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(54) Title: A METHOD FOR UPGRADING AN OIL, A FUEL PRODUCT AND A HYDROCARBON PRODUCT FRACTION

(57) Abstract: A method for upgrading of a pyrolysis oil. The method comprises evaporating water from a mixture of the pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C. The method yields a de-watered pyrolysis oil mixture. In a preferred embodiment, the method additionally comprises converting the de-watered pyrolysis oil mixture in a hydrocarbon conversion process, and separating the product of the hydrocarbon conversion process to obtain hydrocarbon product fractions. Also claimed: a fuel product and a hydrocarbon product fraction.



A METHOD FOR UPGRADING AN OIL, A FUEL PRODUCT AND A
HYDROCARBON PRODUCT FRACTION

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TECHNICAL FIELD OF THE INVENTION

The invention relates to a method for upgrading of a
pyrolysis oil. The method also relates to a fuel product
based on the upgraded pyrolysis oil and a hydrocarbon
product fraction based on the upgraded pyrolysis oil.

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BACKGROUND OF THE INVENTION

With a diminishing supply of crude oil, the use of
renewable energy sources will be increasingly important as a
feedstock for processes for the production of liquid and
gaseous fuels, for example transportation fuels and fuels
for stationary applications. The use of biomass for the
production of fuels has an advantage of improving the CO₂
balance, compared to the use of crude oil.

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Existing processes for the conversion of plant biomass
include the step of pyrolysing the lignocellulosic material
present in the biomass to obtain a pyrolysis oil. The
pyrolysis oil obtained from biomass comprising
lignocellulosic material may generally comprise
hydrocarbons, oxygenated compounds, such as sugars, organic
acids and phenolics, insoluble lignin and water. Suitably a
portion of the water present in the pyrolysis oil may
originate from the starting biomass and another portion may
be a pyrolysis product. The water content may amount to 25 -
30 %wt, or even more. The presence of water and oxygenated
compounds in the pyrolysis oil is disadvantageous for the
caloric value of the pyrolysis oil. The content of
oxygenated compounds may be reduced in a hydrodeoxygenation
step. Water may be removed by evaporation.

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The pyrolysis oil may be upgraded to obtain liquid and/or gaseous fuels. The upgrading process is preferably carried out in standard equipment of an oil refinery.

However, upgrading the pyrolysis oil in refinery equipment

5 can be cumbersome due to its high water content, the presence of organic acids, and incompatibility with hydrocarbon liquids. At present, the upgrading of pyrolysis oil in refinery equipment requires retrofitting to prevent corrosion and fouling. For the purpose of using pyrolysis
10 oil as a fuel component, it has been proposed to improve the compatibility with hydrocarbons by forming emulsions with the help of an emulsifier, but there are instances that the stability of such emulsion has been found unsatisfactory.

The removal of water from the pyrolysis oil would
15 improve the caloric value of the pyrolysis oil and it would improve the compatibility with hydrocarbon liquids. However, the removal of water from the pyrolysis oil by evaporation has led to undesirable results, such as the formation of a highly viscous, tar like material, which could not readily
20 be dissolved in a hydrocarbon liquid. It would be an advancement in the art to provide a method for upgrading a pyrolysis oil that does not have one or more of the above disadvantages.

SUMMARY OF THE INVENTION

25 It has now unexpectedly been found that significantly improved results are obtained in the evaporation of water from the pyrolysis oil if water is evaporated from a mixture of the pyrolysis oil and a relatively high boiling hydrocarbon. Thus, evaporation of water from a mixture of
30 the pyrolysis oil and the high boiling hydrocarbon does not lead to formation of a highly viscous, tar like material, but instead a liquid mixture can be obtained. The formation of insoluble material has been found to be negligibly low. Additionally, the residual liquid obtained suitably

comprises less organic acids and other light oxygenates, compared to the starting pyrolysis oil, when the evaporation is carried out in the presence of the high boiling hydrocarbon.

5 Not wishing to be bound by theory, it is believed that when water is evaporated in the presence of the high-boiling hydrocarbon, substantial quantities of organic acids, such as glycolic acid, acetic acid, formic acid, propionic acid, and butyric acid, which are capable of catalyzing or
10 promoting tar formation from for example aldehyde type and phenol type components present in the pyrolysis oil, evaporate more readily from the mixture than in the absence of the hydrocarbon. An additional advantage of removing of organic acids may be that the oil becomes less acidic and
15 less corrosive.

It has also been found that the stability of mixtures prepared in accordance with this invention can be strongly improved, especially if the high boiling hydrocarbon is of an aromatic nature, for example according to its H/C ratio,
20 more in particular if the high boiling hydrocarbon comprises asphaltenes.

Thus, the present finding advantageously provides new opportunities of using pyrolysis oil as a fuel oil component for marine and/or stationary applications, and as a
25 feedstock for hydrocarbon conversion processes for the production of liquid petroleum gas, gasoline, kerosene, diesel, and fuel oils.

Therefore, the present invention also provides a method for upgrading of a pyrolysis oil, which method comprises
30 evaporating water from a mixture comprising the pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C.

The present invention also provides a fuel product which is obtainable by employing the method of this invention.

Preferably, the method additionally comprises the step
5 of producing the mixture by mixing the pyrolysis oil and the hydrocarbon.

Preferably, the method of the invention comprises
- evaporating water from a mixture comprising the pyrolysis oil and a hydrocarbon having an atmospheric boiling point of
10 at least 130 °C, yielding a de-watered pyrolysis oil mixture,
- converting the de-watered pyrolysis oil mixture in a hydrocarbon conversion process, and
- separating the product of the hydrocarbon conversion process into hydrocarbon product fractions.

15 The present invention also provides a fuel product obtainable by combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C and evaporating water from the mixture to a water content of the mixture of at most 5 %wt.

20 The present invention also provides a fuel product obtainable by combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C and evaporating water from the mixture, which fuel product has a solids content of at most 10 %wt, relative to
25 the weight of the pyrolysis oil, wherein solids content is as measured by using the Hot filtration test according to ASTM D4870, modified in that the prescribed rinsing of the filter employed in the Hot filtration test is followed by rinsing with ethanol.

30 The present invention also provides a fuel product obtainable by combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130°C and evaporating water from the mixture, which fuel product has a kinematic viscosity measured at 50°C which

kinematic viscosity is constant within 15 % during storage of the fuel product at 50 °C for a period of 14 days, wherein kinematic viscosity is as measured according to ASTM D445.

The present invention also provides a fuel product obtainable by combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C and evaporating water from the mixture, which fuel product has a Total acid number of at most 20 % of the quotient A/B, wherein A represents the Total acid number of the pyrolysis oil and B represents the weight fraction of the pyrolysis oil in the mixture comprising the pyrolysis oil and the high boiling hydrocarbon, wherein Total acid number is as measured by using ASTM D664.

The present invention also provides a hydrocarbon product fraction obtainable by

- combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C and evaporating water from the mixture, yielding a de-watered pyrolysis oil mixture,
- converting the de-watered pyrolysis oil mixture in a hydrocarbon conversion process, and
- separating the product of the hydrocarbon conversion process into hydrocarbon product fractions.

DETAILED DESCRIPTION OF THE INVENTION

The pyrolysis oil for use in this invention is obtained or derived from biomass comprising lignocellulosic material. By a lignocellulosic material is herein preferably understood a material containing cellulose, lignin and optionally hemicellulose.

The biomass may generally be of plant origin. For example, the biomass may comprise agriculture waste, forest residue, wood chips, straw, chaff, grain, grasses, corn, corn husks, bagasse, weeds, aquatic plants, hay and any cellulose containing material or material of biological

origin, also including municipal waste, or waste paper. Preferably, the biomass comprises forest residues or agricultural residues.

Pyrolysis of the biomass provides the pyrolysis oil for
5 use in this invention. By pyrolysis is herein preferably understood a process in which the biomass is decomposed at a high temperature, preferably in the absence of oxygen, into gaseous, liquid and solid products. The condensable fraction of pyrolysis vapors forms the pyrolysis oil. The high
10 temperature is preferably in the range of from 400 °C to 800 °C, more preferably in the range of from 450 °C to 700 °C, preferably in the range of from 500 °C to 650 °C. In certain methods, chemicals may be employed for a pretreatment of the biomass, or catalysts may be added to
15 the pyrolysis mixture, cf. for example, H Wang cs., "Effect of acid, alkali, and steam explosion pretreatment on characteristics of bio-oil produced from pinewood", Energy Fuels (2011) 25, p. 3758 - 3764.

In a preferred pyrolysis process, generally referred to
20 as a flash pyrolysis process, the biomass is rapidly heated in the absence of oxygen to a temperature in the range of from 400 °C to 600 °C and kept at that temperature for a short period of time. The water content of the pyrolysis oil has been reported to amount to up to 40 %wt. Such flash
25 pyrolysis processes are known, for example from US-A-5395455.

The pyrolysis oil for use in this invention preferably comprises hydrocarbons, oxygenated compounds and water. The oxygenated compounds may comprise aldehydes, organic acids,
30 carbohydrates, phenols, furfurals, alcohols and ketones. Preferably, the carbon content of the pyrolysis oil may be in the range of from 35 %wt to 75 %wt, more preferably in the range of from 40 %wt to 55 %wt, for example in the range of from 45 %wt to 50 %wt. The hydrogen content may be in the

range of from 4 %wt to 7 %wt, more preferably in the range of from 5 %wt to 6 %wt. The oxygen content may be in the range of from 15 %wt to 55 %wt, more preferably in the range of from 40 %wt to 50 %wt, for example in the range of from 45 %wt to 50 %wt. The nitrogen content may be in the range of from 0.05 %wt to 1 %wt, more preferably in the range of from 0.1 %wt to 0.5 %wt. The sulfur content may be in the range of from 0.005 %wt to 0.05 %wt, more preferably in the range of from 0.01 %wt to 0.02 %wt. Preferably, the water content may be at least 1 %wt or at least 2 %, more preferably in the range of from 15 %wt to 40 %wt, for example 20 %wt tot 35 %wt. Preferably, the Total acid number of the pyrolysis oil may be at most 250 mg KOH/g, more preferably in the range of from 5 mg KOH/g to 200 mg KOH/g, for example in the range of from 10 mg KOH/g to 150 mg KOH/g. As used herein, carbon content, hydrogen content and nitrogen content are as measured by ASTM D5291, and sulfur content is as measured by ASTM D2622. Oxygen content is calculated by difference, such that the sum of carbon content, hydrogen content, oxygen content, nitrogen content and sulfur content is 100 %wt. Water content is as measured by ASTM E203. As used herein, Total acid number is as measured by using ASTM D664.

In accordance with this invention, water is evaporated from the pyrolysis oil, with the pyrolysis oil being present in admixture with a hydrocarbon having an atmospheric boiling point of at least 130 °C. By a hydrocarbon is herein preferably understood a compound containing both hydrogen atoms and carbon atoms, more preferably the hydrocarbon may be a compound consisting of hydrogen atoms and carbon atoms. The hydrocarbon having an atmospheric boiling point of at least 130 °C may be referred to hereinafter by using the term "high boiling hydrocarbon". The skilled person will appreciate that in order to be able to make such an

admixture, the high boiling hydrocarbon is present in addition to any hydrocarbons that may already be present in the pyrolysis oil itself. Such a hydrocarbon that is obtained from a source other than the pyrolysis of the biomass comprising the lignocellulosic material is herein also referred to as an external hydrocarbon. Preferably the high boiling hydrocarbon is a petroleum derived hydrocarbon. By a petroleum derived hydrocarbon is herein preferably understood a hydrocarbon that is derived from a so-called petroleum crude oil.

The high boiling hydrocarbon may be a single hydrocarbon. However, preferably, a high boiling hydrocarbon mixture is employed. Such a high boiling hydrocarbon mixture suitably contains two or more high boiling hydrocarbons.

Preferably, such a high boiling hydrocarbon mixture may comprise a refinery stream, such as a distillation fraction of a mineral crude. Preferably, the high boiling hydrocarbon mixture comprises atmospheric gas oil, vacuum gas oil, flashed distillate, coker gas oil, residual fuel oil, atmospheric residue (also referred to as long residue), or vacuum residue (also referred to as short residue), or blends of such refinery streams. The skilled person will appreciate that when the high boiling hydrocarbon comprises a refinery stream, it may comprise to some extent hydrocarbons having hetero atoms, such as sulfur and/or nitrogen, incorporated in their molecular structure.

In accordance with this invention, the atmospheric boiling point of the high boiling hydrocarbon is at least 130 °C. Preferably, the boiling point of the hydrocarbon is at least 150 °C, more preferably at least 180 °C. In cases that a high boiling hydrocarbon mixture is employed, the initial atmospheric boiling point of the high boiling hydrocarbon mixture may be at least 130 °C, and, preferably, the initial atmospheric boiling point of the high boiling

hydrocarbon mixture may be at least 150 °C, more preferably at least 180 °C. In preferred embodiments, the atmospheric boiling point range of the high boiling hydrocarbon mixture may be from 220 °C to 800 °C, more preferably from 300 °C to 5 700 °C.

In preferred embodiments, the hydrogen to carbon weight ratio (H/C ratio) of the high boiling hydrocarbon mixture may be at most 0.15 w/w, more preferably in the range of from 0.1 to 0.14 w/w, even more preferably in the range of 10 from 0.11 to 0.13 w/w.

In preferred embodiments, the asphaltenes content of the high boiling hydrocarbon mixture may be equal to or more than 0.2 %wt (percent by weight), more preferably equal to or more than 0.7 %wt, still more preferably equal to or more 15 than 2.0 %wt, even more preferably in the range of from 0.8 to 30 %wt, still even more preferably in the range of from 2.0 %wt to 30 %wt, relative to the weight of the high boiling hydrocarbon mixture. Most preferably the asphaltenes content is in the range of from 0.9 to 15 %wt or in the 20 range of from 2.0 to 15 %wt relative to the weight of the high boiling hydrocarbon mixture.

As used herein, boiling point is the atmospheric boiling point, unless indicated otherwise, with the atmospheric boiling point being the boiling point as 25 determined at a pressure of 100 kiloPascal (i.e. 0.1 MegaPascal). As used herein, initial boiling point and boiling point range of the high boiling hydrocarbon mixtures are as determined by ASTM D2887. As used herein, pressure is absolute pressure. As used herein, H/C ratio is as 30 determined by ASTM D5291. As used herein, asphaltenes content or C7-asphaltenes content is as determined by IP143, using n-heptane as a solvent.

The mixture of the pyrolysis oil and the high boiling hydrocarbon can be produced in any manner known to the

skilled person in the art. The pyrolysis oil may be added to the high boiling hydrocarbon, or the high boiling hydrocarbon may be added to pyrolysis oil, or streams of the pyrolysis oil and the high boiling hydrocarbon may be

5 brought together. Suitably the combination of the pyrolysis oil and the high boiling hydrocarbon may be mixed.

Preferably, the pyrolysis oil and the high boiling hydrocarbon may be combined in a weight ratio of pyrolysis oil to high boiling hydrocarbon (grams pyrolysis oil/grams

10 high boiling hydrocarbon) of at least 0.5/99.5, more preferably at least 1/99, still more preferably at least 2/98, respectively. Preferably, the pyrolysis oil and the high boiling hydrocarbon may be combined in a weight ratio of pyrolysis oil to high boiling hydrocarbon (grams

15 pyrolysis oil/grams high boiling hydrocarbon) of at most 75/25, more preferably at most 70/30, even more preferably at most 60/40, and most preferably at most 50/50 respectively. As explained above, the high boiling

hydrocarbon may also be a high boiling hydrocarbon mixture and in such case the same weight ratio's are preferred.

20 In a preferred embodiment the amount of pyrolysis oil in a mixture comprising the pyrolysis oil and a high boiling hydrocarbon mixture, varies depending on the asphaltene content of the high boiling hydrocarbon mixture. This may

25 allow for an optimal stability of the mixture comprising the pyrolysis oil and the high boiling hydrocarbons. For

example, when a high boiling hydrocarbon mixture is used comprising equal to or less than 0.2 wt% of asphaltenes, the weight ratio of pyrolysis oil to high boiling hydrocarbon

30 mixture (grams pyrolysis oil/grams high boiling hydrocarbons) is preferably equal to or less than 10/90, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 10/90. When a high boiling hydrocarbon mixture is used comprising in the range from

more than 0.2 wt% to equal to or less than 0.5wt% of asphaltenes, the weight ratio of pyrolysis oil to high boiling hydrocarbon mixture (grams pyrolysis oil/grams high boiling hydrocarbons) is preferably equal to or less than 15/85, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 15/85. When a high boiling hydrocarbon mixture is used comprising in the range from more than 0.5 wt% to equal to or less than 1.3 wt% of asphaltenes, the weight ratio of pyrolysis oil to high boiling hydrocarbon mixture (grams pyrolysis oil/grams high boiling hydrocarbons) is preferably equal to or less than 20/80, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 20/80. When a high boiling hydrocarbon mixture is used comprising in the range from more than 1.3 wt% to equal to or less than 2.3 wt% of asphaltenes, the weight ratio of pyrolysis oil to high boiling hydrocarbon mixture (grams pyrolysis oil/grams high boiling hydrocarbons) is preferably equal to or less than 30/70, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 30/70. When a high boiling hydrocarbon mixture is used comprising more than 2.3 wt% of asphaltenes, the weight ratio of pyrolysis oil to high boiling hydrocarbon mixture (grams pyrolysis oil/grams high boiling hydrocarbons) is preferably equal to or less than 60/40, more preferably in the range from equal to or more than 0.5/99.5 to equal to or less than 60/40.

The pyrolysis oil and the high boiling hydrocarbon can be mixed in any manner known by the skilled in the art to be suitably for mixing, for example by means of a mixer or via one or more baffles.

Evaporating water may be carried out in a conventional distillation apparatus. Preferably, the distillation apparatus and the conditions of operating the distillation apparatus are selected such that water is evaporated and

condensed as a water rich distillate fraction, and high boiling hydrocarbon remains in the bottom, yielding a bottom fraction which is rich in the high boiling hydrocarbon. In preferred embodiments a flash distillation apparatus or a distillation apparatus having a separation column may be selected. The separation column may preferably be selected and operated such that it comprises at most fifty (inclusive), more preferably at most forty (inclusive), in particular at most thirty (inclusive) theoretical trays.

Preferably, the separation column may preferably be selected and operated such that it comprises at most ten (inclusive) or at most five (inclusive) theoretical trays. Evaporating water may be carried out in a continuous operation or as a batch operation.

Preferably the bottom temperature is selected such that the bottom fraction is sufficiently low in viscosity, and the rate of evaporation of water is sufficiently high at the prevailing pressure and remains sufficiently high at instances that the water content of the bottom fraction is low. Suitably, a bottom temperature in the range of from 50 °C to 200 °C may be selected, more suitable in the range of from 80 °C to 150 °C. The pressure may suitably be selected in the range of from 0.01 kPa to 120 kPa, more suitably in the range of from 0.1 kPa to 60 kPa, preferably in the range of from 0.2 kPa to 10 kPa (kiloPascal).

Although the high boiling hydrocarbon has been defined hereinbefore by its atmospheric boiling point, or atmospheric boiling point range, the skilled person will appreciate that the atmospheric boiling point or atmospheric boiling point range are specified such that a distillation apparatus can be operated at a pressure other than atmospheric pressure while water is evaporated and condensed as a water rich distillate fraction, and high boiling

hydrocarbon remains in the bottom, yielding a bottom fraction which is rich in the high boiling hydrocarbon.

Evaporation of water may preferably be effected to the extent that a bottom fraction is obtained having a water content of at most 5 %wt, more preferably at most 2 %wt, preferably at most 1 %wt, relative to the weight of the bottom fraction. In the normal practice of this invention the water content of the bottom fraction obtained may be at least 0.001 %wt, or at least 0.01 %wt, relative to the weight of the bottom fraction. Hereinafter, the bottom fraction so obtained may be referred to by the term "de-watered pyrolysis oil mixture".

It has unexpectedly been found that the formation of insoluble materials during the evaporation of water in accordance with this invention is low. Preferably, the solids content of the de-watered pyrolysis oil mixture may be at most 1 %wt, more preferably at most 0.5 %wt, relative to the weight of the de-watered pyrolysis oil mixture. In practice the solids content of the de-watered pyrolysis oil mixture may be at least 0.005 %wt, more preferably at least 0.01 %wt, relative to the weight of the de-watered pyrolysis oil mixture. Preferably, the solids content of the de-watered pyrolysis oil mixture may be at most 10 %wt, more preferably at most 5 %wt, relative to the weight of the pyrolysis oil present in the mixture of the pyrolysis oil and the high boiling hydrocarbon, before evaporating water. In practice the solids content of the de-watered pyrolysis oil mixture may be at least 0.05 %wt, more preferably at least 0.1 %wt, relative to the weight of the pyrolysis oil present in the mixture of the pyrolysis oil and the high boiling hydrocarbon, before evaporating water. As used herein, solids content is as measured by using the Hot filtration test according to ASTM D4870, modified in that

the prescribed rinsing of the filter employed in the Hot filtration test is followed by rinsing with ethanol.

It has also unexpectedly been found that the Total acid number of the de-watered pyrolysis oil mixture is remarkably low relative to the Total acid number mixture of at least the pyrolysis oil present in the mixture comprising the pyrolysis oil and the high boiling hydrocarbon prior to evaporating water from the mixture. In particular when the high boiling hydrocarbon itself has a low Total acid number, the Total acid number of the de-watered pyrolysis oil mixture may preferably be at most 20 % of the quotient A/B, wherein A represents the Total acid number of the pyrolysis oil and B represents the weight fraction of the pyrolysis oil in the mixture comprising the pyrolysis oil and the high boiling hydrocarbon prior to evaporating water from the mixture. More preferably, the Total acid number of the de-watered pyrolysis oil mixture is at most 10 %, in particular at most 5 %, of the quotient A/B. Frequently, the Total acid number of the de-watered pyrolysis oil mixture is at least 0.01 %, or at least 0.1 %, of the quotient A/B. In particular in this context, the low Total acid number of the high boiling hydrocarbon amounts preferably to at most 5 mg KOH/g, more preferably at most 1 mg KOH/g. In practice, the low Total acid number of the high boiling hydrocarbon may amount to at least 0.01 mg KOH/g, or at least 0.05 mg KOH/g. The Total acid number of the de-watered pyrolysis oil mixture may preferably be at most 15 mg KOH/g, more preferably at most 10 mg KOH/g. In practice, the low Total acid number of the de-watered pyrolysis oil mixture may amount to at least 0.05 mg KOH/g, or at least 0.1 mg KOH/g.

It has also unexpectedly been found that the storage stability of the de-watered pyrolysis oil mixture as such, or blends comprising the de-watered pyrolysis oil mixture, is remarkably good. Suitably, said blends are made by

blending the de-watered pyrolysis oil mixture with a high boiling hydrocarbon mixture as specified hereinbefore. The improvement in the storage stability is such that a skilled person may not consider the use of an emulsifier for

5 stabilizing the de-watered pyrolysis oil mixture, or such blends. As used herein, storage stability is measured by following the kinematic viscosity at 50 °C as measured according to ASTM D445 during storage at 50 °C. Preferably, during storage at 50 °C for a period of 14 days the value of
10 the kinematic viscosity is constant or variable within at most 15 % of the value at the start of the storage, more preferably within 10 %, in particular with 5 % of the value at the start of the storage.

The de-watered pyrolysis oil mixture may be used, as
15 such, as a component of heavy fuel for marine and/or stationary applications.

Hence the present invention also provides a fuel product which is obtainable by a method for upgrading a pyrolysis oil as described herein, more specifically a fuel product
20 which is obtainable by a method comprises combining in a mixture a pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C and evaporating water from the mixture. This "method comprising combining in a mixture a pyrolysis oil and a hydrocarbon having an
25 atmospheric boiling point of at least 130 °C and evaporating water from the mixture" may be as described herein and the preferences for such a method may also be as described herein. The method preferably comprises combining in a mixture a pyrolysis oil and a hydrocarbon having an
30 atmospheric boiling point of at least 130 °C and evaporating water from the mixture to a water content of the mixture of at most 5 %wt, more preferably at most 2 %wt, and most preferably at most 1 %wt. The fuel product is therefore preferably a fuel product having a water content of at most

5 %wt more preferably at most 2 %wt, and most preferably at most 1 %wt. The fuel product may have a solids content of at most 10 %wt, preferably at most 5 %wt, relative to the weight of the pyrolysis oil, wherein solids content is as measured by using the Hot filtration test according to ASTM D4870, modified in that the prescribed rinsing of the filter employed in the Hot filtration test is followed by rinsing with ethanol. The fuel product may have a kinematic viscosity measured at 50 °C which kinematic viscosity has a value which is constant within 15 %, preferably within 10 %, and most preferably within 5 %, relative to the value at the start of the storage, during storage of the fuel product at 50 °C for a period of 14 days, wherein kinematic viscosity is as measured according to ASTM D445. The fuel product may have a Total acid number (TAN) of at most 20 %, preferably at most 10%, and most preferably at most 5%, of the quotient A/B, wherein A represents the Total acid number of the pyrolysis oil and B represents the weight fraction of the pyrolysis oil in the mixture comprising the pyrolysis oil and the high boiling hydrocarbon, wherein Total acid number is as measured by using ASTM D664.

The de-watered pyrolysis oil mixture may be used, as such, as a component of heavy fuel for marine and/or stationary applications. Alternatively, the de-watered pyrolysis oil mixture may be used as a feedstock for hydrocarbon conversion processes, such as hydrodeoxygenation thermal cracking, fluid catalytic cracking and hydrocracking, residue or crude hydrotreating, or a combination of such processes, for the production of liquefied petroleum gas, gasoline, kerosene and/or diesel. For use as feedstock in these processes, the de-watered pyrolysis oil mixture may be used as such or may be further blended with a high boiling hydrocarbon or high boiling hydrocarbon mixture, as defined hereinbefore.

The hydrocarbon conversion processes are, as such, known in the art. As an example, reference may be made to EP-A-2325281, which discloses a suitable fluid catalytic cracking process, including suitable conditions and catalysts, and a suitable hydrodeoxygenation process, including suitable conditions and catalysts. Preferably the fluid catalytic cracking of a de-watered pyrolysis oil mixture is carried out whilst co-feeding or co-blending a further high boiling hydrocarbon or further high boiling hydrocarbon mixture with it. Preferably the de-watered pyrolysis oil mixture, and optionally any further high boiling hydrocarbons co-fed or blended therewith, is contacted during such fluid catalytic cracking with a fluid catalytic cracking catalyst at a temperature in the range from equal to or more than 480°C to equal to or less than 700°C, preferably in a riser reactor. The fluid catalytic cracking catalyst can be any catalyst known by the person skilled in the art to be suitable therefore. Preferably such a catalyst contains a zeolite Y or X, ultra-stable zeolite Y (USY), Rare Earth zeolite Y (= REY) or Rare Earth USY (REUSY).

The product obtained in the hydrocarbon conversion process may suitably be separated into hydrocarbon product fractions, such as fractions comprising liquefied petroleum gas, gasoline, kerosene and/or diesel. Suitable separation methods, for example distillation, are known in the art. Such hydrocarbon product fractions are suitable for use as transportation fuel or as fuel for stationary application.

The invention will now be illustrated by means of the following Examples.

EXAMPLES 1 - 4

A pyrolysis oil originating from pine forest residue and having a water content of about 22 %wt, obtained from Technical Research Centre of Finland (VTT), was combined and

mixed with a high boiling hydrocarbon mixture. The high boiling hydrocarbon mixture in examples 1 to 3 was a Kuwait Long Residue (further abbreviated as KLR). This Kuwait Long Residue further had a Total Acid Number of about 0.14 mg KOH/g. The high boiling hydrocarbon mixture in example 4 was a Saudi Arabian Short Residue (further abbreviated as SASR). The resultant mixture was placed in a round-bottom flask of a standard laboratory rotary evaporator. After attaching the flask to the rotary evaporator, an oil bath was placed around the flask and heated to 110 °C or 90 °C, while the flask was allowed to rotate. The pressure inside the rotary evaporator was carefully lowered to 0.5 kPa (5 millibar), i.e. such that sudden boiling of the mixture was prevented (for this purpose, additionally some glass beads had been added). A water fraction was distilled off during a period of 2 hours. Table I specifies the type of the high boiling hydrocarbon mixture, the intake of materials, the temperature of the oil bath and the water content of the de-watered pyrolysis oil mixture obtained. The C7-asphaltene content and initial boiling points (IBP) for the high boiling hydrocarbon mixture were as follows:

- Kuwait Long Residue (KLR): 4.2 wt% C7-asphaltenes and IBP > 350°C.
- Saudi Arabian Short Residue (SASR): 12.7 wt% C7-asphaltenes and IBP > 261°C

TABLE I: examples 1 to 4

Example	1	2	3	4
Intake pyrolysis oil (g)	28.13	34.88	22.43	20.81
High boiling hydrocarbon mixture	KLR	KLR	KLR	SASR
Intake high boiling hydrocarbon mixture (g)	35.5	32.43	83.44	136.9
Temperature of the oil bath (°C)	110	110	110	90
Water content of the de-watered pyrolysis oil mixture	0.49	0.38	n.d.	n.d.
*) n.d. : not determined				

In Examples 1 and 2 it was determined that the water
5 fraction comprised a substantial quantity of organic acids,
in particular formic acid, acetic acid, propionic acid,
butyric acid and glycolic acid.

In all examples 1 to 4 a stable product was obtained.
Stability was in this case assessed by means of visual
10 testing immediately after the dewatering step, where
visually no phase separation or solid formation could be
observed.

EXAMPLE 5

In a manner as set out in Examples 1-4, a de-watered
15 pyrolysis oil mixture was obtained from a mixture comprising
51.84 g of the same pyrolysis oil and 206.97 g of a blend
comprising 170.66 g of a vacuum gas oil and 36.31 g of a

Kuwait Long Residue (KLR). The Kuwait Long Residue had an initial boiling point above 350°C and an asphaltene content of 4.2 %wt. This Kuwait Long Residue further had a Total Acid Number of about 0.14 mg KOH/g. The temperature of the oil bath was 110 °C. The water content of the de-watered pyrolysis oil mixture was 0.09 %wt. A sample of the de-watered pyrolysis oil mixture was subjected to catalytic cracking in a small-scale fluidized catalytic cracking reactor. A commercial equilibrium catalyst comprising ultra stable zeolite Y (USY) in an amorphous alumina matrix was used as the cracking catalyst. The cracking catalyst to oil ratio used was 4.31 to achieve 60 % conversion. The reaction temperature was kept at 520 °C and the pressure was kept at 120 kPa. The gas phase product was quantified and characterized by on-line gas chromatography. The liquid product stream was collected at -15 °C and analyzed by True Boiling Point Analysis and two-dimensional gas chromatography. The yield of liquid petroleum gas (LPG) was 10.9 %wt, the yield of gasoline was 42.0 %wt, the yield of light cycle oil was 26.0 %wt and the yield of coke was 5.08 %wt.

For comparison, a sample of the blend comprising 82.5 %wt of a vacuum gas oil and 17.5 %wt of a Kuwait long residue was subjected to catalytic cracking in the same small-scale fluidized catalytic cracking reactor, employing the same conditions. The cracking catalyst to oil ratio used was 4.41 to achieve 60 % conversion. The yield of liquid petroleum gas (LPG) was 10.4 %wt, the yield of gasoline was 42.8 %wt, the yield of light cycle oil was 23.9 %wt and the yield of coke was 4.82 %wt.

EXAMPLE 6

In a manner as set out in Examples 1-4, using an oil bath temperature of 110°C, a de-watered pyrolysis oil mixture was obtained from a mixture comprising 10 %wt of the

same pyrolysis oil and 90 %wt of a blend comprising 82.5 %wt of a vacuum gas oil and 17.5 %wt of the Kuwait Long Residue (KLR) of Example 5.

EXAMPLE 7

5 In a manner as set out in Examples 1-4, a de-watered pyrolysis oil mixture was obtained from a mixture comprising 5 %wt of the same pyrolysis oil and 95 %wt of the Kuwait Long Residue (KLR) of Example 5. The temperature of the oil bath was 110 °C.

10 The Total acid number of the de-watered pyrolysis oil mixture was 1.06 mg KOH/g. Based on the Total acid numbers of the individual components, the Total acid number of the pyrolysis oil mixture before de-watering was calculated to amount to 5 mg KOH/g.

15 EXAMPLE 8

 In a manner as set out in Examples 1-4, a de-watered pyrolysis oil mixture was obtained from a mixture comprising 10 %wt of the same pyrolysis oil and 90 %wt of the Kuwait Long Residue (KLR) of Example 5. The temperature of the oil bath was 110 °C. A water fraction was distilled off during a period of 1 hours.

 In the Hot filtration test the de-watered pyrolysis oil mixture obtained was found to comprise 0.11 %wt insoluble material. The Hot filtration test was carried out according to ASTM D4870, modified in that the prescribed rinsing of the filter employed in the Hot filtration test is followed by rinsing with ethanol. In the same test, the Kuwait origin long residue was found to comprise 0.01 %wt insoluble material.

30 When the pyrolysis oil would have been de-watered by evaporation of water in the absence of the high boiling hydrocarbon (in this case in the absence of Kuwait origin long residue), the pyrolysis oil would have been converted into a substantially insoluble material.

COMPARATIVE EXAMPLE A AND EXAMPLES 9 - 14

In a manner as set out in Examples 1 - 4, a de-watered pyrolysis oil (comparative example A) or a de-watered pyrolysis oil mixture (Examples 9 - 14) was obtained from
5 pyrolysis oil (comparative example A) or from a mixture comprising a pyrolysis oil and a high boiling hydrocarbon mixture (Examples 9 - 14). The pyrolysis oil originated from Biomass Technology Group, Enschede, The Netherlands. Table II specifies the type of the high boiling hydrocarbon
10 mixture, the intake of materials, the temperature of the oil bath, the pressure and the water content of the de-watered pyrolysis oil mixture obtained. The distillate mentioned in table II contains the water fraction that was evaporated, condensed and retrieved. In addition to the water, this
15 distillate may contain condensed acids.

Although examples 12 to 14 do allow for the formation of a mixture and does allow for the dewatering, these examples are less preferred as after dewatering, phase separation and solid formation may occur after a certain
20 amount of time.

Attempts to dissolve the de-watered pyrolysis oil obtained in comparative Example A in Diesel marine fuel Type A failed.

TABLE II: comparative example A and examples 9-14

Example	A*	9	10	11	12	13	14
Intake pyrolysis oil (g)	100.89	104.21	59.17	90.07	99.98	60.46	100.05
High boiling hydrocarbon mixture	-	RFO	RFO	RFO	DMF-A	DMF-A	LCO
initial boiling point of high boiling hydrocarbon mixture	-	about 200°C	about 200°C	about 200°C	about 175°C	about 175°C	about 175°C
C7-Asphaltenes in high boiling hydrocarbon mixture	-	10 wt%	10 wt%	10 wt%	0 wt%	0 wt%	0 wt%
Intake high boiling hydrocarbon mixture (g)	-	102	175.06	91.1	100.12	49.9	100.08
Pressure (kPa)	40	22	20	5	40	40	40
Temperature of the oil bath (°C)	113	126	127	87	110	115	119
Yield of dewatered pyrolysis oil mixture on total intake (%wt)	68.3	80.1	90.0	79.4	80.4	81.4	79.7
Yield of distillate on total intake (%wt)	31.7	19.9	10.0	20.6	19.6	18.6	20.3
Yield of distillate on pyrolysis oil intake (%wt)	31.7	39.4	39.6	41.5	39.2	37.1	40.6

* = For comparison; RFO = Residual Fuel Oil; DMF-A = Diesel Marine Fuel type A ; LCO = Light Cycle Oil

EXAMPLE 15

A de-watered pyrolysis oil mixture similar to the de-watered pyrolysis oil mixture obtained in Example 9 was mixed with Residual fuel oil (RFO, with a C7-asphaltenes content of about 10 wt% and an initial boiling point of about 200°C) to obtain a mixture comprising 10 %wt pyrolysis oil, the balance being Residual fuel oil (Mixture A). For purposes of comparison, a mixture was prepared comprising 10 %wt pyrolysis oil which was not de-watered, the balance being Residual fuel oil (Mixture B). Samples of Mixtures A and B were stored in glass bottles at 50 °C, and their kinematic viscosities at 50 °C were measured at regular intervals. It appeared that the kinematic viscosity of mixture was substantially constant over a storage period of 14 days (i.e. there was a random scatter within 5 %), while the kinematic viscosity of Mixture B increased by a factor of 3 within a storage time of 8 days. As used herein, the kinematic viscosity is as measured according to ASTM D445.

EXAMPLE 16-21

In a manner as set out in Examples 1-4, a de-watered pyrolysis oil mixture was obtained from a mixture comprising a high boiling hydrocarbon mixture and a pyrolysis oil as listed in table III. The temperature of the oil bath was kept at 110°C. A water fraction was distilled off during a period of 1 hour. The C7-asphaltene content and initial boiling points (IBP) for the components of the high boiling hydrocarbon mixture were as follows:

- Kuwait Long Residue (KLR): 4.2 wt% C7-asphaltenes and IBP > 350°C
- Dalia Short Residue (DSR): 1.2 wt% C7-asphaltenes and IBP > 350°C
- Bashra Short Residue (BSR): 4.7 wt% C7-asphaltenes and IBP > 350°C

- Vacuum Gas oil (VGO): 0 wt% C7-asphaltenes and IBP > 239°C

The dewatered mixtures were checked visibly on stability and on solids visible to the eye.

TABLE III: examples 16-21

Example	16	17	18	19	20	21
Intake PO (g)	20.0	30.2	28.0	28.1	10	5
High boiling hydrocarbon mixture (g)	6.0g KLR & 24.0g VGO	37.2g BSR & 7.9g VGO	2.8g KLR & 109.2g VGO	11.2g KLR & 112.1g VGO	12.0g DSR & 28.0g VGO	12.0g DSR & 33g VGO
weight ratio PO/HM	40/60	40/60	20/80	20/80	20/80	10/90
Pressure (kPa)	0.1	1.9	0.1	0.1	0.1	0.1
C7-asphaltene blend (before dewatering)	0.5	2.3	0.08	0.34	0.29	0.29
Oil phase after dewatering (g)	38.1	61.96	122.5	124.3	43.5	45.4
Aqueous phase after dewatering(g)	11.3	11.82	15.6	16.3	5.8	3.8
Stability of the de-watered mixture	not stable, solids	stable, no solids	not stable, solids	stable, no solids	not stable, solids	stable, no solids

PO= pyrolysis oil ; HM= high boiling hydrocarbon mixture

C L A I M S

- 5 1. A method for upgrading of a pyrolysis oil, which method comprises evaporating water from a mixture comprising the pyrolysis oil and a hydrocarbon having an atmospheric boiling point of at least 130 °C.
2. The method as claimed in claim 1, wherein the method
10 additionally comprises the step of producing the mixture by mixing the pyrolysis oil and the hydrocarbon.
3. The method as claimed in claim 2, wherein producing the mixture comprises combining the pyrolysis oil and the hydrocarbon in a weight ratio of pyrolysis oil to
15 hydrocarbon of at most 75/25.
4. The method as claimed in any of claims 1-3, wherein the hydrocarbon has an atmospheric boiling point of at least 150 °C.
5. The method as claimed in any of claims 1-4, wherein the
20 asphaltenes content of the high boiling hydrocarbon mixture is equal to or more than 0.2 %wt.
6. The method as claimed in any of claims 1-5, wherein the hydrocarbon is a hydrocarbon mixture comprising a refinery stream.
- 25 7. The method as claimed in claim 6, wherein the hydrocarbon mixture has an H/C ratio as determined by ASTM D5291 of at most 0.15 w/w and/or the hydrocarbon mixture has an asphaltenes content as determined by IP143, using n-heptane as a solvent of at least 0.7 %wt.
- 30 8. The method as claimed in any of claims 1-7, which method comprises evaporating water employing a bottom temperature in the range of from 50 °C to 200 °C and a pressure in the range of from 0.1 kPa to 60 kPa (absolute).

9. The method as claimed in any of claims 1-8, yielding a de-watered pyrolysis oil mixture, which method additionally comprises

- converting the de-watered pyrolysis oil mixture in a hydrocarbon conversion process, and
- separating the product of the hydrocarbon conversion process into hydrocarbon product fractions.

10. A fuel product which is obtainable by a method as claimed in any of claims 1-8.

11. A fuel product, preferably obtainable by a method as claimed in any of claims 1-8, having

- a solids content of at most 10 %wt, relative to the weight of the pyrolysis oil, wherein solids content is as measured by using the Hot filtration test according to ASTM D4870, modified in that the prescribed rinsing of the filter employed in the Hot filtration test is followed by rinsing with ethanol;

- a kinematic viscosity measured at 50 °C which kinematic viscosity has a value which is constant or variable within at most 15 %, relative to the value at the start of the storage, during storage of the fuel product at 50 °C for a period of 14 days, wherein kinematic viscosity is as measured according to ASTM D445;

- a Total acid number (TAN) of at most 20% of the quotient A/B, wherein A represents the Total acid number of the pyrolysis oil and B represents the weight fraction of the pyrolysis oil in the mixture comprising the pyrolysis oil and the high boiling hydrocarbon, wherein Total acid number is as measured by using ASTM D664.

12. A hydrocarbon product fraction which is obtainable by a method as claimed in claim 9.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101 875 848 A (UNIV TIANJIN) 3 November 2010 (2010-11-03) claim 1; figure 1 -----	1-12
X	DATABASE WPI Week 201140 Thomson Scientific, London, GB; AN 2011-G98201 XP002677672, & RU 2009 115211 A (TECHNOLOGICAL SERVICE CENT LLC) 27 October 2010 (2010-10-27) the whole document -----	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 101875848	A	03-11-2010	NONE	

RU 2009115211	A	27-10-2010	NONE	
