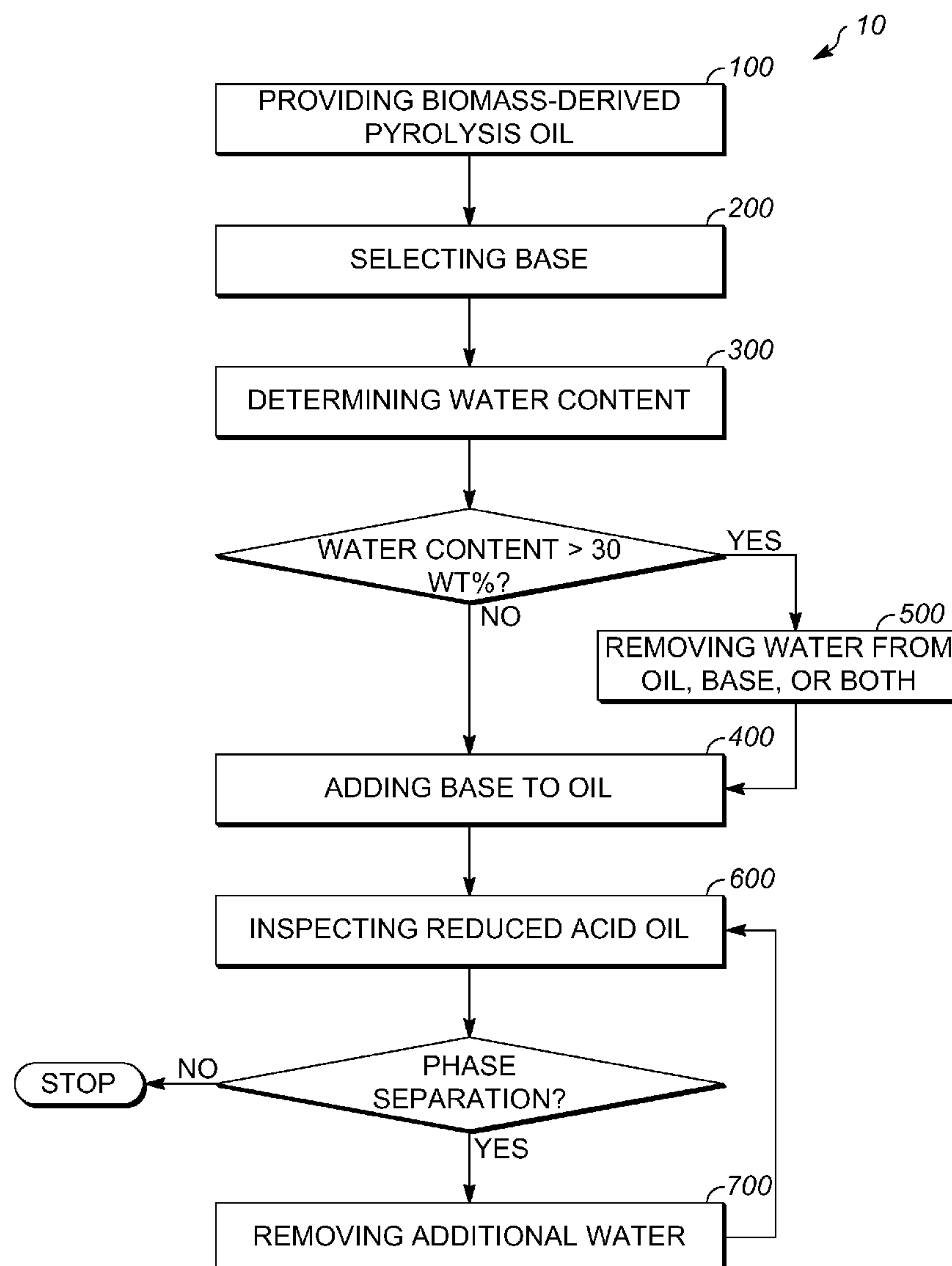


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(19) **United States**(12) **Patent Application Publication**
Koch et al.(10) **Pub. No.: US 2012/0023809 A1**(43) **Pub. Date: Feb. 2, 2012**(54) **METHODS FOR PRODUCING PHASE
STABLE, REDUCED ACID
BIOMASS-DERIVED PYROLYSIS OILS****Publication Classification**(51) **Int. Cl.**
C10L 1/10 (2006.01)(52) **U.S. Cl.** **44/307**(57) **ABSTRACT**

Methods for producing phase stable, reduced acid biomass-derived pyrolysis oils are provided. Biomass-derived pyrolysis oil having a determined water content no greater than about 30% by weight is provided. A base is mixed with the biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil. A base is selected from an inorganic base or a nitrogen-containing base.

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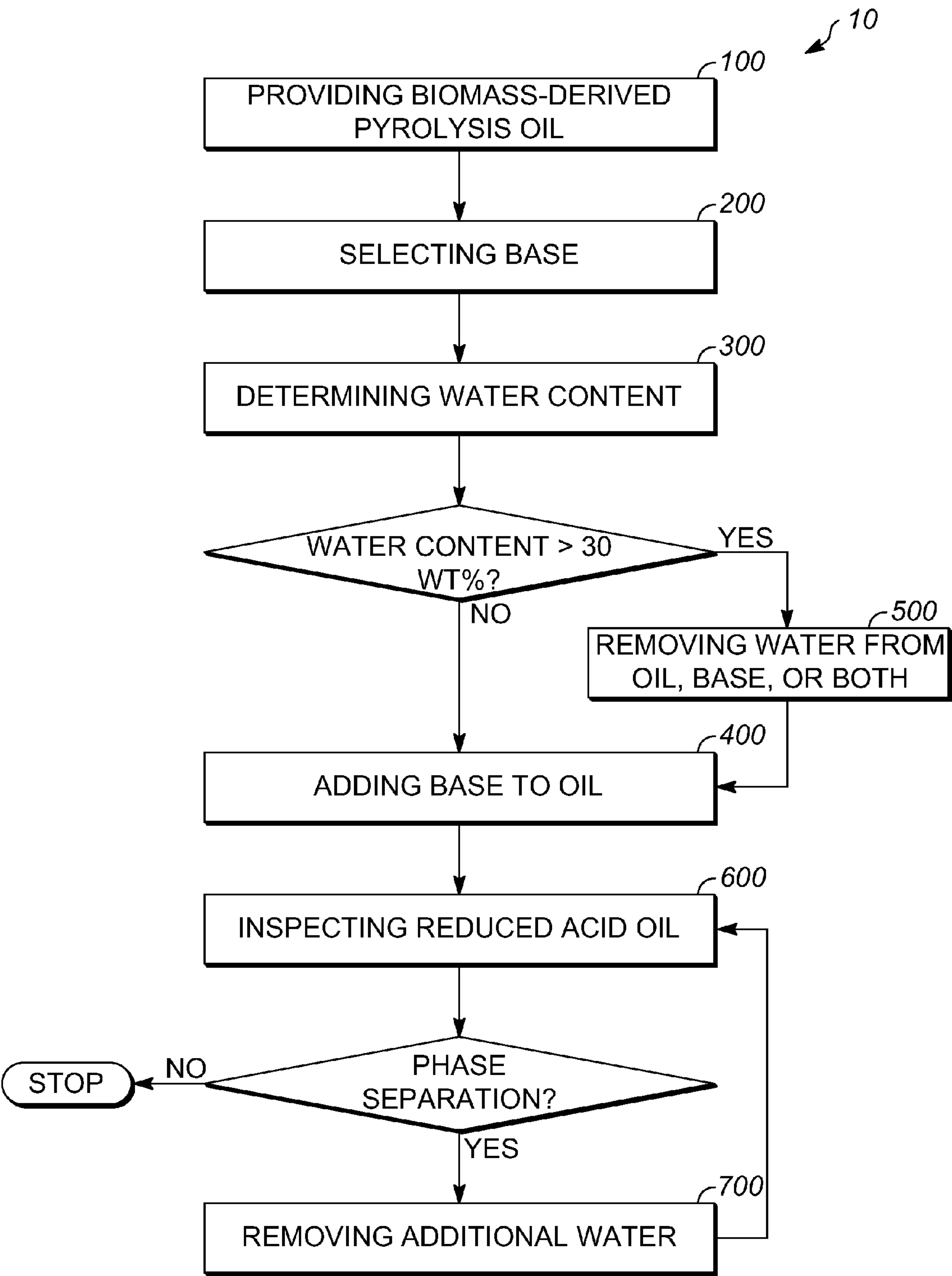


FIG. 1

METHODS FOR PRODUCING PHASE STABLE, REDUCED ACID BIOMASS-DERIVED PYROLYSIS OILS

FIELD OF THE INVENTION

[0001] The present invention generally relates to methods for producing biofuels, and more particularly relates to methods for producing phase stable, reduced acid biomass-derived pyrolysis oils.

DESCRIPTION OF RELATED ART

[0002] Fast pyrolysis is a thermal process during which solid carbonaceous biomass feedstock, i.e., “biomass”, such as wood waste, agricultural waste, etc., is rapidly heated to pyrolysis temperatures of about 300° C. to about 900° C. in the absence of air using a pyrolysis reactor. Under these conditions, solid and gaseous pyrolysis products are formed. A condensable portion (vapors) of the gaseous pyrolysis products is condensed into biomass-derived pyrolysis oil.

[0003] Biomass-derived pyrolysis oil can be burned directly as fuel for certain boiler and furnace applications, and can also serve as a potential feedstock in the production of biofuels in petroleum refineries or in stand-alone process units. Biomass-derived pyrolysis oil has the potential to replace up to 60% of transportation fuels, thereby reducing the dependency on conventional petroleum and reducing its environmental impact. However, biomass-derived pyrolysis oil is a complex, highly oxygenated organic liquid having properties that currently limit its utilization as a fuel/biofuel, particularly for diesel applications. For example, conventional biomass-derived pyrolysis oil has high acidity (with a low pH and high total acid number (TAN)) making it corrosive to storage, pipes, and downstream equipment, with low energy density and susceptibility to increased viscosity over time. Conventional biomass-derived pyrolysis oil typically has a pH of <3 and a TAN >150. The high acidity and low energy density of the biomass-derived pyrolysis oil is attributable in large part to oxygenated hydrocarbons in the oil, particularly carboxylic acids such as formic acid, acetic acid, etc. “Oxygenated hydrocarbons” as used herein are organic compounds containing hydrogen, carbon, and oxygen. The oxygenated hydrocarbons in the oil are derived from oxygenated hydrocarbons in the gaseous pyrolysis products produced during pyrolysis.

[0004] While the direct titration of a base to the biomass-derived pyrolysis oil reduces its acidity (as measured by an increase in pH), phase instability of the biomass-derived pyrolysis oil results. “Phase stability” as used herein means the ability of the oil to resist changes in chemical composition and maintain homogeneity. Phase instability results in phase separation, viscosity increases, and often, solids formation. Such phase instability reduces utilization of the biomass-derived pyrolysis oil as a biofuel.

[0005] Accordingly, it is desirable to provide methods for producing phase stable, reduced acidity biomass derived pyrolysis oils. It is also desirable to produce phase stable, reduced acid biomass-derived pyrolysis oils having increased energy density. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description of the and the appended claims, taken in conjunction with the accompanying drawings and this background of the invention.

SUMMARY OF THE INVENTION

[0006] Methods are provided for producing phase stable, reduced acid biomass-derived pyrolysis oil from biomass-

derived pyrolysis oil. In accordance with one exemplary embodiment, a method for producing phase stable, reduced acid biomass-derived pyrolysis oil comprises providing a biomass-derived pyrolysis oil having a determined water content no greater than about 30% by weight. A base is mixed with the biomass-derived pyrolysis oil.

[0007] Methods are provided for producing phase stable, reduced acid biomass-derived pyrolysis oil from water-containing biomass-derived pyrolysis oil, in accordance with yet another exemplary embodiment of the present invention. The method comprises selecting a base comprising either an inorganic base or a nitrogen-containing base. At least a portion of the water is removed from the water-containing biomass-derived pyrolysis oil, the base, or both. The base is added to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil.

[0008] Methods are provided for producing phase stable, reduced acid biomass-derived pyrolysis oil in accordance with yet another exemplary embodiment of the present invention. The method comprises providing water-containing biomass-derived pyrolysis oil. A base adapted to be added to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil is selected. The water content of the reduced acid biomass-derived pyrolysis oil is determined. If the reduced acid biomass-derived pyrolysis oil is determined to have a water content greater than about 30 wt %, at least a portion of the water is removed from the water-containing biomass-derived pyrolysis oil, the base, or both. The selected base is added to the water-containing biomass-derived pyrolysis oil.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present invention will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

[0010] FIG. 1 is a flow chart of a method for producing phase stable, reduced acid biomass-derived pyrolysis oils, according to exemplary embodiments of the present invention.

DETAILED DESCRIPTION

[0011] The following detailed description of the invention is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description of the invention.

[0012] Various exemplary embodiments of the present invention are directed to a method for producing phase stable, reduced acid biomass-derived pyrolysis oils. It should be appreciated that while the oil produced according to exemplary embodiments of the present invention is generally described herein as a “reduced acid biomass-derived pyrolysis oil”, this term generally includes any oil produced having a lower acidity than the conventional biomass-derived pyrolysis oil from which it is derived. As noted previously, “phase stability” as used herein means the ability of the oil to resist changes in chemical composition and maintain homogeneity. Phase instability results in phase separation, viscosity increases and often, solids formation. In addition, the phase stable, reduced acid biomass-derived pyrolysis oil has higher energy density than conventional biomass-derived pyrolysis oil. “Higher energy density” as used herein means that the phase stable, reduced acid biomass-derived pyrolysis oil has an increased heat of combustion as compared to con-

ventional biomass-derived pyrolysis oil. An increased heat of combustion increases the suitability of the oil as fuel and biofuel.

[0013] Referring to FIG. 1, a method **10** for producing phase stable, reduced acid biomass-derived pyrolysis oil begins by providing conventional biomass-derived pyrolysis oil from a source such as a feed tank or other source operative to provide such oil (step **100**). Biomass-derived pyrolysis oil is available from, for example, Ensyn Technologies Inc., of Ontario, Canada. The composition of biomass-derived pyrolysis oil is somewhat dependent on feedstock and processing variables. The biomass-derived pyrolysis oil may be produced, for example, from fast pyrolysis of wood biomass in a pyrolysis reactor. However, virtually any form of biomass can be considered for pyrolysis to produce biomass-derived pyrolysis oil. In addition to wood, biomass-derived pyrolysis oil may be derived from biomass material such as bark, agricultural wastes/residues, nuts and seeds, algae, grasses, forestry residues, cellulose and lignin, or the like. The biomass-derived pyrolysis oil may also be obtained by different modes of pyrolysis, such as fast pyrolysis, vacuum pyrolysis, catalytic pyrolysis, and slow pyrolysis (also known as carbonization) or the like. Biomass-derived pyrolysis oil typically contains about 20-33% by weight water with a high acidity (TAN >150). The water content in the starting water-containing biomass-derived pyrolysis oil may be measured, for example, by Karl Fischer Reagent Titration Method (ASTM D1364), as known to one skilled in the art. In this regard, biomass-derived pyrolysis oil may alternatively be referred to herein as “water-containing biomass-derived pyrolysis oil.”

[0014] Still referring to FIG. 1, method **10** continues by selecting a base to neutralize the carboxylic acids in the water-containing biomass-derived pyrolysis oil, thereby reducing the acidity of the water-containing biomass-derived pyrolysis oil (step **200**). As used herein, “neutralization” is a chemical reaction whereby the acids in the water-containing biomass-derived pyrolysis oil and the selected base react to form water and a salt. In an aqueous solution, solvated hydrogen ions (hydronium ions, H_3O^+) react with hydroxide ions (OH^-) formed from the base to make two molecules of water. A salt is also formed. In non-aqueous reactions, water is not always formed; however, there is always a donation of protons. Neutralization in accordance with exemplary embodiments raises the pH and lowers the TAN of water-containing biomass-derived pyrolysis oil. In one embodiment, the target pH levels are in the range of about 4.5 to about 4.9. The base may be in an aqueous solution or a solid base. The selected base is adapted to be added to the water-containing biomass-derived pyrolysis oil as hereinafter described.

[0015] The base comprises either an inorganic base or a nitrogen-containing base. The inorganic bases are strong bases. A strong base is a basic chemical compound that is able to deprotonate weak acids in an acid-base reaction. Compounds with a pK_a of more than about 13 are considered strong bases. Very strong bases are even able to deprotonate very weakly acidic C—H groups in the absence of water. Suitable exemplary inorganic bases include metal oxides, metal alkoxides, metal carbonates of the alkali and alkaline earth metals, alkali and alkaline earth exchanged zeolites (e.g., Ca—X zeolite), mixed metal oxides (e.g., hydrotalcite), metal hydroxides, and combinations thereof. Exemplary suitable metal oxides comprise calcium oxide, magnesium oxide, and combinations thereof. Exemplary suitable metal alkoxides comprise sodium ethoxide, potassium tert-butoxide, and

combinations thereof. Exemplary suitable metal carbonates comprise potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and calcium carbonate ($CaCO_3$). Exemplary suitable metal hydroxides comprise lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), rubidium hydroxide (RbOH), caesium hydroxide (CsOH), magnesium hydroxide ($Mg(OH)_2$), calcium hydroxide ($Ca(OH)_2$), strontium hydroxide ($Sr(OH)_2$), barium hydroxide ($Ba(OH)_2$), and combinations thereof. The metal hydroxides generate water when neutralizing carboxylic acids, with the essential reaction being the combination of hydrogen ions with hydroxyl ions to form water. The maximum amount of water produced during neutralization with a metal hydroxide comprises 1 mole eq water to 1 mole eq of neutralized acid. The exact amount of the water produced depends on the selected base.

[0016] The nitrogen-containing base can be a tetraalkylammonium hydroxide, an amine, or combinations thereof. Suitable tetraalkylammonium hydroxides include tetraethylammonium hydroxide, tetramethylammonium hydroxide, tetrapropylammonium hydroxide, and combinations thereof. Amines suitable for use herein include dialkyl amines, trialkyl amines, or combinations thereof. The amine may also comprise pyrrolidine, morpholine, piperidine, N-methylpyrrolidine, and NR^1R^2X wherein R^1 and R^2 are selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, sec. butyl, pentyl, hexyl, cyclohexyl, and benzyl groups; and X is selected from the group consisting of hydrogen, R^1 , and R^2 . Neutralization with non-hydroxyl bases do not generate water.

[0017] In accordance with an exemplary embodiment, the phase stable, reduced acid biomass-derived pyrolysis oil has a water content no greater than about 30 weight percent (wt. %). The terms “about 30 weight percent” and “about 30% by weight” as used herein means ± 3 weight percent of 30 weight percent. In this regard, referring to FIG. 1, prior to adding the selected base to the water-containing biomass-derived pyrolysis oil, the water content of the reduced acid biomass-derived pyrolysis oil after the selected base is added to the water-containing biomass-derived pyrolysis oil, is determined (the “determined water content”) (step **300**). If the water content of the reduced acid biomass-derived pyrolysis oil to be produced is determined to be less than about 30 wt. % (hereinafter, the “threshold value”), the selected base is added to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil. However, if the water content of the reduced acid biomass-derived pyrolysis oil to be produced is determined to be greater than about 30 wt. %, at least a portion of the water is removed from the water-containing biomass-derived pyrolysis oil, the base, or both.

[0018] The water content is determined by the following equation (I) (which takes into account the water in the water-containing biomass-derived pyrolysis oil and the water associated with the base (water in the base and the water produced during neutralization)):

$$x = ((a * b) + (f * d) + g) / (a + f) \quad (I)$$

wherein:

[0019] x = the concentration of water in the phase stable, reduced acid biomass-derived pyrolysis oil expressed as g H_2O /g oil;

[0020] a = the amount of the starting water-containing biomass-derived pyrolysis oil to be treated in grams;

[0021] b=the concentration of water in the starting water-containing biomass-derived pyrolysis oil expressed as g H₂O/g starting oil (as determined by Karl Fischer Reagent Titration Method (ASTM D1364), as noted previously);

[0022] c=the concentration of carboxylic acids in the starting water-containing biomass-derived pyrolysis oil expressed as mol acid/gram oil (determined by the method as hereinafter described);

[0023] d=the concentration of free water in the neutralizing base in gH₂O/gram of base (as determined, for example, by Karl Fischer Reagent Titration Method (ASTM D1364);

[0024] e=the concentration of neutralizing base in mol base/gram as provided by the manufacturer or determined using methods known by those skilled in the art (i.e., dilution of a more concentrated base solution and/or titration against a standard acid); and

[0025] f=the amount of base needed to neutralize the water-containing biomass-derived pyrolysis oil acidity in grams=(a*c)/e.

[0026] g=amount of water in grams produced by neutralization of the pyrolysis oil acids. This is dependent on the nature of the neutralizing base such that for:

Hydroxide bases (sodium hydroxide, tetraethylammonium hydroxide): $g=a*c*18.0$

Oxide and carbonate bases (Calcium oxide, sodium carbonate): $g=(a*c*18.0)/2$

Amine and alkoxide bases (triethylamine, sodium ethoxide): $g=0$

[0027] The concentration of carboxylic acids in the starting water-containing biomass-derived pyrolysis oil ("c" in equation (I) above), is determined by the following method adapted from Dence, C. W., Determination of carboxyl groups [in lignin], Methods Lignin Chem. (1992), p. 458-464: A solution of 0.05N tetra-n-butylammonium hydroxide solution (TnBAH) is prepared by diluting 50.0 milliliters (mL) of 1.0N TnBAH (Aldrich, SAP#1014519, 100 mL) solution to 1.00 liters (L) in isopropanol. The solution is mixed thoroughly before transferring the solution to a Dosimat bottle. 1 mL of concentrated HCl is added to 100 mL of deionized water and mixed thoroughly. 4 mL of this solution is added to about 140 mL of DMF (N,N-dimethylformamide) (available from, for example, Burdick & Jackson of Muskegon, Mich. (USA)) for titration of samples. To standardize the titrant, 0.15-0.20 g of dried benzoic acid is weighed into a titration beaker and the weight recorded to the nearest 0.1 mg. 120 mL of the DMF solution is added to the benzoic acid and titrated with the TnBAH solution. The standardization should be done in duplicate. The Normality is calculated to three significant figures and the standardization repeated every three hours.

$$N = \frac{\text{g Benzoic Acid}}{(\text{mL titrant})(0.12212)}$$

To titrate the samples, and prior to the first sample analysis, 0.05-0.08 g of p-hydroxybenzoic acid is weighed into a titration beaker. The DMF/HCl solution is added to the p-hydroxybenzoic acid. The resultant solution is titrated through the 3rd inflection. This is the blank used to calculate the HCl correction, and can be used as a QC for the phenolic hydroxyl titrations. Next, 0.3-0.4 g of lignin and 0.05-0.08 g of p-hydroxybenzoic acid are weighed into a titration beaker. The DMF/HCl solution is added to the titration beaker. The titra-

tion beaker is blanketed with nitrogen and stirred for 5 minutes before titration. The solution is titrated with 0.05N TnBAH to the 3rd inflection. The theoretical titer of the internal standard used in the blank or sample titration is calculated according to the following equation:

$$a \text{ (mL)} = \frac{\text{g pHBA}}{0.13812(N)}$$

To calculate the HCl interference from the blank,

$$c \text{ (mL)} = [(\text{measured volume to reach } 2^{\text{nd}} \text{ inflection of blank}) - (\text{measured } 1^{\text{st}} \text{ inflection})] - (a \text{ (mL, calculated above)})$$

then,

$$mEq \text{ carboxyl/g sample} = \frac{[(y) - (x) - (c) - (a)]N}{w}$$

$$mEq \text{ phenolic hydroxyl/g sample} = \frac{[(z) - (y) - (a)]N}{w}$$

wherein:

x=mL at first inflection point

y=mL at second inflection point

z=mL at third inflection point

[0028] As noted above, if the water content of the reduced acid biomass-derived pyrolysis oil to be produced is determined to be less than about 30 weight percent, the selected base is added to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil (step 400). The amount of the selected base (f in equation (I) above and equation (II) below) to be added to the water-containing biomass-derived pyrolysis oil to neutralize the starting carboxylic acid content is determined according to the following equation (II):

$$f=(a*c)/e \quad (II)$$

wherein, as noted previously:

[0029] a=the amount of the starting water-containing biomass-derived pyrolysis oil to be treated in grams;

[0030] c=the concentration of carboxylic acids in the starting water-containing biomass-derived pyrolysis oil expressed as mol acid/gram oil (as determined above); and

[0031] e=the concentration of neutralizing base in mol base/gram as provided by the manufacturer or determined using methods known by those skilled in the art (i.e., dilution of a more concentrated base solution and/or titration against a standard acid).

[0032] As neutralization reactions are often exothermic, the base is added at an effective rate to maintain the temperature of the mixture at less than about 40° C. The base is added at a temperature from about 20° C. to about 40° C. A solid base may be dissolved in an organic solvent (thereby producing a base solution) prior to addition of the base to the water-containing biomass-derived pyrolysis oil. Suitable exemplary organic solvents comprise methanol, ethanol, and combinations thereof. The addition of the solvent (about 40% to about 95% by volume) allows the base to be added gradually in a controlled manner, without raising the water content of the resultant phase stable, reduced acid biomass-derived pyrolysis oil above the threshold value. In addition, the solvent raises the solubility of the components in the mixture. Less

solvent is needed when the water produced in the titration (during neutralization) does not exceed the solubility level of the biomass-derived pyrolysis oil. If an excess of base is added, a precipitate may form that may be removed by filtration.

[0033] If the water content of the reduced acid biomass-derived pyrolysis oil to be produced (“x” in equation (I) above) is determined to be greater than about 30 weight percent, at least a portion of the water is removed from the water-containing biomass-derived pyrolysis oil, the base, or both (step **500**) prior to addition of the selected base as described above (step **400**). Water may be removed from the water-containing biomass-derived pyrolysis oil, the base, or both by methods known to one skilled in the art, for example, distillation, evaporation, or the like. It is to be understood that a base may be selected specifically because it does not generate water during the neutralization reaction, for example, the non-hydroxide bases and the nitrogen-containing bases, and therefore little or no water may have to be removed to produce the reduced acid biomass-derived pyrolysis oil with a water content below the threshold value, i.e., a phase stable, reduced acid biomass-derived pyrolysis oil. Similarly, if the water-containing biomass-derived pyrolysis oil has a water content below the threshold value and the selected base does not generate water during neutralization, the removal of water from the reduced acid biomass-derived pyrolysis oil is unnecessary to produce a phase stable, reduced acid biomass-derived pyrolysis oil because the water content thereof has been maintained below the threshold value.

[0034] Referring again to FIG. 1, the reduced acid biomass-derived pyrolysis oil may be inspected (step **600**) to verify that there is no phase separation. Phase separation typically occurs, if at all, within 48 hours after the base is added to the water-containing biomass-derived pyrolysis oil. If phase separation occurs, additional water may be removed from the reduced acid biomass-derived pyrolysis oil (step **700**) by methods known to one skilled in the art, for example distillation and evaporation, until no phase separation is observed on inspection.

[0035] From the foregoing, it is to be appreciated that the phase stable, reduced acid biomass-derived pyrolysis oil having a water content no greater than about 30 wt % is substantially homogenous, with an acidity (as measured by pH) reduced from that of conventional biomass-derived pyrolysis oil. In addition, the energy density of the phase stable, reduced acid biomass-derived pyrolysis oil is higher than that of conventional biomass-derived pyrolysis oil. The increased pH, phase homogeneity, and higher energy density of the phase stable, reduced acid biomass-derived pyrolysis oil produced in accordance with exemplary embodiments as described herein improve its suitability as a fuel and biofuel.

[0036] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without

departing from the scope of the invention as set forth in the appended claims and their legal equivalents.

What is claimed is:

1. A method for producing phase stable, reduced acid biomass-derived pyrolysis oil comprising the steps of:

providing a biomass-derived pyrolysis oil having a determined water content no greater than about 30% by weight; and

mixing a base with the biomass-derived pyrolysis oil.

2. The method of claim 1, wherein the step of mixing comprises selecting the base comprising an inorganic base selected from the group consisting of a metal oxide, a metal hydroxide, a metal alkoxide, and a metal carbonate of the alkali and alkaline earth metals, alkali and alkaline earth exchanged zeolites, a mixed metal oxide, and combinations thereof.

3. The method of claim 2, wherein the step of mixing comprises selecting the metal oxide from the group consisting of calcium oxide, magnesium oxide, and combinations thereof.

4. The method of claim 2, wherein the step of mixing comprises selecting a metal hydroxide from the group consisting of LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂, and combinations thereof.

5. The method of claim 2, wherein the step of mixing comprises selecting a metal alkoxide from the group consisting of sodium ethoxide, potassium tert-butoxide, and combinations thereof.

6. The method of claim 1, wherein the step of mixing comprises selecting a nitrogen-containing base comprising an amine, a tetraalkylammonium hydroxide, or combinations thereof.

7. The method of claim 6, wherein the step of mixing comprises selecting the amine from the group comprising a dialkyl amine, a trialkyl amine, or combinations thereof.

8. The method of claim 7, wherein the step of mixing comprises selecting an amine from the group consisting of pyrrolidine, morpholine, piperidine, N-methyl pyrrolidine, and NR¹R²X wherein:

R¹, R² are selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, sec. butyl, pentyl, hexyl, cyclohexyl, and benzyl; and

X is selected from the group consisting of hydrogen, R¹, and R².

9. The method of claim 6, wherein the step of mixing comprises selecting the tetraalkylammonium hydroxide from the group consisting of tetraethylammonium hydroxide, tetramethylammonium hydroxide, tetrapropylammonium hydroxide, and combinations thereof.

10. The method of claim 1, further comprising the step of dissolving a solid base in an organic solvent to produce a base solution with the total organic solvent concentration in the base solution comprising about 40 to about 95% by volume, the organic solvent selected from the group consisting of methanol, ethanol, and combinations thereof.

11. The method of claim 1, wherein the step of providing comprises:

determining the water content of the phase stable, reduced acid biomass-derived pyrolysis oil; and

removing at least a portion of the water from the biomass-derived pyrolysis oil, the base, or both the biomass-derived pyrolysis oil and the base.

12. The method of claim **11**, further comprising removing additional water upon phase separation of the reduced acid biomass-derived pyrolysis oil.

13. A method for producing phase stable, reduced acid biomass-derived pyrolysis oil from water-containing biomass-derived pyrolysis oil, the method comprising the steps of:

selecting a base comprising either an inorganic base or a nitrogen-containing base;

removing at least a portion of the water from the water-containing biomass-derived pyrolysis oil, the base, or both; and

adding the base to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil.

14. The method of claim **13**, wherein the step of selecting a base comprises selecting the inorganic base from the group consisting of metal oxides, metal hydroxides, metal alkoxides, metal carbonates of the alkali and alkaline earth metals, alkali and alkaline earth exchanged zeolites, mixed metal oxides, and combinations thereof.

15. The method of claim **14**, wherein the step of selecting a base comprises selecting the metal oxide from the group consisting of calcium oxide, magnesium oxide, and combinations thereof; the metal hydroxide from the group consisting of LiOH, NaOH, KOH, RbOH, CsOH, Mg(OH)₂, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂, and combinations thereof; and the metal alkoxide from the group consisting of sodium ethoxide, potassium tert-butoxide, and combinations thereof.

16. The method of claim **13**, wherein the step of selecting a base comprises selecting the nitrogen-containing base comprising an amine, a tetraalkylammonium hydroxide, or combinations thereof, wherein the amine is selected from the group consisting of a dialkyl amine, a trialkyl amine, and

combinations thereof, pyrrolidine, morpholine, piperidine, N-methylpyrrolidine, and NR¹R²X wherein:

R¹, R² are selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, sec. butyl, pentyl, hexyl, cyclohexyl, and benzyl; and

X is selected from the group consisting of hydrogen, R¹, and R².

17. The method of claim **13**, further comprising removing additional water from the reduced acid biomass-derived pyrolysis oil upon phase separation thereof

18. A method for producing phase stable, reduced acid biomass-derived pyrolysis oil, the method comprising the steps of:

providing water-containing biomass-derived pyrolysis oil;

selecting a base adapted to be added to the water-containing biomass-derived pyrolysis oil to produce reduced acid biomass-derived pyrolysis oil;

determining a water content of the reduced acid biomass-derived pyrolysis oil;

wherein if the reduced acid biomass-derived pyrolysis oil is determined to have a water content greater than about 30 wt %, removing at least a portion of the water from the water-containing biomass-derived pyrolysis oil, the base, or both; and

adding the selected base to the water-containing biomass-derived pyrolysis oil.

19. The method of claim **18**, wherein the step of selecting a base comprises selecting a solid base, the method further comprising dissolving the solid base in an organic solvent.

20. The method of claim **18**, further comprising the step of removing additional water from the reduced acid biomass-derived pyrolysis oil upon phase separation thereof.

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