METHOD FOR TREATMENT OF LIQUEFIED WASTE PLASTIC

Technical Field

The present invention relates to improvements in the treatment of liquefied waste plastic. More specifically, the invention relates to an improved method of treating crude (untreated) liquefied waste plastics with an alkaline aqueous medium at elevated temperature.

Background of the Invention

The purification of liquefied waste plastics (LWP) to yield more valuable (pure) substances and the conversion of liquefied waste plastics (LWP) into more valuable material have been studied for several years.

For example, FI 128848 B discloses a method comprising pre-treating liquefied waste plastic material in the presence of an alkaline aqueous medium at elevated temperature, followed by liquid-liquid separation and hydrotreating as well as post-treatment to provide a steam cracker feed.

While pre-treatment of liquefied waste plastics has been employed for some years now, the process is still under development in order to maximize yield and/or purity and to minimize environmental impact of the process. In particular, contaminate waste water results in a significant environmental impact due to complicated and/or highly energy-consuming work-up.

Brief description of drawings

FIG. 1 is a flow chart showing an embodiment of the method and system of the present invention.

FIG. 2 is a flow chart showing an embodiment of the waste water handling

Brief description of the invention

The present invention was made in view of the above-mentioned problems and it is an object of the present invention to provide an improved method for treatment of liquefied waste plastics.

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.

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

1. A method for treating liquefied waste plastics (LWP), said method comprises the steps of

(i) providing a volume of the liquefied waste plastics-based oil (A),

(ii) subjecting the volume of LWP-based oil (A) to a heat treatment (1) with a volume of an alkaline aqueous medium (B) to provide a heat-treated mixture volume (C),

(iii) phase-separating (2) the heat-treated mixture volume (C) into at least two separated phase volumes (D; E), wherein one separated phase volume is a first aqueous phase volume (D), and the other separated phase volume is a first oil phase volume (E),

(iv) isolating (2) the first aqueous phase volume (D),

(v) adjusting (3) the pH of the first aqueous phase volume (D) to pH 9.0 or below by adding an acidic medium (F) into said first aqueous phase volume (D) to form a pH adjusted volume (G),

(vi) phase-separating (4) the pH adjusted volume (G) into at least two separated phase volumes (H; I), wherein one separated phase volume is a second aqueous phase volume (I), and the other separated phase volume is a second oil phase volume (H).

2. The method according to item 1, wherein the acidic medium (F) comprises organic acid and/or inorganic acid, such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid (H_3NSO_3) or a carboxylic acid.

3. The method according to item 1 or 2, wherein the acidic medium (F) is a solution of an acid.

4. The method according to any one of the preceding items, wherein the acidic medium (F) is an aqueous solution of an acid.

5. The method according to item 3 or 4, wherein the acid is at least one selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid (H_3NSO_3), or a carboxylic acid, preferably at least sulfuric acid or hydrochloric acid.

6. The method according to item 5, wherein the acid is at least sulfuric acid.

7. The method according to any one of items 3 to 6, wherein the solution of an acid has a concentration (of the acid) in the range of from 1 to 98 % by mass, preferably 1 to 96 % by mass, more preferably 50 to 70 % by mass.

8. The method according to any of the preceding items, wherein the phase separation (2) in step (iii) is carried out at a temperature in the range of from 15°C to 200°C, preferably 40°C and 200 °C, 50°C to 175°C, or 60°C and 150°C.

9. The method according to any of the preceding items, wherein the phase separation (2) in step (iii) is carried out at a pressure in the range of from 1 bar (absolute) to 15 bar (absolute), preferably 2 bar (absolute) to 15 bar (absolute).

10. The method according to any of the preceding items, wherein the residence time of the pH adjusted volume (G) in the phase separation (4) of step (vi) is in the range of from 1 minute to 600 minutes, such as 1 minute to 240 minutes, or 2 minutes to 180 minutes.

11. The method according to any of the preceding items, wherein the phase separation (4) in step (vi) is performed at the same or at a lower temperature than the phase separation (2) in step (iii).

12. The method according to any of the preceding items, wherein the first oil phase volume (E) and/or the second oil phase volume (H) is further subjected to washing, preferably water washing.

13. The method according to any of the preceding items, wherein the first oil phase volume (E) and the second oil phase volume (H) are each separately subjected to washing, preferably water washing.

14. The method according to any of the preceding items, wherein the second aqueous phase volume (I) is further subjected to evaporation to obtain an impurities concentrate residual and a wastewater stream.

15. The method according to any one of the preceding items, further comprising combining at least part of the second oil phase volume (H) with at least part of the first oil phase volume (E) to provide a combined oil phase volume (K).

16. The method according to item 15, further comprising subjecting at least part of the combined oil phase volume (K) to a further treatment and/or conversion process.

17. The method according to any one of the preceding items, further comprising subjecting at least part of the second oil phase volume (H) and/or at least part of the first oil phase volume (E) to a further treatment and/or conversion process.

18. The method according to any one of the preceding items, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to pH 8.7 or below, such as 8.5 or below, 8.3 or below, or 8.0 or below.

19. The method according to any one of the preceding items, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to pH 1.5 or higher, preferably 2.0 or higher, more preferably 3.0 or higher, 4.0 or higher, 5.0 or higher, 6.0 or higher, or 7.0 or higher.

20. The method according to any one of the preceding items, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to pH 3.0 or higher, such as 4.0 or higher, 5.0 or higher, 6.0 or higher, or 7.0 or higher.

21. The method according to any one of the preceding items, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to a pH in the range of from 1.5 to 9.0, preferably 2.0 to 9.0, 3.0 to 9.0, 4.0 to 8.7, 5.0 to 8.5, 6.0 to 8.3, or 7.0 to 8.0.

22. The method according to any one of the preceding items, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to a pH in the range of from 3.0 to 9.0, such as 3.0 to 8.7, 4.0 to 4.7, 5.0 to 8.7, 5.0 to 8.5, 6.0 to 8.3, or 7.0 to 8.0.

23. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) is an aqueous solution of an alkaline substance.

24. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) is an aqueous solution of a metal hydroxide.

25. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) is an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides.

26. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) is an aqueous solution of a metal hydroxide and

the metal hydroxide is selected from the group consisting of KOH, NaOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$, RbOH, $Sr(OH)_2$ and $Ba(OH)_2$.

27. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) is an aqueous solution of a metal hydroxide and the metal hydroxide is NaOH.

28. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) contains an alkaline substance in an amount in the range of from 0.5 wt.-% to 15.0 wt.-%, such as from 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.-% to 6.0 wt.-%, or 1.5 wt.-% to 6.0 wt.-%.

29. The method according to any one of the preceding items, wherein the alkaline aqueous medium (B) 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.

30. The method according to any one of the preceding items, wherein the water-oil-ratio between the volume of the alkaline aqueous medium (B) and the volume of liquefied waste plastics-based oil (A) in the heat treatment (1) of step (ii) is in the range of from 0.1 to 1.4 by weight, preferably in the range of 0.2 to 1.0, such as 0.2 to 0.7.

31. The method according to any one of the preceding items, wherein the method further comprises a step of cooling the heat-treated mixture volume (C) prior to or in the course of the separation (2) in step (iii).

32. The method according to any one of the preceding items, wherein the separation (2) in step (iii) comprises liquid-liquid separation.

33. The method according to any one of the preceding items, wherein the summed amount of the volume of liquefied waste plastics-based oil (A) and the volume of alkaline aqueous medium (B) in the heat treatment (1) of step

(ii) is 85% to 100% by weight, preferably 90% to 100% by weight, 95% to 100% by weight, 97% to 100% by weight, or 99% to 100% by weight.

34. The method according to any of the preceding items, wherein the heat for carrying out the heat treatment (1) in step (ii) is provided to the volume of the LWP-based oil (A), to the volume of alkaline aqueous medium (B) and/or to a mixture of the volume of the LWP-based oil (A) and the volume of alkaline aqueous medium (B) in a reactor and/or in a heating section as an independent unit preceding a reactor.

35. The method according to item 34, wherein the heat is provided by indirect heating and/or by blowing steam (hot water vapour) into the volume of the LWP-based oil (A), into the volume of alkaline aqueous medium (B) and/or into a mixture of the volume of the LWP-based oil (A) and the volume of alkaline aqueous medium (B).

36. The method according to any one of the preceding items, wherein the heat treatment (1) is carried out in a reactor and the residence time of a mixture of the volume of the LWP-based oil (A) and the volume of alkaline aqueous medium (B) at elevated temperature is at least 10 minutes, preferably in the range of 10 minutes to 600 minutes, such as in the range of 10 minutes to 300 minutes, 15 minutes to 180 minutes, 15 minutes to 120 minutes, or 20 minutes to 60 minutes.

37. The method according to any one of the preceding items, wherein the heat treatment (1) in step (ii) is carried out at a temperature of 150°C or higher, preferably 180°C or higher, such as 200°C or higher, 220°C or higher, or 240°C or higher.

38. The method according to any one of the preceding items, wherein the heat treatment (1) in step (ii) 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.

39. The method according to any one of the preceding items, wherein the heat treatment (1) in step (ii) is carried out at a temperature in the range of 150°C to 450°C, preferably 180°C to 450°C, 200°C to 400°C, 210°C to 350°C, 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C.

40. The method according to any one of the preceding items, wherein the method is carried out as a batch process.

41. The method according to any one of the preceding items, wherein the method is carried out as a continuous process.

42. The method according to any one of the preceding items, wherein the separation (2) in step (iii) comprises a gravity-based separation, such as decantation, or a separation by means of centrifugation.

43. The method according to any one of the preceding items, wherein the second aqueous phase volume (I) is at least partially recycled, after optional purification, back to form part of the volume of alkaline aqueous medium (B).

44. The method according to any one of the preceding items, wherein the volume of the LWP-based oil (A) has a 5% boiling point of 25°C or higher, preferably 30°C or higher, or 35°C or higher, such as in the range of from 25°C to 120°C, in the range of from 25°C to 100°C, in the range of 30°C to 90°C, or in the range of from 35°C to 80°C.

45. The method according to any one of the preceding items, wherein the volume of the LWP-based oil (A) has a 95% boiling point of 700°C or less, preferably 650°C or less, 600°C or less, or 550°C or less, such as in the range of from 180°C to 700°C, 250°C to 700°C, 300°C to 650°C, 350°C to 600°C, 380°C to 500°C, or 400°C to 500°C.

46. The method according to any one of the preceding items, wherein the volume of the LWP-based oil (A) has a density, as measured at 15°C in the range of from 0.780 to 0.850 kg/m^3.

47. The method according to any one of the preceding items, wherein the volume of the LWP-based oil (A) has an olefins content of 5 wt.-% or more, such as 10 wt.-% or more, 15 wt.-% or more, 20 wt.-% or more, 30 wt.-% or more, 40 wt.-% or more, or 50 wt.-% or more.

48. The method according to any one of the preceding items, wherein the volume of the LWP-based oil (A) has an olefins content of 85 wt.-% or less, such as 80 wt.-% or less, 70 wt.-% or less, or 65 wt.-% or less.

49. The method according to any one of the preceding items, wherein the chlorine content of the volume of the LWP-based oil (A) is in the range of from 1 wt.-ppm to 4000 wt.-ppm, such as 100 wt.-ppm to 4000 wt.-ppm, or 300 wt.-ppm to 4000 wt.-ppm.

50. The method according to any one of the preceding items, wherein the separation (4) in step (vi) comprises liquid-liquid separation.

51. The method according to any one of the preceding items, wherein the separation (4) in step (vi) comprises a gravity-based separation, such as decantation, or a separation by means of centrifugation.

52. The method according to any of the preceding items, wherein the phase separation (4) in step (vi) is carried out at a temperature in the range of from 15°C and 200 °C, preferably 30°C and 200 °C, 40°C to 175°C, 50°C and 150°C or 60°C and 140°C.

53. The method according to any of the preceding items, wherein the phase separation (4) in step (vi) is carried out at a pressure in the range of from 1 bar (absolute) to 15 bar (absolute), preferably 2 bar (absolute) to 15 bar (absolute).

54. The method according to any one of the preceding items, further comprising subjecting at least part of the second aqueous phase volume (I) to evaporation.

55. The method according to any one of the preceding items, further comprising adjusting (5) the pH of the second aqueous phase volume (I) to pH 9.5 or higher, preferably 10.0 or higher, or 10.5 or higher.

56. The method according to any one of the preceding items, further comprising adjusting (5) the pH of the second aqueous phase volume (I) to pH 11.0 or higher, preferably 11.5 or higher, or 12.0 or higher.

57. The method according to item 55 or 56, wherein the pH is adjusted by adding an alkaline medium (L).

58. The method according to item 57, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase volume is an aqueous solution of a metal hydroxide.

59. The method according to item 57 or 58, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase volume is an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides.

60. The method according to any one of items 57 to 59, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase volume is an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of KOH, NaOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$, RbOH, $Sr(OH)_2$ and $Ba(OH)_2$.

61. The method according to any one of items 57 to 60, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase

volume is an aqueous solution of a metal hydroxide and the metal hydroxide is NaOH.

62. The method according to any one of items 57 to 61, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase volume contains an alkaline substance in an amount in the range of from 1 wt.-% to 100 wt.-%, such as from 1 wt.-% to 99 wt.-%, 2 wt.-% to 90 wt.-%, 5 wt.-% to 70 wt.-%, 10 wt.-% to 65 wt.-%, 15 wt.-% to 60 wt.-%, or 20 wt.-% to 55.0 wt.-%.

63. The method according to any one of items 57 to 62, wherein the alkaline medium (L) for adjusting (5) the pH of the second aqueous phase volume comprises at least 1 wt.-% water, preferably at least 10 wt.-% water, at least 15 wt.-% water, at least 20 wt.-% water or at least 25 wt.-% water.

64. The method according to any one of items 55 to 63, comprising evaporating (6) at least part of the second aqueous phase volume (M) after adjusting (5) the pH to provide at least one condensate (N) and at least one evaporation residue (P).

65. The method according to item 64, wherein the evaporation (6) is carried out in one, two or more stages.

66. The method according to item 64 or 65, further comprising subjecting at least part of at least one condensate (N) to further work-up, preferably to ammonia removal, such as at least a stripping treatment, in particular a steam stripping treatment.

67. The method according to any one of items 64 to 66, further comprising subjecting at least part of at least one condensate (N), after optional further work-up, to waste-water treatment.

68. The method according to any one of the preceding items, wherein the alkaline aqueous medium has a pH of at least 9.5, preferably at least 10.0, at least 10.5, at least 11.0, more preferably at least 12.0, at least 12.5 or at least 13.0.

69. The method according to any one of the preceding items, wherein the alkaline aqueous medium has a pH in the range of from 9.5 to 14.0, 10.0 to 14.0, 11.0 to 14.0, 12.0 to 14.0, 12.5 to 14.0, 13.0 to 14.0, or 13.0 to 13.9.

70. The method according to any one of the preceding items, further comprising a step of subjecting the isolated first aqueous phase volume (D) of step (iv) to pre-separation to provide an oil-reduced aqueous phase volume and an oil-enriched aqueous phase volume, wherein at least the oil-enriched aqueous phase volume is forwarded to step (v) as the first aqueous phase volume (D).

71. The method according to item 70, wherein the pre-separation comprises at least one of cooling and centrifugation.

72. The method according to item 70 or 71, wherein the pre-separation comprises at least cooling in a heat exchanger followed by phase separation.

73. The method according to any one of items 70 to 72, wherein the oil-reduced aqueous phase volume is separated as a translucent liquid.

74. The method according to any one of items 70 to 73, wherein the oil-enriched aqueous phase volume is separated as an opaque (cloudy/milky) liquid.

Detailed description of the invention

A (volume of) liquefied waste plastics (LWP), such as a pyrolysis product of collected waste plastics (e.g. pyrolysis product of collected consumer plastics), contains large and varying amounts of contaminants which would

be detrimental in downstream processes. Such contaminants include, among others, halogens (e.g. chlorine and bromine) originating from halogenated plastics (such as PVC and PTFE) or flame retardants, sulphur originating from cross-linking agents of rubbery polymers (e.g. in end-of-life tires) and metals or metalloids (e.g. Si, Al) contaminants originating from composite materials and additives (e.g. films coated with metals or metal compounds, end-of-life tires, or plastics processing aids). These contaminants may be present in elemental form, in ionic form, or as a part of organic or inorganic compounds.

These impurities should be removed before the LWP is subjected to further processing. The inventors of the present invention previously proposed a process comprising contacting the (crude) LWP with an alkaline aqueous medium at elevated temperature (also referred to as heat treatment (HT) processing in the following), followed by phase separation. The HT processing may also be referred to as *"reactive extraction"*. That is, the inventors found that an appropriate combination of high pH (of the alkaline aqueous medium) and heat (in the course of HT processing) results in reaction of (e.g. organic-bound) impurities and thus provides benefits over simple *"water washing"* or *"neutralisation treatment"* of LWP. In particular, the reactive extraction process is useful for removing at least part of silicon compounds (of which organic silicon compounds are particularly problematic), as well as chlorine compounds (organic and inorganic forms) and nitrogen-containing compounds. That is, the reactive extraction converts the (organic) impurities into a water-soluble form so that they can be removed (separated) together with the aqueous phase

The present invention is based on the above-mentioned HT processing and provides an improved workup of the aqueous phase (in the following referred to as *"first aqueous phase volume"*) emerging from the HT processing after phase separation. That is, the inventors surprisingly found that a considerable amount of LWP is *"lost"* with the aqueous phase, leading to both yield issues and waste-water workup issues. The present inventors surprisingly found that acidification of the first aqueous phase (volume) to pH 9.0 or below allows

separation of a further amount (volume) of oil phase in a subsequent (second) phase separation step. Thus, both the yield of the LWP eventually obtained is increased and the purity of the aqueous phase is increased (lower total organic carbon content), thus facilitating workup. Based on this finding, the present inventors completed the invention.

In the context of the present invention, liquefied waste plastics (LWP) means a product effluent from liquefaction 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 liquefied waste plastic. Moreover, whenever reference is made to the LWP (which is used as an abbreviation of *"LWP-based oil"*), this shall of course encompass the *"volume of liquefied waste plastics-based oil"*. The same applies to the (volume) of alkaline aqueous medium, the first/second aqueous phase (volume), the first/second oil phase (volume), the pH adjusted (aqueous) volume, and so on.

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-of-life tires (including rubber of natural origin), 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 or any combinations thereof. 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. Waste plastics that are collected consumer plastics or municipal waste products generally would have undergone mechanical sorting thus cellulose-based materials (paper, cardboard) and metals can be

present in the waste plastic feeds of minor quality and should be considered as contaminants.

The liquefaction process is typically 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 effluent from the liquefaction process may be employed as the liquefied waste plastic as such or may be subjected to fractionation (or separation) to provide a fraction (or separated liquid) of the effluent as the liquefied waste plastics. For example, the LWP may be a hydrothermal liquefaction (HTL) oil or a fraction thereof. Similarly, multiple fractionations may be carried out. In addition, two or more liquefaction process effluents and/or fractions thereof may be combined to give the LWP. These effluents and/or fractions may have the same or similar boiling range or may have different boiling ranges. In this context, fractionation comprises fractional distillation and/or fractional evaporation and/or fractional condensation.

In addition to liquid (NTP) hydrocarbons, i.e. hydrocarbons being liquid at normal temperature and pressure (NTP; 20°C, 101.325 kPa absolute), typical product effluents from liquefaction 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.

In the context of the present disclosure, depolymerizing waste plastic means decomposing or degrading the polymer backbones of the waste plastic, typically at least thermally, 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. In other words, as used herein, the liquefied waste plastic does not cover plastics in liquid form obtained merely by melting or by dissolving into a solvent, as these do not involve sufficient cleavage of the polymer backbones, nor waste plastics depolymerized completely to the monomer-level and thus being e.g. of

gaseous (NTP) form. Depolymerizing waste plastics may also involve cleavage of covalently bound heteroatoms such as O, S, and N from optionally present heteroatom-containing compounds.

Initially the waste plastics, or each waste plastics species in mixed waste plastics, to be subjected to liquefaction, is usually in solid state, typically having a melting point in the range of 100°C or higher 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 at least partially melted before and/or during the depolymerisation.

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.

Preferably, the (solid) waste plastics to be subjected to the liquefaction process (depolymerisation), and thus being the base material of the LWP (LWP-based oil), 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. In other words, the LWP-based oil is preferably derived from waste plastics having the stated oxygen content. 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.

In the present disclosure, all embodiments (such as all preferred values and/or ranges within the embodiments, even from Examples) of the present invention may be combined with each other to give (preferred) embodiments, unless explicitly specified otherwise or unless such a combination would result in a contradiction.

The LWP preferably comprises primarily hydrocarbons, typically more than 50 wt.-% based on the total weight of the LWP. Typically the LWP comprises two or more hydrocarbon species selected from paraffins, olefins, naphthenes and aromatics. The composition of the LWP may vary depending e.g. on the composition of the waste plastics, liquefaction process type and condition. Further, the assortment of various species of waste plastics and impurities associated with collected waste may result in a presence of impurities including silicon, sulphur, nitrogen, halogens and oxygen related substances in various quantities in the LWP.

The LWP (LWP-based oil) of the present invention is derived from (crude) LWP and may, for example, be crude LWP (i.e. the liquid fraction directly emerging from the liquefaction process), or a fraction of crude LWP.

The LWP-based oil may specifically refer to an oil or an oil-like product obtainable from liquefaction using non-oxidative thermal or thermocatalytic depolymerisation of (solid) waste plastics (followed by optional subsequent fractionation). In other words, the LWP-based oil may also be referred to as *"depolymerized polymer waste"* or *"liquefied polymer waste"*.

The method of liquefaction is not particularly limited as long as it is a depolymerisation process and one may mention thermal depolymerisation processes, such as pyrolysis (e.g. fast pyrolysis) of waste plastics, or hydrothermal liquefaction of waste plastics.

Further, in the present invention, the term "pH" refers to the pH value of an aqueous medium measured at (or converted to a value corresponding to

measurement at) 20°C. The pH can be measured in accordance with Finnish standard SFS 3021.

The present invention relates to a method for treating liquefied waste plastics (LWP), said method comprises the steps of (i) providing a volume of the liquefied waste plastics-based oil and (ii) subjecting the same to heat treatment (together) with a volume of an alkaline aqueous medium to provide a heat-treated mixture volume, (iii) phase separation to provide at least a first aqueous phase volume and a first oil phase volume, (iv) isolating (at least) the first aqueous phase volume and (v) adjusting (decreasing) the pH thereof to 9.0 or below by adding an acidic medium (e.g. by mixing the first aqueous phase volume and the acidic medium), followed by (vi) phase separating the resulting pH adjusted volume into at least a second oil phase volume and a second aqueous phase volume. In phase separation, the aqueous phase is usually a heavy phase while the oil phase is usually a light phase.

Using the method of the present invention, the total yield of purified LWP can be increased and the TOC content of the waste water (2^{nd} aqueous phase volume) can be reduced, thus facilitating further workup.

The alkaline aqueous medium preferably has a pH of 9.5 or higher, such as 10.0 or higher, 10.5 or higher or 11.0 or higher. More preferably, the alkaline aqueous medium has a pH 12.0 or higher, 12.5 or higher, or 13.0 or higher. For example, the pH may be in the range of from 9.5 to 14.0, 10.0 to 14.0, 11.0 to 14.0, 12.0 to 14.0, 12.5 to 14.0, 13.0 to 14.0, or 13.0 to 13.9. Alkaline aqueous media, in particular strongly alkaline aqueous media, have been found to have very good contaminants (impurities) removal efficiency, in particular with respect to problematic contaminants, such as silicon (e.g. organosilicon compounds). Moreover, when employing strongly alkaline aqueous media (e.g. having a pH of 12.0 or higher, 12.5 or higher or 13.0 or higher), good impurities removal can be achieved while at the same time

keeping the water-to-oil ratio small so that only little contaminated water will be generated.

The alkaline aqueous medium (in the following sometimes simply referred to as aqueous medium) may be an aqueous solution of an alkaline substance. This means that the alkaline substance is dissolved in the aqueous medium, i.e. the aqueous medium contains the alkaline substance in dissolved form. The aqueous medium may particularly be an aqueous solution of a metal hydroxide (the alkaline substance may be a metal hydroxide). The metal hydroxide is preferably selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides. In particular, the aqueous medium (B) may be an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of KOH, NaOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$, RbOH, $Sr(OH)_2$ and $Ba(OH)_2$. The metal hydroxide is preferably NaOH.

Preferably, the aqueous medium contains the alkaline substance (such as metal hydroxide) in an amount in the range of from 0.5 wt.-% to 15.0 wt.-%, such as from 0.5 wt.-% to 10.0 wt.-%, 1.0 wt.-% to 6.0 wt.-%, or 1.5 wt.-% to 6.0 wt.-%. The aqueous medium (B) may comprise 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.

Preferably, the total (summed) amount of alkaline substance and water in the alkaline aqueous medium is 90 wt.-% or more (90-100 wt.-%), more preferably 95 wt.-% or more, or 99 wt.-% or more (relative to the alkaline aqueous medium as a whole).

While such ranges have been shown to be useful, it is also important that the concentration of the alkaline substance in the heat treatment be within a certain range. That is, in case heating is achieved at least partially by injection of steam, as described below, this inevitably results in addition of water and thus dilutes the alkaline substance in the aqueous medium to a certain extent.

Thus, the method preferably takes into account the water added in the form of steam. This can be accomplished by any suitable means, e.g. calculating the concentration of the alkaline substance in consideration of added steam volume and added volume of aqueous medium. Addition amounts (of e.g. steam for heating) can be calculated or taken from tabulated values or both.

In the present invention, it is preferable that the aqueous component of the mixture being subjected to heat treatment has a pH of 9.5 or higher, such as 10.0 or higher, 11.0 or higher, 12.0 or higher, or 13.0 or higher, or in the range of from 9.5 to 14.0, 10.0 to 14.0, 11.0 to 13.9, 12.0 to 13.9, or 13.0 to 13.9.

The water-oil-ratio (water to oil ratio = amount of *"water"* / amount of *"oil"*) between the volume of the alkaline aqueous medium and the liquefied waste plastics in the heat-treated mixture volume is in the range of from 0.1 to 1.4 by weight, preferably in the range of 0.2 to 1.0, such as 0.2 to 0.7. In this context, the *"water"* refers to the total amount of alkaline aqueous medium (including water from admixed aqueous medium and from optionally injected steam); and the *"oil"* refers to the volume of LWP. The water-oil-ratio may be calculated from the feed (admixing / injection) amounts.

The heat treatment in step (ii) is preferably carried out at a temperature of 150°C or higher, more preferably 180°C or higher, such as 200°C or higher, 220°C or higher, or 240°C or higher. The heat treatment may be 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. Accordingly, the heat treatment may be carried out at a temperature in the range of 150°C to 450°C, preferably 180°C to 450°C, 200°C to 400°C, 210°C to 350°C, 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C. Such elevated temperatures (in particular 180°C or higher, even more 200°C or higher) have been found to result in *"reactive extraction"* together with using an alkaline aqueous medium rather than in mere water washing and/or neutralisation of acidic LWP-based oils. Since the heat treatment is typically performed at a temperature that is a

temperature high enough to observe vapour formation, the heat treatment is preferably performed under pressurized conditions and the pressure can vary depending on the operating conditions. The pressure condition is preferably such that the admixture of LWP and aqueous medium is maintained in a liquid state during heat treatment.

The heat for carrying out the heat treatment in step (ii) may be provided to the volume of the LWP-based oil, to the volume of alkaline aqueous medium (B) and/or to a mixture of the volume of the LWP-based oil and the volume of alkaline aqueous medium. The heat may be provided in a reactor and/or in a heating section as an independent unit (preceding a reactor). The heat is provided by indirect heating and/or by direct heating. Direct heating may particularly be achieved by blowing steam (hot water vapour) into the volume of the LWP-based oil, into the volume of alkaline aqueous medium and/or into a mixture of the volume of the LWP-based oil and the volume of alkaline aqueous medium. Direct heating by use of steam provides a particular benefit that fouling due to (local) excessive heat can be significantly reduced.

Favourably, the total amount of liquefied waste plastics and alkaline aqueous medium in the material subjected to heat treatment in step (ii) (and thus in the heat-treated mixture volume) is 85% to 100% by weight, preferably 90% to 100% by weight, 95% to 100% by weight, 97% to 100% by weight, or 99% to 100% by weight. In other words, it is preferable that the material subjected to heat treatment in step (ii) essentially consists of liquefied waste plastics and alkaline aqueous medium (the latter being assumed to include steam used for heating, as the case may be, even if the steam is added only to the LWP). Put in even other words, no significant amounts (15 wt.-% or less, preferably 10 wt.-% or less, 5 wt.-% or less, 3 wt.-% or less or 1 wt.-% or less) of co-feeds or additives are desired.

The method may further comprise holding (maintaining) the heat-treated mixture volume, preferably in a reactor (for treatment). The reactor is preferably a tubular reaction. The reactor may be a packed reactor or a non-

packed reactor, such as a packed tubular reactor or a non-packed tubular reactor. The heating-up for the heat treatment in step (ii) may be performed in a reactor and/or in a dedicated (separate) heating section(s). The heating-up step may be performed in both a heating section and (subsequently or further) in a reactor. Providing a dedicated heating section may facilitate temperature control and handling (as well as integration into existing process lines) while heating within a reactor may require less equipment.

The residence time of the heat-treated mixture volume at elevated temperature (such as the residence time within the reactor) is preferably at least 10 minutes, more preferably in the range of 10 minutes to 600 minutes, such as in the range of 10 minutes to 300 minutes, 15 minutes to 180 minutes, 15 minutes to 120 minutes, or 20 minutes to 60 minutes. The residence time may be defined as the time for which the heat-treated mixture volume is maintained in the reactor at elevated temperatures.

The heat treatment step (ii) may comprise a heating step in which the temperature of an admixture volume of LWP-based oil and alkaline aqueous medium is increased from an initial temperature T1 to a temperature T2 by injecting (blowing in) steam, thus forming a heated admixture volume which in turn results in the heat-treated mixture volume (C). The temperature T2 is preferably 180°C or more, such as 200°C or more, 220°C or more, or 240°C or more. The temperature T2 is preferably 450°C or less, preferably 400°C or less, 350°C or less, 320°C or less, or 300°C or less. The temperature T2 is suitably in the range of 180°C to 350°C, such as 200°C to 350°C, 210°C to 350°C, 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C. It has been found that a (reaction) temperature within the above limits allows efficient pretreatment of the liquefied waste plastics.

The method may further comprise a preheating step before the heat treatment step (ii). In the preheating step, the admixture volume is preheated to the temperature T1. Preheating may be accomplished in a dedicated (separate) preheating section(s), in a heating section(s) or in a reactor for the heat treatment, as long as it is accomplished before the

heating step. Usually, the preheating will be carried out after mixing the volume of LWP-based oil (A) and the volume of an alkaline aqueous medium (B), but it may be partly or fully carried out before such (i.e. preheating the volume of alkaline aqueous medium alone and/or the volume of LWP-based oil alone).

The difference (T2-T1) between temperature T2 and temperature T1 may, for example, be 5°C or more, preferably 10°C or more, such as in the range of from 5°C to 300°C, 10°C to 240°C or 15°C to 200°C.

The method of the present invention may be carried out batchwise (as a batch process) or continuously (a continuous process, also referred to as continuous flow process). A combination of both is possible, e.g. continuous heat treatment, batchwise or semi-batchwise phase separation, and continuous pH adjustment and subsequent (2^{nd}) phase separation.

As will be apparent to the skilled person, a term like *"before"* or *"preceding"* (or similar) can be translated to *"earlier in time"* in a batch process and *"upstream"* in a continuous process, *"afterwards"* (or similar) can be translated to *"later in time"* in a batch process and *"downstream"* in a continuous process, a *"volume" (*or amount, such as relative amount) may be translated to (relative) *"batch size"* (or *"feed amount"*) in a batch process and to (relative) *"flow rate"* (or *"flow rate ratio"*) in a continuous process. The same applies similarly to all expressions used herein.

The method of the present invention comprises a separation step of separating the heat-treated mixture volume (C) into an oil phase volume (first oil phase volume) and an aqueous phase volume (first aqueous phase volume). The oil phase volume predominantly contains *"oil"* (i.e. purified LWP), such as predominantly hydrocarbons. The aqueous phase volume predominantly contains water, and also contains oil material (dissolved and/or emulsified and/or dispersed organic compounds) as well as alkaline substance and/or its reaction products. The term *"predominantly"* in this

respect shall mean *"at least 50 wt.-%"*, such as at least 60 wt.-%, or at least 70 wt.-%.The separation is preferably carried out after cooling down the heat-treated mixture volume to a temperature and pressure which is suitable for separation. Specifically, the phase separation in the separation step of separating the heat-treated mixture volume is preferably carried out at a temperature at which the LWP-based oil (A) in the heat-treated mixture volume (C) is in liquid form, more preferably at a temperature in the range of from 15°C to 200°C, preferably 40°C and 200 °C, such as 50°C to 175°C or 60°C and 150°C. The phase separation may be carried out at a pressure in the range of from 1 bar absolute to 15 bar absolute, such as 2 bar absolute to 15 bar absolute. The separation pressure is not particularly critical. Most suitably, the pressure is adjusted such that no or no substantive gas/vapour formation occurs at the separation temperature. The separation temperature is preferably in the above-identified range. The temperature is most suitably selected depending on the LWP-based oil to be purified, in particular high enough to keep the LWP-based oil liquid (i.e. avoid solidification or precipitation). In addition, higher temperature may accelerate phase separation as it will decrease the viscosities of the liquids to be separated. The separation step preferably comprises liquid-liquid separation.

The separation in step (iii) is preferably carried out after giving the heat-treated mixture volume sufficient time to react (see residence time above for useful time durations), e.g. by maintaining the heat-treated mixture volume at or close to the heat treatment temperature.

The method may further comprise a step of cooling the heat-treated mixture volume. Cooling is particularly favourable to facilitate phase separation. Cooling is carried out after the reaction is finished (i.e. after the residence time). For ease of reference, the heat-treated mixture volume is called *"heat-treated mixture volume"* even after cooling. Cooling (drop of temperature) may also occur in a transfer line or in a storage container. Note that the phase separation is carried out at a temperature which is equal to or lower than the temperature during heat treatment. The method preferably further comprises

phase-separating the heat-treated mixture volume into a first oil volume and a first aqueous volume. The separation step may comprise a gravity-based separation (non-forced separation), such as decantation, or a forced separation, such as separation by means of centrifugation. In other words, it is possible to let the heat-treated mixture volume settle (by natural gravity) to achieve separation or to force the separation e.g. by centrifugation.

In the course of the phase separation process, the first aqueous phase is isolated. That is, not only the phase is separated but the contact between the oil phase and the aqueous phase is actually no longer present, e.g. both the oil phase and the aqueous phase are individually extracted from the phase separator.

After having been isolated, the pH of the first aqueous volume is adjusted to pH 9.0 or below in step (iii) by adding an acidic medium. The pH is preferably adjusted to 8.5 or below, such as 8.0 or below, 7.5 or below or 7.0 or below. In other words, the pH of the resulting pH adjusted volume is preferably within the stated range after the adjustment. In order to avoid excessive use of acidic medium, the pH of the first aqueous volume is suitably adjusted to pH 1.5 or higher, preferably 2.0 or higher, more preferably 3.0 or higher, 4.0 or higher, 5.0 or higher, 6.0 or higher, or 7.0 or higher. The pH of the first aqueous volume may be adjusted to a pH in the range of from 1.5 to 9.0, preferably 2.0 to 9.0, 3.0 to 9.0, 4.0 to 8.7, 5.0 to 8.5, 6.0 to 8.3, or 7.0 to 8.0.

The inventors surprisingly found that adjusting the first aqueous phase volume to pH 9.0 or below significantly facilitates (or even enables) separation of a significant further amount of oil phase (second oil phase volume). Although the reasons for this effect are not fully understood and it is not desired to be bound to theory, it is assumed that some components of the (crude) LWP-based oil react with the alkaline aqueous medium to result in water-soluble or water-dispersible compounds, some of which might even act as surfactants to emulsify hydrocarbon compounds (considering that LWP

mostly comprises apolar hydrocarbon compounds which would actually be expected to be water-insoluble, regardless of the pH). It is further assumed that such dissolved/dispersed compounds are converted to a water-insoluble form and/or the dispersion state of dispersed compounds is destabilized by reducing the pH to 9.0 or below, such as close to neutral or even acidic. Thus, these compounds can be separated after adjusting the pH. The inventors surprisingly found that a significant amount of oil phase (in the range of several percent of the original LWP-based oil volume) can thus be recovered which would otherwise be lost.

The acidic medium preferably comprises at least one organic acid and/or at least one inorganic acid. Suitable acids are at least one (preferably exactly one) selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid (H_3NSO_3) and a carboxylic acids.

The acidic medium may be a solution of an acid. The acidic medium may particularly be an aqueous solution of an acid. The acid is preferably at least one (more suitably exactly one) selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid (H_3NSO_3), or a carboxylic acid, preferably at least sulfuric acid or hydrochloric acid. The acid may particularly preferably be at least sulfuric acid.

The solution of an acid preferably has a concentration (of the acid) in the range of from 1 to 98 % by mass, preferably 1 to 96 % by mass, more preferably 50 to 70 % by mass.

According to a preferred embodiment, the method further comprises a step of subjecting the isolated first aqueous phase volume of step (iv) to pre-separation to provide an oil-reduced aqueous phase volume and an oil-enriched aqueous phase volume. Usually, no heating will occur between the (first) phase separation and the pre-separation, while cooling may occur e.g.

in a heat exchanger or in a transfer line. At least the oil-enriched aqueous phase volume (and preferably only the oil-enriched aqueous phase volume) is forwarded to acidification step (v) as the first aqueous phase volume for pH adjustment. That is, the inventors surprisingly found that part the aqueous phase after separation (1st aqueous phase volume) can be further separated into an aqueous phase containing substantially no oil (or having significantly reduced oil content) and into an aqueous phase having significantly increased oil content (oil-enriched aqueous phase). Although it is not intended to be bound to theory, it is assumed that the oil-enriched aqueous phase mainly contains water as well as dispersed or emulsified oil. That is, this phase separation does not form a distinct oil phase and a distinct aqueous phase but rather forms at least an intermediate phase (oil-enriched aqueous phase) containing both water and oil in substantial amounts.

This oil-enriched aqueous phase may then be subjected to pH adjustment (in which case it is referred to as the 1st aqueous phase employed in step (v)). This provides the benefit that significant oil recovery can be achieved while only very little acidic medium is required for pH adjustment. Accordingly, this embodiment provides a further improvement regarding economic and ecological aspects. Furthermore, it is assumed that this procedure furthermore increases the quality of the second oil phase because the amount of impurities that is potentially transferred back to the oil phase upon acidification is minimized.

Although it is not intended to be bound by theory, the inventors observed that the progress of the phase separation (and thus the reduction of the oil content in the oil-reduced aqueous phase volume) can be visually inspected because the oil-reduced aqueous phase gets clearer (less opaque) as the oil content thereof decreases. This clear (but usually dark coloured) liquid is also referred to as translucent liquid. At the same time, an opaque (cloudy/milky, as the case may be even solid-like) oil-enriched phase is formed.

The pre-separation may comprise at least one of cooling and centrifugation. The pre-separation may comprise both of these and/or may further comprise other treatments. Preferably, the pre-separation comprises at least phase separation after the cooling or centrifugation.

After pH adjustment in step (v), a further phase separation is carried out in step (vi) using the pH adjusted (aqueous) volume. The further (second) phase separation results in a second oil phase volume and a second aqueous phase volume. As already said for the first oil/water phase volume, the oil phase volume predominantly contains *"oil"* (i.e. purified LWP), such as predominantly hydrocarbons. The aqueous phase volume predominantly contains water, and also contains oil material (dissolved and/or emulsified and/or dispersed organic compounds) as well as alkaline substance and/or its reaction products. Again, the term *"predominantly"* in this respect shall mean *"at least 50 wt.-%"*, such as at least 60 wt.-%, at least 70 wt.-% or at least 80 wt.-%.

The residence time of the pH adjusted volume in the phase separation (in the phase separator) of step (vi) is preferably in the range of from 1 minute to 600 minutes, such as 1 minute to 240 minutes, or 2 minutes to 180 minutes. That is, depending on e.g. pH and temperature the phase separation may spontaneously (or forcedly) proceed rather fast or it may take a while. The phase separation in step (vi) preferably comprises liquid-liquid separation. The phase separation in step (vi) may comprise a gravity-based separation, such as decantation, or a separation by means of centrifugation.

Suitably, the phase separation in step (vi) is performed at the same or at a lower temperature than the phase separation in step (iii). The phase separation in step (vi) is preferably carried out at a temperature in the range of from 15°C and 200°C, such as 30°C and 200°C, 40°C to 175°C, 50°C and 150°C or 60°C and 140°C. The phase separation may be carried out at a pressure in the range of from 1 bar (absolute) to 15 bar (absolute), preferably 2 bar (absolute) to 15 bar (absolute).

After the phase separation in step (iv), the second oil phase volume may further be subjected to washing, e.g. to water washing.

The method may further comprise combining at least part of (such as all of) the second oil phase volume with at least part of (such as all of) the first oil phase volume to provide a combined oil phase volume. In other words, it is possible to combine the obtained oil phase volumes. The method may further comprise subjecting at least part of the combined oil phase volume to a further treatment and/or conversion process. A further treatment or conversion process may comprise any known process (or series of processes), including known petrochemical processes such as fractionation, cracking (e.g. steam cracking or hydrocracking), finishing, hydrotreatment, and others.

The method may alternatively or in addition comprise subjecting at least part of the second oil phase volume and/or at least part of the first oil phase volume) to a further treatment and/or conversion process. In other words, the oil phases may be further used (or treated) separately or combined or both. Unless specifically stated to the contrary, the treatment(s) for (and uses of) the first and/or second oil phase volume described herein similarly apply to the first oil phase volume alone, the second oil phase volume alone and the combined oil phase volume. Moreover, such treatment(s) may be performed on the first and second oil phase volume separately and only thereafter these (treated) volumes are optionally combined.

In an embodiment, the second oil phase volume and the first oil phase volume are subjected to washing, e.g. water washing, separately and are optionally combined thereafter.

The second aqueous phase volume may further be subjected to evaporation to obtain an impurities concentrate residual and a wastewater stream. Depending on local regulations and/or standards, the wastewater stream may be ready for disposal, such as being released to nature. In most cases,

however, the wastewater stream will be treated further (e.g. by conventional wastewater treatment) before disposal in order to minimize environmental impact. Wastewater treatment may, for example, include a biological refinery (microbial treatment), such as bacterial digestion or breakdown of organic material (organic compounds).

The first and/or second (preferably the second) aqueous volume may at least partially be recycled, after optional purification, back to the process (to form part of the alkaline aqueous medium), e.g. by recycling it into the heat treatment of step (ii). In this case, the (amount of the) recycled aqueous volume is counted as being part of the (volume of the) alkaline aqueous medium, even if admixed with the LWP separately.

The method may further comprise subjecting at least part of (such as all of) the second aqueous phase volume to evaporation. The evaporation provides at least one condensate (evaporate) and further provides at least an evaporation residue. At least one of the condensate(s) is an aqueous phase volume (purified water). Most of the impurities concentrate in the evaporation residue.

The evaporation may be suited to further separate oil-based components and/or other impurities from the second aqueous phase volume. In any case, the evaporation is suited to provide further purified water (more suitable for waste water treatment or for direct use as *"fresh"* water, depending on the use case) while the evaporation residue usually contains at least inorganic compounds (such as residual alkaline substance or acidic substance or reaction products thereof) and high-boiling reaction products of the LWP.

The inventors surprisingly found that evaporation of a second aqueous phase volume obtained directly after phase separation in step (vi) (and thus having a pH of 9.0 or below, often around neutral pH or even acidic) may result in significant presence of organic compounds in the purified water (condensate). Although the reasons for this phenomenon is not fully understood, and it is

not desired to be bound to theory, it is assumed that e.g. carboxylic acids and/or phenols which are present in their protonated form in the second aqueous phase volume are evaporated under the conditions of the evaporation.

The inventors then found that adjusting the pH of the second aqueous phase volume back to basic, more specifically to a pH of 9.5 or higher, preferably 10.0 or higher, or 10.5 or higher, most suitably to pH 11.0 or higher, such as 11.5 or higher, or 12.0 or higher, results in a significant decrease of TOC (total organic carbon) in the purified water (evaporate). Such an adjustment of the pH of the 2nd aqueous phase volume is thus preferred, in particular in case the 2nd aqueous phase is subjected to evaporation thereafter.

In this step (pH adjustment of 2nd aqueous phase volume), the pH may be adjusted by adding an alkaline medium. The alkaline medium may be an aqueous solution of a metal hydroxide. The alkaline medium may be an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides. The alkaline medium may be an aqueous solution of a metal hydroxide. The metal hydroxide may be selected from the group consisting of KOH, NaOH, LiOH, $Ca(OH)_2$, $Mg(OH)_2$, RbOH, $Sr(OH)_2$ and $Ba(OH)_2$. Specifically, the alkaline medium may be an aqueous solution of NaOH.

The alkaline medium (employed in the pH adjustment of 2nd aqueous phase volume) preferably contains an alkaline substance in an amount in the range of from 1 wt.-% to 100 wt.-%, such as from 1 wt.-% to 99 wt.-%, 2 wt.-% to 90 wt.-%, 5 wt.-% to 70 wt.-%, 10 wt.-% to 65 wt.-%, 15 wt.-% to 60 wt.-%, or 20 wt.-% to 55 wt.-%. Suitably, the concentration of the alkaline substance in the alkaline medium of this step is higher than the concentration of an alkaline substance in the alkaline aqueous medium employed in step (ii) so as to ensure easy pH adjustment and further considering that accurate adjustment in this step is not critical. For example, the alkaline medium comprises at least 1 wt.-% water, preferably at least 10 wt.-% water, at least

15 wt.-% water, at least 20 wt.-% water or at least 25 wt.-% water. Preferably, the total (summed) amount of alkaline substance and water in the alkaline medium employed for adjusting the pH of the second aqueous phase volume is 90 wt.-% or more (90-100 wt.-%), more preferably 95 wt.-% or more, or 99 wt.-% or more (relative to the alkaline aqueous medium as a whole). Most suitably, stirring is performed during and/or after adjusting the pH.

The method preferably comprises evaporating at least part of the second aqueous phase volume after adjusting the pH to provide at least one condensate and at least one evaporation residue. The evaporation may be carried out in one, two or more stages. Preferably, at least part of at least one condensate is subjected to further work-up. The further work-up may comprise at least ammonia removal, preferably a stripping treatment, in particular steam stripping treatment. Stripping is particularly suitable to remove ammonia or amines.

At least part of at least one condensate (purified water), after optional further work-up, may be forwarded to waste-water treatment.

The liquefied waste plastics-based oil, which is a feed to be (pre)treated by the method of the present invention, may have a 5% boiling point of 25°C or higher, preferably 30°C or higher, or 35°C or higher, such as in the range of from 25°C to 120°C, in the range of from 25°C to 100°C, in the range of 30°C to 90°C, or in the range of from 35°C to 80°C. The liquefied waste plastics-based oil may have a 95% boiling point of 700°C or less, preferably 650°C or less, 600°C or less, or 550°C or less, such as in the range of from 180°C to 700°C, 250°C to 700°C, 300°C to 650°C, 350°C to 600°C, 380°C to 500°C, or 400°C to 500°C. The LWP may particularly be a crude LWP or a fraction thereof.

The LWP may have a density, as measured at 15°C, in the range of from 0.780 to 0.850 kg/m^3. The LWP may have an olefins content of 5 wt.-% or

more, such as 10 wt.-% or more, 15 wt.-% or more, 20 wt.-% or more, 30 wt.-% or more, 40 wt.-% or more, or 50 wt.-% or more. The LWP may have an olefins content of 85 wt.-% or less, such as 80 wt.-% or less, 70 wt.-% or less, or 65 wt.-% or less. Such an olefins content is usual for thermally produced LWP (e.g. pyrolysis oil or HTL oil) but may vary with depolymerisation temperature. The chlorine content of the LWP may be in the range of from 1 wt.-ppm to 4000 wt.-ppm, such as 100 wt.-ppm to 4000 wt.-ppm, or 300 wt.-ppm to 4000 wt.-ppm.

In the following, a preferred embodiment of the present invention will be briefly described with reference to the FIGs.

FIG. 1 shows a flow chart of the base process of the present invention. In this embodiment, a volume of the liquefied waste plastics-based oil (A) and a volume of an alkaline aqueous medium (B) are subjected to heat treatment (1). The heat treatment may be carried out in a reactor. After completion, the resulting heat-treated mixture volume (C) is forwarded to phase-separation (2), yielding a first aqueous phase volume (D) and a first oil phase volume (E). The first oil phase volume (E) may be used as such (as a purified LWP) or may be combined with the later-obtained second oil-phase volume (H), as shown in FIG. 1. Separation as well as isolation of the first aqueous phase volume (D) may be achieved by means of a separator. The isolated first aqueous phase volume (D) is subjected to pH adjustment (3), wherein the pH is adjusted to pH 9.0 or below by adding an acidic medium (F) into said first aqueous phase volume (D). The resulting pH adjusted volume (G) is forwarded to a further phase-separation (4) to provide a second aqueous phase volume (I) and a second oil phase volume (H). As shown in FIG. 1, the second oil phase volume (H) may be combined with the first oil phase volume (E) to provide a combined oil phase volume (K).

FIG. 2 shows a further workup procedure of a preferred embodiment of the present invention. In this embodiment, the second aqueous phase volume (I) emerging from the phase separation (4) is subjected to pH adjustment (5)

by addition of an alkaline medium (L). The resulting second aqueous phase after pH adjustment (M) is then subjected to evaporation, thus providing a condensate (purified water, N) and an evaporation residue (P). The residue (P) may be disposed or burnt (not shown).

EXAMPLES

In the following, the invention is further illustrated by means of Examples. While the Examples represent preferred embodiment of the invention and numerical values of specific process steps may be used and combined with values or ranges disclosed in the description or claims to generate more limited (e.g. preferred) ranges, it is to be understood that the invention is defined by the appended claims and not limited to the illustrated Examples.

Example 1

A sample of LWP was heat treated with aqueous NaOH in a continuous flow tubular reactor system (test reactor). The inner diameter of the reactor was 23 mm and the effective volume was approximately 325 ml. The reactor was a packed reactor including a woven steel wire matrix (200 micrometre wire) for enhancing the dispersion/mixing of the LWP-alkali water mixture. The conditions of the test run are provided in the following table. The absolute amount of NaOH (flow and concentration) was set such that it results in a pH value of the first aqueous phase of at least 12 after the heat treatment process and the phase separation.

Table 1: HT processing conditions

Reaction temperature	280°C
LWP flow	156 g/h
Aqueous NaOH flow	53 g/h
NaOH concentration	2 wt.-%
Reactor pressure	90 bar (gauge)

After exiting the reactor, the effluent flow (heat-treated mixture volume) was cooled down and depressurized down to 2.5 bar (gauge). The effluent flow was then directed to a vertical decanter (diameter 42 mm, height 500 mm) for phase separation. The decanter had two outlets: one at the bottom of the decanter for removing the used NaOH solution (heavy phase; first aqueous phase volume) and another one (height 350 mm from bottom) for removing the product LWP (light phase; first oil-phase volume). The levels of both liquid phases could be set independently, and were controlled via a combination of control valves and level/interface measurements in the decanter. The pH in the continuous decanter heavy phase (aqueous phase) flow was about pH 13. The residence time was on average 1 hour for phase separation in the decanter. In this Example, the decanter was operated in continuous run for 12 h at a temperature of 100°C and a pressure of 2 bar (gauge). In order to maintain the desired level for the heavy phase, the average outflow during the 12 h experiment was approximately 60 g/h (heavy phase). The light phase water content was determined to be 0.87 wt.-% on average. This resulted in calculated LWP yield loss of approximately 5.46 wt.-% into the heavy phase (first aqueous phase volume).

After the end of the separation test run, a 200 g sample of the first aqueous phase volume was taken from the unified aqueous phase collected during the test run (about 12 h), placed in a 500 ml glass vessel, agitated using magnetic stirring and heated to a temperature of 80°C. The pH of this sample was then adjusted in 5 minutes to approximately 8.9 by dropwise addition of 50 wt.-% sulfuric acid. After this, 10 wt.-% sulfuric acid was further added during 5 minutes until a colour/appearance change (from opaque yellowish to translucent/clear brown) was observed at approximately pH 7.4. The neutralised mixture was then allowed to settle and phase separate spontaneously (gravity settling) for 60 min to ensure full separation. The amount of separated oil from the 200 g sample was approximately 42.4 g.

After allowing the acidified mixture to settle for 60 minutes, the light phase (2^{nd} oil phase volume) water content was analysed as 30.1 wt.-%. The overall

yield of treated LWP from the process increased from its original value of 94.5 wt.-% (after the first separation and before acidification) to approximately 99.7 wt.-% (after acidification and second separation).

Even though this value may not be 100% accurate due to the small sample size of this test run, it can be clearly seen that the method of the present invention provides a significant yield increase and consequently provides an aqueous phase having significantly reduced TOC (total organic carbon) content.

Example 2

A test run was performed in a pilot plant to evaluate a preferred embodiment of the invention. 149 kg LWP and 45 kg of a 2 wt.-% solution of aqueous NaOH were transferred into a 500 litres mixed batch reactor vessel. The filling rate of the reactor was approximately 46 volume-%. The mixture was heated to 240°C and then maintained at that temperature for 30 minutes. The reactor pressure was approximately 41 bar(g) at 240°C. After heat treatment the reactor mixture was cooled down to approximately 70°C. Mixing was stopped after reaching 70°C and the light (first oil) and heavy (first aqueous) phases were separated by gravity and isolated.

The pH value of the first aqueous phase volume thus produced was adjusted to about 8 using 50 wt.-% sulfuric acid. The mixture was allowed to spontaneously (gravity) phase separate allowing the precipitated oil to be collected or removed from the aqueous solution..

One part of the roughly neutral (pH about 8) first aqueous phase was directly subjected to evaporation according to the procedure described below. For a second part thereof, the pH value was adjusted to about 12 using 50 wt.-% aqueous NaOH before evaporation.

Both evaporation tests were performed in a 10-litre rotary evaporator at a constant pressure of 200 mbar (absolute). The condensates were collected in

three stages and each sample was analysed separately for its total organic carbon (TOC; SFSEN1484), chemical oxygen demand (COD; ISO15705) and phenols content (ISO14402) using the respective standards.

Table 2 below shows the results from the experiment where the pH value of the evaporation feed (2nd aqueous phase volume) was 8. In this evaporation, the yield of the evaporation residue was 5 wt.-% of the original feed.

Table 2: Evaporation test pH 8 feed

	evaporation feed	1st condensate	2nd condensate	3rd condensate
Yield in evaporation (wt.-%)	-	68	15	17
TOC (mg/ml)	17000	2790	1090	944
COD (mg/l)	n.a.	9560	3940	3001
Phenols (mg/l)	n.a.	2175	929	516

* n.a.= not available

Table 3 below shows the results from the experiment where the pH value of the evaporation feed (2nd aqueous phase volume after pH adjustment) was about 13.

Table 3: Evaporation test pH 13 feed

	evaporation feed	1st condensate	2nd condensate	3rd condensate
Yield in evaporation (wt.-%)	-	72	14	14
TOC (mg/ml)	17200	552	141	177
COD (mg/l)	n.a.	1630	543	503
Phenols (mg/l)	n.a.	46	54	73

When comparing the results, one can clearly observe that the TOC, COD and phenol concentrations of the condensates obtained with the pH adjusted

second aqueous phase volume were clearly lower than in the case of employing the non-pH adjusted second aqueous phase volume. In other words, when evaporating the second aqueous phase volume from LWP pretreatment that was neutralized for improved oil recovery, better quality condensates could be obtained after the pH value of the solution was re-adjusted back to basic conditions prior to evaporation, thus providing a further benefit to the present invention.

CLAIMS

1. A method for treating liquefied waste plastics (LWP), said method comprises the steps of

(i) providing a volume of the liquefied waste plastics-based oil (A),

(ii) subjecting the volume of LWP-based oil (A) to a heat treatment (1) with a volume of an alkaline aqueous medium (B) to provide a heat-treated mixture volume (C),

(iii) phase-separating (2) the heat-treated mixture volume (C) into at least two separated phase volumes (D; E), wherein one separated phase volume is a first aqueous phase volume (D), and the other separated phase volume is a first oil phase volume (E),

(iv) isolating (2) the first aqueous phase volume (D),

(v) adjusting (3) the pH of the first aqueous phase volume (D) to pH 9.0 or below by adding an acidic medium (F) into said first aqueous phase volume (D) to form a pH adjusted volume (G),

(vi) phase-separating (4) the pH adjusted volume (G) into at least two separated phase volumes (H; I), wherein one separated phase volume is a second aqueous phase volume (I), and the other separated phase volume is a second oil phase volume (H).

2. The method according to claim 1, wherein the acidic medium (F) comprises organic acid and/or inorganic acid, such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid (H_3NSO_3) or a carboxylic acid.

3. The method according to claim 1 or 2, wherein the acidic medium (F) is a solution of an acid, preferably an aqueous solution of an acid.

4. The method according to claim 3, wherein the acid is at least one selected from the group consisting of hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), sulfamic acid

(H_3NSO_3), or a carboxylic acid, preferably at least sulfuric acid or hydrochloric acid.

5. The method according to claim 3 or 4, wherein the solution of an acid has a concentration (of the acid) in the range of from 1 to 98 % by mass, preferably 1 to 96 % by mass, more preferably 50 to 70 % by mass.

6. The method according to any of the preceding claims, wherein the phase separation (2) in step (iii) is carried out at a temperature in the range of from 15°C to 200°C, preferably 40°C and 200 °C, 50°C to 175°C, or 60°C and 150°C.

7. The method according to any of the preceding claims, wherein the first oil phase volume (E) and/or the second oil phase volume (H) is further subjected to washing, preferably water washing.

8. The method according to any one of the preceding claims, wherein the pH of the first aqueous volume (D) is adjusted in step (v) to a pH in the range of from 1.5 to 9.0, preferably 2.0 to 9.0, more preferably 3.0 to 9.0, 4.0 to 8.7, 5.0 to 8.5, 6.0 to 8.3, or 7.0 to 8.0.

9. The method according to any one of the preceding claims, wherein the alkaline aqueous medium (B) is an aqueous solution of a metal hydroxide and the metal hydroxide is selected from the group consisting of alkali metal hydroxides and alkaline earth metal hydroxides.

10. The method according to any one of the preceding claims, wherein the water-oil-ratio between the volume of the alkaline aqueous medium (B) and the volume of liquefied waste plastics-based oil (A) in the heat treatment (1) of step (ii) is in the range of from 0.1 to 1.4 by weight, preferably in the range of 0.2 to 1.0, such as 0.2 to 0.7.

11. The method according to any one of the preceding claims, wherein the heat treatment (1) in step (ii) is carried out at a temperature in the range of 150°C to 450°C, preferably 180°C to 450°C, 200°C to 400°C, 210°C to 350°C, 220°C to 330°C, 240°C to 320°C, or 260°C to 300°C.

12. The method according to any one of the preceding claims, further comprising adjusting (5) the pH of the second aqueous phase volume (I) to pH 9.5 or higher, preferably 10.0 or higher, or 10.5 or higher, preferably further comprising evaporating (6) at least part of the second aqueous phase volume (M) after adjusting (5) the pH to provide at least one condensate (N) and at least one evaporation residue (P).

13. The method according to any one of the preceding claims, further comprising combining at least part of the second oil phase volume (H) with at least part of the first oil phase volume (E) to provide a combined oil phase volume (K).