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(54) REMOVAL OF SILICON FROM DEPOLYMERIZED OIL

(57) The present invention relates to an improved method of removing silicon from depolymerized oil, more specifically to a method of producing a pyrolysis oil, said method comprising the steps of adding alumina in the form of granules to organic silicon-containing waste plastic to form a mixture, feeding said mixture to a pyrolysis reactor, pyrolysing said mixture in said reactor, recovering at least a pyrolysis gas and a solid residue from said reactor, and condensing the pyrolysis gas to provide an oil product, wherein the solid residue comprises the alumina reacted with silicon.

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Description

Technical Field

[0001] The present invention relates to an improved method of removing silicon from depolymerized oil, more specifically to in-situ reduction of silicon content during pyrolysis of waste plastic and to a use of alumina for in-situ reduction of silicon content during pyrolysis of waste plastic.

Background of the Invention

[0002] The purification of liquefied waste plastics (LWP), which may also be referred to as depolymerized oil, to yield more valuable (pure) substances has been studied for several years.

[0003] LWP is typically produced by pyrolysis or hydrothermal liquefaction (HTL) of waste plastics. Depending on the source of the waste plastics, LWP has variable levels of impurities.

[0004] The feed for chemical recycling of plastics usually comprises mixed plastics waste which can originate for example from separately collected plastics from households from which the cleaner plastics fractions have been taken out for mechanical recycling, or from plastics separated from municipal solid waste (MSW). However, sorting the waste even close to 100% plastics content is not economically feasible. Thus, the waste plastic material (waste plastic feed) for producing LWP usually contains also materials other than plastics. These other materials, including biomass, are also possible sources of impurities which end up in the LWP.

[0005] In particular, consumer waste including waste packaging often comprise compositions other than hydrocarbons. Silicon is one common nonhydrocarbon element in plastic waste coming from various sources, such as silicones. Therefore, plastic waste that is being subjected to chemical recycling often encounters high amounts of silicon impurities. Other typical impurity components are chlorine, nitrogen, sulphur, and oxygen.

[0006] No matter whether the LWP is merely subjected to common refinery processing (e.g. fractionation) or is forwarded to a subsequent petrochemical conversion process, the LWP feed needs to meet the impurity levels for these processes so as to avoid deterioration of the facility, such as catalyst poisoning. In this respect, silicon impurities may cause catalyst deactivation e.g. in hydrotreatment steps and thus techniques for reducing the silicon content in LWP have been studied.

[0007] WO2021/80899 A1 discloses passing LWP (i.e. depolymerized oil) over an absorbent in the presence of hydrogen at temperatures of 80°C to 360°C.

[0008] However, further improvements regarding the removal of silicon from an LWP product are desirable.

Brief description of the invention

[0009] The present invention was made in view of the above-mentioned problems and it is an object of the present invention to provide a method of reducing the content of silicon in LWP obtained by a pyrolysis process.

[0010] The present invention is based on the finding that the content of silicon in LWP can be reduced in-situ already during pyrolysis by employing alumina as a reactant. That is, other than in the prior art, it is not necessary to provide a dedicated step of removing silicon from already-produced LWP. Rather, the amount of silicon in the LWP is reduced already in the pyrolysis step.

[0011] The problem underlying the invention is solved by the subject-matters set forth in the independent claims. Further beneficial developments are set forth in dependent claims.

[0012] In brief, the present invention relates to one or more of the following items:

1. A method of producing a pyrolysis oil, said method comprising the steps of

   adding alumina in the form of granules to organic silicon-containing waste plastic to form a mixture,
   feeding said mixture to a pyrolysis reactor,
   pyrolysing said mixture in said reactor,
   recovering at least a pyrolysis gas and a solid residue from said reactor, and condensing the pyrolysis gas to provide an oil product, wherein
   the solid residue comprises the alumina reacted with silicon.

2. The method according to item 1, wherein the alumina is added in an amount of 0.2 to 40.0 wt.-%, preferably 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.- %, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.- %, 4.0 to 12.0 wt.-%. 5.0 to 11.0 wt.-%, 5.5 to 10.0 wt.-%, or 6.0 to 9.0 wt.-%.

3. The method according to item 1 or 2, wherein said adding alumina to form a mixture is carried out at elevated temperatures.

4. The method according to any one of the preceding items, wherein said adding alumina to form a mixture is carried out at a temperature in the range of from 50°C to 280°C, preferably in the range of from 60°C to 270°C, 80°C to 260°C, 100°C to 250°C, 110°C to 250°C, 120°C to 250°C, 130°C to 240°C, 140°C to 230°C, or 150°C to 220°C.

5. The method according to any one of the preceding items, wherein said adding alumina to form a mixture comprises melting the waste plastic.

6. The method according to any one of the preceding items, wherein said adding alumina to form a mixture comprises melting the waste plastic and the addition of alumina is carried out before and/or during and/or after melting the waste plastic, preferably at least before melting.

7. The method according to any one of the preceding items, wherein the waste plastic predominantly contains thermoplastic compounds.

8. The method according to any one of the preceding items, wherein said adding alumina to form a mixture is carried out in an extruder, preferably in a melt extruder.

9. The method according to any one of the preceding items, wherein said adding alumina to form a mixture is carried out by blending the alumina with waste plastic, preferably solid waste plastic, without external heating.

10. The method according to any one of the preceding items, wherein the alumina has an average particle size in the range of from 50 nm to 10 mm, preferably in the range of from 10 μm to 2.0 mm, in the range from 50 μm to 1.8 mm or in the range from 100 μm to 1.5 mm.

11. The method according to any one of the preceding items, wherein the alumina is activated alumina.

12. The method according to any one of the preceding items, wherein the alumina has an open pore structure.

13. The method according to any one of the preceding items, wherein the alumina has pore sizes in the range of from 30 angstroms to 10000 angstroms, preferably from 40 angstroms to 1000 angstroms, from 50 angstroms to 500 angstroms, from 55 angstroms to 300 angstroms, or from 60 angstroms to 200 angstroms.

14. The method according to any one of the preceding items, wherein the alumina has a BET specific surface area in the range of from 50 m^2/g to 500 m^2/g, preferably above 50 m^2/g, above 100 m^2/g, or 150 m^2/g or more, such as in the range of from 150 to 300 m^2/g.

15. The method according to any one of the preceding items, further comprising post-processing the oil product recovered from the pyrolysis reactor.

16. The method according to item 15, wherein post-processing comprises subjecting the oil product to heat treatment with an aqueous solution of a basic substance, preferably an aqueous solution of a metal hydroxide, more preferably of sodium hydroxide, followed by phase separation (liquid-liquid separation) to provide an oil product which is further purified.

17. The method according to item 16, wherein the aqueous solution comprises at least 50 wt.-% water, preferably at least 70 wt.-% water, more preferably at least 85 wt.-% water, at least 90 wt.-% water or at least 95 wt.-% water.

18. The method according to item 16 or 17, wherein the aqueous solution comprises at least 0.3 wt.-% of the basic substance, more preferably at least 0.5 wt.-%, at least 1.0 wt.-%, or at least 1.5 wt.-% of the basic substance, such as 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.-% to 6.0 wt.-%, or 1.5 wt.-% to 4.0 wt.-%.

19. The method according to any one of items 16 to 18, wherein the aqueous solution comprises at least 0.5 wt.-%, preferably at least 1.0 wt.- %, or at least 1.5 wt.-% of a metal hydroxide or of an alkali metal hydroxide, such as from 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.-% to 6.0 wt.-%, or 1.5 wt.- % to 4.0 wt.-%.

20. The method according to any one of items 16 to 19, wherein the heat treatment is carried out at a temperature of 150°C or more, preferably 190°C or more.

21. The method according to any one of items 16 to 20, wherein heat treatment is carried out at a temperature of 200°C or more, such as 210°C or more, 220°C or more, 240°C or more or 260°C or more.

22. The method according to any one of items 16 to 21, wherein the heat treatment is carried out at a temperature of 450°C or less, preferably 400°C or less, 350°C or less, 320°C or less, or 300°C or less.

23. The method according to any one of items 16 to 22, wherein the heat treatment is carried out at a temperature in the range of 200°C to 350°C, preferably 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C.

24. The method according to any one of items 15 to 23, wherein post-processing comprises hydrotreating the oil product to provide a hydrotreated oil product.

25. The method according to any one of the preceding items, wherein the pyrolysis is carried out in two or more steps.

26. The method according to item 25, wherein the first pyrolysis step is carried out in the absence of a pyrolysis catalyst and at least one of the subsequent pyrolysis step(s) is carried out in the presence of a pyrolysis catalyst.

27. The method according to any one of the preceding items, wherein a Group II metal oxide or Group II metal hydroxide (Group II metal oxide/hydroxide) is furthermore added in the step of adding alumina to form a mixture and/or directly to the pyrolysis reactor.

28. The method according to item 27, wherein the Group II metal is magnesium or calcium.

29. The method according to item 27 or 28, wherein the Group II metal oxide/hydroxide is at least one selected from the group consisting of calcium oxide and calcium hydroxide.

30. The method according to any one of items 27 to 29, wherein the Group II metal oxide/hydroxide is added in an amount in the range of 0.2 to 40.0 wt.-%, preferably in an amount in the range of 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.-%, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.-%, 4.0 to 12.0 wt.-%, 5.0 to 11.0 wt.-%, 5.0 to 10.0 wt.-%, or 5.5 to 9.0 wt.-%.

31. The method according to any one of the preceding items, wherein the alumina is added in such an amount that the silicon content (by weight) in the oil product recovered from the pyrolysis reactor is reduced by at least 15% as compared to the silicon content in the oil product recovered from the pyrolysis reactor when no alumina is added.

32. The method according to any one of the preceding items, wherein the alumina is acidic or basic alumina, preferably acidic alumina.

33. The method according to any one of the preceding items, wherein the pyrolysis is carried out at a temperature in the range of from 250°C to 850°C.

34. A use of alumina in the form of granules for in-situ reduction of the amount of organic silicon in a waste plastic pyrolysis process.

35. The use according to item 34 in a waste plastic pyrolysis process as defined in any one of claims 1 to 33.

36. The use according to item 34 or 35 in a method of producing a pyrolysis oil, said method comprising the steps of

adding alumina in the form of granules to organic silicon-containing waste plastic to form a mixture,
feeding said mixture to a pyrolysis reactor,
pyrolysing said mixture in said reactor,
recovering at least a pyrolysis gas and a solid residue from said reactor, and condensing the pyrolysis gas to provide an oil product, wherein
the solid residue comprises the alumina reacted with silicon.

37. The use according to any one of items 34 to 36, wherein the alumina is added in an amount of 0.2 to 40.0 wt.-%, preferably 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.-%, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.-%, 4.0 to 12.0 wt.-%. 5.0 to 11.0 wt.-%, 5.5 to 10.0 wt.-%, or 6.0 to 9.0 wt.-%.

38. The use according to any one of items 34 to 37, wherein said adding alumina to form a mixture is carried out at elevated temperatures.

39. The use according to any one of items 34 to 38, wherein said adding alumina to form a mixture is carried out at a temperature in the range of from 50°C to 280°C, preferably in the range of from 60°C to 270°C, 80°C to 260°C, 100°C to 250°C, 110°C to 250°C, 120°C to 250°C, 130°C to 240°C, 140°C to 230°C, or 150°C to 220°C.

40. The use according to any one of items 34 to 39, wherein said adding alumina to form a mixture comprises melting the waste plastic.

41. The use according to any one of items 34 to 40, wherein said adding alumina to form a mixture comprises melting the waste plastic and the addition of alumina is carried out before and/or during and/or after melting the waste plastic, preferably at least before melting.

42. The use according to any one of items 34 to 41, wherein the waste plastic predominantly contains thermoplastic compounds.

43. The use according to any one of items 34 to 42, wherein said adding alumina to form a mixture is carried out in an extruder, preferably in a melt extruder.

44. The use according to any one of items 34 to 43, wherein said adding alumina to form a mixture is carried out by blending the alumina with waste plastic, preferably solid waste plastic, without external heating.

45. The use according to any one of items 34 to 44, wherein the alumina has an average particle size in the range of from 50 nm to 10 mm.

46. The use according to any one of items 34 to 45, wherein the alumina has an average particle size in the range of from 10 μm to 2.0 mm, preferably in the range from 50 μm to 1.8 mm or in the range from 100 μm to 1.5 mm.

47. The use according to any one of items 34 to 46, wherein the alumina has an open pore structure.

48. The use according to any one of items 34 to 47, wherein the alumina is added to the waste plastic before the pyrolysis reaction (before the waste plastic enters the pyrolysis reactor).

49. The use according to any one of items 34 to 48, wherein the alumina has pore sizes in the range of from 30 angstroms to 10000 angstroms, preferably from 40 angstroms to 1000 angstroms, from 50 angstroms to 500 angstroms, from 55 angstroms to 300 angstroms, or from 60 angstroms to 200 angstroms.

50. The use according to any one of items 34 to 49, wherein the alumina has a BET specific surface area in the range of from 50 m^2/g to 500 m^2/g, preferably above 50 m^2/g, above 100 m^2/g, or 150 m^2/g or more, such as in the range of from 150 to 300 m^2/g.

51. The use according to any one of items 34 to 50, wherein the pyrolysis is carried out in two or more steps.

52. The use according to any one of items 34 to 51, wherein the first pyrolysis step is carried out in the absence of a pyrolysis catalyst and at least one of the subsequent pyrolysis step(s) is carried out in the presence of a pyrolysis catalyst.

53. The use according to any one of items 34 to 52, wherein a Group II metal oxide or Group II metal hydroxide (Group II metal oxide/hydroxide) is furthermore added to the pyrolysis reactor.

54. The method according to item 53, wherein the Group II metal is magnesium or calcium.

55. The method according to item 52 or 54, wherein the Group II metal oxide/hydroxide is at least one selected from

the group consisting of calcium oxide and calcium hydroxide.

56. The method according to any one of items 52 to 55, wherein the Group II metal oxide/hydroxide is added in an amount in the range of 0.2 to 40.0 wt.-%, preferably in an amount in the range of 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.-%, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.-%, 4.0 to 12.0 wt.-%, 5.0 to 11.0 wt.-%, 5.0 to 10.0 wt.-%, or 5.5 to 9.0 wt.-%.

57. The use according to any one of items 34 to 56, wherein the alumina is added in such an amount that the silicon content (by weight) in the oil product recovered from the pyrolysis reactor is reduced by at least 15% as compared to the silicon content in the oil product recovered from the pyrolysis reactor when no alumina is added.

58. The use according to any one of items 34 to 57, wherein the alumina is acidic or basic alumina, preferably acidic alumina.

59. The use according to any one of items 34 to 58, wherein the alumina is activated alumina.

60. The use according to any one of items 34 to 59, wherein the pyrolysis is carried out at a temperature in the range of from 250°C to 850°C.

Detailed description of the invention

[0013] The present invention relates to relates to an improved method of reducing silicon content in depolymerized oil.

[0014] The content of silicon impurities should be reduced before the LWP is subjected to further processing. The present invention focusses on a method of in-situ removal of silicon during the pyrolysis step (i.e. during depolymerisation of waste plastic). The present invention specifically relates to a method making use of alumina in the form of granules (also referred to as granulated alumina or alumina granules) which is added to the waste plastic before pyrolysis and which reacts with the silicon compounds produced from organic silicon in the waste plastic during pyrolysis so that the silicon which has undergone reaction with the alumina ends up in the solid residue of the pyrolysis reaction whereas the gas product (gas effluent) is minimized in silicon content and this gas product is then condensed to provide a depolymerized oil (liquefied waste plastic; LWP).

[0015] In the context of the present invention, liquefied waste plastics (LWP) means a product effluent from pyrolysis process comprising at least depolymerising waste plastics. LWP is thus a material which is obtainable by depolymerizing waste plastics. LWP may also be referred to as polymer waste-based oil or as depolymerized oil.

[0016] The waste plastics may be derived from any source, such as (recycled or collected) consumer plastics, (recycled or collected) industrial plastics or (recycled or collected) end-life-tires (ELT). In particular, the term waste plastics refers to an organic polymer material which is no longer fit for its use or which has been disposed of for any other reason. Waste plastics may more specifically refer to end-life tires, collected consumer plastics (consumer plastics referring to any organic polymer material in consumer goods, even if not having "plastic" properties as such), collected industrial polymer waste. In the sense of the present invention, the term waste plastics or "polymer" in general does not encompass purely inorganic materials (which are otherwise sometimes referred to as inorganic polymers). Polymers in the waste plastics may be of natural and/or synthetic origin and may be based on renewable and/or fossil raw material.

[0017] The liquefaction process (pyrolysis) is carried out at elevated temperature, and preferably under non-oxidative conditions. The liquefaction process may be carried out at elevated pressure. The liquefaction process may be carried out in the presence of a catalyst. The liquefaction process provides a gas effluent and a solid residue, wherein the gas effluent is condensed to yield an oil product. The oil product may be employed as the pyrolysis oil (LWP; i.e. as the product of the process) as such or may be subjected to fractionation (or separation) to provide a fraction (or separated liquid) and may also be subjected to other work-up, in particular to further purification. In this context, fractionation refers to fractional distillation and/or fractional evaporation.

[0018] In addition to liquid (NTP) hydrocarbons, i.e. hydrocarbons being liquid at normal temperature and pressure (NTP; 20°C, 101.325 kPa absolute), typical oil products from the pyrolysis processes comprise gaseous (NTP) hydrocarbons, and hydrocarbons that are waxy or solid at NTP but become liquids upon heating, for example upon heating to 80°C.

[0019] In the context of the present disclosure, depolymerizing waste plastic means decomposing or degrading the polymer backbones of the waste plastic by pyrolysis to the extent yielding polymer and/or oligomer species of smaller molecular weight compared to the starting waste plastic, but still comprising at least liquid (NTP) hydrocarbons. Depolymerizing waste plastics may also involve cleavage of covalently bound heteroatoms such as O, S, and N from optionally present heteroatom-containing compounds.

[0020] Initially the waste plastics, or each waste plastics species in mixed waste plastics, to be subjected to pyrolysis,

is usually in solid state, typically having a melting point in the range of 100°C or more as measured by DSC as described by Larsen et al. ("Determining the PE fraction in recycled PP", Polymer testing, vol. 96, April 2021, 107058). However, the waste plastics, or each waste plastics species, may be melted before and/or during the depolymerisation.

[0021] Solid waste plastics may contain various further components such as additives, reinforcing materials, etc., including fillers, pigments, printing inks, flame retardants, stabilizers, antioxidants, plasticizers, lubricants, labels, metals, paper, cardboard, cellulosic fibres, fibre-glass, even sand or other dirt. Some of the further components may be removed, if so desired, from the solid waste plastics, from melted waste plastic, and/or from liquefied waste plastic using commonly known methods.

[0022] Preferably, the (solid) waste plastics to be subjected to the pyrolysis has an oxygen content of 15 wt.-% or less, preferably 10 wt.-% or less, more preferably 5 wt.-% or less, of the total weight of the (solid) waste plastics. The oxygen content may be 0 wt.-% and may preferably be in the range of 0 wt.-% to 15 wt.-% or 0 wt.-% to 10 wt.%. Oxygen content in wt.-% can be determined by difference using the formula 100 wt.-% - (CHN content + ash content), wherein CHN content refers to combined content of carbon, hydrogen and nitrogen, as determined in accordance with ASTM D5291, and ash content refers to ash content as determined in accordance with ASTM D482/EN15403.

[0023] In the present disclosure, when reference is made to a standard, the latest revision available on January 31, 2022 shall be meant, unless stated to the contrary. Furthermore, all embodiments (such as all preferred values and/or ranges within the embodiments) of the present invention may be combined with each other to give new (preferred) embodiments, unless explicitly specified otherwise or unless such a combination would result in a contradiction.

[0024] In the present invention, the term *"granules"* or "*in granulated form"* encompasses all kinds of powders, grains, agglomerates and the like and is not limited to a specific shape.

[0025] The term "*pyrolysis reactor"* refers to the pyrolysis zone of an apparatus carrying out a pyrolysis reaction. That is, the "*pyrolysis reactor"* is the place where the actual pyrolysis reaction takes place.

[0026] The term "*solid residue*" means a material which is not transferred to the gas phase in the course of the pyrolysis reaction. Usually, such a solid residue contains tar and inorganic impurities which are not evaporated. In the present invention, the solid residue comprises the alumina reacted with silicon. This means that the alumina has a higher Si content than at the time of addition (i.e. a higher Si content than the granulated alumina). The reaction may comprise or be a physical reaction (e.g. adsorption) and/or a chemical reaction. Preferably, Si is chemically reacted with the alumina, preferably bonded to the alumina surface (accessible surface, including permeating into the open pores). Although the mechanism is not fully clear, it is assumed that Si reacts with alumina mainly on its surface when added to the pyrolysis reactor to form a layer-like structure, and it is assumed that this layer-like structure is formed of a Si-Al-oxide type material.

[0027] It is assumed that most organic silicon in waste plastic is in the form of polysiloxanes, which form volatile oligosiloxanes during pyrolysis and are thus transferred to the oil product. Inorganic silicon, e.g. in the form of silica, on the other hand, is not reactive (and not volatile) under pyrolysis conditions and thus ends up in the solid residue in any case.

[0028] The method of the present invention is characterized by mixing granulated alumina with waste plastic and subjecting this mixture to pyrolysis in a pyrolysis reactor so that silicon in the waste plastic reacts with the alumina and is transferred to the solid residue.

[0029] Specifically, the present invention relates to a method of producing a pyrolysis oil, said method comprising the steps of adding alumina in the form of granules to organic silicon-containing waste plastic to form a mixture, feeding said mixture to a pyrolysis reactor, pyrolysing said mixture in said reactor, recovering at least a pyrolysis gas and a solid residue from said reactor, and condensing the pyrolysis gas to provide an oil product, wherein the solid residue comprises the alumina reacted with silicon.

[0030] The mixture is thus prepared before the mixture enters the pyrolysis reactor (i.e. the pyrolysis reaction zone). For example, the mixture may be prepared in advance or in a feed unit, such as an extruder. The step of adding alumina to form a mixture may also be referred to as mixing step

[0031] The alumina is preferably added in an amount of 0.2 wt.-% to 40.0 wt.-% (relative to 100 wt.-% of pyrolysis feed), more preferably 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.-%, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.-%, 4.0 to 12.0 wt.-%. 5.0 to 11.0 wt.-%, 5.5 to 10.0 wt.-%, or 6.0 to 9.0 wt.-%. The term "*relative to 100* wt.-% *of pyrolysis feed"* refers to the summed amount of waste plastic (including all impurities and contaminations such as biomass), alumina and other feeds (but excluding pyrolysis catalyst if present). That is, as pointed out above, the waste plastic may be derived from municipal waste and may include some biomass even after sorting.

[0032] The step of adding alumina to form a mixture (i.e. the mixing step) may be carried out at elevated temperature. In this respect, "*elevated temperature"* means that external heating is applied to the mixing device (such that the components to be mixed are heated).

[0033] For example, the mixing step may be carried out at a temperature in the range of from 50°C to 280°C, preferably in the range of from 60°C to 270°C, 80°C to 260°C, 100°C to 250°C, 110°C to 250°C, 120°C to 250°C, 130°C to 240°C, 140°C to 230°C, or 150°C to 220°C. By employing elevated temperature in the mixing step, the processing can be facilitated and a more intimate mixture can be prepared. In some embodiments, it can be beneficial to limit the temperature

in the mixing step to 180°C or less, such as in the range of from 50°C to 180°C, in order to minimize the generation of hydrochloric acid in the mixing stage. In the context of the present invention, the "*temperature"* at which the mixing step is carried out refers to the temperature of the mixed materials (not to the temperature of the heating medium).

[0034] In particular, said adding alumina to form a mixture may comprises (at least partially) melting the waste plastic. When the waste plastic is melted, a more intimate mixture can be prepared. In addition, a melted material further facilitates handling thereof. The addition of alumina may be carried out before and/or during and/or after melting the waste plastic, but is preferably carried out at least before melting.

[0035] Melting the waste plastic (at least partially) requires the presence of thermoplastic compounds. Accordingly, the waste plastic in the present invention preferably predominantly contains thermoplastic compounds. The term "*predominantly contains*" thermoplastic compounds means that at least 50 wt.-% (preferably at least 60 wt.-%, at least 70 wt.-%, at least 80 wt.- %, at least 90 wt.-%) of the waste plastic is formed of thermoplastic compounds based on the waste plastic as a whole.

[0036] In an embodiment, the mixing step is carried out in an extruder, preferably in a melt extruder. Since an extruder is often used as a feed unit to supply waste plastic to a pyrolysis reactor, the addition of alumina at this stage can be easily achieved while at the same time achieving intimate mixing.

[0037] In the alternative, or in addition, the mixing step may be carried out without external heating, such as at room temperature. In this case, handling is facilitated since it is not necessary to take care of high temperatures and/or cooling effects in the mixing step.

[0038] Pyrolysis may be carried out as a batch or continuous method, preferably a continuous method.

[0039] The alumina (alumina granules) preferably has an average particle size in the range of from 50 nm to 10 mm, preferably in the range of from 10 μm to 2.0 mm, in the range from 50 μm to 1.8 mm or in the range from 100 μm to 1.5 mm. Average particle sizes can be measured for example by laser diffraction (ISO 13320) or by optical or electron microscopy (ISO13322) methods. Specific surface areas and pore sizes (pore diameters) of alumina can be determined by gas adsorption measurements, e.g. based on ISO 9277 or ISO 15901-2. In the case of agglomerates, the particle size refers to the size of the agglomerate rather than to the primary particle size. The alumina (alumina granules) may for example have a porosity in the range of 20-85%.

[0040] The alumina (alumina granules) preferably has an open pore structure. The inventors found that the silicon mainly reacts with the alumina surface and therefore an open pore structure (having a high accessible alumina surface) is preferable. Preferably, the alumina has pore sizes in the range of from 30 Å to 10000 Å, preferably from 40 Å to 1000 Å, from 50 Å to 500 Å, from 55 Å to 300 Å, or from 60 Å to 200 Å.

[0041] The alumina (alumina granules) preferably has a BET specific surface area in the range of from in the range of from 50 m^2/g to 500 m^2/g, preferably above 50 m^2/g, above 100 m^2/g, or 150 m^2/g or more, such as in the range of from 150 to 300 m^2/g.

[0042] The method of the present invention may further comprise post-processing the oil product recovered from the pyrolysis reactor. Although the oil product produced by the method of the present invention may be sufficiently pure to be added to the value chain (such as being used in a crude oil refinery process), it is preferable to post-process the oil product to improve its purity or usability. The post-processing thus may in particular comprise purification process(es), such as fractionation or extraction, and/or upgrading process(es), such as hydrotreatment. Nevertheless, any known petrochemical process may be used for post-processing and, in particular, the oil product may be used as a co-feed in a petrochemical process.

[0043] In an embodiment, the post-processing comprises subjecting the oil product to heat treatment with an aqueous solution of a basic substance, preferably an aqueous solution of a metal hydroxide, more preferably of sodium hydroxide, followed by liquid-liquid separation to provide an oil product which was further purified. Such processing is suited to further remove impurities, in particular chlorine-containing impurities, from the oil product in a very efficient manner. The aqueous solution preferably comprises at least 50 wt.- % water, more preferably at least 70 wt.-% water, more preferably at least 85 wt.-% water, at least 90 wt.-% water or at least 95 wt.-% water. The aqueous solution preferably comprises at least 0.3 wt.-% of the basic substance, more preferably at least 0.5 wt.-%, at least 1.0 wt.-%, or at least 1.5 wt.-% of the basic substance, such as 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.- % to 6.0 wt.-%, or 1.5 wt.-% to 4.0 wt.-%. For example, the aqueous solution comprises at least 0.5 wt.-%, preferably at least 1.0 wt.-%, or at least 1.5 wt.-% of a metal hydroxide or of an alkali metal hydroxide, such as from 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.-% to 6.0 wt.-%, or 1.5 wt.-% to 4.0 wt.-%. The heat treatment may be carried out at a temperature of 150°C or more, preferably 190°C or more, or 200°C or more, such as 210°C or more, 220°C or more, 240°C or more or 260°C or more. In order to keep heating efforts within usual limits and to avoid excessive side reactions, the heat treatment is preferably carried out at a temperature of 450°C or less, preferably 400°C or less, 350°C or less, 320°C or less, or 300°C or less. In particular, the heat treatment may be carried out at a temperature in the range of 200°C to 350°C, preferably 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C.

[0044] The post-processing may comprise hydrotreating the oil product to provide a hydrotreated oil product. Hydrotreatment may in particular be used for removal of heteroatoms and/or for olefin saturation. Hydrotreatment is particularly favourable in the present invention because organic silicon may act as a catalyst deactivator. Thus, the method of the

present invention can protect the hydrotreatment catalyst from being deteriorated and increase its service life.

[0045] The pyrolysis step in the method of the present invention can be further implemented with a second step (as a two-step process). In this embodiment, the two steps can vary in reactor types also with reaction temperatures. Usually, the first step is to perform cracking with solid residue removed in the first reactor. The second step is then to treat the pyrolysis gas by contacting it with catalyst to selective crack long (carbon) chains. For example, the mixture of waste plastic and alumina is fed to the first step and a solid residue is removed from the first step while a product stream (e.g. oil or gas) is forwarded to the second (and optional subsequent) step(s). The first step may be a step of cracking the waste plastic into (long chain) compounds whereas the second step mainly serves to crack (long chain) compounds of the already-cracked material. Employing such a two-step process, the product distribution is improved. In particular, the viscosity of the oil product is reduced, thus facilitating handling and storage.

[0046] The cracking in the second step is preferably a selective cracking step. It is therefore preferable that the second pyrolysis step (and even more preferably subsequent pyrolysis step(s)) be carried out in the presence of a catalyst. In the first pyrolysis step, a catalyst is not as beneficial and thus may preferably be omitted. Accordingly, it is preferable that the first pyrolysis step be carried out in the absence of a pyrolysis catalyst and at least one of the subsequent pyrolysis step(s) be carried out in the presence of a pyrolysis catalyst. It is particularly preferable that at least the last pyrolysis step be carried out in the presence of a catalyst. A solid catalyst is preferred, such as an acidic solid catalyst, for example an acidic FCC catalyst, an acidic zeolite catalyst or an acidic silica-alumina catalyst, such as ZSM-5 or H-ultrastable Y-zeolite.

[0047] In order to further improve the product distribution (in particular to reduce chlorine content of the oil product), it is preferable that a wherein a Group II metal oxide or Group II metal hydroxide (in the following sometimes collectively referred to as Group II metal oxide/hydroxide) be furthermore added in the step of adding alumina to form a mixture and/or directly to the pyrolysis reactor. A Group II metal oxide/hydroxide is suited to reduce chlorine impurities during pyrolysis (in situ) and the inventors furthermore found that the additional presence of a Group II metal oxide/hydroxide further reduces the silicon content of the oil product. In view of procedural efficiency, it is preferable that the alumina and the Group II metal oxide/hydroxide be added in the same step, be it simultaneously and/or one after another, such as first adding the alumina and then adding the Group II metal oxide/hydroxide.

[0048] The Group II metal of the Group II metal oxide/hydroxide is preferably at least one selected from the group consisting of calcium and magnesium. Specifically, the Group II metal oxide/hydroxide is preferably at least one selected from the group consisting of calcium oxide and calcium hydroxide. The Group II metal oxide/hydroxide is preferably added in an amount in the range of 0.2 wt.-% to 40.0 wt.-%, more preferably in an amount in the range of 0.5 wt.-% to 35.0 wt.-%, 1.0 wt.-% to 30.0 wt.-%, 1.5 wt.-% to 25.0 wt.- %, 2.0 wt.-% to 20.0 wt.-%, 2.5 wt.-% to 15.0 wt.-%, 3.0 wt.-% to 13.0 wt.-%, 4.0 wt.-%to 12.0 wt.-%, 5.0 wt.-% to 11.0 wt.-%, 5.0 wt.-% to 10.0 wt.-%, or 5.5 wt.-% to 9.0 wt.-%. The amount of Group II metal oxide/hydroxide is calculated in terms of Group II metal oxide. That is, if a Group II metal hydroxide (e.g. $Ca(OH)_2$) is added, a Group II metal oxide (e.g. CaO) equivalent amount is calculated assuming that all Group II metal-containing compounds are present as Group II metal oxide (e.g. CaO), i.e. using the content of Group II metal (e.g. Ca) as a basis.

[0049] The alumina is preferably added in such an amount that the silicon content (by weight) in the oil product recovered from the pyrolysis reactor is reduced by at least 15% as compared to the silicon content in the oil product recovered from the pyrolysis reactor when no alumina is added. The amount of silicon may be determined based on ASTM D5185. In this respect, the oil product refers to the oil product directly after pyrolysis (i.e. condensed product) from which only gaseous (NTP) products are removed and no further work-up or post-processing is applied. Further, the term "*when no alumina is added"* means that the reaction is carried out under the same conditions but without addition of alumina. Adjusting the Si content reduction may preferably be achieved by means of a feedback control or feed-forward control, e.g. feed-forward control using tabulated values for known waste plastic compositions.

[0050] The alumina may be acidic, neutral or basic alumina, and is preferably neutral or acidic alumina, more preferably acidic alumina. Alumina is called acidic, when it gives a pH (of the water) below 6 when placed in water. Alumina is called basic, it gives a pH (of the water) above 8 when placed in water. Alumina is called neutral, when the pH of the water between is 6 and 8. It is assumed that acidic and/or neutral alumina more easily forms chemical bonds with Si and thus results in better Si removal efficiency.

[0051] Moreover, in order to improve reactivity, the alumina is preferably activated alumina, more preferably acidic activated alumina. Activated alumina is a highly porous form of aluminium oxide which is used in chemistry for example as drying agent. Its surface area is high, typically above 100 m^2/g, often even exceeding 200 m^2/g. Activated alumina may be produced by dehydroxylating aluminium hydroxide such that a highly porous material is formed. The activated alumina may have an open pore structure, in particular tunnel-like pores. Activated alumina may comprise or consist of gamma alumina (γ-Al_2O_3) .

[0052] The temperature in the pyrolysis step is not particularly limited and a conventional range may be employed. In a case where multiple pyrolysis steps are employed, the temperature is preferably adjusted to the presence or absence of a catalyst.

[0053] Thermal non-catalytic pyrolysis preferably employs a temperature in the range from 300°C to 850°C, such as from 400°C to 800°C. This process is typically conducted at atmospheric pressure, usually under non-oxidative conditions, especially in the absence of air. The non-oxidative conditions may be achieved for example by purging the liquefaction equipment with an inert gas such as nitrogen.

[0054] Thermal catalytic pyrolysis preferably employs a temperature in the range from 250°C to 500°C, such as from 300°C to 450°C. This process is typically conducted at atmospheric pressure, usually under non-oxidative conditions, especially in the absence of air. The process typically employs a solid catalyst, preferably an acidic solid catalyst, for example an acidic FCC catalyst, an acidic zeolite catalyst or an acidic silica-alumina catalyst, such as ZSM-5 or H-ultrastable Y-zeolite, just to name a few. The non-oxidative conditions may be achieved for example by purging the liquefaction equipment with an inert gas such as nitrogen.

[0055] The waste plastic may be mixed waste plastic or sorted waste plastic. Since the present invention is particularly suited for highly contaminated waste plastic, it is possible to reduce the reliance on the quality of sorted waste plastic and thus sorted waste plastic of lower quality may be used. Waste plastic, in particular non-processed mixed waste plastic, may contain high amounts of silicon from various sources. The waste plastic may for example have a silicon content in the range of from 300 to 50000 ppm, such as from 300 to 20000 ppm or from 500 to 10000 ppm. The silicon content may be determined with any conventional method, such as ICP-MS (Inductively coupled plasma mass spectrometry) or XRF (X-ray fluorescence).

[0056] The present invention further relates to a use of alumina granules for in-situ reduction of the amount of organic silicon in a waste plastic pyrolysis process. In this respect, in-situ reduction means that the organic silicon species (which may be originally present or generated in the course of the pyrolysis reaction) are removed, accumulate in a solid residue and are reduced in content in the product stream (gas/oil product) while carrying out the pyrolysis. In this use, the alumina is preferably added before starting the pyrolysis reaction (e.g. before feeding the waste plastic to the reaction zone). The embodiments set forth for the method of the present invention may be similarly applied to the process of the present invention.

[0057] The present invention provides a pyrolysis oil having reduced organic silicon content and an efficient method for achieving this.

Examples

[0058] In the following, the present invention is illustrated by means of non-limiting Examples. Nevertheless, it is to be understood that the Examples represent preferred embodiment of the invention and, in particular, numerical values and range recited in the Examples may be combined with other ranges and values disclosed in the specification to give ranges embodying the invention.

Comparative Example 1

[0059] Pyrolysis was carried out using sorted waste plastic (industry grade DKR310, commonly used in Germany) to which 1 wt.-% PVC (relative to final waste plastic mixture) was added and to which 0.5 wt.-% PDMS (polydimethylsiloxane; 0.5 wt.-%) was further added to mimic an organic silicon-containing waste plastic material having a high organic silicon content.

[0060] The pyrolysis was carried out without catalyst at a temperature (pyrolysis temperature inside the reactor) of 380°C. Generated gases were condensed and collected to provide an oil product. The oil product was analysed. Si content in the oil was analysed based on ASTM D5185, with the procedure adjusted as necessary for measurement of pyrolysis oil. Results are shown in Table 1.

Example 1

[0061] Comparative Example 1 was repeated under the same conditions, except that 20 wt.-% activated acidic alumina powder (BET SSA 155 m^2/g, pore size 58 Å, average particle size 150 mesh, corresponding to 105 μm) was further added (to give a mixture containing 20 wt.-% alumina and 80 wt.-% mixed waste plastic) by mixing without external heating. The oil product was analysed. Results are shown in Table 1.

Comparative Example 2

[0062] Comparative Example 1 was repeated under the same conditions, except that DKR350 (industry grade) sorted waste plastic (originally having a high Si content) was used without addition of PVC or PDMS. The oil product was analysed. Results are shown in Table 1

Examples 2 to 4

[0063] Comparative Example 2 was repeated under the same conditions, except that varying amounts of the alumina specified in Example 1 alumina were added. Specifically, 3 wt.-% (Example 2) and 7 wt.-% (Example 3) were added in a double screw melt extruder at a temperature of 165°C. In Example 4, 7 wt.- % alumina was added and 6.7 wt.-% CaO were further added. The oil products were analysed. Results are shown in Table 1.

Table 1

	C.Ex. 1	Ex. 1	C.Ex. 2	Ex. 2	Ex. 3	Ex. 4
alumina addition	0	20%	0	3%	7%	7% (+CaO)
Si content in oil [ppm]	2000	440	490	430	260	220
Si content reduction	-	78%	-	12%	47%	55%

[0064] The results show that a significant reduction of Si content in the oil product can be achieved by simple addition of alumina to the pyrolysis raw material.

Claims

1. A method of producing a pyrolysis oil, said method comprising the steps of

   adding alumina in the form of granules to organic silicon-containing waste plastic to form a mixture,
   feeding said mixture to a pyrolysis reactor,
   pyrolysing said mixture in said reactor,
   recovering at least a pyrolysis gas and a solid residue from said reactor, and condensing the pyrolysis gas to provide an oil product, wherein
   the solid residue comprises the alumina reacted with silicon.

2. The method according to claim 1, wherein the alumina is added in an amount of 0.2 to 40.0 wt.-%, preferably 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.- %, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.- %, 4.0 to 12.0 wt.-%. 5.0 to 11.0 wt.-%, 5.5 to 10.0 wt.-%, or 6.0 to 9.0 wt.-%.

3. The method according to claim 1 or 2, wherein said adding alumina to form a mixture is carried out at a temperature in the range of from 50°C to 280°C, preferably in the range of from 60°C to 270°C, 80°C to 260°C, 100°C to 250°C, 110°C to 250°C, 120°C to 250°C, 130°C to 240°C, 140°C to 230°C, or 150°C to 220°C.

4. The method according to any one of the preceding claims, wherein said adding alumina to form a mixture comprises melting the waste plastic.

5. The method according to any one of the preceding claims, wherein said adding alumina to form a mixture is carried out in an extruder, preferably in a melt extruder.

6. The method according to any one of the preceding claims, wherein the alumina has an open pore structure.

7. The method according to any one of the preceding claims, wherein the alumina has a BET specific surface area in the range of from 50 m^2/g to 500 m^2/g, preferably above 50 m^2/g, above 100 m^2/g, or 150 m^2/g or more, such as in the range of from 150 to 300 m^2/g.

8. The method according to any one of the preceding claims, wherein the pyrolysis is carried out in two or more steps.

9. The method according to claim 24, wherein the first pyrolysis step is carried out in the absence of a pyrolysis catalyst and at least one of the subsequent pyrolysis step(s) is carried out in the presence of a pyrolysis catalyst.

10. The method according to any one of the preceding claims, wherein a Group II metal oxide or Group II metal hydroxide (Group II metal oxide/hydroxide) is furthermore added in the step of adding alumina to form a mixture and/or directly

to the pyrolysis reactor.

11. The method according to claim 10, wherein the Group II metal is magnesium or calcium.

12. The method according to claim 10 or 11, wherein the Group II metal oxide/hydroxide is at least one selected from the group consisting of calcium oxide and calcium hydroxide.

13. The method according to any one of claims 10 to 12, wherein the Group II metal oxide/hydroxide is added in an amount in the range of 0.2 to 40.0 wt.-%, preferably in an amount in the range of 0.5 to 35.0 wt.-%, 1.0 to 30.0 wt.-%, 1.5 to 25.0 wt.-%, 2.0 to 20.0 wt.-%, 2.5 to 15.0 wt.-%, 3.0 to 13.0 wt.-%, 4.0 to 12.0 wt.-%, 5.0 to 11.0 wt.-%, 5.0 to 10.0 wt.-%, or 5.5 to 9.0 wt.-%.

14. The method according to any one of the preceding claims, wherein the alumina is acidic alumina, preferably activated acidic alumina.

15. A use of alumina in the form of granules for in-situ reduction of the amount of organic silicon in a waste plastic pyrolysis process.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 18 4304

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	CN 114 507 542 A (CHINESE PETROCHEMICAL INDUSTRY LTD COMPANY ET AL.) 17 May 2022 (2022-05-17) * claim 1 * * paragraphs [0071], [0072] * * examples 11, 14 *	1-14	INV. C10G1/00 C10G1/08 C10G1/10
X	WO 2021/204818 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]) 14 October 2021 (2021-10-14) * claims 1, 9, 10 * * page 19, lines 8-20 *	15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10G C10B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23 November 2022	Pardo Torre, J

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23-11-2022

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 114507542 A	17-05-2022	NONE	
WO 2021204818 A1	14-10-2021	WO 2021204817 A1	14-10-2021
		WO 2021204818 A1	14-10-2021
		WO 2021204819 A1	14-10-2021
		WO 2021204820 A1	14-10-2021
		WO 2021204821 A1	14-10-2021

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Patent documents cited in the description

- WO 202180899 A1 **[0007]**

Non-patent literature cited in the description

- **LARSEN et al.** Determining the PE fraction in recycled PP. *Polymer testing,* April 2021, vol. 96, 107058 **[0020]**