlorinated plastics, such as polyvinylchloride (PVC), polyvinylidene chloride (PVDC), etc., nitrogen-containing plastics, such as polyamides (PA), polyurethanes (PU), acrylonitrile butadiene styrene (ABS), etc., oxygen-containing plastics such as polyesters, e.g. polyethylene terephthalate (PET), polycarbonate (PC), etc.), silicones and/or sulfur bridges crosslinked rubbers. PET plastic waste is often sorted out before pyrolysis, since PET has a profitable resale value. Accordingly, the plastic waste to be pyrolyzed often contains less than about 10 wt.%, preferably less than about 5 wt.% and most preferably substantially no PET based on the dry weight of the plastic material.

[0051] As used herein, "biomass" refers to any plant or animal based material such as wood residues, lignocellulosic biomass, paper, cardboard, energy crops, agricultural residues, and food waste from industry, households and farms.

[0052] Haoxi et al, "A comprehensive Characterization of Pyrolysis Oil from Softwood Barks", Polymers 2019, 11, 1387, provides an example of crude pyrolysis oil derived from pyrolysis of biomass.

[0053] In step b) of the process, the crude pyrolysis oil is in-situ hydrogenated in the presence of an organic hydrogen donor and a supported Pd catalyst in a reactor to obtain a hydrogenated crude pyrolysis oil. The obtained hydrogenated crude pyrolysis oil comprises the hydrocarbons and hydrogenated impurities.

[0054] The organic hydrogen donor comprises a compound containing a formate group. Preferably, the organic hydrogen donor comprises a compound containing a formate group and a metal selected from Group 1 and Group 2, preferably the organic hydrogen donor comprises or consists of sodium formate, potassium formate, calcium formate, magnesium formate or a mixture thereof. More preferably, the organic hydrogen donor is sodium formate.

[0055] Preferably, in step b) the organic hydrogen donor is present in an amount of from 15 mmol/l to 3 000 mmol/l, more preferably 70 mmol/l to 1 500 mmol/l, based on the total volume of the crude pyrolysis oil.

[0056] Preferably, the organic hydrogen donor is present as a solid or dissolved in a polar solvent.

[0057] Preferably, the polar solvent comprises water, an alkanol or any mixture thereof. The alkanol is preferably methanol or ethanol or a mixture thereof. Most preferably, the polar solvent comprises water.

[0058] Preferably, in step b) the temperature in the reactor is from 20 to 350 °C, more preferably from 50 to 200 °C, more preferably from 70 to 150 °C, and most preferably from 90 to 125 °C.

[0059] Step b) of the process is conducted in the presence of a supported Pd catalyst. The amounts of supported Pd catalyst depends on whether the organic hydrogen donor is present as a solid or present in a polar solvent.

[0060] Preferably, in step b) the supported Pd catalyst is present either in an amount of from 0.1 to 10 g/l, more preferably 0.2 to 5 g/l, preferably 0.3 to 1 g/l, preferably 0.4 to 0.6 g/l, based on the total volume of the crude pyrolysis oil in case the organic hydrogen donor is present as a solid, or

in an amount of from 1 to 50 g/l, more preferably 2 to 25 g/l, preferably 5 to 15 g/l, preferably 8 to 12 g/l, based on the total volume of the crude pyrolysis oil in case the organic hydrogen donor is present in a polar solvent.

[0061] Preferably, the supported Pd catalyst is a carbon supported Pd catalyst, the Pd present in an amount of preferably 1 to 15 wt.%, more preferably 5 to 12 wt.%, based on the total weight of the carbon supported Pd catalyst.

[0062] Preferably, the process further comprises the step

c) washing the hydrogenated crude pyrolysis oil with a polar washing solvent to obtain a purified pyrolysis oil phase and a polar washing solvent phase, the polar washing solvent phase comprising at least a part of the hydrogenated impurities.

[0063] It is preferred that washing step c) is performed in case the organic hydrogen donor is present as a solid. In such a case, reacting products and/or impurities are removed from the hydrogenated crude pyrolysis oil via the washing step c).

[0064] Step c) can take place either in the reactor of hydrogenating step b) or in a second reactor other than the reactor used in the hydrogenating step b). In the latter, the hydrogenated crude pyrolysis oil obtained in step b) is transferred to the second reactor. The reactor of step b) and, if present, the second reactor can be any reactor in the art, such as a vessel, suitable for carrying out step b) and step c), respectively.

[0065] Preferably, in step c) the polar washing solvent comprises water, more preferably, the polar washing solvent comprises water and further comprises an acid or a base.

[0066] Preferably, the polar washing solvent comprises water and an acid or a base, wherein the acid is selected from sulphuric acid, phosphoric acid, hydrochloric acid and any mixture thereof, or

wherein the base comprises a hydroxide or alkoxide of a metal of Group 1 or Group 2, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, sodium alkoxide, potassium alkoxide, calcium alkoxide, magnesium alkoxide or a mixture thereof.

[0067] As disclosed above, the organic hydrogen donor may preferably be dissolved in a polar solvent in step b). Preferably, the polar solvent of step b) is used as the polar washing solvent in step c). In case the polar solvent of step b) is used as the polar washing solvent in step c), then the polar washing solvent in step c) preferably comprises water, an alkanol or any mixture thereof. The alkanol is preferably methanol or ethanol or a mixture thereof.

[0068] Preferably, in step c) the temperature is from 10 to 350 °C, more preferably from 15 to 150 °C, and most preferably from 20 to 30 °C.

[0069] Preferably, the process further comprises the step of

c1) separating the polar washing solvent phase from the purified pyrolysis oil phase of step c) to obtain a purified pyrolysis oil, wherein step c1) takes place after step c).

[0070] Separation may be performed by, for example, centrifugation, settling followed by decanting of polar washing solvent phase from the purified pyrolysis oil phase or phase separation filtration.

[0071] Optionally, the process further comprises adding an acid or a base to the crude pyrolysis oil prior to step b) and/or adding an acid or a base to the hydrogenated pyrolysis oil prior to step c). The acid preferably comprises sulphuric acid, phosphoric acid, hydrochloric acid or any mixture thereof, and the base preferably comprises a hydroxide or alkoxide of a metal of Group 1 or Group 2, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, sodium alkoxide, potassium alkoxide, calcium alkoxide, magnesium alkoxide or a mixture thereof.

[0072] For further reducing the concentration of impurities and/or hydrogenated impurities from the crude pyrolysis oil and/or hydrogenated crude pyrolysis oil, an adsorption step may be performed before or after the in-situ hydrogenation and/or washing step to further purify the crude pyrolysis oil. Preferably, the process further comprises the step of

d) adsorbing impurities and/or hydrogenated impurities from the crude pyrolysis oil and/or hydrogenated crude pyrolysis oil in the presence of an adsorption means, wherein step d) takes place either before step b) or after step b) or before step c) or after step c).

[0073] Preferably, the adsorption means comprises, or consists of, activated carbon. Alternatively or in addition, the adsorption means can be other commercially available adsorption agents.

[0074] Step d) can be carried out in the reactor of step b) or in the reactor of step c) or in a reactor other than the reactor of step b) or of step c).

[0075] A further option can also be to include an adsorbing step for purification completely or partly in the pyrolysis process for obtaining the crude pyrolysis oil of step a), allowing to utilize the high temperature used during pyrolysis. As discussed above, the crude pyrolysis oil preferably originates at least partially from the pyrolysis of plastic waste. Preferably, the process comprises the step of
e) adsorbing impurities from the crude pyrolysis oil in the presence of an adsorption means, wherein step e) takes place before step a).

[0076] Preferably, the adsorption means comprises, or consists of, activated carbon. Alternatively or in addition, the adsorption means can be other commercially available adsorption agents.

[0077] The invention further provides a method for producing a cracker feedstock comprising the step of blending 1 to 100 wt.% of a purified pyrolysis oil based on the total weight of the cracker feedstock and 99 to 0 wt.% of fossil naphtha based on the total weight of the cracker feedstock, wherein the purified pyrolysis oil is obtained by the process for the purification of a crude pyrolysis oil according to the invention.

[0078] All preferred embodiments of the process for the purification of a crude pyrolysis oil according to the invention are also preferred embodiments of the method for producing a cracker feedstock, if applicable.

[0079] Preferably, the cracker feedstock is a steam cracker feedstock.

[0080] In an embodiment, the cracker feedstock, or the steam cracker feedstock, comprises at least 5 wt.% of the purified pyrolysis oil and not more than 95 wt.% of fossil naphtha based on the total weight of the cracker feedstock, preferably the cracker feedstock, or the steam cracker feedstock, comprises at least 10 wt.% of the purified pyrolysis oil and not more than 90 wt.% of fossil naphtha based on the total weight of the cracker feedstock, more preferably the cracker feedstock, or the steam cracker feedstock, comprises at least 30 wt.% of the purified pyrolysis oil based on the total weight of the cracker feedstock and not more than 70 wt.% of fossil naphtha based on the total weight of the cracker feedstock, particularly the cracker feedstock, or the steam cracker feedstock, comprises at least 40 wt.% of the purified pyrolysis oil based on the total weight of the cracker feedstock and not more than 60 wt.% of fossil naphtha based on the total weight of the cracker feedstock.

[0081] The invention further provides the use of the purified pyrolysis oil as a cracker feedstock. Preferably, the cracker feedstock is a steam cracker feedstock.

[0082] The invention is further directed to the use an organic hydrogen donor comprising a compound containing a formate group and a supported Pd catalyst for removing impurities from a crude pyrolysis oil.

[0083] All preferred embodiments of the process for the purification of a crude pyrolysis oil according to the invention are also preferred embodiments of the use of an oxidation agent, if applicable.

[0084] Preferably, the impurities comprise inorganic compounds, the inorganic compounds preferably comprising metals or metal ions, the metals preferably being heavy metals and the metal ions being preferably heavy metal ions, and/or organic compounds containing heteroatoms, the heteroatoms preferably being oxygen, nitrogen, sulfur, silicon and/or a halogen.

[0085] The invention is further described and illustrated below by means of non-limiting examples.

Experimental Part

Analytical methods

Chlorine content in pyrolysis oil

[0086] Instrument: 2019.010 (combustion) and 2019.080 (fraction collector) Xprep C-IC from TE Instruments with Archie injection and liquid boat, 19250020 ECO IC from Metrohm

[0087] Testing method: ASTM D7359 - 18 (Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and Their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC))

[0088] Each pyrolysis oil sample was measured in triplicate.

Nitrogen content in pyrolysis oil

Instrument: Xplorer-NS from TE Instruments with Archie injection and liquid boat

Testing methods:

[0089] ASTM D5762 - 18a (Standard Test Method for Nitrogen in Liquid Hydrocarbons, Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence) ASTM D4629 - 17 (Standard Test Method for Trace Nitrogen in Liquid Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection)

[0090] ASTM D4629 was used for analyzing pyrolysis oil with a nitrogen concentration below 1 000 ppm, whereas ASTM D5762 was used for analyzing pyrolysis oil with a nitrogen concentration above 1 000 ppm.
[0091] Each sample was measured in triplicate.

Sulfur content in pyrolysis oil

Instrument: Xplorer-NS from TE Instruments with Archie injection and liquid boat

[0092] Testing method: ASTM D5453 - 19a (Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence)
[0093] Each sample was measured in triplicate.

Materials

[0094] Commercially available batches of crude pyrolysis oil (Recycled Carbon Fuel) from Renasci Oostende Recycling NV was used in the following examples. The crude pyrolysis oil is characterized by a boiling point from 50°C to 482.5°C. Properties of the different batches of the crude pyrolysis oil for the examples are given in Table 1 below.
[0095] The Pd/C hydrogenation catalyst (palladium on activated carbon, 10 % Pd, unreduced, dry) was obtained from Acros Organics. Sodium formate (≥99%, AnalaR NORMAPUR®) was obtained from VWR Chemicals. A saturated aqueous solution of sodium formate (about 98 g of sodium formate in 100 ml of water) was prepared by adding 120 g of sodium formate to 100 ml of demineralized water and mixing this suspension at a temperature of 20°C for 10 minutes, followed by removing of undissolved sodium formate by filtration.

Examples

Example 1

[0096] In a 50 ml glass reactor equipped with magnetic stirring 2 ml of a saturated solution of sodium formate in water and 0.1 g of the Pd/C hydrogenation catalyst were added to 10 ml of pyrolysis oil. The reactions mixture was heated to 95°C and mixing at this temperature was continued for 2 hours. After cooling to room temperature, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm. Finally, Pd/C hydrogenation catalyst residues were removed from the pyrolysis oil by filtration (PES syringe filter, 0.45 μm pore size).

Comparative example CE1

[0097] As Example 1 except that no Pd/C hydrogenation catalyst was used.

Example 2

[0098] In a 50 ml glass reactor equipped with magnetic stirring 2 ml of a saturated solution of sodium formate in water and 0.1 g of the Pd/C hydrogenation catalyst were added to 10 ml of pyrolysis oil. The reactions mixture was heated to 95°C and mixing at this temperature was continued for 2 hours. After cooling to room temperature, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm. 1 ml of demineralized water was then added to the pyrolysis oil and after 1 minute of mixing at room temperature the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm. Finally, Pd/C hydrogenation catalyst residues were removed from the pyrolysis oil by filtration (PES Syringe filter, 0.45 μm pore size).

Comparative example CE2

[0099] As Example 2 except that no Pd/C hydrogenation catalyst was used.

Example 3

[0100] In a 50 ml glass reactor equipped with magnetic stirring 0,05 g of solid sodium formate and 0.005 g of the Pd/C catalyst were added to 10 ml of pyrolysis oil. The reactions mixture was heated to 120°C and mixing at this temperature was continued for 1 hour. After cooling to room temperature, the Pd/C catalyst and unreacted sodium formate were removed from the pyrolysis oil by centrifugation for 5 minutes at 4 000 rpm. 1 ml of demineralized water was then added to the pyrolysis oil and after 1 minute of mixing at room temperature the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm. Finally, Pd/C catalyst residues were removed from the pyrolysis oil by filtration (PES Syringe filter, 0.45 μm pore size).

Comparative example CE3

[0101] As Example 2 except that no Pd/C hydrogenation catalyst was used.

[0102] Results are provided in Table 1 and Table 2 below.

Table 1. Chlorine and nitrogen concentrations

	Chlorine			Nitrogen		
	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)
Example 1	22.4	15.3	31.6	222.1	180.5	18.7
CE1	16.7	12.4	25.7	223.4	239.5	-7.2
Example 2	22.4	11.9	46.6	222.1	147.0	33.8
CE2	16.7	12.3	26.2	223.4	197.0	11.8
Example 3	24.4	15.6	35.8	720.1	420.7	41.6
CE3	17.7	12.4	30.0	216.0	142.7	33.9

Table 2. Sulfur concentrations

	Sulfur		
	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)
Example 1	15.6	11.5	26.3
CE1	15.2	12.7	16.1
Example 2	15.6	11.2	28.5
CE2	15.2	12.7	16.6
Example 3	26.1	24.7	5.6
CE3	13.9	13.1	6.4

$$\text{Reduction} = \frac{c(\text{crude oil}) - c(\text{purified oil})}{c(\text{crude oil})} \times 100\%$$

c(crude oil): Concentration in ppm of the respective impurity in the pyrolysis oil before purification

c(purified oil): Concentration in ppm of the respective impurity in the pyrolysis oil after purification

Claims

1. Process for the purification of a crude pyrolysis oil, the process comprising the steps of

a) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities,
b) hydrogenating the crude pyrolysis oil in the presence of an organic hydrogen donor and a supported Pd

catalyst in a reactor to obtain a hydrogenated crude pyrolysis oil, the hydrogenated crude pyrolysis oil comprising the hydrocarbons and hydrogenated impurities,

wherein the organic hydrogen donor comprises a compound containing a formate group.

2. The process according to any one of the preceding claims, wherein the organic hydrogen donor comprises a compound containing a formate group and a metal selected from Group 1 and Group 2, preferably the organic hydrogen donor comprises sodium formate, potassium formate, calcium formate, magnesium formate or a mixture thereof.

3. The process according to any one of the preceding claims, wherein the organic hydrogen donor is present as a solid or dissolved in a polar solvent.

4. The process according to claim 3, wherein the polar solvent comprises water, an alkanol or any mixture thereof.

5. The process according to any one of the preceding claims, wherein in step b) the temperature in the reactor is from 20 to 350 °C.

6. The process according to any one of the preceding claims, wherein in step b) the organic hydrogen donor is present in an amount of from 15 mmol/l to 3 000 mmol/l based on the total volume of the crude pyrolysis oil.

7. The process according to claim 3, wherein in step b) the supported Pd catalyst is present either in an amount of from 0.1 to 10 g/l based on the total volume of the crude pyrolysis oil in case the organic hydrogen donor is present as a solid, or
in an amount of from 1 to 50 g/l based on the total volume of the crude pyrolysis oil in case the organic hydrogen donor is present in a polar solvent.

8. The process according to claim 7, wherein the supported Pd catalyst is a carbon supported Pd catalyst.

9. The process according to any one of the preceding claims, wherein the process further comprises the step
c) washing the hydrogenated crude pyrolysis oil with a polar washing solvent to obtain a purified pyrolysis oil phase and a polar washing solvent phase, the polar washing solvent phase comprising at least a part of the hydrogenated impurities.

10. The process according to claim 9, wherein in step c) the polar washing solvent comprises water, optionally further comprising an acid or a base.

11. The process according to claim 10, wherein the polar washing solvent comprises water and an acid or a base, wherein the acid is selected from sulphuric acid, phosphoric acid, hydrochloric acid and any mixture thereof, or wherein the base comprises a hydroxide or alkoxide of a metal of Group 1 or Group 2, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, sodium alkoxide, potassium alkoxide, calcium alkoxide, magnesium alkoxide or a mixture thereof.

12. The process according to any one claims 3 to 11, wherein the polar solvent of step b) is used as the polar washing solvent in step c).

13. The process according to any one of the preceding claims, wherein in step c) the temperature is from 10 to 350 °C.

14. The process according to any one of claims 1 to 13, wherein the process further comprises adding an acid or a base to the crude pyrolysis oil prior to step b) and/or adding an acid or a base to the hydrogenated pyrolysis oil prior to step c).

15. A method for producing a cracker feedstock comprising the step of blending 1 to 100 wt.% of a purified pyrolysis oil based on the total weight of the cracker feedstock and 0 to 99 wt.% of fossil naphtha based on the total weight of the cracker feedstock, wherein the purified pyrolysis oil is obtained by the process according to any one of claims 1 to 14.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 21 4609

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	HANSEN SAMUEL ET AL: "A comprehensive state-of-technology review for upgrading bio-oil to renewable or blended hydrocarbon fuels", RENEWABLE AND SUSTAINABLE ENERGY REVIEWS, ELSEVIERS SCIENCE, NEW YORK, NY, US, vol. 118, 13 November 2019 (2019-11-13), XP085940265, ISSN: 1364-0321, DOI: 10.1016/J.RSER.2019.109548 [retrieved on 2019-11-13] * paragraphs [0001], [3.3.3], [0005]; tables 1,7 *	1-15	INV. C10G1/00 C10G1/10 C10G45/24 C10G67/02
X	STRUHS ETHAN ET AL: "Ultrasonic-assisted catalytic transfer hydrogenation for upgrading pyrolysis-oil", ULTRASONICS SONOCHEMISTRY, BUTTERWORTH-HEINEMANN, GB, vol. 73, 23 February 2021 (2021-02-23), XP086541518, ISSN: 1350-4177, DOI: 10.1016/J.ULTSONCH.2021.105502 [retrieved on 2021-02-23] * paragraphs [0001], [02.1], [02.2], [03.3]; figure 1; table 3 *	1-15	TECHNICAL FIELDS SEARCHED (IPC) C10G
A	WO 2020/178597 A1 (OXFORD SUSTAINABLE FUELS LTD [GB]) 10 September 2020 (2020-09-10) * claims 1-7 *	1-15	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	10 May 2023	Deurinck, Patricia

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 22 21 4609

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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10-05-2023

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		EP 3935138 A1	12-01-2022
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- **KUSENBERG et al.** Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation. *Waste Management,* 2022, vol. 141, 104-114 **[0003]**
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