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(54) **PYROLYSIS OIL PURIFICATION**

(57) The present invention relates to a process for purifying a crude pyrolysis oil at least partially originating 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 comprising the purified pyrolysis oil.

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Description

[0001] The present invention relates to a process for purifying a crude pyrolysis oil at least partially originating 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 containing hydrocarbons 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 purification of the pyrolysis oil is required. Purification of crude pyrolysis oil can for example be done by a costly hydrotreatment step or simply by a washing step, i.e. by extracting the impurities with a solvent that is immiscible with the oil. However, even if such a washing step can be efficient for the removal of polar impurities, only a low removal efficiency can be found in case of non-polar impurities with a high solubility in the oil, e.g. certain organic chlorides.

[0006] Oxidative desulfurization of waste tire pyrolysis fuel having high sulfur content using hydrogen peroxide and subsequent methanol extraction or silicagel adsorption has been suggested (Al-Lal et al, "Desulfurization of pyrolysis fuels obtained from waste: Lube oils, tires and plastics", Fuel 150 (2015), p. 208-216).

[0007] Generally, pyrolysis oil at least partially originating from the pyrolysis of plastic waste requires dehalogenation (particularly dechlorination), denitrogenation and deoxygenation to reduce the concentrations of these impurities and allow use in cracker feedstock, such as steam cracker feedstock.

[0008] WO 2021/224287 A1 is directed to a process for purifying a crude pyrolysis oil originating from the pyrolysis of plastic waste. The process comprises the steps of (i) subjecting the crude pyrolysis oil to a treatment with a trapping agent selected from an elemental metal, an oxide of metals, an alkoxide of metals, a solid sorption agent or a combination of at least two trapping agents, and (ii) separating the product obtained into a purified pyrolysis oil fraction having a reduced nitrogen, sulfur and halogen content in relation to the crude pyrolysis oil and a fraction comprising the trapping agent which has bound at least a part of the sulfur, nitrogen and halogen present in the crude pyrolysis oil.

[0009] A process for upgrading a pyrolysis oil is disclosed in WO 2020/178597. The process comprises the steps of treating a pyrolysis oil with an aqueous solution and optionally a hydrocarbon fluid, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof. An upgraded pyrolysis oil prepared by said process is also disclosed.

[0010] 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.

[0011] It is a further object of the present invention to provide a process for purifying a crude pyrolysis oil at least partially originating from the pyrolysis of plastic waste which reduces the content of polar and non-polar impurities in the crude pyrolysis oil.

[0012] It is still a further object of the present invention to provide a process for purifying a crude pyrolysis oil at least partially originating from the pyrolysis of plastic waste having an improved removal efficiency for impurities present in

the crude pyrolysis oil.

[0013] 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.

[0014] 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 and in a second aspect a process for purifying a crude pyrolysis oil according to claim 2.

[0015] In the first aspect, a process for the purification of a crude pyrolysis oil is provided, the process comprising the steps of

A1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,

A2) oxidising the crude pyrolysis oil, preferably the pre-treated crude pyrolysis oil, in the presence of an oxidation agent in a first reactor, the first reactor preferably being a stirred tank reactor, to obtain an oxidised crude pyrolysis oil comprising oxidised impurities,

A2a) optionally separating reacted oxidation agent obtained in step A2) from the oxidised crude pyrolysis oil, wherein step A2a) takes place after step A2) and before step A3);

A3) mixing either in the first reactor or in a second reactor the oxidised crude pyrolysis oil, preferably the pre-treated oxidised 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 oxidised impurities,

A4) separating the polar washing solvent phase from the purified pyrolysis oil phase to obtain a purified pyrolysis oil,

wherein the oxidation agent comprises hydrogen peroxide and a metal salt, the metal salt preferably comprising an iron salt, the iron salt preferably comprising iron (III) nitrate.

[0016] Optionally, in step A4) separating also reacted oxidation agent obtained in step A2) from the purified pyrolysis oil phase.

[0017] In a second aspect, a process for the purification of a crude pyrolysis oil is provided, the process comprising the steps of

B1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,

B2) mixing the crude pyrolysis oil, preferably the pre-treated crude pyrolysis oil, with a polar washing solvent in a first reactor, the first reactor preferably being a stirred tank reactor, to obtain a washed crude pyrolysis oil phase and a polar washing solvent phase, the polar washing solvent phase comprising at least a part of the impurities,

B3) separating the polar washing solvent phase from the washed crude pyrolysis oil phase,

B4) oxidising either in the first reactor or in a second reactor the washed crude pyrolysis oil phase in the presence of an oxidation agent to obtain an oxidised purified pyrolysis oil comprising oxidised impurities,

B5) separating the oxidised impurities from the oxidised purified pyrolysis oil to obtain a purified pyrolysis oil,

wherein the oxidation agent comprises hydrogen peroxide and a metal salt, the metal salt preferably comprising an iron salt, the iron salt preferably comprising iron (III) nitrate.

[0018] Optionally, in step B5) separating also reacted oxidation agent obtained in step B4) from the oxidised purified pyrolysis oil. Particularly, the present invention provides processes 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.

[0019] More particularly, the present invention provides processes 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.

[0020] 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.

[0021] In a specific embodiment, the present invention provides a process for purifying a crude pyrolysis oil at least partially originating from the pyrolysis of plastic waste to obtain a purified pyrolysis oil, typically having a chlorine content of 10 ppm by weight or less and/or typically having a nitrogen content of 100 ppm by weight or less. In addition, the purified pyrolysis oil typically has an olefins content of 30 wt.% or less.

[0022] As used herein, the term "olefins" refers to unsaturated open-chain (linear) hydrocarbons.

[0023] As used herein, the term "hydrocarbon" refers to organic compounds consisting of carbon and hydrogen.

[0024] In step A1) of the process according to the first aspect and on step B1) of the process according to the second aspect a crude pyrolysis oil is provided. The crude pyrolysis oil comprises hydrocarbons and impurities and the crude pyrolysis oil at least partially originates from pyrolysis of plastic waste. Preferably, the crude pyrolysis oil is a crude plastic waste pyrolysis oil.

[0025] In the present invention, the term "pyrolysis" relates to a thermal decomposition or degradation of a feedstock, such as end of life plastics (plastic waste) or plastic waste combined with biomass, under inert conditions and results in a gas, a liquid and a solid char fraction. During pyrolysis of plastic waste, 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.

[0026] The term "pyrolysis" includes slow pyrolysis, fast pyrolysis, flash catalysis and catalytic pyrolysis. These type 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.

[0027] In the context of the present invention, the term "crude pyrolysis oil" is understood to mean any 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.

[0028] As used herein, "crude plastic waste pyrolysis oil" means pyrolysis oil derived from pyrolysis of a feedstock consisting of plastic waste.

[0029] As used herein, "crude biomass pyrolysis oil" means pyrolysis oil derived from pyrolysis of a feedstock consisting of biomass.

[0030] 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.

[0031] Depending on the plastic waste 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.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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 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.

[0036] 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 4000 mg/l, often 900 to 3000 mg/l, relative to the total volume of

the crude pyrolysis oil.

[0037] In one embodiment, the crude pyrolysis oil has a halogen content of 10 mg/l or more, such as 20 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 a halogen content of 100 to 1000 mg/l, often 120 to 900 mg/l, relative to the total volume of the crude pyrolysis oil.

[0038] 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.

[0039] 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 10 mg/ml or more, such as 20 mg/ml or more.

[0040] 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.

[0041] 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 5 mg/l to 15 mg/l, or 5 to 20 mg/l relative to the total volume of the crude pyrolysis oil.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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, 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.

[0047] The process according to the invention may provide purified pyrolysis oil having the nitrogen content reduced by 10 to 95%, such as at least 50% or at least 60% or at least 70%, relative the nitrogen content of the crude pyrolysis oil.

[0048] The process according to the invention may provide purified pyrolysis oil having the chlorine content reduced by 10 to 95%, such as at least 50% or at least 60% or at least 70% or at least 80% or at least 90%, relative the chlorine content of the crude pyrolysis oil.

[0049] Preferably, the pyrolysis oil comprises paraffins, preferably n-paraffins and/or i-paraffins, olefins, naphthenes and/or aromatics. The crude pyrolysis oil originating from plastic waste is further characterized by, but not limited to

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.

[0050] 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.

[0051] The feedstock for the pyrolysis is typically plastic waste or plastic waste combined with biomass.

[0052] As used herein, the term "plastic waste" refers to any plastic or rubber 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" may also include used petroleum-based hydrocarbon material such as used motor oil, machine oil, greases, waxes, etc. Preferably, the plastic waste essentially consists of plastic and/or rubber materials.

[0053] 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.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.

[0054] 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.

[0055] An oxidation agent is used in step A2) of the process according to the first aspect to oxidise the crude pyrolysis oil, and in step B4) of the process according to the second aspect to oxidise the washed crude pyrolysis oil.

[0056] The oxidation agent comprises hydrogen peroxide and a metal salt. The oxidation agent is usually added in the form of an aqueous solution comprising the hydrogen peroxide and the metal salt. The hydrogen peroxide may be added as pure hydrogen peroxide, as an aqueous hydrogen peroxide solution and/or in the form of sodium percarbonate ($Na_2CO_3 \cdot 3H_2O_2$). Preferably, the oxidation agent comprises or consists of an aqueous solution of the metal salt and hydrogen peroxide. More preferably, the oxidation agent comprises or consists of an aqueous solution of the metal salt and 20 to 50 wt.% hydrogen peroxide, particularly within the range of from 30 to 50 wt.% hydrogen peroxide, based on the total weight of the aqueous solution.

[0057] The advantage of using hydrogen peroxide is, for example, that it is able to oxidize most of the impurities but not the pyrolysis oil as such. In other words, it does not modify the pyrolysis oil but only oxidizes undesired components.

[0058] The main decomposition products of the oxidation agent are O_2 and water, i.e. volatile compounds that can be easily removed. It is known that O_2 catalyses the oligomerization/polymerization of dienes in the pyrolysis oil, resulting in the formation of solids or gels during storage/transportation of the oil, e.g. when in contact with air. Such dienes are now to a certain degree already advantageously removed during the oxidation or washing step according to the present invention in form of solids because of the O_2 from the peroxide.

[0059] Finally, hydrogen peroxide does not contain any other heteroatoms than O. In other words, hydrogen peroxide does not increase e.g. the concentration of sulfur, which is often a strong poison in following processing steps of the pyrolysis oil.

[0060] The metal salt preferably comprises an iron salt, a copper salt, a cerium salt, a cobalt salt, a chromium salt and mixtures thereof, more preferably comprises, or consists of, an iron salt.

[0061] The iron salt preferably comprises, or consists of, iron nitrate, such as iron (III) nitrate, iron sulphate iron

phosphate, iron chloride and mixtures thereof, more preferably comprises, or consists of, iron (III) nitrate.

[0062] The copper salt preferably comprises, or consists of, copper sulphate. The cerium salt preferably comprises, or consists of, cerium sulphate and/or cerium oxide. The cobalt salt preferably comprises, or consists of, cobalt sulphate. The chromium salt preferably comprises, or consists of, potassium chromium sulphate.

[0063] Apart from hydrogen peroxide and the metal salt, the oxidation agent may further comprise one or more further component(s). The oxidation agent may further comprise oxone, sodium persulfate, sodium hypochlorite, sodium perchlorate, sodium borate, sodium bismuthate, ammonium cerium nitrate, peroxyacetic acid, sodium peroxide, potassium superoxide and mixtures thereof. In other embodiments, the oxidation agent further comprises sodium chlorite.

[0064] Preferably, the hydrogen peroxide is added in step A2) or in step B4) in an amount from 0.15 mol/l to 3.5 mol/l with respect to the crude pyrolysis oil.

[0065] Preferably, the metal salt is added in step A2) or in step B4) in an amount from 0.2 mmol/l to 25 mmol/l with respect to the pyrolysis oil.

[0066] Preferably, in step A2) a polar solvent is present, the polar solvent preferably comprising water and/or wherein the polar solvent of step A2) is used as polar washing solvent in step A3).

[0067] Preferably, the process further comprises step A2a) of separating a reacted oxidation agent obtained in step A2) from the oxidised crude pyrolysis oil, wherein step A2a) takes place after step A2) and before step A3). In step A2) preferably an aqueous phase and a non-aqueous phase is formed. The non-aqueous phase comprises the pyrolysis oil and the aqueous phase comprises the reacted oxidation agent. Preferably, separating the reacted oxidation agent in step A2a) is done by separating an aqueous phase comprising the reacted oxidation agent from a non-aqueous phase comprising the pyrolysis oil.

[0068] Preferably, in step A2) or B4) the temperature in the reactor is from 15 to 100 °C, preferably from 20 to 75 °C, more preferably from 20 to 50 °C, such as from 35 to 50 °C. The mixing time in step A2) or B4) is preferably within the range of from 1 minute to 3 hours, more preferably within the range of from 10 min to 1 hour.

[0069] Preferably, in step A3) or B2) the temperature is from 10 to 600 °C, preferably from 15 to 400 °C, more preferably from 20 to 360 °C, most preferably 250 to 350°C. The mixing time in step A3) or B2) is preferably within the range of from 1 minute to 3 hours, more preferably within the range of from 10 min to 30 minutes.

[0070] Preferably, the polar washing solvent used in step A3) or step B2) comprises, or consists of, water, an alkanol or any mixture thereof, preferably the polar washing solvent comprises, or consists of, water. The water is preferably distilled water.

[0071] An alkanol is defined as an alkane alcohol, i.e. R-OH with R being an alkyl group, preferably an alkyl group having one to 12 carbon atoms. Preferably, the alkanol selected from C1 to C4 alkanols, such as methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, and 2-methylpropan-1-ol, preferably methanol or ethanol.

[0072] Preferably, the polar washing solvent further comprises, or consists of, an acid or a base, more preferably comprises, or consists of, a base.

[0073] Preferably, the acid comprises hydrochloric acid, sulfuric acid or phosphoric acid. Preferably, the base comprises a hydroxide or alkoxide of a metal of Group 1 or Group 2, preferably the hydroxide or alkoxide of a metal of Group 1 or Group 2 comprises sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium methoxide or potassium methoxide.

[0074] Preferably, the base, such as sodium hydroxide, can be added to the process as an aqueous solution or as a solid prior to adding the polar washing solvent, such as water. Adding the base as a solid has the advantage that the pressure in the process is not significantly increased.

[0075] In embodiments where the base, such as sodium hydroxide, is added as a solid to the optionally pre-treated oxidised crude pyrolysis oil from step A2) or the optionally pre-treated crude pyrolysis oil from step B1) prior to adding the polar washing solvent in step A3) or step B2), the base and the oil are preferably mixed at a temperature above 100°C, more preferably at a temperature within the range of from 250°C to 350°C for a time period within the range of from 1 minute to 3 hours, preferably from 10 min to 30 minutes, thereafter cooled to below 100°C, such as about 20°C, and the polar washing solvent of step A3) or step B2) is then added to the cooled mixture.

[0076] Preferably, the ratio of the weight of the acid or the weight of the base with respect to the volume of the oxidised crude pyrolysis oil in step A3) is 0.1 to 1 mol/l, more preferably 0.1 to 0.5 mol/l and most preferably 0.1 to 0.2 mol/l, or the ratio of the weight of the acid or the weight of the base with respect to the volume of the crude pyrolysis oil in step B2) is 0.1 to 1 mol/l, more preferably 0.1 to 0.5 mol/l and most preferably 0.1 to 0.2 mol/l.

[0077] In a preferred embodiment, the polar washing solvent comprises, or consists of, water and a hydroxide of a metal of Group 1 or Group 2. Preferably, the hydroxide of a metal of Group 1 or Group 2 comprises, or consists of, sodium hydroxide, potassium hydroxide or calcium hydroxide.

[0078] In specific embodiments, the polar washing solvent is an 10 to 30 wt.% aqueous solution of sodium hydroxide, such as 20 wt.% aqueous solution of sodium hydroxide.

[0079] In other specific embodiments, the polar washing solvent is a 10 to 30 wt.% solution of sodium methoxide in methanol, such as 30 wt.% solution of sodium methoxide in methanol.

[0080] It has been found that addition of a base or acid to the polar washing solvent allows transforming certain non-polar compounds that can easily be protonated (when acid added) or deprotonated (when base added) into polar compounds with a high solubility in the polar washing solvent, thereby allowing improved removal of such non-polar compounds. For example, amines can be easily protonated by adding an acid and fatty acids can be easily deprotonated by adding a base.

[0081] Alternatively or additionally, the process may further comprise adding an acid or a base together with the oxidation agent in step A2) or step B4).

[0082] Alternatively, the process may comprise a pre-treatment comprising step B1a) of adding an acid or a base to the crude pyrolysis oil prior to mixing the pre-treated crude pyrolysis oil with the polar washing solvent, wherein step B1a) takes place after step B1) and before step B2).

[0083] Alternatively, the process may further comprise a pre-treatment comprising step A1a) of adding an acid or a base to the crude pyrolysis oil prior to oxidising the pre-treated crude pyrolysis oil in the presence of the oxidation agent, wherein step A1 a) takes place after step A1) and prior to step A2).

[0084] Still alternatively, the process may further comprise a pre-treatment comprising step A2b) of adding an acid or a base to the oxidised crude pyrolysis oil prior to mixing the pre-treated oxidised crude pyrolysis oil with the polar washing solvent, wherein step A2b) takes place after step A2) or, if present, after step A2a) and before step A3).

[0085] Particularly, the respective pre-treatment steps B1a), A1a) or A2b) may comprise adding the acid or the base as an aqueous solution to the crude pyrolysis oil, allowing water/oil phase separation and removing the aqueous phase from the pre-treated crude pyrolysis oil phase prior to subsequent steps of the process.

[0086] In a particular embodiment, the process comprises:

A1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,

A1a) adding an aqueous solution of an acid, such as hydrochloric acid, sulfuric acid or phosphoric acid, particularly sulfuric acid, to the crude pyrolysis oil in a pre-reactor (or in the first reactor) thereby providing a pre-treated crude pyrolysis oil,

A1b) optionally allowing water/oil phase separation and removing the aqueous phase from the pre-treated crude pyrolysis oil,

A2) oxidising the pre-treated crude pyrolysis oil in the presence of an oxidation agent in a first reactor, the first reactor preferably being a stirred tank reactor, to obtain an oxidised crude pyrolysis oil, wherein the oxidation agent comprises an aqueous solution of hydrogen peroxide and a metal salt, such as an iron salt, particularly iron (III) nitrate,

A2a) separating reacted oxidation agent obtained in step A2) from the oxidised crude pyrolysis oil by allowing water/oil phase separation and removing the aqueous phase from the oxidised crude pyrolysis oil,

A3) mixing either in the first reactor or in a second reactor the oxidised 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 oxidised impurities, wherein the polar washing solvent is water comprising a base, such as a hydroxide of a metal of Group 1 or Group 2, particularly sodium hydroxide, and

A4) separating the polar washing solvent phase from the purified pyrolysis oil phase to obtain a purified pyrolysis oil.

[0087] In another particular embodiment, the process comprises:

A1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,

A1a) adding an aqueous solution of an acid, such as hydrochloric acid, sulfuric acid or phosphoric acid, particularly sulfuric acid, to the crude pyrolysis oil in a pre-reactor (or in the first reactor) thereby providing a pre-treated crude pyrolysis oil,

A1b) optionally allowing water/oil phase separation and removing the aqueous phase from the pre-treated crude pyrolysis oil,

A2) oxidising the pre-treated crude pyrolysis oil in the presence of an oxidation agent in a first reactor, the first

reactor preferably being a stirred tank reactor, to obtain an oxidised crude pyrolysis oil, wherein the oxidation agent comprises an aqueous solution of hydrogen peroxide and a metal salt, such as an iron salt, particularly iron (III) nitrate,

A2a) separating reacted oxidation agent obtained in step A2) from the oxidised crude pyrolysis oil by allowing water/oil phase separation and removing the aqueous phase from the oxidised crude pyrolysis oil,

A2b) adding either in the first reactor or in a second reactor a base, such as sodium hydroxide, in solid form to the oxidised crude pyrolysis oil,

A3) mixing either in the first reactor or in a second or third reactor the oxidised 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 oxidised impurities, wherein the polar washing solvent is water, and

A4) separating the polar washing solvent phase from the purified pyrolysis oil phase to obtain a purified pyrolysis oil.

[0088] In step A1a), mixing the aqueous solution of an acid and the crude pyrolysis oil is preferably performed at a temperature within the range of from 10°C to 95°C, such as from 20 to 50°C or from 30 to 50°C. Preferably in step A1a), the aqueous solution of an acid and the crude pyrolysis oil are mixed for a period within the range of from 1 minute to 1 hour, more preferably from 1 minute to 30 minutes.

[0089] In step A2b), mixing of the base (when added in solid form) and the oxidised crude pyrolysis oil is preferably performed at a temperature above 100°C, more preferably from 250°C to 350°C. In step A2b), the base (when added in solid form) and the oxidised crude pyrolysis oil are preferably mixed for a period within the range of from 10 minutes to 3 hours, more preferably from 10 minutes to 1 hour. When the mixing of the base (when added in solid form) and the oxidised crude pyrolysis oil in step A2b) is performed at a temperature above 100°C, the process preferably further comprises step A2c) of cooling said mixture to ambient temperature, such as 20°C, prior to step A3).

[0090] In step A4) or step B5) of the process, separation may be performed by, for example, centrifugation, settling followed by decanting of water phase from oil phase or phase separation filtration.

[0091] As discussed above, the crude pyrolysis oil contains a number of various impurities. 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. The concentration of these impurities is disclosed herein above.

[0092] 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.

[0093] 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.

[0094] Preferably, the cracker feedstock is a steam cracker feedstock.

[0095] 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.

[0096] The invention further provides the use of the purified pyrolysis oil as a cracker feedstock.

[0097] Preferably, the cracker feedstock is a steam cracker feedstock.

[0098] The invention is further directed to the use of an oxidation agent for removing impurities from a crude pyrolysis oil.

[0099] The invention thus further provides the use of an oxidation agent comprising a an aqueous solution of hydrogen peroxide and a metal salt, the metal salt preferably comprising an iron salt, the iron salt preferably comprising iron (III) nitrate for removing impurities from a crude pyrolysis oil, the crude pyrolysis oil comprising a pyrolysis oil and impurities.

[0100] 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.

[0101] 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.

[0102] The invention is further described and illustrated below by means of non-limiting examples.

EXAMPLE SECTION

Materials

[0103] Commercially available batches of crude pyrolysis oils (Recycled Carbon Fuel) from Renasci Oostende Recycling NV were 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 used different batches of the crude pyrolysis oils for the examples are given in Table 1 below.

[0104] A 35 wt.% aqueous hydrogen peroxide solution was obtained from Merck. The 50 wt.% aqueous hydrogen peroxide solution, iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium hydroxide, and a 30 wt.% solution of sodium methoxide in methanol were obtained from Sigma-Aldrich Handels GmbH.

Analytical methods

Chlorine content in pyrolysis oil

[0105] 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

[0106] 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))

[0107] Each pyrolysis oil sample was measured in triplicate.

Nitrogen content in pyrolysis oil

[0108] Instrument: Xplorer-NS from TE Instruments with Archie injection and liquid boat

Testing methods:

[0109]

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)
ASTM D4629 was used for analyzing pyrolysis oil with a nitrogen concentration below 1000 ppm, whereas ASTM D5762 was used for analyzing pyrolysis oil with a nitrogen concentration above 1000 ppm.

[0110] Each sample was measured in triplicate.

Sulfur content in pyrolysis oil

[0111]

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

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)

Each sample was measured in triplicate.

Examples

[0112] The following examples 1 to 5, 10 and Comparative Example 4 were carried out in a 100 ml glass reactor (EasyMax reactor system from Mettler Toledo) and a 100 ml high pressure steel autoclave (Parr GmbH, maximum pressure 200 bar), both equipped with electrical heating.

Example 1

Fenton oxidation:

[0113] In a 100 ml glass reactor equipped with mechanical stirring 50 ml of pyrolysis oil was heated to 45°C. 1.0 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was then added to the pyrolysis oil under stirring, followed by the addition of 5 ml of 50 wt.% aqueous solution of hydrogen peroxide. After one hour mixing at 45°C, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm.

High temperature caustic wash:

[0114] 40 ml of the pyrolysis oil from the Fenton oxidation step was transferred to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 1.0 g of an aqueous 20 wt.% sodium hydroxide solution was then added at room temperature to the stirred pyrolysis oil. The autoclave was then heated to 350°C and mixing of the reaction mixture was continued for one hour at this temperature. After cooling of the reaction mixture to room temperature, 10 ml of water was added and stirring at this temperature was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 2

High temperature caustic wash:

[0115] 40 ml of pyrolysis oil was added to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 1.0 g of an aqueous 20 wt.% sodium hydroxide solution was then added at room temperature to the stirred pyrolysis oil. The autoclave was then heated to 350°C and mixing of the reaction mixture was continued for one hour at this temperature. After cooling of the reaction mixture to room temperature, 10 ml of water was added and stirring at this temperature was continued for 1 minute. The aqueous phase was then separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Fenton oxidation:

[0116] In a 100 ml glass reactor equipped with electrical heating and mechanical stirring the pyrolysis oil from the high temperature caustic wash step was heated to 45°C. 0.8 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was then added to the pyrolysis oil under stirring, followed by the addition of 4 ml of 50 wt.% aqueous solution of hydrogen peroxide. After one hour mixing at 45°C the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm.

Example 3

[0117] In a 100 ml glass reactor equipped with electrical heating and mechanical stirring 50 ml of pyrolysis oil was heated to 45°C. 1 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was then added to the pyrolysis oil under stirring, followed by the addition of 5 ml of 50 wt.% aqueous solution of hydrogen peroxide. After one hour of mixing at 45°C the temperature was decreased to room temperature and the reactor content was transferred to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 1.0 g of an aqueous 20 wt.% sodium hydroxide solution was then added at room temperature to the stirred pyrolysis oil. The autoclave was then heated to 350°C and mixing of the reaction mixture was continued for one hour at this temperature. After cooling of the reaction mixture to room temperature, 10 ml of water were added and stirring at this temperature was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 4

[0118] As Example 2 except that in the high temperature caustic wash, instead of 1.0 g of an aqueous 20 wt.% sodium hydroxide solution, 1.0 g of a 30 wt.% solution of sodium methoxide in methanol was used.

Example 5

[0119] As Example 2 except that in the high temperature caustic wash instead of 1.0 g of an aqueous 20 wt.% sodium hydroxide solution, 1.0 g of a 30 wt.% solution of sodium methoxide in methanol was used and the temperature was

120°C instead of 350°C.

Example 6

Fenton oxidation:

[0120] In a 1 000 ml glass bottle equipped with mechanical stirring 800 ml of pyrolysis oil was heated to 45°C. 8.0 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was added to the pyrolysis oil under stirring, followed by the addition of 120 ml of a 35 wt.% aqueous solution of hydrogen peroxide. After 30 minutes mixing at 45°C, the aqueous phase was separated from the pyrolysis oil by decanting and filtration (phase separating paper filter, size 185 mm, grade 108 H).

High temperature caustic wash:

[0121] 40 ml of the pyrolysis oil from the Fenton oxidation step was transferred to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 0.29 g of solid sodium hydroxide was then added at room temperature to the stirred pyrolysis oil. The autoclave was heated to 350°C and mixing of the reaction mixture was continued for 10 minutes at this temperature. After cooling of the reaction mixture to room temperature 10 ml of water was added and stirring was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 7

Fenton oxidation:

[0122] In a 1 000 ml glass bottle equipped with mechanical stirring 800 ml of pyrolysis oil was heated to 45°C. 8.0 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$, 24 ml of 1 wt.% sulfuric acid and 12 ml of water was added to the pyrolysis oil under stirring, followed by slow addition of 120 ml of a 35 wt.% aqueous solution of hydrogen peroxide. After 30 minutes mixing at 45°C, the aqueous phase was separated from the pyrolysis oil by decanting and filtration (phase separating paper filter, size 185 mm, grade 108 H).

High temperature caustic wash:

[0123] 40 ml of the pyrolysis oil from the Fenton oxidation step was transferred to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 0.29 g of solid sodium hydroxide was then added at room temperature to the stirred pyrolysis oil. The autoclave was heated to 350°C and mixing of the reaction mixture was continued for 10 minutes at this temperature. After cooling of the reaction mixture to room temperature 10 ml of water was added and stirring was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 8

Sulfuric acid wash:

[0124] 500 ml of 0.2% sulfuric acid was added at room temperature in a 1 500 ml separation funnel to 500 ml of the pyrolysis oil. After one minute of vigorous shaking the two phases were allowed to separate and the aqueous phase was removed from the pyrolysis oil.

Fenton oxidation:

[0125] In a 1 000 ml glass bottle equipped with mechanical stirring 700 ml of pyrolysis oil washed with sulfuric acid was heated to 45°C. 7.0 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was added to the pyrolysis oil under stirring, followed by slow addition of 105 ml of a 35 wt.% aqueous solution of hydrogen peroxide. After 30 minutes mixing at 45°C, the aqueous phase was separated from the pyrolysis oil by decanting and filtration (phase separating paper filter, size 185 mm, grade 108 H).

High temperature caustic wash:

[0126] 40 ml of the pyrolysis oil from the Fenton oxidation step was transferred to a 100 ml steel autoclave equipped

with electrical heating and a magnetic stir bar. 0.29 g of solid sodium hydroxide was then added at room temperature to the stirred pyrolysis oil. The autoclave was heated to 350°C and mixing of the reaction mixture was continued for 10 minutes at this temperature. After cooling of the reaction mixture to room temperature 10 ml of water was added and stirring was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 9

Sulfuric acid wash:

[0127] 500 ml of 0.2% sulfuric acid was added at room temperature in a 1 500 ml separation funnel to 500 ml of the pyrolysis oil. After one minute of vigorous shaking the two phases were allowed to separate and the aqueous phase was removed from the pyrolysis oil.

Fenton oxidation:

[0128] In a 1 000 ml glass bottle equipped with mechanical stirring 60 ml of pyrolysis oil from the sulfuric acid wash was heated to 45°C. 0.6 ml of a 10 wt.% aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$ was added to the pyrolysis oil under stirring, followed by slow addition of 0.9 ml of a 35 wt.% aqueous solution of hydrogen peroxide. After 30 minutes mixing at 45°C, the aqueous phase was separated from the pyrolysis oil by decanting and filtration (phase separating paper filter, size 185 mm, grade 108 H).

High temperature caustic wash:

[0129] 40 ml of the pyrolysis oil from the Fenton oxidation step was transferred to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 0.29 g of solid sodium hydroxide was then added at room temperature to the stirred pyrolysis oil. The autoclave was heated to 350°C and mixing of the reaction mixture was continued for 10 minutes at this temperature. After cooling of the reaction mixture to room temperature 10 ml of water was added and stirring was continued for 1 minute. Finally, the aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Example 10

[0130] As Example 8 except that in the high temperature washing step instead of 0.29 g of solid NaOH, 1 ml of an aqueous 29 wt% sodium hydroxide solution was added and that the mixing time at 350°C was 3 hours instead of 10 minutes.

Example 11

Fenton oxidation:

[0131] In a 100 ml glass reactor equipped with mechanical stirring 10 ml of pyrolysis oil was heated to 45°C. 1.0 ml of a 35 wt.% aqueous hydrogen peroxide solution and 0.01 g of $Fe(NO_3)_3 \cdot 9H_2O$ was then added under stirring and mixing of the reaction mixture was continued at this temperature for three hours. The aqueous phase was separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm.

[0132] 1.0 ml water was added to the oil at room temperature, followed by mixing for one minute. The aqueous phase was then separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 5 minutes at 4 000 rpm.

Comparative example CE1

High temperature caustic wash:

[0133] 40 ml of pyrolysis oil was added to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 1.0 g of an aqueous 20 wt.% sodium hydroxide solution was then added at room temperature to the stirred pyrolysis oil. The autoclave was then heated to 150°C and mixing of the reaction mixture was continued for one hour at this temperature. After cooling of the reaction mixture to room temperature, 10 ml of water was added and stirring at this temperature was continued for 1 minute. The aqueous phase was then separated from the pyrolysis oil by decanting

after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Comparative example CE2

High temperature aqueous wash:

[0134] 40 ml of pyrolysis oil was added to a 100 ml steel autoclave equipped with electrical heating and a magnetic stir bar. 1.0 g of water was then added at room temperature to the stirred pyrolysis oil. The autoclave was then heated to 150°C and mixing of the reaction mixture was continued for one hour at this temperature. After cooling of the reaction mixture to room temperature, 10 ml of water was added and stirring at this temperature was continued for 1 minute. The aqueous phase was then separated from the pyrolysis oil by decanting after centrifugation of the reaction mixture for 10 minutes at 4 000 rpm.

Comparative example CE3

[0135] As Comparative example CE2 except that in the high temperature aqueous wash instead of 150°C a temperature of 350°C was applied.

Comparative example CE4

[0136] As Example 6 except that no $Fe(NO_3)_3 \cdot 9H_2O$ was used.

Table 1 Chlorine, nitrogen, and sulfur concentration of crude and purified pyrolysis oil

	Chlorine concentration			Nitrogen concentration			Sulfur concentration		
	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)
Example 1	18.8	4.4	76.6	200.3	23.5	88.3	9.7	6.5	32.8
Example 2	18.8	3.8	79.9	200.3	22.0	89.0	9.7	6.9	28.8
Example 3	18.8	6.0	68.3	200.3	75.9	62.1	9.7	7.0	27.7
Example 4	19.9	1.7	91.5	200.7	39.1	80.5	15.4	12.3	19.9
Example 5	16.8	8.0	52.7	203.4	54.4	70.5	14.5	11.7	19.3
Example 6	12.1	1.8	84.8	998.6	99.0	90.1	17.6	13.1	25.9
Example 7	12.1	1.4	88.5	998.6	44.0	95.6	17.6	12.5	29.2
Example 8	12.1	1.4	88.5	998.6	51.0	94.9	17.6	12.1	31.6
Example 9	N.D.	N.D.	N.D.	1140.8	104.9	90.8	N.D.	N.D.	N.D.
Example 10	12.1	1.7	85.8	998.6	64.7	93.5	17.6	8.3	52.9
Example 11	18.2	13.1	28.0	220.7	73.8	66.5	16.1	14.1	12.7
CE1	18.9	12.2	35.4	218.8	124.4	43.2	16.0	15.2	5.2
CE2	18.9	16.1	14.5	218.8	136.9	37.4	16.0	15.7	2.2

(continued)

	Chlorine concentration			Nitrogen concentration			Sulfur concentration		
	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)	Crude oil (ppm)	Purified oil (ppm)	Reduction (%)
CE3	26.4	11.6	56.2	202.8	116.6	42.5	13.7	14.4	-5.1
CE4	18.2	14.0	23.0	220.7	118.3	46.4	16.1	15.1	6.2
N.D. = Not determined									

[0137] The reduction in table 1 was calculated as follows:

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

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

A1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,
A2) oxidising the crude pyrolysis oil in the presence of an oxidation agent in a first reactor, the first reactor preferably being a stirred tank reactor, to obtain an oxidised crude pyrolysis oil, the oxidised crude pyrolysis oil comprising oxidised impurities,
A3) mixing either in the first reactor or in a second reactor the oxidised 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 oxidised impurities,
A4) separating the polar washing solvent phase from the purified pyrolysis oil phase to obtain a purified pyrolysis oil,
wherein the oxidation agent comprises hydrogen peroxide and a metal salt.

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

B1) providing a crude pyrolysis oil, the crude pyrolysis oil comprising hydrocarbons and impurities, the crude pyrolysis oil at least partially originating from pyrolysis of plastic waste,
B2) mixing the crude pyrolysis oil with a polar washing solvent in a first reactor, the first reactor preferably being a stirred tank reactor, to obtain a washed crude pyrolysis oil phase and a polar washing solvent phase, the polar washing solvent phase comprising at least a part of the impurities,
B3) separating the polar washing solvent phase from the washed crude pyrolysis oil phase,
B4) oxidising either in the first reactor or in a second reactor the washed crude pyrolysis oil phase in the presence of an oxidation agent to obtain an oxidised purified pyrolysis oil, the oxidised purified pyrolysis oil comprising oxidised impurities,
B5) separating the oxidised impurities from the oxidised purified pyrolysis oil to obtain a purified pyrolysis oil,
wherein the oxidation agent comprises hydrogen peroxide and a metal salt.

3. The process according to claim 1, wherein the process further comprises the step

A2a) separating reacted oxidation agent obtained in step A2) from the oxidised crude pyrolysis oil,
wherein step A2a) takes place after step A2) and before step A3).

4. The process according to any one of the preceding claims, wherein in step A2) or B4) the temperature in the reactor is from 15 to 100 °C.

5. The process according to any one of the preceding claims, wherein the hydrogen peroxide is added in step A2) or in step B4) in an amount from 0.15 mol/l to 3.5 mol/l with respect to the crude pyrolysis oil, and the metal salt is added in step A2) or in step B4) in an amount from 0.2 mmol/l to 25 mmol/l with respect to the crude pyrolysis oil.

6. The process according to any one of the preceding claims, wherein the polar washing solvent comprises water, an alkanol or a mixture thereof.

7. The process according to claim 6, wherein the alkanol is methanol or ethanol.

8. The process according to any one of the preceding claims, wherein the polar washing solvent further comprises an acid or a base.

9. The process according to claim 8, wherein the acid comprises hydrochloric acid, sulfuric acid or phosphoric acid, or wherein the base comprises a hydroxide or alkoxide of a metal of Group 1 or Group 2.

10. The process according to any one of the preceding claims, wherein the polar washing solvent comprises sodium hydroxide in water or sodium methoxide in methanol.

11. The process according to any one of claims 1 to 10, wherein the process further comprises a pre-treatment step B1a) adding an acid or a base to the crude pyrolysis oil prior to mixing the pre-treated crude pyrolysis oil with the polar washing solvent, wherein step B1a) takes place after step B1) and before step B2); or A1a) adding an acid or a base to the crude pyrolysis oil prior to oxidising the pre-treated crude pyrolysis oil in the presence of the oxidation agent, wherein step A1a) takes place after step A1) and prior to step A2); or A2b) adding an acid or a base to the oxidised crude pyrolysis oil prior to mixing the pre-treated oxidised crude pyrolysis oil with the polar washing solvent, wherein step A2b) takes place after step A2) or, if present, after step A2a) and before step A3).

12. The process according to any one of claims 1 and 3 to 11, wherein in step A2) a polar solvent is present, the polar solvent preferably comprising water and/or wherein the polar solvent of step A2) is used as polar washing solvent in step A3.

13. The process according to any one of the preceding claims, wherein in step A3) or B2) the temperature is from 10 to 600 °C.

14. The process according to any one of the preceding claims, wherein the impurities comprise inorganic compounds and/or organic compounds containing heteroatoms.

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 4607

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	9 May 2023	Deurinck, Patricia

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