

PROCESS FOR PRODUCING AN UPGRADED PYROLYSIS OIL PRODUCT**INTRODUCTION**

[001] Described herein is an improved process for producing an upgraded pyrolysis oil product. The process is of particular use for upgrading pyrolysis oil derived from the pyrolysis of plastic or rubber, or a combination thereof. The process uses low cost materials to efficiently and sustainably produce stable pyrolysis oil, allowing safe storage, transportation and/or its use as fuel, as a component of fuels and/or as a chemical feedstock.

BACKGROUND OF THE INVENTION

[002] Managing the disposal and recycling of plastic waste has become a significant global challenge; it is estimated, in 2019, that 353 million tonnes of plastic waste was generated. While recycling has gained more recognition recently only 9% of waste in 2019 was actually recycled by mechanical methods. This compares to 50% being sent to landfill to accumulate, 18% to incineration with associated CO₂ emissions and 23% mismanaged to potentially enter the environment uncontrolled¹.

[003] Chemical recycling is a potential alternative to increase utilization of waste material and pyrolysis has long been regarded for its potential to produce a liquid oil. However, the chemical challenges of pyrolysis oils have limited adoption.

[004] Pyrolysis is a conversion process where hydrocarbon-based material, including plastics, are heated to high temperatures, in the absence of oxygen, to thermally crack large molecules to produce shorter chain molecules. This process could be carried out with or without a catalyst to promote cracking.

[005] From the pyrolysis reactor a hydrocarbon stream is separated into non-condensable gas and liquid pyrolysis oil. A solid char is also produced in the reactor. It is the liquid oil that is of greatest interest for use in refining and petrochemical applications. While reactor conditions play a significant role in the characteristics of the resulting pyrolysis oils, the table below shows typical yield of hydrocarbon type from various plastic sources².

Plastic Type	Polyethylene (PE)	Polypropylene (PP)	Municipal Plastic Waste
Fraction			
Total-paraffin	35.6	30.4	32.5
Total-olefin	42.6	44.7	37.3

Plastic Type	Polyethylene (PE)	Polypropylene (PP)	Municipal Plastic Waste
Fraction			
Naphthene	19.6	21.5	20.7
Aromatics	5.8	1.4	7.9
Others	1.4	2.0	1.6

[006] Post consumer plastics, such as municipal wastes, are not pure substances. They contain many substances in addition to the polymer themselves. These can include dyes, additives, adhesives and contamination such as organic material. These materials are a source of heteroatoms in the pyrolysis system and ultimately the pyrolysis oil. Elements such as sulphur, chlorine, oxygen, nitrogen and silicon and metals are present in both organic and inorganic forms³. The liquid stream can also often contain solid residue such as char carried over from the reactor which can be removed by means of filtration or centrifuge.

[007] It is known that nitrogen, oxygen and sulphur can play a significant role in gum formation in hydrocarbons when combined with olefin and di-olefin content. This process is also known to be catalyzed by the presence of transition metals⁴. With the presence of all components sometimes in high concentrations it is no wonder that pyrolysis oils suffer poor stability and cause significant fouling during storage and in process equipment, such as heat exchangers and catalyst beds.

[008] Silicon is also found within pyrolysis oils and is known to be a hydrotreatment catalyst poison causing irreversible deactivation⁵. Hydrotreatment is a known refining step to improve the quality of the oil to the extent that it can be used without hinderance in steam cracking or in fuels by saturation of olefin and diolefin components, denitrification, deoxygenation and desulfurization.

[009] Previous work⁶ with polar aprotic solvents (such as NMP or propylene carbonate) has shown reduction of nitrogen, oxygen and halides in plastic pyrolysis oils through a mechanism of polar extraction. However, polar extraction methods alone are not suitable to remove non-polar contaminants from the oil, such as silicon.

[0010] Polar aprotic solvents do not remove silicon and are of concern from environmental and health and safety grounds. In particular, restrictions on the use of commonly employed dipolar aprotic solvents, such as NMP and DMF, have been recently introduced⁷.

[0011] There is a need in the art for improved methods for upgrading pyrolysis oils derived from plastic, rubber or a combination thereof. Suitably, new methods will provide higher quality pyrolysis oil in improved yield which have at least one or more advantages selected from improved impurity profile (e.g. decreased levels of heteroatoms, such as silicon) and improved stability. The upgraded pyrolysis oil products may be utilised as a transportation fuel, for blending with fuels and/or as a chemical feedstock.

SUMMARY OF THE INVENTION

[0012] In a first aspect, the present invention relates to a process for producing an upgraded pyrolysis oil product comprising:

(i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;

(ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and

(iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;

wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[0013] In a second aspect, the present invention relates to the use of a solution comprising a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water for decreasing the heteroatom content of a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[0014] In a third aspect, the present invention relates to an upgraded pyrolysis oil obtainable by a process according to the first aspect of the invention.

[0015] In a fourth aspect, the present invention relates to the use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination to stabilise a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[0016] Preferred, suitable, and optional features of any one particular aspect of the present invention are also preferred, suitable, and optional features of any other aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Figure 1 provides a schematic diagram of an embodiment of the claimed process involving liquid/liquid extraction and distillation of the extract phase.

[0018] Figure 2 provides a schematic diagram of an embodiment of the claimed process involving liquid/liquid extraction, further extraction of the raffinate with aqueous KOH and distillation of the extract phase.

[0019] Figure 3 provides a schematic diagram of an embodiment of the claimed process involving liquid/liquid extraction, further extraction of the raffinate with water and distillation of the extract phase.

[0020] Figure 4 provides a schematic diagram of an embodiment of the claimed process involving liquid/liquid extraction, further extractions of the raffinate with methanol and water and distillation of the extract phase(s).

[0021] Figure 5 provides a schematic diagram of an embodiment of the use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in a method to stabilise a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0022] As used herein, in each aspect of the invention, the term “upgrading” and “upgraded” used in relation to a pyrolysis oil refers to removing or reducing the concentration of one or more unwanted substances in the pyrolysis oil.

[0023] As used herein the term “plastic” refers to a solid material which comprises one or more thermoplastic or thermosetting polymers. Suitably, the plastic (essentially) consists of one or more thermoplastic or thermosetting polymers. Suitably the plastic (essentially) consists of one or more thermoplastic polymers. Suitably, the plastic is waste plastic which may be a mixture of various plastics. Plastics may be referred to by the name of the polymer of which they consist of. Examples of common plastics are polyethylene, polypropylene and polystyrene.

[0024] As used herein the term “thermoplastic polymer” refers to a polymer which becomes pliable or mouldable above a certain temperature and solidifies upon cooling but can be remelted on heating. Typically, thermoplastic polymers have a melting temperature from

about 60°C. to about 300°C, from about 80°C to about 250°C, or from about 100°C to about 250°C.

[0025] Suitably, the thermoplastic polymer is one which is commonly comprised in commercial plastic products. Suitable thermoplastic polymers generally include polyolefins, polyesters, polyamides, copolymers thereof, and combinations thereof. Examples of thermoplastic polymers include polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), polyamideimide, polymethylmethacrylate (PMMA), polytetrafluoroethylene, polyethylene terephthalate (PET), natural rubber (NR), and polycarbonate (PC), polyvinylidene chloride (PVDC), acrylonitrile butadiene styrene (ABS), polyurethanes (PU).

[0026] As used herein the term “thermosetting polymer” refers to a polymer which is irreversibly cured and cannot be reworked upon reheating. Examples of thermosetting polymers are polyurethane and polyoxybenzylmethylenglycolanhydride (Bakelite™).

[0027] As used herein the term “specific gravity (20/4)” refers to the true density of a sample at 20°C divided by water density at 4°C.

[0028] As used herein the term “liquid” refers to the liquid matter state at standard ambient temperature and pressure (SATP) (i.e. at a temperature of about 298.15 K (25 °C) and a pressure of about 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm)) unless otherwise provided.

Extraction Process

[0029] In one aspect, the present invention relates to a process for producing an upgraded pyrolysis oil product comprising:

(i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;

(ii) mixing the product of (i) and then allowing the mixture to form two phases consisting of a raffinate phase and an extract phase, and

(iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;

wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[0030] In one embodiment, “upgraded” used in relation to a pyrolysis oil refers to the removal or reduction the concentration of one or more unwanted substances in the pyrolysis oil.

Typically, upgraded/upgrading is assessed relative to the pyrolysis to be upgraded, i.e. the starting pyrolysis oil prior to being subjected to the process of the invention.

[0031] In one embodiment, the unwanted substances to be removed or reduced are selected from one or more compounds containing heteroatoms, such as sulphur, nitrogen, oxygen, halogens, transition metals and/or silicon.

[0032] In another embodiment, the unwanted substances comprise or (essentially) consist of compounds containing heteroatoms, suitably the compounds containing heteroatoms are selected from one or more of sulphur compounds, nitrogen compounds, oxygen compounds, halogen compounds, silicon compounds, transition metal compounds; or combinations thereof. Suitably, the compounds containing heteroatoms are sulphur, nitrogen, oxygen, chlorine and silicon compounds. Suitably, the compounds containing heteroatoms are silicon compounds.

[0033] In one embodiment, the sulphur compounds reduced/removed by the process of the invention comprise or essentially consist of organic sulphur compounds (OSCs). In another embodiment, the sulphur compounds reduced/removed comprise compounds selected from thiols, thioethers, disulphides, thiophenes and benzothiophenes. In another embodiment, the sulphur compounds reduced/removed are selected from thiols, thioethers, disulphides, thiophenes and benzothiophenes.

[0034] In one embodiment, the halogen compounds are halogen compounds commonly found in plastic or rubber pyrolysis oils. These compounds include for instance halogenated acids (such as HCl and HBr) and halogenated aromatics, such a polyhalogenated dibenzodioxins and dibenzofurans.

[0035] In one embodiment, the nitrogen compounds are molecules containing nitrogen which are commonly found in pyrolysis products. In one embodiment, the nitrogen compounds reduced/removed by the process of the invention comprise organic nitrogen compounds, such as ammonia and organic amines and imines.

[0036] In one embodiment, the transition metal compounds are molecules containing transitional metals which are commonly found in pyrolysis products. In one embodiment, the transition metals reduced/removed by the process of the invention comprise copper or iron or compounds thereof which are often used in dyes, inks and additives within plastics.

[0037] In one embodiment, the silicon compounds are molecules containing silicon which are commonly found in pyrolysis products. In one embodiment, the silicon compounds

reduced/removed by the process of the invention comprise one or more of a silane, an organosilane and a siloxane.

[0038] In one embodiment, the oxygen compounds are molecules containing oxygen which are commonly found in pyrolysis products. In one embodiment, the oxygen compounds reduced/removed by the process of the invention comprise phenols and carboxylic acids.

[0039] In step (i), the pyrolysis oil, C₁₋₃ alcohol, the base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water may be combined by any means known in the art. Typically, each component will be delivered (e.g. pumped) to a vessel, reactor or mixer commonly used in the art, either simultaneously, sequentially or in combination, suitably in combination.

[0040] In one embodiment, the C₁₋₃ alcohol, the base and the water are added simultaneously to the pyrolysis oil. In this embodiment, one or more of the C₁₋₃ alcohol, the base, and the water may be added in combination with one or more of the others. For instance, in one embodiment the C₁₋₃ alcohol is added in one entry stream and the water and alkali metal hydroxide are added in a second entry stream.

[0041] In another embodiment, the C₁₋₃ alcohol, the base and the water are added in combination. In one embodiment, the C₁₋₃ alcohol, the base and the water are pre-mixed before they are combined with the pyrolysis oil. Pre-mixing may be achieved using any suitable technique known in the art. For instance, the C₁₋₃ alcohol, the base and the water may be combined in an agitate tank before being transferred to pyrolysis oil in a separate vessel. Alternatively, the C₁₋₃ alcohol, the base and the water can be combined by an in-line mixing step.

[0042] In one embodiment, the pyrolysis oil is combined with the C₁₋₃ alcohol, the base and the water at a temperature of between about 10°C to about 50°C, suitably between about 15°C and about 45°C, suitably between about 18°C and about 40°C, suitably between about 25°C and about 40°C. Typically, the pyrolysis oil is combined with the C₁₋₃ alcohol, the base and the water at ambient pressure, for instance a pressure of about 1 atm (101 kPa). Accordingly, expense and other problems associated with high pressure conditions are avoided.

[0043] In one embodiment, the C₁₋₃ alcohol, the base and the water are combined at a pressure of about 101 kPa to about 160 KPa, suitably about 101 KPa to about 140 KPa.

[0044] In one embodiment, the base and water are added to the pyrolysis oil together, suitably in the form of an aqueous base solution. In one embodiment, the aqueous base solution has

a concentration of about 0.3 M to about 4 M. Suitably, the concentration in the aqueous solution is about 0.3 M to about 2 M, suitably about 0.3 M to about 1 M, suitably about 0.5 M to about 0.8 M.

[0045] In another embodiment, the C₁₋₃ alcohol, the base and the water are added together via a single entry stream.

[0046] In another embodiment, the C₁₋₃ alcohol, the base and the water may be each added separately, suitably separately but simultaneously.

[0047] In one embodiment, the C₁₋₃ alcohol is added in an amount such that the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 5:1 to about 1:2. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 3:1 to about 1:2. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 3:1 to about 2:3. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 2:1 to about 2:3. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:1 to about 2:3. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:1 to about 4:5.

[0048] In another embodiment, the water is added in an amount such that the mass ratio of water to pyrolysis oil is about 1:2 to about 1:20. Suitably, the mass ratio of water to pyrolysis oil is about 1:2 to about 1:15. Suitably, the mass ratio of water to pyrolysis oil is about 1:2 to about 1:12. Suitably, the mass ratio of water to pyrolysis oil is about 1:5 to about 1:12. Suitably, the mass ratio of water to pyrolysis oil is about 1:8 to about 1:10.

[0049] In another embodiment, the base is added in an amount such that the mass ratio of base to pyrolysis oil is about 1:4 to about 1:250. Suitably, the mass ratio of base to pyrolysis oil is about 1:10 to about 1:200. Suitably, the mass ratio of base to pyrolysis oil is about 1:10 to about 1:175. Suitably, the mass ratio of base to pyrolysis oil is about 1:50 to about 1:150. Suitably, the mass ratio of base to pyrolysis oil is about 1:75 to about 1:150. Suitably, the mass ratio of base to pyrolysis oil is about 1:90 to about 1:110. Suitably, the mass ratio of base to pyrolysis oil is about 1:100.

[0050] In one embodiment, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 3:1 to about 1:2, the mass ratio of water to pyrolysis oil is about 1:2 to about 1:15 and the mass ratio of alkali metal hydroxide to pyrolysis oil is about 1:50 to about 1:200. In another embodiment, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 3:1 to about 2:3, the mass ratio of water to pyrolysis oil is about 1:2 to about 1:12 and the mass ratio of alkali metal hydroxide to pyrolysis oil is about 1:10 to about 1:175. In another embodiment, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:1 to about 4:5, the mass ratio of water to pyrolysis oil is about

1:8 to about 1:10, and the mass ratio of alkali metal hydroxide to pyrolysis oil is about 1:90 to about 1:110.

[0051] In another embodiment, the C₁₋₃ alcohol, the base and the water are added to the pyrolysis oil simultaneously as a combined solution. Suitably, the combined solution comprises about 5% to about 20% (w/w) of water, suitably about 5% to about 15% (w/w) water, suitably about 12.5% (w/w) of water. Suitably, the combined solution comprises about 80% to about 95% (w/w) of C₁₋₃ alcohol, suitably about 85% to about 90% (w/w) C₁₋₃ alcohol, suitably about 86.5% (w/w) of C₁₋₃ alcohol. Suitably, the combined solution comprises about 0.5% to about 5% (w/w) of the base, suitably about 0.5% to about 3% (w/w) of the base, suitably about 0.5% to about 1.2% (w/w) of the base, suitably about 1% (w/w) of the base.

[0052] In one embodiment, the base is present in a concentration of about 0.05 M to about 1 M in the combined solution. Suitably, the concentration in the combined solution is about 0.05 M to about 0.5 M, suitably about 0.05 M to about 0.2 M, suitably about 0.09 M to about 0.2 M.

[0053] In one embodiment, the combined solution comprises:

about 70% to about 95% (w/w) of the C₁₋₃ alcohol;
about 3% to about 20% (w/w) of the water; and
about 0.5% to about 10% (w/w) of the base.

[0054] In another embodiment, the combined solution comprises:

about 80% to about 95% (w/w) of the C₁₋₃ alcohol;
about 5% to about 20% (w/w) of the water; and
about 0.5% to about 5% (w/w) of the base.

[0055] In another embodiment, the combined solution comprises:

about 85% to about 90% (w/w) of the C₁₋₃ alcohol;
about 5% to about 15% (w/w) of the water; and
about 0.5% to about 3% (w/w) of the base.

[0056] In another embodiment, the combined solution comprises:

about 85% to about 90% (w/w) of the C₁₋₃ alcohol;
about 5% to about 15% (w/w) of the water; and
about 0.5% to about 1.5% (w/w) of the base.

[0057] In another embodiment, the combined solution comprises:

about 85% to about 90% (w/w) of the C₁₋₃ alcohol;
about 5% to about 15% (w/w) of the water; and
about 0.5% to about 1.2% (w/w) of the base.

[0058] In another embodiment, the combined solution comprises:

about 85% to about 90% (w/w) of the C₁₋₃ alcohol;
about 8% to about 15% (w/w) of the water; and
about 0.5% to about 1.2% (w/w) of the base.

[0059] In another embodiment, the combined solution comprises:

about 80% to about 90% (w/w) of the C₁₋₃ alcohol;
about 8% to about 15% (w/w) of the water; and
about 0.5% to about 2% (w/w) of the base.

[0060] In one embodiment, the C₁₋₃ alcohol is selected from methanol, ethanol and 1-propanol. In another embodiment, the C₁₋₃ alcohol is methanol or ethanol. Suitably, the C₁₋₃ alcohol is methanol.

[0061] In one embodiment, the base is a Group I hydroxide or oxide or a Group II hydroxide or oxide selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide, potassium oxide, sodium oxide, lithium oxide, caesium hydroxide, caesium oxide, barium hydroxide, barium oxide, calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide.

[0062] In one embodiment, the base is a Group I hydroxide or a Group II hydroxide. Suitably, the base is selected from potassium hydroxide, sodium hydroxide, lithium hydroxide, caesium hydroxide, barium hydroxide, calcium hydroxide and magnesium hydroxide.

[0063] In one embodiment, the base is a Group I hydroxide. Suitably, the base is selected from potassium hydroxide, sodium hydroxide, lithium hydroxide and caesium hydroxide.

[0064] In one embodiment, the base is an alkali metal hydroxide. Suitably the base is an alkali metal hydroxide selected from potassium hydroxide or sodium hydroxide, suitably potassium hydroxide.

[0065] In one embodiment, step (i) comprises or (essentially) consists of combining the pyrolysis oil with methanol, potassium hydroxide and water. Suitably, a combined solution (essentially) consisting of methanol, potassium hydroxide and water. In one embodiment, the

combined solution of step (i), (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 3% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water.

[0066] In another embodiment, the combined solution of step (i) (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 3% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water.

[0067] In another embodiment, the combined solution of step (i) (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 1.2% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water.

[0068] In another embodiment, the combined solution of step (i) (essentially) consists of about 86.5% (w/w) methanol, about 1.0% (w/w) of potassium hydroxide and about 12.5% (w/w) water.

[0069] In another embodiment, the combined solution of step (i) (essentially) consists of about 85% (w/w) methanol, about 1.5% (w/w) of potassium hydroxide and about 13.5% (w/w) water.

[0070] Typically, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, the base and water combined is from about 95:5 to about 10:90. In one embodiment, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, base and water combined is about 60:40 to about 30:70, or suitably about 50:50 to about 30:70, or suitably about 50:50.

[0071] In one embodiment, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, base and water combined is from about 60:40 to about 20:80, suitably about 60:40 to about 40:60.

[0072] In one embodiment, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, base and water combined is from about 2:1 to about 1:2, suitably about 2:1 to about 1:1.

[0073] In step (ii), the pyrolysis oil, C₁₋₃ alcohol, base and water may be mixed by any means known in the art. For instance, each component may be added to vessels, reactors or mixers commonly used in the art, either simultaneously or sequentially and the components may be mixed. Mixing may comprise vigorous agitation of the components by a mixing means. For instance, the components may be mixed together by stirring or by shaking.

[0074] In one embodiment, the combination of pyrolysis oil with the C₁₋₃ alcohol, the base and the water is allowed to mix for period of time, suitably about 1 minute to about 24 hours, suitably about 1 minute to 12 hours; suitably about 1 minute to about 6 hours. The mixing may take place in a separate vessel.

[0075] In one embodiment, the pyrolysis oil is mixed with the C₁₋₃ alcohol, the base and the water at a temperature of between about 10°C to about 50°C, suitably between about 15°C and about 45°C, suitably between about 18°C and about 40°C, suitably between about 25°C and about 40°C. Typically, the pyrolysis oil is mixed with the C₁₋₃ alcohol, the base and the water at ambient pressure, for instance a pressure of about 1 atm (101 kPa). Accordingly, expense and other problems associated with high pressure conditions are avoided.

[0076] In one embodiment, the C₁₋₃ alcohol, the base and the water are mixed at a pressure of about 101 kPa to about 160 KPa, suitably about 101 KPa to about 140 KPa.

[0077] In one embodiment, the mixing of the components may occur more than once. For instance, after mixing the pyrolysis oil with the C₁₋₃ alcohol, base and water for the first time, the resulting two phases may be mixed again, possible numerous times. In one embodiment, the mixing results in two liquid phases, i.e. an extract phase and a raffinate phase.

[0078] The pyrolysis oil may be repeatedly mixed multiple times with fresh batches of C₁₋₃ alcohol, base and water. For instance, the pyrolysis oil may be mixed with a first batch to provide a first raffinate phase and a first extract phase. Following separation of the raffinate phase from the extract phase the raffinate phase may be mixed with a second batch to provide a second raffinate phase and a second extract phase. This cycle may be repeated multiple times.

[0079] In one embodiment the cycle of mixing the pyrolysis oil or its raffinate with fresh batches of C₁₋₃ alcohol, base and water is repeated between 1 and 9 times. In another embodiment, the cycle is repeated between 1 and 4 times. In another embodiment, the cycle is repeated 1, 2, 3 or 4 times. In another embodiment, the cycle is repeated 4 times.

[0080] The steps of contacting and formation of two phases may be continuous. Thus, in another embodiment the components may pass through a mixing means before entering a separating chamber in which the first and second phases are formed. The contacting of the components may be performed using a propeller, in-line mixers, counter-current flow means, an agitation means, a column (e.g. a Scheibel® column or a KARR® column) or a centrifugal extractor.

[0081] Typically, the pyrolysis oil, C₁₋₃ alcohol, base and water are mixed to the extent to allow effective reactive extraction of the pyrolysis oil by the C₁₋₃ alcohol, base and water. In respect of two immiscible solutions, the skilled person would understand that typically these solutions are intimately mixed until an emulsion is formed which is subsequently allowed to separate into two liquid phases.

[0082] In one embodiment, each mixing is carried out at a temperature of between about 10°C to about 65°C, suitably each mixing is carried out at a temperature of between about 10°C to about 50°C, suitably between about 15°C and about 45°C, suitably between about 18°C and about 40°C.

[0083] As used herein the term “raffinate phase” refers to the phase comprising/consisting essentially of/consisting of the upgraded pyrolysis oil.

[0084] As used herein, the term “extract phase” refers to the phase typically comprising the C₁₋₃ alcohol, the base and water. Typically, the extract phase will comprise the majority of the C₁₋₃ alcohol, the base and water after mixing with the pyrolysis oil. Typically, the extract phase will be denser than the raffinate phase and will form the lower layer. In addition to the C₁₋₃ alcohol, the base and water, the extract phase may comprise one or more undesirable substances extracted from the pyrolysis oil (e.g. such as heteroatom compounds).

[0085] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of undesirable substances compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0086] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of one or more of heteroatoms compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0087] In one embodiment, the concentration of sulphur compounds in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 80% (wt.%) relative to the concentration of sulphur compounds in the starting pyrolysis oil. In another embodiment, the concentration of sulphur compounds in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 70% (wt.%) relative to the concentration of sulphur compounds in the starting pyrolysis oil. In another embodiment, the concentration of sulphur compounds in the raffinate phase/upgraded pyrolysis oil is reduced by about 30% to about 80% (wt.%) relative to the concentration of sulphur compounds in the starting pyrolysis oil. In another embodiment, the concentration of sulphur compounds in the raffinate phase/upgraded pyrolysis oil is reduced by about 30% to about 70% (wt.%) relative to the concentration of sulphur compounds in the starting pyrolysis oil. In another embodiment, the concentration of sulphur compounds in the raffinate phase/upgraded pyrolysis oil is reduced by about 40% to about 60% (wt.%) relative to the concentration of sulphur compounds in the starting pyrolysis oil.

[0088] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of chlorine compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0089] In one embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 80% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil. In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 70% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil. In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 60% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil.

[0090] In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 30% to about 80% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil. In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 30% to about 70% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil. In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 30% to about 60% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil.

[0091] In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 40% to about 60% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil. In another embodiment, the concentration of chlorine in the raffinate phase/upgraded pyrolysis oil is reduced by about 50% to about 60% (wt.%) relative to the concentration of chlorine in the starting pyrolysis oil.

[0092] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of silicon compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0093] In one embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 80% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil. In another embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 70% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil. In another embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 10% to about 60% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil.

[0094] In another embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 25% to about 80% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil. In another embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 25% to about 70% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil. In another embodiment, the concentration of silicon in the raffinate phase/upgraded pyrolysis oil is reduced by about 25% to about 60% (wt.%) relative to the concentration of silicon in the starting pyrolysis oil.

[0095] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of oxygen compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0096] In one embodiment, the concentration of oxygen in the raffinate phase/upgraded pyrolysis oil is reduced by about 50% to about 90% (wt.%) relative to the concentration of oxygen in the starting pyrolysis oil. In another embodiment, the concentration of oxygen in the raffinate phase/upgraded pyrolysis oil is reduced by about 50% to about 80% (wt.%) relative to the concentration of oxygen in the starting pyrolysis oil. In another embodiment, the concentration of oxygen in the raffinate phase/upgraded pyrolysis oil is reduced by about 50% to about 70% (wt.%) relative to the concentration of oxygen in the starting pyrolysis oil. In another embodiment, the concentration of oxygen in the raffinate phase/upgraded pyrolysis oil is reduced by about 60% to about 70% (wt.%) relative to the concentration of oxygen in the starting pyrolysis oil.

[0097] In one embodiment, the raffinate phase/upgraded pyrolysis oil will have a reduced concentration of nitrogen compared to the pyrolysis oil prior to treatment with the C₁₋₃ alcohol, the base and water.

[0098] In one embodiment, the concentration of nitrogen in the raffinate phase/upgraded pyrolysis oil is reduced by about 50% to about 90% (wt.%) relative to the concentration of nitrogen in the starting pyrolysis oil. In another embodiment, the concentration of nitrogen in the raffinate phase/upgraded pyrolysis oil is reduced by about 60% to about 80% (wt.%) relative to the concentration of nitrogen in the starting pyrolysis oil. In another embodiment, the concentration of nitrogen in the raffinate phase/upgraded pyrolysis oil is reduced by about 70% to about 80% (wt.%) relative to the concentration of nitrogen in the starting pyrolysis oil.

[0099] In the process of the present invention, the raffinate phase tends to be of lower density than the extract phase and thus the raffinate phase will typically be the upper phase and the extract phase will typically be the lower phase.

[00100] In one embodiment, the process comprises an optional step of filtering the two liquid phases prior to separating the raffinate from the extract phase. Filtration may be carried by processes known in the art.

[00101] The process further comprises separating the raffinate phase to yield an upgraded pyrolysis oil (step (iii)). The raffinate phase may be separated by any means used in the art and is typically separated by a physical process. Said separating typically comprises physically isolating the raffinate phase, or at least some of the raffinate phase. Thus, said separating typically comprises separating at least some of the raffinate phase from the extract phase.

[00102] As the two phases will typically already be separate in the same container due to their immiscibility, said separating may simply comprise removing (e.g. by draining or decanting) at least part of the extract phase from the container comprising the extract phase and the raffinate phase. Alternatively, the raffinate phase may be removed (e.g. by draining or decanting) from the container to leave the extract phase.

[00103] In one embodiment, the separation of the raffinate and extract phase is conducted at a temperature of between about 10°C to about 65°C, or about 10°C to about 50°C, suitably between about 15°C and about 45°C, suitably between about 18°C and about 40°C, suitably between about 25°C and about 40°C. Typically, the separation is conducted at ambient pressure, for instance a pressure of about 1 atm. (101 kPa). In one embodiment, the separation is conducted at a pressure of about 101 kPa to about 160 KPa, suitably about 101 KPa to about 140 KPa.

[00104] In one embodiment, the raffinate is further treated with the base and/or water. In one embodiment, and in the same manner as any of the embodiments described above, the raffinate is mixed with the base and/or water and allowed to form two layered phases. The top layer being a further raffinate essentially consisting of the upgraded pyrolysis oil and the bottom layer being a further extract layer essentially consisting of aqueous base or water and potentially a small amount of extracted C₁₋₃ alcohol. In one embodiment, this further extract may be recycled in order to treat further batches of pyrolysis oil.

[00105] In another embodiment, the raffinate is further treated with the C₁₋₃ alcohol and/or water. In one embodiment, and in the same manner as any of the embodiments described above, the raffinate is mixed with the C₁₋₃ alcohol and/or water and allowed to form two layered phases. The top layer being a further raffinate essentially consisting of the upgraded pyrolysis oil and the bottom layer being a further extract layer essentially consisting

of C₁₋₃ alcohol and/or water and potentially a small amount of base, or Group I or II metal. In one embodiment, this further extract may be combined with preceding extract phases for further processing, e.g., distillation.

[00106] In one embodiment, the raffinate is further treated with (i) a combination of C₁₋₃ alcohol and water, and raffinate derived therefrom is further treated with water.

[00107] In one aspect, the present invention relates to a raffinate phase obtainable by a process as defined in any of the above embodiments.

[00108] In another aspect, the present invention relates to a raffinate phase obtained by a process as defined in any of the above embodiments.

[00109] In another aspect, the present invention relates to an upgraded pyrolysis oil obtained by a process as defined in any of the above embodiments. In one embodiment, the upgraded pyrolysis oil obtained/obtainable by the process of the invention is suitable for use as a substitute for naphtha used to produce fuel (e.g. gasoline and diesel) or hydrocarbon chemicals (e.g. ethylene and propylene). The upgraded pyrolysis has a reduced tendency to form gum on storage and thus can be stored or transported for longer periods than untreated pyrolysis oils.

Pyrolysis oil

[00110] Pyrolysis oil is a substance known to the skilled person. Pyrolysis oil may be obtained from a number of sources. The present invention concerns pyrolysis oil derived from plastic, rubber or a combination thereof. In one embodiment, the pyrolysis oil is derived from plastic. In another embodiment, the pyrolysis oil is derived from rubber. In another embodiment, the pyrolysis oil is derived from a combination of plastic and rubber.

[00111] In one embodiment, the pyrolysis oil to be upgraded is obtainable or obtained by pyrolysis of plastic, rubber or a combination thereof. Typically, pyrolysis is carried out at high temperature (greater than 400°C) and with very high heating rates in the absence of oxygen.

[00112] In another embodiment, the pyrolysis oil is obtainable or obtained by pyrolysis of plastic. In another embodiment, the pyrolysis oil is obtainable or obtained by pyrolysis of rubber. In another embodiment, the pyrolysis oil is obtainable or obtained by pyrolysis of a combination of plastic and rubber.

[00113] In one embodiment, the combination of rubber and plastic comprises at least about 50% w/w of plastic and rubber, suitably at least about 60% w/w of plastic and rubber, suitably at least about 70% w/w of plastic and rubber, suitably at least about 80% w/w of plastic and rubber, suitably at least about 90% w/w of plastic and rubber, suitably at least about 95% w/w of plastic and rubber.

[00114] In another embodiment, the combination of plastic and rubber comprises about 50% to about 100% (w/w) of plastic and rubber, suitably about 60% to about 100% (w/w) of plastic and rubber, about 70% to about 100% (w/w) of plastic and rubber, about 80% to about 100% (w/w) of plastic and rubber, about 90% to about 100% (w/w) of plastic and rubber.

[00115] Suitably, in each of the above-mentioned embodiments the rubber is obtained from tyres.

[00116] Suitably, in each of the above embodiments the plastic (essentially) consists of one or more thermoplastic polymers. Suitably, the plastic is waste plastic which may be a mixture of various plastics. Plastics may be referred to by the name of the polymer of which they consist of. Examples of common plastics are polyethylene, polypropylene and polystyrene.

[00117] In one embodiment, the pyrolysis oil is obtainable or obtained by pyrolysis of waste plastic, for instance waste plastic from the residue of a material recovery facility (MRF). Typically, such sources of waste plastic will additionally contain contamination from organic and inorganic materials which will be pyrolyzed and/or carried through into the resultant pyrolysis oil resulting in the pyrolysis oil containing water, organic acids, organic halides such as chlorides and bromides; oxygenated compounds such as phenol, alcohol, ketone carboxylic acids; silanes, organic sulphides; organic nitrogen compounds such as amides and amines; and transition metals, such as iron and vanadium.

[00118] In another embodiment, the pyrolysis oil is obtainable or obtained by pyrolysis of plastic comprising one or more of polyethylene, polypropylene and polystyrene.

[00119] In one embodiment, the waste plastic comprises at least about 50% w/w of plastic, suitably at least about 60% w/w of plastic, suitably at least about 70% w/w of plastic, suitably at least about 80% w/w of plastic, suitably at least about 90% w/w of plastic, suitably at least about 95% w/w of plastic.

[00120] In another embodiment, the waste plastic comprises about 50% to about 100% (w/w) of plastic, suitably about 60% to about 100% (w/w) of plastic, about 70% to about 100%

(w/w) of plastic, about 80% to about 100% (w/w) of plastic, about 90% to about 100% (w/w) of plastic.

[00121] In one embodiment, the pyrolysis oil to be upgraded has a specific gravity (20/4) of about 1 or less, suitably about 0.95 or less, or about 0.90 or less. In one embodiment, the pyrolysis oil to be upgraded has a specific gravity (20/4) of from about 0.7 to about 0.95, suitably about 0.8 to about 0.95, or about 0.7 to about 0.85.

[00122] In one embodiment, the pyrolysis oil to be upgraded is not miscible with water at standard ambient temperature and pressure (SATP), i.e. at a temperature of 298.15 K (25 °C) and at 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm).

[00123] Suitably, the pyrolysis oil to be upgraded is not miscible with water at standard ambient temperature and pressure (SATP), i.e. at a temperature of 298.15 K (25 °C) and at 100,000 Pa (1 bar, 14.5 psi, 0.9869 atm), and has a specific gravity (20/4) of from about 0.7 to about 0.95, suitably about 0.8 to about 0.95, or about 0.7 to about 0.85.

[00124] In one embodiment, the process comprises a preceding step of pyrolyzing plastic, rubber or a combination thereof, before combining the pyrolysis oil derived therefrom with a C₁₋₃ alcohol, an alkali metal hydroxide and water (i.e. step (i)).

[00125] In one embodiment, the pyrolysis is conducted on plastic or a combination of plastics as defined in any of the above embodiments. In one embodiment, the pyrolysis is conducted using waste plastic, suitably waste plastic from the residue of a material recovery facility (MRF).

[00126] Typically pyrolysis of polymers (e.g. plastic) can occur with or without a catalyst in temperature range of about 300°C to about 900°C in the absence of oxygen. In one embodiment, the pyrolysis is conducted at a temperature in the range of about 300°C to about 500°C, suitably about 300°C to about 450°C, suitably about 400°C to about 450°C. The reactor can be of batch or continuous design. Products produced include non-condensable gases, a (liquid) pyrolysis oil and char. A filter system or gravitational method of separation may be employed to remove solids from the pyrolysis oil, such as char carried over via entrainment from the reactor.

[00127] In one embodiment, the pyrolysis oil is or has been filtered prior to performing the claimed method. In another embodiment, the pyrolysis oil is or has been dewatered prior to performing the claimed method. In another embodiment, the pyrolysis oil is a dewatered, filtered and/or fractionated pyrolysis oil prior to performing the claimed method. In another

embodiment, the pyrolysis oil is a dewatered, and/or filtered pyrolysis oil prior to performing the claimed method.

[00128] In another embodiment, the pyrolysis oil, suitably a plastic pyrolysis oil, used in step (i) is obtained directly from the pyrolysis reactor.

Further Process Steps

[00129] In one embodiment, the process comprises the further step of recovering the C₁₋₃ alcohol from the extract phase. Suitably, the recovered C₁₋₃ alcohol from the extract is then recycled for use in step (i).

[00130] In one embodiment, the C₁₋₃ alcohol is recovered from the extract phase by distillation. Distillation may be performed by conventional techniques familiar to the skilled person and may or may not take place under vacuum. Suitably means of distillation would be known to the skilled person and include rotary evaporator, rising film evaporator and distillation tower.

[00131] In one embodiment, the distillation is conducted at atmospheric pressure at a temperature of about 60°C to about 80°C, suitably about 65°C to about 70°C.

[00132] In one embodiment, the present invention provides a process for producing an upgraded pyrolysis oil product comprising:

(i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;

(ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and

(iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;

(iv) optionally performing one or more further extractions of the raffinate phase with C₁₋₃ alcohol, water or a mixture thereof to provide a second raffinate phase and a second extract phase; and

(v) recovering C₁₋₃ alcohol from the extract phase(s), suitably via distillation;

wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00133] In one embodiment, the process is carried out a temperature of about 50°C or less, suitably 45°C or less, suitably 40°C or less. In another embodiment, the process is carried out at a temperature of about 15°C to about 45°C, suitably about 18°C to about 40°C, about 25°C to about 40°C.

[00134] In one embodiment, the process is carried out at ambient pressure, for instance a pressure of about 1 atm. (101 kPa). In one embodiment, the process is carried out at a pressure of about 101 kPa to about 160 KPa, suitably about 101 KPa to about 140 KPa.

[00135] The raffinate produced by the process disclosed herein is suitably purified for further processing, storage or transportation. In one embodiment, further processing is selected from one or more of hydrotreatment, cracking, adsorption, absorption and distillation.

[00136] In one embodiment, the process further comprises a step of recovering water from the residue of the extract phase after methanol has been recovered from the extract phase via distillation. Suitable techniques for water recovery would be known to the skilled person, such as passing the distillation residue through a membrane or by a further distillation step.

[00137] In one embodiment, the present invention provides a process for producing an upgraded pyrolysis oil product comprising:

(i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;

(ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and

(iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;

(iv) optionally performing one or more further extractions of the raffinate phase with C₁₋₃ alcohol, water or a mixture thereof to provide a second raffinate phase and a second extract phase; and

(v) recovering C₁₋₃ alcohol from the extract phase(s), suitably via distillation; and

(vi) recovering water from the residue of step (v);

wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00138] Suitably, the recovered water from the extract is then recycled for use in step (i) or (iv).

[00139] One embodiment of the present process will now be described with reference to Figure 1. Figure 1 provides a schematic of a process according to the present invention. The process comprises pumping methanol (101) and aqueous potassium hydroxide solution (102) via a shared entry stream to a separator with heating device (103) charged with pyrolysis oil (109) derived from plastic, rubber or a combination thereof. The separator (103) is suitably a column, mixer settler or centrifuge.

[00140] In separator (103) the pyrolysis oil is intensely mixed with the methanol (101) and the aqueous potassium hydroxide solution (102) in order to extract contaminants from the oil via a reactive liquid-liquid extraction and then allowed to settle. Said contaminants include sulphur, silicon, nitrogen, oxygen and chlorine containing compounds. The extraction in separator (103) may take place at ambient temperature to about 40°C and at substantially ambient pressure (i.e. about 1 atm.).

[00141] In this embodiment, the upper raffinate phase (104) comprising upgraded pyrolysis oil is isolated via one exit stream and the lower extract phase (105) from separator (103) comprising mostly methanol, water and potassium hydroxide along with impurities extracted from the pyrolysis oil is fed via an exit stream to a distillation device (106) in order to separate a recycle stream of methanol (107) which may be combined with or used as methanol stream (101) for use in the extraction of separator (103).

[00142] The distillation is typically performed at atmospheric pressure and at a temperature of about 60°C to about 80°C.

[00143] Another embodiment of the present process will now be described with reference to Figure 2. Figure 2 provides a schematic of a process according to the present invention. The process comprises pumping methanol (201) and aqueous potassium hydroxide solution (202) via a shared entry stream to a separator with heating device (203) charged with pyrolysis (212) oil derived from plastic, rubber or a combination thereof. The separator (203) is suitably a column, mixer settler or centrifuge.

[00144] In separator (203) the pyrolysis oil is intensely mixed with the methanol (201) and the aqueous potassium hydroxide solution (202) in order to extract contaminants from the oil via a reactive liquid-liquid extraction and then allowed to settle.

[00145] In this embodiment, the upper phase (204) comprising extracted pyrolysis oil exits separator (203) and is fed to another separator (205) for further extraction with aqueous potassium hydroxide solution (207). Any residual methanol remaining in the oil is removed and the lower phase extract can be recycled as part of the aqueous KOH feed (202) to be combined with methanol (201) for use in separator (203). The upgraded pyrolysis oil (206) product is isolated as an exit stream from separator (205).

[00146] The extractions in separators (203) and (205) may take place at ambient temperature to about 40°C and at substantially ambient pressure (i.e. about 1 atm.).

[00147] The lower extract phase (208) from separator (203) comprising mostly methanol, water and potassium hydroxide along with impurities extracted from the pyrolysis oil is fed via an exit stream to a distillation device (209) in order to separate a recycle stream of methanol (211) which may be combined with or used as methanol stream (201) for use in the extraction of separator (203).

[00148] The distillation is typically performed at atmospheric pressure and at a temperature of about 60°C to about 80°C.

[00149] An alternative embodiment is described below with reference to Figure 3.

[00150] Similar to the process of Figure 2, the process comprises pumping methanol (301) and aqueous potassium hydroxide solution (302) via a shared entry stream to a separator with heating device (303) charged with pyrolysis oil (312) derived from plastic, rubber or a combination thereof. The separator (303) is suitably a column, mixer settler or centrifuge.

[00151] In separator (303) the pyrolysis oil is intensely mixed with the methanol (301) and the aqueous potassium hydroxide solution (302) in order to extract contaminants from the oil via a reactive liquid-liquid extraction and then allowed to settle.

[00152] In this embodiment, the upper phase (304) comprising extracted pyrolysis oil exits separator (303) and is fed to another separator (305) for further extraction with water (307). Any residual methanol remaining in the oil is removed and the lower phase extract from separator (305) can be recycled as part of the aqueous KOH feed (302) to be combined with methanol (301) for use in separator (303). The upgraded pyrolysis oil (306) product is isolated as an exit stream from separator (305).

[00153] Distillation of the lower phase (308) from separator (303) is conducted in a similar manner as the process described in Figure 2. In particular, lower extract phase (308) comprising mostly methanol, water and potassium hydroxide along with impurities extracted from the pyrolysis oil is fed via an exit stream to a distillation device (309) in order to separate a recycle stream of methanol (311) which may be combined with or used as methanol stream (301) for use in the extraction of separator (303).

[00154] A further embodiment is described below with reference to Figure 4. A feed stream of aqueous potassium hydroxide (402), an water stream (401) and a methanol stream (403) is delivered, suitably pumped, to a mixer tank (404). The combined methanol, KOH and water solution is then transferred to a reaction tank (405) where it is combined with the pyrolysis oil derived from plastic, rubber or a combination thereof (406). The reaction tank (405) comprises a heating device. Typically the contents are mixed (e.g. stirred) for 1 minute to 6 hours at a temperature of about 15°C to about 40°C in order to extract contaminants from the oil via a reactive liquid-liquid extraction.

[00155] Once the desired time has elapsed, the contents of the reaction tank (405) is transferred to a separator with heating device (407). The separator (407) is suitably a column, mixer settler or centrifuge.

[00156] In the separator (407) the oil, methanol, KOH and water mixture is allowed to settle under gravity for a desired time, typically 30 minutes to 24 hours and typically at a temperature of about 15°C to about 40°C. The upper phase (408) comprising upgraded pyrolysis oil exits the separator (407) and is fed to another separator with heating device (409) for further extraction with methanol and water (418). The separator (409) is suitably a column, mixer settler or centrifuge. After mixing the inputs the contents are allowed to settle under gravity for a desired time, typically 30 minutes to 24 hours and typically at a temperature of about 15°C to about 40°C. In the separator (409), any residual potassium and other heteroatoms remaining in the oil are removed to the extract phase. The lower phase extract (413) from the separator (409) can be combined with the extract from the previous separator (407) to form a feed (414) to a distillation apparatus (415).

[00157] In this embodiment, the upper phase (410) comprising extracted pyrolysis oil exits separator (409) and is fed to a further separator (411) for washing with a water (420). The further separator (411) is suitably a column, mixer settler or centrifuge. The water is fed (420) to the separator (411) and after mixing the inputs the contents are allowed to settle under gravity for a desired time, typically 30 minutes to 24 hours and typically at a temperature of about 15°C to about 40°C. Any residual methanol from the oil is removed to a lower aqueous

extract phase (419) which may be combined with recovered methanol (417) as a methanol and water feed (418). The upgraded pyrolysis oil (412) product is isolated as an exit stream from the further separator (411).

[00158] Distillation of the lower extract phase (414) from separator (407) and optionally the lower phase (413) from the next separator (409) is conducted in a similar manner as the process described in Figure 2. In particular, the lower extract phase(s) comprising mostly methanol, water and potassium hydroxide along with impurities extracted from the pyrolysis oil is fed to a distillation device (415) in order to separate extracted impurities, KOH and water (416) from the methanol. The recycle stream of purified methanol (417) obtained from the distillation may be combined with water for use as extractant stream (418) in a separator (409), and/or may be recycled as the methanol feed (403) to the mixer tank (404).

[00159] The residue (416) of the distillation device (415) is fed to a water recovery system (421) in order to recover water (422) which may be recycled as one or more of the water feeds (401, 420).

Sorbent

[00160] In another embodiment, the raffinate may be treated with a sorbent.

[00161] Accordingly, in one embodiment, the present invention relates to a process for producing an upgraded pyrolysis oil product comprising:

(i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;

(ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and

(iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product; and

(iv) treating the separated raffinate phase of step (iii) with a sorbent;

wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00162] The raffinate/upgraded pyrolysis oil may be treated with the sorbent by any means known in the art. For instance, the raffinate/upgraded pyrolysis oil and sorbent may

be combined and either left to stand, stirred or shaken together, or a combination thereof. Alternatively, the raffinate/upgraded pyrolysis oil may be flowed over a bed of the sorbent.

[00163] Suitably, the sorbent is capable of absorbing and/or adsorbing one or more heteroatoms (suitably sulfur and/or chloride) from the raffinate/upgraded pyrolysis oil. Particular examples of suitable sorbents are zeolites, aluminosilicates, activated carbon and mixtures thereof.

[00164] In one embodiment, the sorbent is a commercially available molecular sieve. Suitably, the sorbent is a microporous molecular sieve (i.e. pore diameter of 2nm or less).

[00165] In one embodiment, the sorbent is a zeolite molecular sieves suitably selected from 3A, 4A, 5A, 10X, 13X. Suitably, the sorbent is zeolite molecular sieves 13X.

[00166] In one embodiment, the zeolite is a zeolite of the faujasite series, suitably a zeolite Y (e.g. zeolite Na-Y or La-Y).

[00167] In one embodiment the sorbent is selected from a zeolite molecular sieves 3A, 4A, 5A, 10X, 13X, or zeolite Na-Y and La-Y. In another embodiment, the sorbent is selected from zeolite molecular sieves 13X and zeolite Na-Y or La-Y. In another embodiment, the sorbent is selected from zeolite molecular sieves 13X and zeolite Na-Y.

[00168] In one embodiment, the sorbent is an adsorbent.

[00169] Optionally, the sorbent treated raffinate may be further subjected to hydrotreatment.

Use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water

[00170] The process of the invention utilises a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination to upgrade the pyrolysis oil. Without being bound by theory, it is believed that the methanol removes polar heteroatom containing compounds but has minimal impact on silicon containing compounds and can lead to mass loss from the hydrocarbon oil, in part due to poor phase separation. As demonstrated for the first time herein, the addition of water and a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide maintains effective removal of polar heteroatom containing compounds, vastly improves removal of silicon containing compounds whilst increasing the selectivity of the extraction and subsequent yield of the upgraded pyrolysis oil.

[00171] Thus, in one embodiment, a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination is capable of removing or reducing the concentration of undesirable substances in the pyrolysis oil, wherein the undesirable substances are selected from one or more of polar heteroatom compounds (e.g. compounds containing sulphur, nitrogen, oxygen and halogens) and silicon containing compounds.

[00172] In another aspect, the present invention relates to the use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination for decreasing the heteroatom content of a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00173] In one embodiment, the heteroatoms are selected from sulphur, nitrogen, oxygen, halogens (e.g. chlorine) and silicon.

[00174] In another embodiment, the heteroatoms include sulphur, nitrogen, oxygen, halogens (e.g. chlorine) and silicon.

[00175] In one embodiment, the present invention relates to the use of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination for decreasing the silicon content of a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00176] Suitably, the silicon content is decreased by about 25% to about 80% (wt.%) relative to the silicon content in the pyrolysis oil initially. In another embodiment, the silicon content is decreased by about 25% to about 70% (wt.%) relative to the silicon content in the pyrolysis oil initially. In another embodiment, the content is decreased by about 25% to about 60% (wt.%) relative to the silicon content in the pyrolysis oil initially.

[00177] In one embodiment, the combination (essentially) consists of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water.

[00178] In one embodiment, the C₁₋₃ alcohol is methanol or ethanol. Suitably, the C₁₋₃ alcohol is methanol.

[00179] In one embodiment, the base is an alkali metal hydroxide, suitably selected from potassium hydroxide or sodium hydroxide, suitably potassium hydroxide.

[00180] In one embodiment of each of the above aspects, the C₁₋₃ alcohol, the base and water are used as a combined solution.

[00181] In one embodiment, the combined solution (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 3% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water. In another embodiment, the combined solution (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 1.2% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water. In another embodiment, the combined solution (essentially) consists of about 86.5% (w/w) methanol, about 1.0% (w/w) of potassium hydroxide and about 12.5% (w/w) water.

[00182] In another aspect, the present invention relates to the use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination to stabilise a pyrolysis oil wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00183] In particular, addition of the C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination can prevent gum formation within the pyrolysis oil, thus small amounts of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination may be added to the pyrolysis oil during storage or transport in order to reduce or prevent gum formation and thus stabilise the oil.

[00184] In another aspect, the present invention relates to a method of stabilising a pyrolysis oil wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof, wherein said method comprises combining a mixture of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water with the pyrolysis oil.

[00185] In one embodiment, the pyrolysis oil and mixture of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water are combined in a suitable container, such as a bulk tank, drum or intermediate bulk container (IBC).

[00186] In one embodiment, the pyrolysis oil and mixture of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water are stored, suitably at ambient temperature. In one embodiment, the combination of pyrolysis oil and mixture of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water are stored for at least one week, suitably at least two weeks, suitably at least one month. In another embodiment, the combination of pyrolysis oil and mixture of C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II

hydroxide or oxide; and water are stored for between 1 day and 1 year, suitably between 1 week and 1 year, suitably between 1 month and 1 year.

[00187] In one embodiment, the mixture/combination (essentially) consists of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water.

[00188] In one embodiment, the C₁₋₃ alcohol is methanol or ethanol. Suitably, the C₁₋₃ alcohol is methanol.

[00189] In one embodiment, the base is an alkali metal hydroxide, suitably selected from potassium hydroxide or sodium hydroxide, suitably potassium hydroxide.

[00190] In one embodiment of each of the above aspects, the C₁₋₃ alcohol, the base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water are used as a combined solution.

[00191] In one embodiment, the combined solution is added such that the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:100 to about 1:5. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:50 to about 1:5. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:50 to about 1:8. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:20 to about 1:8. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:20 to about 1:5. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:10 to about 1:5. Suitably, the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:10 to about 1:8.

[00192] In one embodiment, the combined solution (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 3% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water. In another embodiment, the combined solution (essentially) consists of about 85% to about 90% (w/w) methanol, about 0.5% to about 1.2% (w/w) of potassium hydroxide and about 5% to about 15% (w/w) water. In another embodiment, the combined solution (essentially) consists of about 86.5% (w/w) methanol, about 1.0% (w/w) of potassium hydroxide and about 12.5% (w/w) water. In another embodiment, the combined solution (essentially) consists of about 85% (w/w) methanol, about 1.5% (w/w) of potassium hydroxide and about 13.5% (w/w) water.

[00193] In one embodiment, the C₁₋₃ alcohol is added in an amount such that the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:100 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:50 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:20 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:10.

[00194] In another embodiment, the water is added in an amount such that the mass ratio of water to pyrolysis oil is about 1:500 to about 1:100. Suitably, the mass ratio of water to pyrolysis oil is about 1:300 to about 1:100. Suitably, the mass ratio of water to pyrolysis oil is about 1:200.

[00195] In another embodiment, the base is added in an amount such that the mass ratio of base to pyrolysis oil is about 1:5000 to about 1:1000. Suitably, the mass ratio of base to pyrolysis oil is about 1:3000 to about 1:1000. Suitably, the mass ratio of base to pyrolysis oil is about 1:2000.

[00196] In one embodiment, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:20 to about 2:15, the mass ratio of water to pyrolysis oil is about 1:300 to about 1:100 and the mass ratio of alkali metal hydroxide to pyrolysis oil is about 1:3000 to about 1:1000.

[00197] In another aspect, the present invention relates to a mixture comprising a pyrolysis oil, a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00198] In one embodiment, the mixture (essentially) consists of a pyrolysis oil, a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

[00199] In one embodiment, the C₁₋₃ alcohol is methanol or ethanol. Suitably, the C₁₋₃ alcohol is methanol.

[00200] In one embodiment, the base is an alkali metal hydroxide, suitably selected from potassium hydroxide or sodium hydroxide, suitably potassium hydroxide.

[00201] In one embodiment, the C₁₋₃ alcohol is present in an amount such that the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:100 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:50 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:50 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:50 to about 2:15.

to pyrolysis oil is about 1:20 to about 2:15. Suitably, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:10.

[00202] In another embodiment, the water is present in an amount such that the mass ratio of water to pyrolysis oil is about 1:500 to about 1:100. Suitably, the mass ratio of water to pyrolysis oil is about 1:300 to about 1:100. Suitably, the mass ratio of water to pyrolysis oil is about 1:200.

[00203] In another embodiment, the base is present in an amount such that the mass ratio of the base to pyrolysis oil is about 1:5000 to about 1:1000. Suitably, the mass ratio of the base to pyrolysis oil is about 1:3000 to about 1:1000. Suitably, the mass ratio of the base to pyrolysis oil is about 1:2000.

[00204] In one embodiment, the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:20 to about 2:15, the mass ratio of water to pyrolysis oil is about 1:300 to about 1:100 and the mass ratio of the base to pyrolysis oil is about 1:3000 to about 1:1000.

[00205] Typically, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, the base and water combined is from about 12:1 to about 5:1. In one embodiment, the mass ratio of pyrolysis oil to C₁₋₃ alcohol, the base and water combined is about 11:1 to about 8:1, suitably about 10:1.

[00206] A further embodiment is described below with reference to Figure 5. A feed stream of aqueous potassium hydroxide (502), an water stream (501) and a methanol stream (503) is delivered, suitably pumped, to a mixer tank (504). The combined methanol, KOH and water solution is then transferred to a storage vessel, such as a bulk tank, a drum, an IBC or other suitable container (505) where it is combined with the pyrolysis oil derived from plastic, rubber or a combination thereof (506). The storage vessel may optionally comprise an agitation means. The oil and the methanol, KOH and water solution in the storage vessel (505) may be left in contact with or without agitation for extended time period up to or more than 1 year, suitably at ambient temperature, in order to inhibit accumulation and deposition of gums or solids in the storage vessel. Following storage, the contents of the storage vessel is transferred to a separator with heating device (507). The separator (507) is suitably a column, mixer settler or centrifuge. In the separator (507) the oil, methanol, KOH and water mixture is allowed to settle under gravity for a desired time, typically 30 minutes to 24 hours and typically at a temperature of about 15°C to about 40°C. The upper phase (508) comprising pyrolysis oil is recovered from the separator (507).

Numbered Clauses

[00207] The invention will now be further described by way of the following numbered clauses (which are not claims):

1. A process for producing an upgraded pyrolysis oil product comprising:
 - (i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;
 - (ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and
 - (iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.
2. A process according to clause 1, wherein each of the C₁₋₃ alcohol, the base and water are added simultaneously to the pyrolysis oil.
3. A process according to clause 1 or 2, wherein the base and water are added in combination, suitably at a concentration of about 0.3 M to about 4 M.
4. A process according to any one of clauses 1 to 3, wherein the C₁₋₃ alcohol, the base and water are added in combination.
5. A process according to clause 4, wherein the combination comprises about 80% to about 95% (w/w) of C₁₋₃ alcohol, suitably about 85% to about 90% (w/w).
6. A process according to clause 4 or 5, wherein the combination comprises about 5% to about 20% (w/w) of water, suitably about 5% to about 15% (w/w) water.
7. A process according to any one of clauses 4 to 6, wherein the combination comprises about 12% to about 15% (w/w) of water.
8. A process according to any one of clauses 4 to 7, wherein the combination comprises about 12.5% to about 13.5% (w/w) of water.
9. A process according to any one of clauses 4 to 8, wherein the combination comprises about 0.5% to about 5% (w/w) of the base, suitably about 0.5% to about 3% (w/w).

10. A process according to any one of clauses 4 to 9, wherein the combination comprises about 1% (w/w) of the base.

11. A process according to clause 4, wherein the combination consists of:

- about 70% to about 95% (w/w) of C₁₋₃ alcohol;
- about 3% to about 20% (w/w) of water; and
- about 0.5% to about 10% (w/w) of the base.

12. A process according to clause 4, wherein the combination consists of:

about 85% to about 90% (w/w) of C₁₋₃ alcohol;

about 8% to about 15% (w/w) of water; and

about 0.5% to about 1.2% (w/w) of the base.

13. A process according to clause 4, wherein the combination consists of about 86.5% (w/w) C₁₋₃ alcohol, about 12.5% (w/w) water and about 1% (w/w) of the base; or wherein the combination consists of about 85% (w/w) C₁₋₃ alcohol, about 13.5% (w/w) water and about 1.5% (w/w) of the base.

14. A process according to any one of the preceding clauses, wherein the C₁₋₃ alcohol is added in an amount such that the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 5:1 to about 1:2, suitably about 1:1 to about 2:3.

15. A process according to any one of the preceding clauses, wherein the water is added in an amount such that the mass ratio of water to pyrolysis oil is about 1:2 to about 1:20, suitably about 1:5 to about 1:12.

16. A process according to any one of the preceding clauses, wherein the base is added in an amount such that the mass ratio of the base to pyrolysis oil is about 1:4 to about 1:250, suitably about 1:90 to about 1:110.

17. A process according to any one of the preceding clauses, wherein:

- the ratio of C₁₋₃ alcohol to pyrolysis oil is 3:1 to about 1:2;
- the ratio of water to pyrolysis oil is 1:2 to about 1:15; and
- the ratio of the base to pyrolysis oil is 1:50 to about 1:200.

18. A process according to any one of the preceding clauses, wherein:

- the ratio of C₁₋₃ alcohol to pyrolysis oil is 3:1 to about 2:3;
- the ratio of water to pyrolysis oil is 1:2 to about 1:12; and
- the ratio of the base to pyrolysis oil is about 1:90 to about 1:110.

19. A process according to any one of the preceding clauses, wherein in step (i), the pyrolysis oil is combined with the C₁₋₃ alcohol, the base and water at a temperature of about 10°C to about 50°C, suitably about 15°C to about 40°C.

20. A process according to any one of the preceding clauses, wherein in step (i) the pyrolysis oil is combined with the C₁₋₃ alcohol, the base and water at a pressure of about 101 kPa to about 160 KPa, suitably about 101 KPa to about 140 KPa.

21. A process according to any one of the preceding clauses, wherein in step (ii), the two liquid phases are filtered before separation in step (iii).

22. A process according to any one of the preceding clauses, further comprising a step of recovering the C₁₋₃ alcohol from the extract phase, which is optionally recycled for use in step (i).

23. A process according to clause 22, wherein the C₁₋₃ alcohol is recovered from the extract phase by distillation.

24. A process according to any one of the preceding clauses, wherein the raffinate is further treated with (i) C₁₋₃ alcohol and/or water, and optionally the raffinate derived therefrom is further treated with water.

25. A process according to any one of the preceding clauses, further comprising the step of treating the raffinate with a sorbent.

26. A process according to clause 25, wherein the sorbent is an adsorbent.

27. A process according to clause 25, wherein the sorbent is selected from zeolites, aluminosilicates, activated carbon and mixtures thereof.

28. A process according to any one of the preceding clauses, wherein the process comprises a preceding step of pyrolyzing plastic, rubber or a combination thereof, before combining the pyrolysis oil derived therefrom with a C₁₋₃ alcohol, the base and water.

29. A process according to any one of the preceding clauses, wherein the pyrolysis oil is derived from the pyrolysis of plastic, suitably waste plastic.

30. A process according to any one of the preceding clauses, wherein the pyrolysis oil is a full range (i.e. unfractionated) pyrolysis oil.
31. A process according to any one of the preceding clauses, wherein the C₁₋₃ alcohol is selected from methanol or ethanol.
32. A process according to any one of the preceding clauses, wherein the C₁₋₃ alcohol is methanol.
33. A process according to any one of the preceding clauses, wherein the base is a Group I hydroxide or oxide and a Group II hydroxide or oxide from potassium hydroxide, sodium hydroxide, lithium hydroxide, potassium oxide, sodium oxide, lithium oxide, caesium hydroxide, caesium oxide, barium hydroxide, barium oxide, calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide
34. A process according to any one of the preceding clauses, wherein the base is an alkali metal hydroxide, suitably selected from potassium hydroxide or sodium hydroxide.
35. A process according to any one of the preceding clauses, wherein the base is potassium hydroxide.
36. An upgraded pyrolysis oil obtained or obtainable according to the process of clauses 1 to 35.
37. Use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination for decreasing the heteroatom content of a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.
38. Use according to clause 37, wherein the heteroatoms are selected from one or more of sulphur, nitrogen, chlorine, oxygen and silicon.
39. Use according to clause 37 or 38, wherein the heteroatoms content reduced includes silicon.
40. Use according to any one of clauses 37 to 39, wherein the C₁₋₃ alcohol is methanol or ethanol.
41. Use according to any one of clauses 37 to 40, wherein the C₁₋₃ alcohol is methanol

42. Use according to any one of clauses 37 to 41, wherein the base is an alkali metal hydroxide, suitably potassium hydroxide.
43. Use according to any one of clauses 37 to 42, wherein the C₁₋₃ alcohol, the base and water are used as a combined solution.
44. Use according to any one of clauses 37 to 43, wherein the combined solution comprises about 80% to about 95% (w/w) of C₁₋₃ alcohol, suitably about 85% to about 90% (w/w).
45. Use according to any one of clauses 37 to 44, wherein the combined solution comprises about 5% to about 20% (w/w) of water, suitably about 5% to about 15% (w/w) water.
46. Use according to any one of clauses 37 to 45, wherein the combined solution comprises about 12% to about 15% (w/w) of water, suitably about 12.5% (w/w) of water.
47. Use according to any one of clauses 37 to 46, wherein the combined solution comprises about 0.5% to about 5% (w/w) of the base, suitably about 0.5% to about 3% (w/w).
48. Use according to any one of clauses 37 to 46, wherein the combined solution comprises about 1% (w/w) of the base.
49. Use according to clause 43, wherein the combined solution consists of:
- about 70% to about 95% (w/w) of C₁₋₃ alcohol;
 - about 3% to about 20% (w/w) of water; and
 - about 0.5% to about 10% (w/w) of the base.
50. Use according to clause 43, wherein the combined solution consists of:
- about 85% to about 90% (w/w) of C₁₋₃ alcohol;
 - about 8% to about 15% (w/w) of water; and
 - about 0.5% to about 1.2% (w/w) of the base.
51. Use according to clause 43, wherein the combined solution consists of about 86.5% (w/w) C₁₋₃ alcohol, about 12.5% (w/w) water and about 1% (w/w) of the base; or about 85% (w/w) C₁₋₃ alcohol, about 13.5% (w/w) water and about 1.5% (w/w) of the base.
52. Use of a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water in combination to stabilise a pyrolysis oil wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.

53. Use according to clauses 52, wherein the C₁₋₃ alcohol is methanol or ethanol.
54. Use according to clauses 52 or 53, wherein the C₁₋₃ alcohol is methanol
55. Use according to any one of clauses 52 to 54, wherein the base is an alkali metal hydroxide, suitably potassium hydroxide.
56. Use according to any one of clauses 52 to 55, wherein the C₁₋₃ alcohol, the base and water are used as a combined solution.
57. Use according to any one of clauses 52 to 56, wherein the combined solution is added such that the mass ratio of combination of C₁₋₃ alcohol, the base and water to pyrolysis oil is about 1:100 to about 1:5, suitably about 1:20 to about 1:8, more suitably about 1:10.
58. Use according to any one of clauses 52 to 57, wherein the combined solution comprises about 80% to about 95% (w/w) of C₁₋₃ alcohol, suitably about 85% to about 90% (w/w).
59. Use according to any one of clauses 52 to 58, wherein the combined solution comprises about 5% to about 20% (w/w) of water, suitably about 5% to about 15% (w/w) water.
60. Use according to any one of clauses 52 to 59, wherein the combined solution comprises about 12% to about 15% (w/w) of water, suitably about 12.5% (w/w) of water.
61. Use according to any one of clauses 52 to 60, wherein the combined solution comprises about 0.5% to about 5% (w/w) of the base, suitably about 0.5% to about 3% (w/w).
62. Use according to any one of clauses 52 to 61, wherein the combined solution comprises about 1% (w/w) of the base.
63. Use according to clause 56, wherein the combined solution consists of:
- about 70% to about 95% (w/w) of C₁₋₃ alcohol;
 - about 3% to about 20% (w/w) of water; and
 - about 0.5% to about 10% (w/w) of the base.
64. Use according to clause 56, wherein the combined solution consists of:
- about 85% to about 90% (w/w) of C₁₋₃ alcohol;
 - about 8% to about 15% (w/w) of water; and
 - about 0.5% to about 1.2% (w/w) of the base.

65. Use according to clause 56, wherein the combined solution consists of about 86.5% (w/w) C₁₋₃ alcohol, about 12.5% (w/w) water and about 1% (w/w) of the base; or about 85% (w/w) C₁₋₃ alcohol, about 13.5% (w/w) water and about 1.5% (w/w) of the base.
66. A mixture comprising a pyrolysis oil, a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.
67. A mixture according to clause 66, wherein the C₁₋₃ alcohol is methanol or ethanol.
68. A mixture according to clauses 66 or 67, wherein the C₁₋₃ alcohol is methanol
69. A mixture according to any one of clauses 66 to 68, wherein the base is an alkali metal hydroxide, suitably potassium hydroxide.
70. A mixture according to any one of clauses 66 to 69, wherein the pyrolysis oil is derived from the pyrolysis of plastic, suitably waste plastic.
71. A mixture according to any one of clauses 66 to 70, wherein the pyrolysis oil is a full range (i.e. unfractionated) pyrolysis oil.
72. A mixture according to any one of clauses 66 to 71, wherein the C₁₋₃ alcohol is present in an amount such that the mass ratio of C₁₋₃ alcohol to pyrolysis oil is about 1:100 to about 2:15, suitably about 1:20 to about 2:15.
73. A mixture according to any one of clauses 66 to 72, wherein the water is present in an amount such that the mass ratio of water to pyrolysis oil is about 1:500 to about 1:100, suitably about 1:300 to about 1:100.
74. A mixture according to any one of clauses 66 to 73, wherein the base is present in an amount such that the mass ratio of alkali metal hydroxide to pyrolysis oil is about 1:5000 to about 1:1000, suitably about 1:3000 to about 1:1000.
75. A mixture according to any one of clauses 66 to 74, wherein the mass ratio of pyrolysis oil to C₁₋₃ alcohol, the base and water combined is from about 12:1 to about 5:1, suitably about 11:1 to about 8:1, more suitably about 10:1.

EXAMPLES

A. Materials and Methods

[00208] Methanol, analytical reagent grade; potassium hydroxide, ca. 85% pellets; demineralised water; and propylene carbonate 98.5% were purchased from Fisher Scientific UK. Sodium hydroxide, > 98% pellets was purchased from Sigma Aldrich. N-Methyl-2-pyrrolidone (NMP), 98% was obtained from Acros Organic. Plastic pyrolysis oil was sourced from industrial pyrolysis facilities in Thailand processing post-consumer waste plastic.

[00209] Experiments were conducted as follows. Extraction solutions were pre-prepared by addition of components to a glass bottle by weight and mixing by shaking until solids, if used, dissolved.

[00210] Both the pyrolysis oil and extraction solution were warmed in a water bath set to desired temperature to ensure oil is above its cloud point. If the oil shows no wax formation at ambient room temperature of 18 to 22°C the water bath is not required

[00211] Into a clean bottle, pyrolysis oil was added and then the extraction solution in the desired quantity by weight.

[00212] The bottle was mixed vigorously by shaking for one minute and then placed into the water bath (if used) and allowed to separate into upper and lower phases.

[00213] Once the upper oil phase (raffinate) was clear and bright, the lower phase (extract) was removed completely by syringe to a clean bottle and weighed.

[00214] Demineralised water is optionally warmed to the set temperature and is measured into the treated pyrolysis oil. The mixture is mixed by shaking for 1 minute and the allowed to separate by gravity in the water bath (if used). The lower aqueous phase is removed by syringe and weighed to determine quantity of water-soluble species present in the upgraded oil.

[00215] Analysis of the oil is carried out using XOS Petramax XRF to determine sulphur and chlorine content.

[00216] Analysis for nitrogen (ASTM D5762), oxygen (ASTM D5622) and silicon (ASTM D5185) is carried out by ITS Testing Services (UK) Ltd

B. Results

B.1 Reduction of polar heteroatoms

[00217] It was found that the combination of 89.3 wt.% methanol/2.7 wt.% KOH/ 8 wt.% water has similar performance in terms of reducing key heteroatoms affecting the stability of the pyrolysis oil as dipolar aprotic solvents such as propylene carbonate and NMP (Table 1).

Table 1 - Comparison of performance at 1:1 mass ratio solvent to oil

	Base Oil	Propylene Carbonate	NMP (90%) /water	Methanol (89.3%) /KOH (2.7%) / Water (8%)
Sulphur, ppm	87.89	47.99	44.88	46.92 (-47%)
Chlorine, ppm	511.2	213.9	220.5	210.3 (-59%)
Oxygen, % mass	0.45	0.19	0.3	0.15 (-67%)
Nitrogen, mg/kg	740	140	270	200 (-71.5%)
Yield %		95.20%	93.60%	95.19%

[00218] It was surprisingly found that the water content in the MeOH/KOH/water combination has several effects on extraction performance, including the quantity of methanol retained in upper phase, the phase separation and the total oil extracted (yield) (Table 2). Mass loss of the oil in the extract phase was significantly higher for methanolic KOH compared to the MeOH/KOH/water combination. Furthermore, water soluble species in the upgraded oil was reduced with increasing water content whilst heteroatom removal was comparable.

Table 2 - Effect of water content on extraction performance in same base oil

wt.% water in solvent	0.0%	8.0%	10.0%	12.5%	15.0%
wt.% Oil extracted	11.17%	4.81%	4.50%	3.05%	2.86%
wt.% Water soluble species in upper oil phase	0.94%	0.26%	0.19%	0%	0%
Nitrogen, mg/kg	160	200		190	230
Chlorine, ppm	170	210	207	191	224
Oxygen % m/m	0.14	0.15		0.22	0.19

[00219] With respect to extraction of silicon compounds, it was found that silicon concentrations in the oil after extraction with aprotic dipolar solvents, such as NMP and propylene carbonate, showed an increase as these silicon compounds showed preference for the oil phase. Methanol alone showed a small reduction in silicon concentration. However, methanol/KOH/water solution showed significant reduction in silicon compounds (Table 3).

Table 3 - Comparison of silicon reduction performance

Extraction Solution	Si, wt. % change from Base Oil	Base Oil Si, mg/kg	Treated oil Si mg/ kg	Oil mass loss (wt.%)
Propylene Carbonate	6%	34	36	4.8%
NMP	23%	44	54	6.4%
Methanol	-6%	64	60	17.63%
90wt% Methanol 10wt% water	2%	64	65	2.36%
89.3wt% Methanol/2.7 wt% KOH/ 8wt% Water	-56%	34	15	4.8%
86.5wt% Methanol/ 1wt% KOH/ 12.5wt% Water	-27%	44	32	4.5%

B.2 Ratio of oil to extraction solution

[00220] An extraction solution consisting of 85 wt.% methanol/1.50 wt.% KOH/ 13.5 wt.% water were prepared as described above. A pyrolysis oil and the extraction solution were weighed into a bottle in the desired ratio and mixed vigorously by shaking for two minutes and then placed into the water bath at 40°C and allowed to separate into upper and lower phases under gravity.

[00221] Details of heteroatom removal and oil yield are provided in Table 4.

Table 4 - Comparison of heteroatom reduction performance for different oil to extraction solvent (85 wt.% methanol/1.50 wt.% KOH/ 13.5 wt.% water) ratios

Oil ID	Ratio (mass) solvent/oil	Base Value	0.11	0.25	0.5	1	2	3
Oil 1	Sulphur, (XRF)	80 ppm	-10%	-28%	-42.50%	-47.50%	-52.50%	-60.00%
Oil 1	Chlorine, (XRF)	453 ppm	-22%	-39%	-54.21%	-61.18%	-70.61%	-75.47%
Oil 2	Oxygen (Oxycube)	0.35%			-74.29%	-77.14%	-82.86%	-85.71%
Oil 1	Nitrogen (ASTM D 4629)	830 ppm			-68.61%	-77.60%	-80.19%	-83.10%
Oil 1	Silicon (ICP)	26 ppm			-26.32%	-39.77%	-45.03%	-52.83%
Oil 1	Oil Mass Loss		0.78%	1.51%	2.13%	3.30%	5.91%	7.64%
Oil 2	Oil Mass Loss				2.53%	3.56%	6.37%	8.21%

[00222] In summary, while methanol removes polar compounds it has minimal impact on removal of silicon compounds. Furthermore, on its own it suffers poor selectivity with high mass loss from the hydrocarbon oil. Phase separation is also poor due to density being close to that of pyrolysis oils. In some cases it forms upper phase and others the lower. The addition of water improves phase separation, however solubility of extracted components also quickly declines.

[00223] However, it has been found that a combination of methanol/KOH/water will remove oxygen, nitrogen, sulphur, chlorine and silicon from plastic derived pyrolysis oil with high selectivity of extraction and thus provides improvements in the subsequent yield and stability of the pyrolysis oil.

[00224] Furthermore, aprotic solvents such as dipolar NMP and polar propylene carbonate are more difficult to recover from the extract phase. In particular, elevated temperatures required during recovery represent a high energy cost and carry a significant risk of deterioration and permanent loss due to instability. For example, NMP and PC suffer from ring opening at elevated temperatures which can be accelerated by the presence of extracted species. In contrast, for the methanol/KOH/water system, methanol can be easily recovered by direct distillation at relatively low temperature offering significant energy savings.

[00225] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference in their entirety and to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein (to the maximum extent permitted by law).

[00226] All headings and sub-headings are used herein for convenience only and should not be construed as limiting the invention in any way.

[00227] The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise paragraphed. No language in the specification should be construed as indicating any non-paragraphed element as essential to the practice of the invention.

[00228] The citation and incorporation of patent documents herein is done for convenience only and does not reflect any view of the validity, patentability, and/or enforceability of such patent documents.

[00229] This invention includes all modifications and equivalents of the subject matter recited in the paragraphs appended hereto as permitted by applicable law.

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CLAIMS

1. A process for producing an upgraded pyrolysis oil product comprising:
 - (i) combining a pyrolysis oil with a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide; and water;
 - (ii) mixing the product of (i) and then allowing the mixture to form two liquid phases consisting of a raffinate phase and an extract phase, and
 - (iii) separating the raffinate phase from the extract phase to yield an upgraded pyrolysis oil product;wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.
2. A process according to claim 1, wherein each of the C₁₋₃ alcohol, the base and water are combined simultaneously with the pyrolysis oil.
3. A process according to claim 1 or 2, wherein the C₁₋₃ alcohol, the base and water are added in combination.
4. A process according to claim 3, wherein the combination comprises about 5% to about 20% (w/w) of water.
5. A process according to claim 3 or 4, wherein the combination comprises about 12% to about 15% (w/w) of water.
6. A process according to any one of claims 3 to 5, wherein the combination comprises about 12.5% (w/w) of water.
7. A process according to any one of claims 3 to 6, wherein the combination comprises about 1% (w/w) of the base.
8. A process according to any one of claims 3 to 7, wherein the combination consists of:
 - about 80% to about 94% (w/w) C₁₋₃ alcohol;
 - about 5% to about 15% (w/w) water;
 - about 0.9% to about 5% (w/w) of the base.

9. A process according to any one of claims 3 to 8, wherein the combination consists of about 86.5% (w/w) C₁₋₃ alcohol, about 12.5% (w/w) water and about 1% (w/w) of the base; or about 85% (w/w) C₁₋₃ alcohol, about 13.5% (w/w) water and about 1.5% (w/w) of the base.
10. A process according to any one of claims 1 to 8, wherein:
- the ratio of C₁₋₃ alcohol to pyrolysis oil is 3:1 to about 2:3;
 - the ratio of water to pyrolysis oil is 1:2 to about 1:12; and
 - the ratio of the base to pyrolysis oil is about 1:90 to about 1:110.
11. A process according to any one of the preceding claims, wherein in step (i), the pyrolysis oil is treated with the C₁₋₃ alcohol, the base and water at a temperature of about 18 to about 40°C.
12. A process according to any one of the preceding claims, further comprising a step of recovering the C₁₋₃ alcohol from the extract phase, which is optionally recycled for use in step (i).
13. A process according to claim 12, wherein the C₁₋₃ alcohol is recovered from the extract phase by distillation.
14. A process according to any one of the preceding claims, further comprising the step of treating the raffinate with a sorbent.
15. A process according to any one of the preceding claims, wherein the C₁₋₃ alcohol is selected from methanol or ethanol.
16. A process according to any one of the preceding claims, wherein the C₁₋₃ alcohol is methanol.
17. A process according to any one of the preceding claims, wherein the base is selected from the group consisting of potassium hydroxide, sodium hydroxide, lithium hydroxide, potassium oxide, sodium oxide, lithium oxide, caesium hydroxide, caesium oxide, barium hydroxide, barium oxide, calcium hydroxide, calcium oxide, magnesium hydroxide and magnesium oxide.
18. A process according to any one of the preceding claims, wherein the base is potassium hydroxide.

19. A process according to any one of the preceding claims, wherein the pyrolysis oil is derived from the pyrolysis of waste plastic.
20. Use of a solution comprising a C₁₋₃ alcohol, a base selected from a Group I hydroxide or oxide and a Group II hydroxide or oxide, and water for decreasing the heteroatom content of a pyrolysis oil, wherein the pyrolysis oil is derived from the pyrolysis of plastic or rubber, or a combination thereof.
21. Use according to claim 20, wherein the heteroatoms are selected from one or more of sulphur, nitrogen, chlorine, oxygen and silicon.
22. Use according to claim 20 or claim 21, wherein the heteroatoms content reduced includes silicon.
23. Use according to any one of claims 20 to 22, wherein the C₁₋₃ alcohol is methanol or ethanol.
24. Use according to any one of claims 20 to 23, wherein the C₁₋₃ alcohol is methanol
25. Use according to any one of claims 20 to 24, wherein the base is potassium hydroxide.