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(54) **Title:** PRE-PROCESSING BIO-OIL BEFORE HYDROTREATMENT

(57) **Abstract:** Described are methods and systems for preparing stabilized bio-oil suitable for subsequent hydrotreatment and forming a hydrocarbon product from a stabilized bio-oil. For example, preparing stabilized bio-oil suitable for subsequent hydrotreatment may include filtering bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers; treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil; and catalytically stabilizing the bio-oil to provide the stabilized bio-oil suitable for subsequent hydrotreatment. Forming a hydrocarbon product from a stabilized bio-oil may include hydrotreating the stabilized bio-oil by, for example, contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the hydrocarbon product. Also included are stabilized bio-oil and hydrocarbon products derived therefrom.



Pre-processing Bio-oil Before Hydrotreatment**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims priority to U.S. Provisional Pat. App. Nos. 62/129,007, filed on March 5, 2015, and 62/245,423, filed October 23, 2015, each of which is entirely incorporated by reference herein.

**STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY-
SPONSORED RESEARCH AND DEVELOPMENT**

[0002] This invention was made with Government support under Contract Nos. DE-AC0576RLO1830 and DE-EE0004391, awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND

[0003] Pyrolytic bio-oil derived from biomass may have limited commercial applications because of poor heating value (~17 MJ/kg), high oxygen content (~45 wt %), high viscosity (>200 cP), and corrosiveness. It is highly desirable that such liquid hydrocarbon products produced from bio-oil be substantially reduced in water content, viscosity, and corrosiveness in order to provide miscibility with petroleum-based fuels and compatibility with petroleum refining unit operations.

[0004] Bio-oil may be hydrotreated using heterogeneous catalysts and may be used to produce improved liquid hydrocarbon products such as gasoline, kerosene, and diesel fractions. With existing technology, hydrotreatment catalysts may unfortunately become deactivated due to carbon deposition from bio-oil polymerization and coke formation, leading to a low "Time On Stream" (TOS) of a few hundred hours before a hydrotreatment apparatus must be shut down for catalyst maintenance. This substantially increases the cost of such operations and limits the rate and economic viability of liquid hydrocarbon products produced from bio-oil.

[0005] The lack of solutions in the art to these significant barriers have substantially limited the production viability of improved liquid hydrocarbon products from pyrolytic bio-

oil. In recognition of these issues, the U.S. Department of Energy has called for solutions, for example, in “Upgrading of Biomass Fast Pyrolysis Oil (Bio-oil),” Funding Opportunity Announcement Number: DE-FOA-0000342, the entire contents of which are incorporated herein by reference.

[0006] The present application appreciates that production of improved liquid hydrocarbon products from pyrolytic bio-oil may be a challenging endeavor.

SUMMARY

[0007] In one embodiment, a method for preparing stabilized bio-oil suitable for subsequent hydrotreatment is provided. The method may include providing the bio-oil. The method may include filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers. The method may include treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil. The method may include catalytically stabilizing the bio-oil. The method may thereby provide the stabilized bio-oil suitable for subsequent hydrotreatment.

[0008] In another embodiment, a method for forming a hydrocarbon product from a stabilized bio-oil is provided. The method may include providing the stabilized bio-oil. The method may include hydrotreating the stabilized bio-oil by thereby providing the hydrocarbon product.

[0009] In one embodiment, a system for forming a hydrocarbon product from biomass is provided. The system may include a pyrolysis reactor configured to pyrolyze a biomass input and provide a bio-oil output. The system may include an inline filter operatively coupled to receive the bio-oil output. The inline filter may be configured to remove at least a portion of particles having an effective diameter greater than about 10 micrometers from the bio-oil output to provide a coarse-filtered bio-oil output. The system may include a fine filtration module configured to receive the coarse-filtered bio-oil output. The fine filtration module may be configured to remove at least a portion of particles having an effective diameter greater than about 5 micrometers to provide a fine-filtered bio-oil output. The system may include a bed configured to contain an ion exchange resin effective to receive the fine-filtered

bio-oil. The bed may be configured to remove at least a portion of inorganic species from the fine filtered bio-oil to produce a reduced-inorganic bio-oil output. The system may include a first catalytic unit configured to contain a stabilizing catalyst effective to receive the reduced-inorganic bio-oil. The first catalytic unit may be configured to stabilize the reduced-inorganic bio-oil to produce a stabilized bio-oil output. The system may include a second catalytic unit configured to contain a hydrotreatment catalyst effective to receive the stabilized bio-oil. The second catalytic unit may be configured to hydrotreat the stabilized bio-oil to provide a hydrocarbon output. The system may include a hydrogen source operatively coupled to provide hydrogen to one or more of the first catalytic unit and the second catalytic unit.

[0010] In another embodiment, a method for forming a hydrocarbon product from a bio-oil is provided. The method may include providing the bio-oil. The method may include filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers. The method may include treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil. The method may include catalytically stabilizing the bio-oil to provide a stabilized bio-oil. The method may include hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the hydrocarbon product.

[0011] In another embodiment, a stabilized bio-oil is provided. The stabilized bio-oil may be prepared according to any of the methods described herein or prepared using any of the systems described herein.

[0012] In one embodiment, a stabilized bio-oil is provided. The stabilized bio oil may be characterized by one or more of: a total acid number (TAN) value less than 100 mg KOH/g; a water content of at least about 17 wt.%; a hydrogen to carbon ratio greater than 1.4:1; and an average percentage of aldehyde and ketone groups of less than about 5%.

[0013] In another embodiment, a hydrocarbon product derived from bio-oil is provided. The hydrocarbon product derived from bio-oil may be prepared according to any of the methods described herein or prepared using any of the systems described herein.

[0014] In one embodiment, a hydrocarbon product derived from bio-oil is provided. The hydrocarbon product may be characterized by one or more of the following. The hydrocarbon product may be characterized by one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% nC₅-C₆ alkanes, and about 2.4% olefins. The hydrocarbon product may be characterized by one or more of: a density in grams/mL of 0.78-0.86; a total sulfur weight percent of less than 0.08%; a pour point in °C of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 1.5:1 to about 2.2:1; and an energy value in mega Joules per kilogram of about 40 to 45.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The accompanying figures, which are incorporated in and constitute a part of the specification, illustrate example methods and apparatuses, and are used merely to illustrate example embodiments.

[0016] **FIG. 1** is a schematic depicting the preparation of stabilized bio-oil and hydrocarbon products derived therefrom.

[0017] **FIG. 2** is a flow diagram of an example method **200** for preparing a stabilized bio-oil.

[0018] **FIG. 3A** is a flow diagram of an example method **300** for preparing a hydrocarbon product.

[0019] **FIG. 3B** is a flow diagram of an example method **350** for preparing a hydrocarbon product.

[0020] **FIG. 4** is a block diagram of an example system **400** for preparing a hydrocarbon product from biomass.

[0021] **FIG. 5** is a table of ICP analyses of bio-oil and synthetic bio-oil.

- [0022] **FIG. 6A** is a flow diagram illustrating hydrotreatment of synthetic bio-oil.
- [0023] **FIG. 6B** is a table of conditions used in the hydrotreatment of synthetic bio-oil without inorganic additives.
- [0024] **FIG. 6C** is a table of conditions used in the hydrotreatment of synthetic bio-oil without inorganic additives and results obtained at various time intervals.
- [0025] **FIG. 6D** is a graph illustrating the percentage volume of C2-C6 hydrocarbon gases detected after hydrotreatment of synthetic bio-oil without inorganic additives relative to time on stream.
- [0026] **FIG. 6E** is a graph illustrating the density of the product organic phase obtained after hydrotreatment of synthetic bio-oils with and without inorganic additives relative to time on stream.
- [0027] **FIG. 6F** is a graph illustrating the percentage of water in the product organic phase obtained after hydrotreatment of synthetic bio-oils with and without inorganic additives relative to time on stream.
- [0028] **FIG. 6G** is a graph illustrating the percentage volume of C2-C6 hydrocarbon gases detected after hydrotreatment of synthetic bio-oils with and without inorganic additives relative to time on stream.
- [0029] **FIG. 7** is a flow diagram illustrating hydrotreatment of pyrolysis bio-oil.
- [0030] **FIG. 8** is a table summarizing the results of thermogravimetric experiments.
- [0031] **FIG. 9A** is a transmission electron microscope (TEM) photo illustrating a metal particle size and metal dispersion of a fresh catalyst.
- [0032] **FIG. 9B** is a transmission electron microscope (TEM) photo illustrating a metal particle size and metal dispersion of a spent catalyst.
- [0033] **FIG. 10** is a graph of ICP analyses of fresh and spent (post 500 h TOS) catalysts showing that deposition of inorganic contaminants such as Ca, Fe and S are associated with deactivated catalyst.

[0034] **FIG. 11** is a table reporting the concentration of various inorganic species measured for the fine-filtered bio-oil before and after contact with the polystyrene sulfonic acid ion exchange resin under various conditions.

[0035] **FIG. 12** is a table summarizing the conditions used in cycle 1.

[0036] **FIG. 13** is a graph illustrating liquid and dry yield ratios of stabilized bio-oil product/cleaned bio-oil feed.

[0037] **FIG. 14** is a graph illustrating the pH of the stabilized bio-oil product versus time on stream.

[0038] **FIG. 15** is graph illustrating the water content in the liquid phase as determined by the Karl Fisher method.

[0039] **FIG. 16A** is a graph illustrating the molar hydrogen/carbon ratio (H/C) of the stabilized bio-oil as function of time on stream.

[0040] **FIG. 16B** is a graph illustrating the Total Acidity Number, TAN (mg KOH/ gram of sample) as a function of time on stream.

[0041] **FIG. 17A** is a graph illustrating the density of the hydrocarbon product of Zone II versus time on stream.

[0042] **FIG. 17B** is a graph illustrating the consumption of hydrogen versus time on stream.

[0043] **FIG. 18A** is an image of overlay ^1H NMR spectra from about 6 ppm to 13 ppm of fine-filtered bio-oil and reduced-inorganic bio-oil.

[0044] **FIG. 18B** is an image of overlay ^1H NMR spectra from 0 ppm to about 6 ppm of fine-filtered bio-oil and reduced-inorganic bio-oil.

[0045] **FIG. 19A** is an image of overlay ^1H NMR spectra from about 6 ppm to 13 ppm of reduced inorganic bio-oil at TOS = 0 h and stabilized bio-oil at TOS = 55-60 h, 106-112 h, 242-252 h, and 312-324 h.

[0046] **FIG. 19B** is an image of overlay ^1H NMR spectra from 0 ppm to about 6 ppm of reduced inorganic bio-oil at TOS = 0 h and stabilized bio-oil at TOS = 55-60 h, 106-112 h, 242-252 h, and 312-324 h.

[0047] **FIG. 20A** is an image of overlay ^1H NMR spectra from about 6 ppm to 13 ppm of reduced inorganic bio-oil at TOS = 0 h and stabilized bio-oil at TOS = 466-478 h, 502-514 h, 676-700 h, 773-797 h, 820-844 h, 916-940 h, and 964-1010 h.

[0048] **FIG. 20B** is an image of overlay ^1H NMR spectra from 0 ppm to about 6 ppm of reduced inorganic bio-oil at TOS = 0 h and stabilized bio-oil at TOS = 466-478 h, 502-514 h, 676-700 h, 773-797 h, 820-844 h, 916-940 h, and 964-1010 h.

DETAILED DESCRIPTION

[0049] Pyrolytic bio-oil, as produced, includes contaminants that may tend to foul conventional methods and catalysts for hydrogenating and cracking bio-oil to form hydrocarbon products. Such contaminants may include particulates, e.g., of char and ash, as well as compounds including inorganic atoms such as Al, Ca, Fe, K, Mg, Na, Si, and S. Such contaminants may arise from the source biomass, from pyrolysis, by leaching from components of pyrolysis systems, and the like. As described in the **EXAMPLES**, such contaminants were found to foul and deactivate catalysts. Further, as described in the **EXAMPLES**, removal of these contaminants may tend to reduce fouling and catalyst deactivation, leading to benefits such as better catalyst performance, easier catalyst regeneration, longer Time On Stream (TOS) operation, and the like. In particular, embodiments described herein lead to substantially improved TOS values compared to the prior art.

[0050] Accordingly, **FIG. 1** is an example reaction flow diagram **100** illustrating an overview of various aspects of embodiments detailed herein. Reaction flow diagram **100** shows that a pyrolytic bio-oil **102** may be directed into a filtering step **104** that may produce a filtered bio-oil **106**. The filtered bio-oil **106** may be cleaned of at least some inorganic species in an ion exchange process **108**, followed by the output of a cleaned bio-oil **110** with reduced content of the inorganic species. The cleaned bio-oil **110**, which may still contain sulfur species, may be subjected to a mild catalytic stabilization in a Zone I process **112** to produce a stabilized bio-oil **114**. The stabilized bio-oil **114**, which may still contain sulfur

species, may be further hydrotreated and cracked using a hydrotreatment catalyst, e.g., a sulfided catalyst in a Zone II process **116**, which may output a hydrocarbon fuel product **118**.

[0051] **FIG. 2** is a flow diagram illustrating an example method **200** for preparing stabilized bio-oil for subsequent hydrotreatment. In various embodiments, the method may include **202** providing the bio-oil. The method may include **204** filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers. The method may include **206** treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil. The method may include **208** catalytically stabilizing the bio-oil. The method may thereby provide the stabilized bio-oil suitable for subsequent hydrotreatment.

[0052] In some embodiments, providing the bio-oil may include pyrolyzing biomass to produce the bio-oil. Providing the bio-oil may include pyrolyzing biomass to produce the bio-oil. The biomass may be substantially free of small or large biomass particulates. For example, the biomass may be characterized by a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters. The method may include preparing the biomass prior to the pyrolyzing by selecting the biomass in a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters. Providing the bio-oil may include pyrolyzing biomass to produce the bio-oil at a temperature in °C of between about one or more of: 400 to 600, 400 to 550, and 450 to 500, for example, 450-500 °C.

[0053] In several embodiments, providing the bio-oil may include pyrolyzing biomass to produce the bio-oil in a downflow reactor. For example, providing the bio-oil may include pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor. Filtering the bio-oil may include in-line filtering the bio-oil vapor produced by the pyrolysis effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers. Further, for example, providing the bio-oil may include pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor and condensing the bio-oil vapor to provide the bio-oil in condensed form. Filtering the bio-oil may include in-line filtering the

bio-oil in condensed form effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

[0054] In various embodiments, filtering the bio-oil may include removing at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1, for example, an effective particulate diameter greater than about 0.8 micrometers or greater than about 0.2 micrometers. Filtering the bio-oil may include a first filtering process effective to remove at least a portion of the particles having an effective particulate diameter greater than about 10 micrometers. Filtering the bio-oil may include a second filtering process effective to remove at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1, for example, an effective particulate diameter greater than about 0.8 micrometers or greater than about 0.2 micrometers. Filtering the bio-oil may include a second filtering process conducted on the bio-oil offline from a pyrolysis process used to provide the bio-oil. Filtering the bio-oil may include a second filtering process conducted using a pressure differential in pounds per square inch (PSI) of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200, for example, a pressure differential of about 80 PSI. Filtering the bio-oil may include a second filtering process conducted at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100, for example, at least about 40 °C or at least about 80 °C.

[0055] In some embodiments, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to one or more of: an ion exchange resin, a zeolite, and activated carbon. The ion exchange resin may include any ion exchange resin described herein. The zeolite may include any zeolite described herein. For example, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin in a fixed-bed column reactor or a slurry bed reactor. For example, the fixed-bed column reactor may be operated in intermittent or continuous flow mode. For example, the slurry bed reactor may

be operated in batch mode. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40, for example, 40 °C.

[0056] Suitable ion-exchange resins may include strongly acidic cation-exchange resins. The ion exchange resin may be used in protonated form, for example, including active SO₃H groups or CO₂H groups. Neutralized sulfonic acid resins, in which some or all of the protons have been exchanged by a cation such as lithium, sodium, potassium, magnesium, and calcium may also be suitable. Resins having a counterion (i.e., sodium, Na⁺), may be converted to protonated form by treatment with aqueous acid, e.g., hydrochloric acid, nitric acid, sulfuric acid, substituted sulfonic acids such as p-toluene sulfonic acid, and the like. This is commonly known in the art as ion-exchange resin activation. The ion exchange resin may include sulfonated or carboxylated polymers or copolymers of styrene. For example, the ion exchange resin may include one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid).

[0057] Example ion exchange resins may include macroreticular resins. As used herein, “macroreticular resins” may include two continuous phases--a continuous pore phase and a continuous gel polymeric phase. The continuous gel polymeric phase may be structurally composed of small spherical microgel particles agglomerated together to form clusters that may form interconnecting pores. The surface area may correspond to the exposed surface of the microgel clusters. Macroreticular ion exchange resins may be made with different surface areas ranging from 7 to 1500 m²/g, and average pore diameters ranging from about 5 to about 10000 nm.

[0058] Example ion exchange resins may include gel-type resins. “Gel-type resins” may be translucent. Gel-type resins may lack permanent pore structures. Gel-type resins may

include molecular-scale micropores. The pore structures may be determined by the distance between the polymer chains and crosslinks that may vary with the crosslink level of the polymer, the polarity of the solvent, and the operating conditions. Macroreticular resins may be used for continuous column flow processes where minimization of resin swelling/shrinking may be desirable. Gel-type resins may be used for slurry bed batch processes. Macroreticular resins and gel-type resins may be used in either continuous column flow or slurry bed batch processes.

[0059] Suitable ion-exchange resins may include those provided by Dow Chemical Co., Midland, MI under the tradenames/trademarks DOWEX® MARATHON C, DOWEX® MONOSPHERE C-350, DOWEX® HCR-S/S, DOWEX® MARATHON MSC, DOWEX® MONOSPHERE 650C, DOWEX® HCR-W2, DOWEX® MSC-1, DOWEX® HGR NG (H), DOWE® DR-G8, DOWEX® 88, DOWEX® MONOSPHERE 88, DOWEX® MONOSPHERE C-600 B, DOWEX® MONOSPHERE M-31, DOWEX® MONOSPHERE DR-2030, DOWEX® M-31, DOWEX® G-26 (H), DOWEX® 50W-X4, DOWEX® 50W-X8, DOWEX® 66, AMBERLYST™ 131, AMBERLYST™ 15, AMBERLYST™ 16, AMBERLYST™ 31, AMBERLYST™ 33, AMBERLYST™ 35, AMBERLYST™ 36, AMBERLYST™ 39, AMBERLYST™ 40 AMBERLYST™ 70, AMBERLITE™ FPC11, AMBERLITE™ FPC22, AMBERLITE™ FPC23, and the like. Suitable ion-exchange resins may include those provided by Brotech Corp., Bala Cynwyd, PA (USA) under the trade names/trademarks PUROFINE® PFC150, PUROLITE® C145, PUROLITE® C150, PUROLITE® C160, PUROFINE®PFC100, PUROLITE® C100, and the like. Suitable ion-exchange resins may include those provided by Thermax Limited Corp., Novi, MI under the tradename/trademark MONOPLUS™. 5100, TULUSION® T42, and the like.

[0060] For example, the poly(styrene sulfonic acid) may be characterized by one or more of: a surface area of about 28 to 37 square meters per gram, a particle diameter of 0.60 to 0.850 millimeters, a particle diameter uniformity coefficient of less than about 1.6, a total pore volume of 0.15 to 0.25 milliliters per gram, an average pore diameter of about 200 to 280 angstroms, and an exchange capacity of at least about 5 milli-equivalents per gram.

[0061] In several embodiments, the inorganic species may include one or more of: Al, Ca, Na, K, Mg, Fe, P, Si, S, and Zn. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include reducing the amount of one or more inorganic species in the bio-oil to a concentration in parts per million (ppm) of less than one or more of about: 25, 20, 15, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1, for example, less than about 6 ppm or less than about 3 ppm. For example, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include reducing a content or amount of one or more of, or each of: Al, Ca, Na, K, Mg, and Fe in the bio-oil to a corresponding concentration in ppm of less than one or more of about: 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1, for example, less than about 6 ppm or less than about 3 ppm.

[0062] In various embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst. The stabilizing catalyst may include a metal dispersed on a solid support, e.g., a metal oxide, a zeolite, carbon, and the like. The metal dispersed on a solid support may be acidic. For example, the metal may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal oxide may include one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

[0063] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil. The method may include diluting the bio-oil in an organic solvent to form a diluted bio-oil. The organic solvent may include a protic organic solvent, e.g., an alcohol. The organic solvent may include an aprotic organic solvent. The organic solvent may include a polar solvent. The organic solvent may include a polar protic solvent. The organic solvent may include a polar aprotic solvent. The organic solvent may include a nonpolar solvent. The diluting medium may include an organic solvent including one or more of: a protic solvent, an aprotic solvent, a polar solvent, and a nonpolar solvent. The diluting medium may include an organic solvent including one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, diethyl ether,

acetonitrile, dimethyl formamide, dimethylsulfoxide, and the like. The method may include diluting the bio-oil in a petroleum fuel to form a diluted bio-oil. The petroleum fuel may include one or more of: diesel, gasoline, kerosene, jet fuel, fuel oil, naptha, fractions thereof, combinations thereof, and the like. The method may include diluting the bio-oil in a portion of the stabilized bio-oil to form the diluted bio-oil. The portion of the stabilized bio-oil may include a light phase. The light phase may include water. The portion of the stabilized bio-oil may include a heavy phase. The heavy phase may include the bio-oil. The portion of the stabilized bio-oil may include one or more of: the light phase and the heavy phase. The method may include diluting the bio-oil to form the diluted bio-oil in one or more of: an organic solvent, a petroleum fuel, water, and a portion of the stabilized bio-oil.

[0064] The method may include diluting the bio-oil in a diluting medium to form a diluted bio-oil. Diluting the bio-oil in the diluting medium may include diluting the bio-oil to a percentage by weight of the diluting medium of about one or more of: 5 to 50, 10 to 45, 15 to 40, 20 to 35, 25 to 35, and 30.

[0065] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil using a positive pressure differential in pounds per square inch compared to atmospheric pressure of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 500, 1000, 1500, 1800, and 2000.

[0066] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil and catalytically stabilizing the bio-oil. Catalytically stabilizing the bio-oil may include contacting the diluted bio-oil to the stabilizing catalyst.

[0067] The method may include removing at least a portion of the diluting medium from the diluted bio-oil after catalytically stabilizing the diluted bio-oil. The diluting medium may include one or more of: the organic solvent, the petroleum fuel, and the water. The removed diluting medium may be recycled.

[0068] In some embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst that includes a zeolite. Further, the solid support may be a zeolite, e.g., an acidic zeolite. The zeolite may include one or more of: a Y zeolite, a Beta

zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[0069] In various embodiments, the stabilizing catalyst may include the metal dispersed on an acidic metal oxide. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica. For example, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst including Ru/TiO₂.

[0070] In some embodiments, the stabilizing catalyst may include the metal dispersed on an acidic zeolite. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[0071] In several embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, and 170. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst in the presence of hydrogen. Catalytically stabilizing the bio-oil may include providing a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500. Catalytically stabilizing the bio-oil may include flowing the bio-oil past a stabilizing catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst for a Time On Stream (TOS) in hours of at least about one or more of: 200, 300, 400, 500, 600, 700,

800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

[0072] In several embodiments, the method may include regenerating the stabilizing catalyst, for example, by rinsing the stabilizing catalyst with an organic solvent. The organic solvent may include a protic organic solvent, e.g., an alcohol. The organic solvent may include one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, acetonitrile, and dimethyl formamide. The method may include regenerating the stabilizing catalyst by contacting the stabilizing catalyst with hydrogen at a temperature in °C of about one or more of: 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400. For example, the hydrogen may chemically reduce carbon accumulation on the stabilizing catalyst to produce gaseous methane. Such reducing may be desirable compared to oxidative methods of removing carbon, because hydrogen reduction of carbon to methane may be less exothermic than carbon oxidation in the presence of oxygen, leading to less heating and less thermal damage to the stabilizing catalyst, e.g., by sintering.

[0073] In various embodiments, the stabilized bio-oil may be characterized compared to the bio-oil. For example, the stabilized bio-oil may be characterized compared to the bio-oil by a decreased content of aldehydes and free carboxylic acids. The stabilized bio-oil may be characterized compared to the bio-oil by an increase in pH of at least one or more of about: 0.25, 0.5, 0.75, 1, 1.25, and 1.5. The stabilized bio-oil may be characterized compared to the bio-oil by a percent increase in dry hydrogen:carbon ratio of one or more of about: 5, 10, 15, 20, and 25. The stabilized bio-oil may be characterized compared to the bio-oil by one or more of the characteristics recited in this paragraph.

[0074] In some embodiments, the bio-oil may be characterized by one or more of: a density of about 1 to 1.2 grams per milliliter, a dry hydrogen:carbon ratio of about 1.4:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 30% to 45%. The stabilized bio-oil may be characterized by one or more of: a density of

about 1 to 1.1 grams per milliliter, a dry hydrogen:carbon ratio of about 1.2:1 to 1.8:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 20% to 35%.

[0075] In several embodiments, the method may include cooling the stabilized bio-oil prior to the subsequent hydrotreatment, insulating the stabilizing catalyst from heat of the subsequent hydrotreatment, or cooling the stabilizing catalyst against heat of the subsequent hydrotreatment.

[0076] The method may include conveying the stabilized bio-oil directly from the catalytically stabilizing to the subsequent hydrotreatment, for example, as a continuous process.

[0077] The method may include a stabilized bio-oil including one or more of: a light phase and a heavy phase. The method may include feeding at least the heavy phase directly from the catalytically stabilizing to the subsequent hydrotreatment. The method may include separating the light phase from the heavy phase and feeding the heavy phase to the subsequent hydrotreatment. The method may include feeding the light phase and the heavy phase in parallel to the subsequent hydrotreatment. The method may include controlling a ratio between the light phase and the heavy phase and feeding the ratio of the light phase and the heavy phase in parallel to the subsequent hydrotreatment. The light phase:heavy phase may include a ratio between about 1:20 and about 20:1.

[0078] The method may include conducting at least a portion of the method under an inert atmosphere. The inert atmosphere may include one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis.

[0079] **FIGS. 3A** and **3B** are flow diagrams illustrating methods of forming a hydrocarbon product. For example, **FIG. 3A** is a flow diagram illustrating an example method **300** for forming a hydrocarbon product from a stabilized bio-oil. In various embodiments, the method may include **302** providing the stabilized bio-oil. The method may include **304** hydrotreating the stabilized bio-oil by, for example, contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the

hydrocarbon product. Further, for example, **FIG. 3B** is a flow diagram illustrating an example method **350** for forming a hydrocarbon product from a bio-oil. In various embodiments, the method may include **352** providing the bio-oil. The method may include **354** filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers. The method may include **356** treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil. The method may include **358** catalytically stabilizing the bio-oil to provide a stabilized bio-oil. The method may include **360** hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the hydrocarbon product. Methods **300** and **350** may incorporate of the following aspects.

[0080] For example, the stabilized bio-oil may be characterized by one or more of: a total acid number (TAN) value less than 100 mg KOH/g; a water content of at least about 17 wt.%; a hydrogen to carbon ratio greater than 1.4:1; and an average percentage of aldehyde and ketone groups of less than about 5%. The TAN may be, for example, a value in milligrams of potassium hydroxide per gram of less than one or more of: 100, 90, 80, 70, 60, 50, 40, and 35. The water content may be, for example, a percent by weight of one or more of: 17 to 35, 20 to 35, 20 to 30, and 25 to 30. The hydrogen:carbon ratio may be, for example, one or more of: 1.4:1 to 1.9:1, 1.5:1 to 1.9:1, 1.6:1 to 1.9:1, 1.7:1 to 1.9:1, 1.4:1 to 1.8:1, 1.6:1 to 1.8:1, and 1.7:1 to 1.8:1. The average percentage of aldehyde and ketone groups, e.g., as measured by ^1H NMR may be a weight percentage of one or more of: less than about 5%, less than about 4.5%, less than about 4%, less than about 3.5%, between about 1.5% and about 3.5%, and between about 2% and about 3%.

[0081] In some embodiments, hydrotreating the stabilized bio-oil may include contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen at a temperature in $^{\circ}\text{C}$ of about one or more of: 200 to 420, 220 to 400, 240 to 380, 260 to 360, 280 to 340, 300 to 320, and 310. Hydrotreating the stabilized bio-oil may include contacting the stabilized bio-oil to the hydrotreatment catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

[0082] In various embodiments, the hydrotreatment catalyst may be an active metal catalyst or a sulfided catalyst.

[0083] For example, the active metal catalyst may include a metal dispersed on a solid support, e.g., a metal oxide, a zeolite, carbon, and the like, each of which may be acidic. For example, the metal may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal oxide may include one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica. The hydrotreatment catalyst may include a zeolite. Further, the solid support may be a zeolite, e.g., an acidic zeolite. The zeolite may include one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[0084] In various embodiments, the hydrotreatment catalyst may include the metal dispersed on an acidic metal oxide. For example, the hydrotreatment catalyst may include a metal including one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal may be dispersed on a solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, silica, a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, a Chabazite zeolite, and carbon. For example, the active metal catalyst may include one or more of Ru/TiO₂, Ru/TiO₂-ZSM5, Pd/C, Pd/SiO₂-Al₂O₃, Pd/Nb/Al₂O₃, Pd/Nb/TiO₂-SiO₂, Pt/ZrO₂-Al₂O₃, and Pd/Mg/Al₂O₃.

[0085] Further, for example, the hydrotreatment catalyst may include a sulfided catalyst, e.g., including one or more of: Ni, Nb, Mo, Co, and W. For example, the sulfided catalyst may include one or more of sulfided: Ni, Nb, Mo, Co, W, NiMo, and CoMo.

[0086] In some embodiment, hydrotreating the stabilized bio-oil may include contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500

to 1800, and 1000 to 1500. Hydrotreating the stabilized bio-oil may include contacting the stabilized bio-oil to the hydrotreatment catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr^{-1} to 1 hr^{-1} . Hydrotreating the stabilized bio-oil may include contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

[0087] In several embodiments, the hydrocarbon product may include a liquid fraction characterized compared to the stabilized bio-oil at 25°C and 1 atmosphere. The liquid fraction may be characterized compared to the stabilized bio-oil by one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% $\text{nC}_5\text{-C}_6$ alkanes, and about 2.4% olefins. The liquid fraction may be characterized compared to the stabilized bio-oil by one or more of: a density in grams/mL of 0.78-0.86; a total sulfur weight percent of less than 0.08%, or less than about 0.01%; a pour point in $^\circ\text{C}$ of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 1.5:1 to about 2.2:1, e.g., about 2.1:1; and an energy value in mega Joules per kilogram of about 40 to 45 or about 41 to 44... The liquid fraction may be characterized compared to the stabilized bio-oil by one or more of the characteristics described in this paragraph.

[0088] In various embodiments, the hydrocarbon product may include a $\text{C}_1\text{-C}_4$ gas fraction, e.g., one or more of methane, ethane, propane, butane, and the like. The hydrocarbon product may include a liquid fraction characterized by one or more of: a density of about 0.8 to about 0.86 grams per milliliter, a hydrogen:carbon ratio of about 1.5:1 to about 2.2:1, a dry oxygen weight percentage of about 0% to about 5%, e.g., less than about 0.5%, and a water weight percentage of about 0% to about 5%, e.g., less than about 0.5%.

[0089] In some embodiments, the method may include conducting at least a portion of the method under an inert atmosphere. The inert atmosphere may include one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis.

[0090] In several embodiments, providing the stabilized bio-oil may include: providing a bio-oil; filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers; treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil; and catalytically stabilizing the bio-oil, thereby providing the stabilized bio-oil.

[0091] The method may include one or more of: cooling the stabilized bio-oil prior to hydrotreating the stabilized bio-oil, insulating the stabilizing catalyst from heat of hydrotreating the stabilized bio-oil, and cooling the stabilizing catalyst against heat of hydrotreating the stabilized bio-oil. The method may include conveying the stabilized bio-oil directly from the catalytically stabilizing to the hydrotreating.

[0092] The method may include a stabilized bio-oil including one or more of: a light phase and a heavy phase. The method may include feeding at least the heavy phase directly from the catalytically stabilizing to the hydrotreating. The method may include separating the light phase from the heavy phase and feeding the heavy phase to the hydrotreating. The method may include feeding the light phase and the heavy phase in parallel to the hydrotreating. The method may include controlling a ratio between the light phase and the heavy phase and feeding the ratio of the light phase and the heavy phase in parallel to the hydrotreating. The light phase:heavy phase may include a ratio between about 1:20 and about 20:1.

[0093] In some embodiments, providing the bio-oil may include pyrolyzing biomass to produce the bio-oil. Providing the bio-oil may include pyrolyzing biomass to produce the bio-oil. The biomass may be substantially free of small or large biomass particulates. For example, the biomass may be characterized by a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters. The method may include preparing the biomass prior to the pyrolyzing by selecting the biomass in a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters. Providing the bio-oil may include pyrolyzing biomass to produce the bio-oil at a temperature in °C of between about one or more of: 400 to 600, 400 to 550, and 450 to 500, for example, 450-500 °C.

[0094] In several embodiments, providing the bio-oil may include pyrolyzing biomass to produce the bio-oil in a downflow reactor. For example, providing the bio-oil may include pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor. Filtering the bio-oil may include in-line filtering the bio-oil vapor produced by the pyrolysis effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers. Further, for example, providing the bio-oil may include pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor and condensing the bio-oil vapor to provide the bio-oil in condensed form. Filtering the bio-oil may include in-line filtering the bio-oil in condensed form effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

[0095] In various embodiments, filtering the bio-oil may include removing at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1, for example, an effective particulate diameter greater than about 0.8 micrometers or greater than about 0.2 micrometers. Filtering the bio-oil may include a first filtering process effective to remove at least a portion of the particles having an effective particulate diameter greater than about 10 micrometers. Filtering the bio-oil may include a second filtering process effective to remove at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1, for example, an effective particulate diameter greater than about 0.8 micrometers or greater than about 0.2 micrometers. Filtering the bio-oil may include a second filtering process conducted on the bio-oil offline from a pyrolysis process used to provide the bio-oil. Filtering the bio-oil may include a second filtering process conducted using a pressure differential in pounds per square inch (PSI) of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200, for example, a pressure differential of about 80 PSI. Filtering the bio-oil may include a second filtering process conducted at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100, for example, at least about 40 °C or at least about 80 °C.

[0096] In some embodiments, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to one or more of: an ion exchange resin, a zeolite, and activated carbon. The ion exchange resin may include any ion exchange resin described herein. The zeolite may include any zeolite described herein. For example, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin in a fixed-bed column reactor or a slurry bed reactor. For example, the fixed-bed column reactor may be operated in intermittent or continuous flow mode, and the slurry bed reactor may be operated in batch mode. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include contacting the bio-oil to an ion exchange resin at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40, for example, 40 °C. The ion exchange resin may include one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid). For example, the poly(styrene sulfonic acid) may be characterized by one or more of: a surface area of about 28 to 37 square meters per gram, a particle diameter of 0.60 to 0.850 millimeters, a particle diameter uniformity coefficient of less than about 1.6, a total pore volume of 0.15 to 0.25 milliliters per gram, an average pore diameter of about 200 to 280 angstroms, and an exchange capacity of at least about 5 milliequivalents per gram

[0097] In several embodiments, the inorganic species may include one or more of: Al, Ca, Na, K, Mg, Fe, P, Si, S, and Zn. Treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include reducing one or more inorganic species in the bio-oil to a concentration in parts per million (ppm) of less than one or more of about: 25, 20, 15, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1, for example, less than about 6 ppm or less than about 3 ppm. For example, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil may include reducing a content of one or more of, or each of: Al, Ca,

Na, K, Mg, and Fe in the bio-oil to a corresponding concentration in ppm of less than one or more of about: 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1, for example, less than about 6 ppm or less than about 3 ppm.

[0098] In various embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst. The stabilizing catalyst may include a metal dispersed on a solid support, e.g., a metal oxide, a zeolite, carbon, and the like, which may be acidic. For example, the metal may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal oxide may include one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

[0099] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil. The method may include diluting the bio-oil in an organic solvent to form a diluted bio-oil. The organic solvent may include a protic organic solvent, e.g., an alcohol. The organic solvent may include an aprotic organic solvent. The organic solvent may include a polar solvent. The organic solvent may include a polar protic solvent. The organic solvent may include a polar aprotic solvent. The organic solvent may include a nonpolar solvent. The diluting medium may include an organic solvent including one or more of: a protic solvent, an aprotic solvent, a polar solvent, and a nonpolar solvent. The diluting medium may include an organic solvent including one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, diethyl ether, acetonitrile, dimethyl formamide, dimethylsulfoxide, and the like. The method may include diluting the bio-oil in a petroleum fuel to form a diluted bio-oil. The petroleum fuel may include one or more of: diesel, gasoline, kerosene, jet fuel, fuel oil, naptha, fractions thereof, combinations thereof, and the like. The method may include diluting the bio-oil in a portion of the stabilized bio-oil to form the diluted bio-oil. The portion of the stabilized bio-oil may include a light phase. The light phase may include water. The portion of the stabilized bio-oil may include a heavy phase. The heavy phase may include the bio-oil. The portion of the

stabilized bio-oil may include one or more of: the light phase and the heavy phase. The method may include diluting the bio-oil to form the diluted bio-oil in one or more of: an organic solvent, a petroleum fuel, water, and a portion of the stabilized bio-oil.

[00100] The method may include diluting the bio-oil in a diluting medium to form a diluted bio-oil. Diluting the bio-oil in the diluting medium may include diluting the bio-oil to a percentage by weight of the diluting medium of about one or more of: 5 to 50, 10 to 45, 15 to 40, 20 to 35, 25 to 35, and 30.

[00101] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil using a positive pressure differential in pounds per square inch compared to atmospheric pressure of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 500, 1000, 1500, 1800, and 2000.

[00102] The method may include contacting the bio-oil to a diluting medium to form a diluted bio-oil and catalytically stabilizing the bio-oil. Catalytically stabilizing the bio-oil may include contacting the diluted bio-oil to the stabilizing catalyst.

[00103] The method may include removing at least a portion of the diluting medium from the diluted bio-oil after catalytically stabilizing the diluted bio-oil. The diluting medium may include one or more of: the organic solvent, the petroleum fuel, and the water. The removed diluting medium may be recycled.

[00104] In some embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst that includes a zeolite. Further, the solid support may be a zeolite, e.g., an acidic zeolite. The zeolite may include one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[00105] In various embodiments, the stabilizing catalyst may include the metal dispersed on an acidic metal oxide. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica. For example, catalytically

stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst including Ru/TiO₂.

[00106] In some embodiments, the stabilizing catalyst may include the metal dispersed on an acidic zeolite. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[00107] In several embodiments, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, and 170. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst in the presence of hydrogen. Catalytically stabilizing the bio-oil may include providing a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500. Catalytically stabilizing the bio-oil may include flowing the bio-oil past a stabilizing catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹. Catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

[00108] In several embodiments, the method may include regenerating the stabilizing catalyst, for example, by rinsing the stabilizing catalyst with an organic solvent. The organic solvent may include a protic organic solvent, e.g., an alcohol. The organic solvent may include one or more of methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, acetonitrile, dimethyl formamide. The

method may include regenerating the stabilizing catalyst by contacting the stabilizing catalyst with hydrogen at a temperature in °C of about one or more of: 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400. For example, the hydrogen may chemically reduce carbon accumulation on the stabilizing catalyst to produce gaseous methane. Such reducing may be desirable compared to oxidative methods of removing carbon, because hydrogen reduction of carbon to methane may be less exothermic than carbon oxidation in the presence of oxygen, leading to less heating and less thermal damage to the stabilizing catalyst, e.g., by sintering.

[00109] In various embodiments, the stabilized bio-oil may be characterized compared to the bio-oil. For example, the stabilized bio-oil may be characterized compared to the bio-oil by a decreased content of aldehydes and free carboxylic acids. The stabilized bio-oil may be characterized compared to the bio-oil by an increase in pH of at least one or more of about: 0.25, 0.5, 0.75, 1, 1.25, and 1.5. The stabilized bio-oil may be characterized compared to the bio-oil by a percent increase in dry hydrogen:carbon ratio of one or more of about: 5, 10, 15, 20, and 25. The stabilized bio-oil may be characterized compared to the bio-oil by one or more of the characteristics recited in this paragraph.

[00110] In some embodiments, the bio-oil may be characterized by one or more of: a density of about 1 to 1.2 grams per milliliter, a dry hydrogen:carbon ratio of about 1.4:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 30% to 45%. The stabilized bio-oil may be characterized by one or more of: a density of about 1 to 1.1 grams per milliliter, a dry hydrogen:carbon ratio of about 1.2:1 to 1.8:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 20% to 35%.

[00111] **FIG. 4** is a block diagram illustrating an example system **400** for forming a hydrocarbon product from biomass. In various embodiments, system **400** may include a pyrolysis reactor **402** configured to pyrolyze a biomass input and provide a bio-oil output. System **400** may include an inline filter **404** operatively coupled to receive the bio-oil output. Inline filter **404** may be configured to remove at least a portion of particles having an

effective diameter greater than about 10 micrometers from the bio-oil output to provide a coarse-filtered bio-oil output. System **400** may include a fine filtration module **406** configured to receive the coarse-filtered bio-oil output. Fine filtration module **406** may be configured to remove at least a portion of particles having an effective diameter greater than about 5 micrometers to provide a fine-filtered bio-oil output. System **400** may include a bed **408** configured to receive the fine-filtered bio-oil. Bed **408** may be configured to remove at least a portion of inorganic species from the fine filtered bio-oil to produce a reduced-inorganic bio-oil output. Bed **408** may be configured to contain one or more of: an ion exchange resin, a zeolite, and activated carbon. The ion exchange resin may include any ion exchange resin described herein. The zeolite may include any zeolite described herein. System **400** may include a first catalytic unit **410** configured to contain a stabilizing catalyst effective to receive the reduced-inorganic bio-oil. First catalytic unit **410** may be configured to stabilize the reduced-inorganic bio-oil to produce a stabilized bio-oil output. System **400** may include a second catalytic unit **412** configured to contain a hydrotreatment catalyst effective to receive the stabilized bio-oil. Second catalytic unit **412** may be configured to hydrotreat the stabilized bio-oil to provide a hydrocarbon output. System **400** may include a hydrogen source **414** operatively coupled to provide hydrogen to one or more of first catalytic unit **410** and second catalytic unit **412**.

[00112] In some embodiments, pyrolysis reactor **402** may include a downflow pyrolysis reactor. Pyrolysis reactor **402** may be configured to heat to a temperature in °C of at least about one or more of: 400 to 600, 400 to 550, and 450 to 500.

[00113] In several embodiments, system **400** may include a condenser module **416**. Condenser module **416** may include a three-stage condenser. Condenser module **416** may include an electrostatic precipitator. Condenser module **416** may be operatively coupled between pyrolysis reactor **402** and inline filter **404** such that inline filter **404** is configured to receive the bio-oil output in condensed form from condenser module **416**. Inline filter **404** may be directly coupled to pyrolysis reactor **402** such that inline filter **404** may be configured to receive the bio-oil output in vapor form from pyrolysis reactor **402**. Inline filter **404** may

include one or more of: a bag filter element, a metal mesh filter element, and a ceramic filter element. Inline filter **404** may be configured to remove at least a portion of particles having a diameter in micrometers greater than one or more of about: 10, 9, 8, 7, 6, 5, 4, and 2.

[00114] In various embodiments, fine filtration module **406** may be a stand-alone unit (not shown). Fine filtration module **406** may operatively couple inline filter **404** and bed **408** such that fine filtration module **406** may be configured for inline operation. Fine filtration module **406** may be configured to remove at least a portion of particles having a diameter in micrometers greater than one or more of about: 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1. Fine filtration module **406** may include one or more of: a bag filter element, a metal mesh filter element, and a ceramic filter element. Fine filtration module **406** may be operatively coupled to a pressure source **406A** configured to operate fine filtration module **406** using a pressure differential in pounds per square inch of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200. Fine filtration module **406** may be operatively coupled to a heat source **406B** configured to operate fine filtration module **406** at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100.

[00115] In some embodiments, bed **408** may be configured in the form of a fixed-bed column reactor or a slurry bed reactor. For example, the fixed-bed column reactor may be configured for continuous or intermittent flow operation. The slurry bed reactor may be configured for batch operation. Bed **408** may include the ion exchange resin. Bed **408** may be operatively coupled to a pressure source **408A** configured to operate bed **408** at a pressure in pounds per square inch of at least about one or more of: gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20. Bed **408** may be operatively coupled to a heat source **408B** configured to operate bed **408** at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40, for example, 40 °C. Bed **408** may include as the ion exchange resin one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid). For example, the ion exchange resin may include a poly(styrene sulfonic acid)

characterized by one or more of: a surface area of about 28 to 37 square meters per gram, a particle diameter of 0.60 to 0.850 millimeters, a particle diameter uniformity coefficient of less than about 1.6, a total pore volume of 0.15 to 0.25 milliliters per gram, an average pore diameter of about 200 to 280 angstroms, and an exchange capacity of at least about 5 milliequivalents per gram.

[00116] In several embodiments, first catalytic unit **410** may include the stabilizing catalyst. The stabilizing catalyst may include a metal dispersed on a solid support, e.g., a metal oxide, a zeolite, carbon, and the like, which may be acidic. The metal may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal oxide may include one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

[00117] In some embodiments, the stabilizing catalyst may include a zeolite, e.g., an acidic zeolite. Further, the solid support may be a zeolite, e.g., an acidic zeolite. The zeolite may include one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[00118] In various embodiments, the stabilizing catalyst may include the metal dispersed on an acidic metal oxide. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica. For example, catalytically stabilizing the bio-oil may include contacting the bio-oil to a stabilizing catalyst including Ru/TiO₂.

[00119] In some embodiments, the stabilizing catalyst may include the metal dispersed on an acidic zeolite. For example, the stabilizing catalyst may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os; dispersed on one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[00120] In various embodiments, first catalytic unit **410** may be operatively coupled to a pressure source **410A** configured to operate first catalytic unit **410** at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500. First catalytic unit **410** may be operatively coupled to a heat source **410B** configured to operate first catalytic unit **410** at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, 170, 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400. First catalytic unit **410** may be configured to operate at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹. First catalytic unit **410** may be configured to operate for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000. First catalytic unit **410** may be operatively coupled to an organic solvent source **410C**.

[00121] In some embodiments, system **400** may include a heat exchanger **418** operatively coupled between first catalytic unit **410** and second catalytic unit **412**. Heat exchanger **418** may be configured to actively or passively limit heating of first catalytic unit **410** by heat from second catalytic unit **412**.

[00122] In several embodiments, second catalytic unit **412** may include the hydrotreatment catalyst. The hydrotreatment catalyst may be an active metal catalyst or a sulfided catalyst. For example, the active metal catalyst may include a metal dispersed on a solid support, e.g., a metal oxide, a zeolite, carbon, and the like, each of which may be acidic. For example, the metal may include one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal oxide may include one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica. The hydrotreatment catalyst may include a zeolite. Further, the solid support may be a zeolite, e.g., an acidic zeolite. The zeolite may include one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

[00123] In various embodiments, the hydrotreatment catalyst may include the metal dispersed on an acidic metal oxide. For example, the hydrotreatment catalyst may include a metal including one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os. The metal may be dispersed on a solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, silica, a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, a Chabazite zeolite, and carbon. For example, the active metal catalyst may include one or more of Ru/TiO₂, Ru/TiO₂-ZSM5, Pd/C, Pd/SiO₂-Al₂O₃, Pd/Nb/Al₂O₃, Pd/Nb/TiO₂-SiO₂, Pt/ZrO₂-Al₂O₃, and Pd/Mg/Al₂O₃.

[00124] Further, for example, the hydrotreatment catalyst may include a sulfided catalyst, e.g., including one or more of: Ni, Nb, Mo, Co, and W. For example, the sulfided catalyst may include one or more of sulfided: Ni, Nb, Mo, Co, W, NiMo, and CoMo.

[00125] In several embodiments, second catalytic unit **412** may include a pressure source **412A** configured to pressurize second catalytic unit **412** to a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500. Second catalytic unit **412** may include a heat source **412B** configured to heat second catalytic unit **412** to a temperature in °C of about one or more of: 200 to 420, 220 to 400, 240 to 380, 260 to 360, 280 to 340, 300 to 320, and 310. Second catalytic unit **412** may be configured to operate at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹. Second catalytic unit **412** may be configured to operate for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

[00126] In various embodiments, system **400** may include an inert gas source **420** operatively coupled to provide an inert atmosphere to at least a portion of system **400**. Inert gas source **410** may be configured to provide one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis. Inert gas source **410** may be coincident with, the same as, or operatively coupled to one or more of pressure sources **406A**, **408A**,

410A, and **412A**. Hydrogen source **414** may be coincident with, the same as, or operatively coupled to one or more of pressure sources **406A**, **408A**, **410A**, and **412A**. Two or more of pressure sources **406A**, **408A**, **410A**, and **412A** may be coincident, the same as each other, or operatively coupled to each other. Two or more of heat sources **406B**, **408B**, **410B**, and **412B** may be coincident, the same as each other, or operatively coupled to each other.

[00127] In some embodiments, pyrolysis reactor **402**, inline filter **404**, fine filtration module **406**, bed **408**, first catalytic unit **410**, and second catalytic unit **412** may be operatively coupled to provide a continuous process for converting the biomass input to the hydrocarbon output.

[00128] In several embodiments, system **400** may be configured to operate for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

[00129] In various embodiments, a stabilized bio-oil is provided, prepared according to any of the methods described herein or prepared using any of the systems described herein. In various embodiments, a hydrocarbon product derived from bio-oil is provided, prepared according to any of the methods described herein or prepared using any of the systems described herein.

[00130] In some embodiments, a stabilized bio-oil is provided. The stabilized bio oil may be characterized by one or more of: a total acid number (TAN) value less than 100 mg KOH/g; a water content of at least about 17 wt.%; a hydrogen to carbon ratio greater than 1.4:1; and an average percentage of aldehyde and ketone groups of less than about 5%.

[00131] In several embodiments, a hydrocarbon product derived from bio-oil is provided. The hydrocarbon product may be characterized by one or more of the following. The hydrocarbon product may be characterized by one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% nC₅-C₆ alkanes, and about 2.4% olefins. The hydrocarbon product may be characterized by one or more of: a density in grams/mL of 0.78-0.86; a total sulfur weight percent of less than 0.08%; a pour

point in °C of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 1.5:1 to about 2.2:1; and an energy value in mega Joules per kilogram of about 40 to 45. The hydrocarbon product may be characterized by one or more of: a density of about 0.8 to about 0.86 grams per milliliter, a hydrogen:carbon ratio of about 1.5:1 to about 2.2:1, a dry oxygen weight percentage of about 0% to about 5%, and a water weight percentage of about 0% to about 5%.

EXAMPLES

EXAMPLE 1: Preparation of Synthetic Bio-oils with and without Inorganic Species

[00132] Four synthetic bio-oil compositions were prepared to determine the effects inorganic species had in deactivating the hydrotreatment catalyst. The synthetic bio-oils included a mixture of chemicals with functional groups similar to those found in pyrolytic bio-oil. The synthetic bio-oil compositions included carboxylic acids, aldehydes, phenols, polyols, and water, effective to give the synthetic bio-oil a similar oxygen concentration (28% wt) as pyrolytic bio-oil. Inorganic species were provided in synthetic bio-oil compositions that included metal concentrations comparable to that of pyrolytic bio-oil. The table in **FIG. 5** reports species concentrations determined from inductively coupled plasma (ICP) atomic analyses of pyrolytic bio-oil and synthetic bio-oil.

[00133] A first synthetic bio-oil composition without inorganic species was prepared by mixing acetic acid (6.8% by volume), hydroquinone (9.1% by volume), D-glucose (7.8% by volume), 4-hydroxybenzoic acid (8.0% by volume), methanol (50.7% by volume) and water (17.6% by volume). The methanol was added to the mixture in order to solubilize hydroquinone and 4-hydroxybenzoic acid.

[00134] A second synthetic bio-oil composition with inorganic species was prepared by mixing acetic acid (6.8% by volume), hydroquinone (9.1% by volume), D-glucose (7.8% by volume), 4-hydroxybenzoic acid (8.0% by volume), methanol (50.7% by volume), water (17.6% by volume), calcium (101 ppm) in the form of calcium hydroxide, zinc (52 ppm) in the form of zinc acetate, sodium (49 ppm) in the form of sodium hydroxide, potassium (49 ppm) in the form of potassium carbonate, magnesium (99 ppm) in the form of magnesium

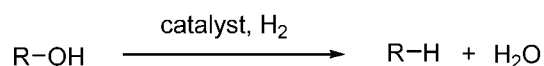
carbonate, iron (148 ppm) in the form of iron acetate, aluminum (287 ppm) in the form of aluminum lactate, phosphorus (50 ppm) in the form of phosphorus pentoxide, and sulfur (50 ppm).

[00135] A third synthetic bio-oil composition with heteroatom-containing species was prepared by mixing acetic acid (6.8% by volume), hydroquinone (9.1% by volume), D-glucose (7.8% by volume), 4-hydroxybenzoic acid (8.0% by volume), methanol (50.7% by volume), water (17.6% by volume), calcium (101 ppm) in the form of calcium hydroxide, zinc (52 ppm) in the form of zinc acetate, sodium (49 ppm) in the form of sodium hydroxide, potassium (49 ppm) in the form of potassium carbonate, magnesium (99 ppm) in the form of magnesium carbonate, iron (148 ppm) in the form of iron acetate, aluminum (287 ppm) in the form of aluminum lactate, and phosphorus (50 ppm) in the form of phosphorus pentoxide. The third synthetic bio-oil composition with inorganic species did not include a sulfur additive. A fourth synthetic bio-oil composition with inorganic species was prepared by mixing acetic acid (6.8% by volume), hydroquinone (9.1% by volume), D-glucose (7.8% by volume), 4-hydroxybenzoic acid (8.0% by volume), methanol (50.7% by volume), water (17.6% by volume), and iron (148 ppm) in the form of iron acetate.

EXAMPLE 2: Hydrotreatment of Synthetic Bio-oil without Inorganic Species

[00136] The first synthetic bio-oil without inorganic species was subjected to hydrotreatment under various conditions. The efficiency of the catalyst system was determined by analyzing the products obtained from the hydrotreatment process:

[00137] 1) The catalyst was considered to be active if a biphasic product resulted with an organic phase with a density of less than 0.8 g/cm³ and a water content of less than 5%. An aqueous phase with a density of approximately 1 g/cm³ and a water content greater than 90% was desirable. The hydro-deoxygenation reaction scheme is illustrated below:



[00138] Catalyst deactivation was indicated by an increase in the density of the organic phase corresponding to an increase in water content in the organic phase. An increase in density and water content in the organic phase may result from remaining bio-oil hydroxyls

that may effectively hydrogen bond with water, thus drawing the water into the organic phase. Remaining bio-oil hydroxyls may be indicative of an inefficient or deactivated catalyst.

[00139] 2) Measurement of non-condensable gases (R-H at higher temperatures; C₁-C₆ hydrocarbons) released from the reaction mixture indicated catalyst activity since the detection of such gases suggested that hydro-deoxygenation was successful. Methanol used to solubilize the synthetic bio-oil composition was converted to methane under hydro-deoxygenation conditions. Thus, assessment of the catalyst activity was made by detection of the gaseous C₂-C₆ hydrocarbons by gas chromatography (GC) analysis.

[00140] The first synthetic bio-oil without inorganic species was subjected to hydrotreatment under the conditions illustrated in **FIGS. 6A-6C**. The synthetic bio-oil was subjected to Zone I at 150 °C and passed over a Ru/TiO₂ catalyst at a liquid hourly space velocity (LHSV) of 0.2 h⁻¹ in the presence of H₂ at a 400 mL/min flow rate. The reaction mixture from Zone I was subsequently subjected to Zone II at 280 °C and passed over a Ru/TiO₂ – ZSM5 catalyst at a LHSV of 0.2 h⁻¹ in the presence of H₂ at a 400 mL/min flow rate (entry 1, **FIG. 6C**). Samples were analyzed every 4-8 h for a duration of 0-40 h Time on Stream (TOS) (see graph in **FIG. 6D**, and sections **A** and **B** in **FIG. 6D** for parameters). The majority of the synthetic bio-oil was released as gaseous hydrocarbons. The condensed liquid phase obtained was mostly aqueous.

[00141] At 40 h TOS to 48 h TOS, the H₂ flow rate had been increased from 400 mL/min to 600 mL/min, and the LHSV was increased from 0.2 h⁻¹ to 0.4 h⁻¹. The Zone I temperature was maintained at 150 °C and the Zone II temperature was maintained at 280 °C (entry 2, **FIG. 6C**). Samples were analyzed every 4-8 h by GC (see graph in **FIG. 6D**, and sections **B**, **C**, and **D** in **FIG. 6D**). Increasing the H₂ flow and the LHSV did not lead to a biphasic mixture.

[00142] At 48 h TOS to 60 TOS, the temperature of Zone II was decreased from 280 °C to 150 °C. The Zone I temperature was maintained at 150 °C, the H₂ flow rate was maintained at 600 mL/min, and the LHSV was maintained at 0.4 h⁻¹ (entry 3, **FIG. 6C**). Samples were

analyzed every 4-8 h (see graph in **FIG. 6D**, and sections **C**, **D**, **E**, and **F** in **FIG. 6D**). Decreasing the temperature in Zone II, the hydro-deoxygenation zone, led to poor catalytic activity. Although a biphasic mixture was obtained, the organic phase contained approximately 30% water.

[00143] At 60 h TOS to 170 h TOS, the temperature of Zone I was increased from 150 °C to 200 °C and the temperature of Zone II was increased from 150 °C to 200 °C. The H₂ flow rate was maintained at 600 mL/min and the LHSV was maintained at 0.4 h⁻¹ (entry 4, **FIG. 6C**, see sections **C**, **D**, and **G** in **FIG. 6D**). A biphasic mixture of hydrocarbons and water was obtained. The organic phase had less than 1% water content and the aqueous phase was more than 90% water.

EXAMPLE 3: Hydrotreatment of Synthetic Bio-oils with and without Inorganic

Species: Analysis of Organic Phase Density

[00144] Based on the results of **EXAMPLE 2**, operative conditions of Zone I and Zone II at 200 °C and a LHSV of 0.2 h⁻¹ were used for studying the hydrotreatment of synthetic bio-oils with and without inorganic species. **FIG. 6E** illustrates the density of the organic phase obtained relative to time on system (TOS) for the first, second, third, and fourth synthetic bio-oil compositions described in **EXAMPLE 1**. The density of the organic phase did not increase over time for the first synthetic bio-oil composition without inorganic species. The addition of iron in the fourth synthetic bio-oil did not adversely affect the density of the organic phase product until after 24 h, which indicated that the catalyst had begun to lose activity. The addition of other heteroatoms, such as those of the second and third synthetic bio-oils described in **EXAMPLE 1**, corresponded to a rapid increase in the density of the organic phase product. From this experiment, it was concluded that inorganic species deactivate the catalyst.

EXAMPLE 4: Hydrotreatment of Synthetic Bio-oils with and without Inorganic

Species: Analysis of Organic Phase Water Content

[00145] Based on the results of **EXAMPLE 2**, operative conditions of Zone I and Zone II at 200 °C and a LHSV of 0.2 h⁻¹ were used for studying the hydrotreatment of synthetic bio-

oils with and without inorganic species. **FIG. 6F** illustrates the water content of the organic phase obtained relative to the TOS for the first, second, third, and fourth synthetic bio-oil compositions described in **EXAMPLE 1**. The water content of the organic phase remained low throughout the TOS, which indicated that the catalytic reduction was sustainable. Had the catalyst become deactivated over time, it was expected that the unreacted hydroxyl-containing moieties in the organic phase would effectively increase the organic phase water content. Complimentary to the results in **EXAMPLE 3**, the addition of iron as in the fourth synthetic bio-oil did not adversely affect the water content of the organic phase product until after 24 h, which indicated that the catalyst had begun to lose activity. The addition of other heteroatoms, such as those provided in the second and third synthetic bio-oils described in **EXAMPLE 1**, corresponded to a rapid increase in the water content of the organic phase product. In conjunction with **EXAMPLE 3**, this experiment suggests that inorganic species deactivate the catalyst.

EXAMPLE 5: Hydrotreatment of Synthetic Bio-oils with and without Inorganic

Species: Analysis of Gaseous C₂-C₆ Hydrocarbons Produced

[00146] Based on the results of **EXAMPLE 2**, operative conditions of Zone I and Zone II at 200 °C and a LHSV of 0.2 h⁻¹ were used for studying the hydrotreatment of synthetic bio-oils with and without inorganic species. **FIG. 6G** illustrates the C₂-C₆ hydrocarbon concentration in the non-condensable gas relative to the TOS in the hydrotreatment process for the first, second, third, and fourth synthetic bio-oil compositions described in **EXAMPLE 1**. The concentration of C₂-C₆ hydrocarbons remained constant throughout TOS for the first synthetic bio-oil without inorganic species, which indicated that the catalytic reduction was sustainable. Complimentary to the results in **EXAMPLES 3 and 4**, the addition of iron as in the fourth synthetic bio-oil did not adversely affect the concentration of C₂-C₆ hydrocarbons released until after 24 h, which indicated that the catalyst had begun to lose activity. The addition of other heteroatoms, such as those provided in the second and third synthetic bio-oils described in **EXAMPLE 1**, corresponded to a rapid decrease in the concentration of C₂-

C₆ hydrocarbons released. In conjunction with **EXAMPLES 3** and **4**, this experiment suggests that inorganic species deactivate the catalyst.

EXAMPLE 6: Hydrotreatment of Pyrolysis Bio-oil

[00147] The results described in **EXAMPLES 2-5** suggested that inorganic species in the bio-oil deactivated the hydrotreatment catalysts. It was hypothesized that pyrolytic bio-oil would be a better feedstock for hydrotreatment in that the fluid-cracking catalyst (FCC) used in the vapor phase catalytic reactor may have removed some of the inorganic species during the pyrolysis process. The organic phase obtained from the pyrolysis process was blended with methanol (10% wt) to improve the homogeneity of the bio-oil feedstock. The pyrolysis bio-oil composition was subjected to hydrotreatment for 50 h TOS with fresh catalyst, as illustrated in **FIG. 7**. Samples were analyzed every 8 h. After 50 h, the density of the organic phase obtained had increased from 0.7 g/cm³ to 0.9 g/cm³, which indicated degradation of product quality and suggested deactivation of the catalyst. The catalyst was regenerated by rinsing with methanol at room temperature, and reducing with H₂ at 400 °C. Hydrotreatment was resumed and revealed an increase in deactivation rate (the organic phase densities increased at a faster rate). The catalyst was regenerated two additional times, and each subsequent hydrotreatment process produced a decrease in product quality at increasingly faster rates. The increase in deactivation rates from cycle to cycle suggested non-reversible catalyst deactivation. The C₂-C₆ hydrocarbon non-condensable gases were also monitored during the experiments. The data from gaseous C₂-C₆ hydrocarbon detection correlated with the data obtained in the organic phase analyses.

[00148] The pyrolysis bio-oil used in **EXAMPLE 6** was obtained from a pyrolysis process using a spent FCC catalyst. Bio-oil obtained from the use of fresh FCC catalyst may effectively increase the removal of inorganic species prior to hydrotreatment. However, the focus in removing inorganic species prior to hydrotreatment turned to other means as described below.

EXAMPLE 7: Production of Intermediate Bio-Oil

[00149] Bio-oil was produced using a continuous feed pyrolysis system having a 1 ton per day capacity. A pine saw dust with a particle size between 2 to 5 mm was continuously fed into the pyrolysis system as a feedstock. The pyrolysis temperature was between 450°C and 500°C. The yield was approximately 65-70% bio-oil by weight based on initial biomass weight with a water content of 35-40%. The bio-oil was condensed and filtered via a two filter system as follows. A 10 micrometer filter was coupled to the pyrolysis output just after condensation to provide a coarse-filtered bio-oil. The coarse-filtered bio-oil was then directed to an ex-situ filter module that included a 0.8 micron. Using pressure up to 80 psi, the coarse-filtered bio-oil was driven through the 0.8 micron to provide a fine-filtered bio-oil. This fine-filtered bio-oil was collected and reserved for further **EXAMPLES** as described below.

EXAMPLE 8: Deactivation of Stabilization Catalyst is Associated with Inorganic

Contaminants

[00150] It is known that stabilization catalysts are readily deactivated in contact with bio-oil. To determine the root cause of catalyst deactivation, fresh and spent stabilization catalysts were characterized after 500 h TOS.

[00151] The fresh (reduced at 400 °C), spent (500 h TOS and washed with methanol) and regenerated (spent, washed with methanol and reduced) catalysts were analyzed by thermogravimetric analysis in the presence of air from 120 °C (held for 30 min) to 700 °C (held for 30 min) at a rate of 10 °C/min. The weight loss for the spent catalyst was approximately 24%. Reduction of the catalyst at 400 °C, 450 °C, and 500 °C successively removed 90%, 93% and 95% of material. This removal was attributed to the oxidation of carbon on the catalyst to CO₂. The remaining carbon (<10%) was thought to be bonded strongly to the high active metal sites located in the micro pores. These active sites are thought to be difficult access, for example, due to diffusion limitations, which may tend to prevent such sites from actively contributing to catalysis at steady state. As a consequence, the regeneration of the catalyst was judged to be efficient and the coke formation was not judged to be the main

cause of catalyst deactivation. **FIG. 8** summarizes the results of the thermogravimetric experiments.

[00152] **FIGS. 9A and 9B** are transmission electron microscope (TEM) photos showing that the fresh and spent catalysts, respectively, had similar metal particle sizes (2 to 8 nanometers) and metal dispersions. However, hydrogen adsorption data at room temperature indicated that the fresh reduced catalyst had a metal dispersion of 12% and the regenerated spent catalyst had a metal dispersion of less than 1%. This data indicates that the catalyst deactivation is not due to a loss of surface area due to sintering.

[00153] **FIG. 10** is a graph of ICP analysis of fresh and spent (post 500 h TOS) catalysts showing that deposition of inorganic contaminants such as Ca, Fe and S are associated with deactivated catalyst. The increase in certain inorganic metal contaminants not present in the bio-oil feed, such as the 1,500 ppm of Fe, may indicate that such species are leaching out of the steel of the hydrotreatment reactor.

[00154] By contrast, the small amounts of sulfur in the feed (8.92 ppm) compared to the 1,800 ppm of sulfur on the catalyst after 500 h TOS was judged to occur by accumulation of sulfur from the bio-oil feed on the catalyst.

[00155] In view of these results, **EXAMPLE 9** was devised to remove inorganic contaminants from the bio-oil prior to Zone I stabilization in order to reduce catalyst deactivation.

EXAMPLE 9: Ion Exchange Media Removes Inorganic species from Bio-Oil

[00156] **EXAMPLE 8** corresponds to **EXAMPLES 2-5** in describing inorganic species poisoning as the most probable cause of permanent deactivation of hydrotreatment catalysts, with the poisoning being associated with inorganic salts and covalent sulfur containing compounds. Consequently, a variety of media were tested to remove the inorganic species and covalent sulfur containing compounds from the bio-oil.

[00157] Preliminary tests showed that a polystyrene sulfonic acid ion exchange resin (AMBERLYSTTM 36, Dow Chemical Company, Midland, MI) effectively removed many inorganic species. Samples of unfiltered, coarse-filtered, and fine-filtered bio-oil from both

batch and flow reactors were contacted to the polystyrene sulfonic acid ion exchange resin in a slurry reactor at about 40 °C for about 1 h. **FIG. 11** reports the concentration in parts per million of various inorganic species measured via inductively coupled plasma (ICP) atomic analysis for the fine-filtered bio-oil of **EXAMPLE 7** before and after contact with the polystyrene sulfonic acid ion exchange resin under various conditions.

[00158] A fixed bed flow reactor was prepared by loading the polystyrene sulfonic acid ion exchange resin into a column. A slurry bed batch reactor was prepared by loading the polystyrene sulfonic acid ion exchange resin into a 2L three-necked flask equipped with a stirrer and a thermocouple. Both reactors were supplied with the fine-filtered bio-oil of **EXAMPLE 7** under nitrogen and at 40 °C.

[00159] **FIG. 11** shows that the content of inorganic elements such as Al, Ca, Fe, K, Mg, Na, Si and S could be decreased, in many cases below 3.0 ppm, which suggested a successful removal of these inorganics from bio-oil. The fixed bed flow reactor worked well to remove inorganic species from the fine-filtered bio-oil to produce a reduced-inorganic bio-oil as shown for trial #1 in **FIG. 11**. However, with the benchtop equipment available, the fixed bed flow reactor operated at an undesirably low space velocity. The slurry bed batch reactor required far less time to remove the inorganic contaminants. Accordingly, the slurry bed batch reactor was selected for use in further tests to produce the reduced-inorganic bio-oil.

[00160] In trial #2, operation of the slurry bed batch reactor on a fine-filtered bio-oil with a relatively higher initial amounts of most inorganic species was able to remove most species to a concentration below about 6 ppm. In trial #3, operation of the slurry bed batch reactor on a fine-filtered bio-oil with a somewhat lower overall amounts of inorganic species was able to remove most species to a concentration below about 3 ppm. The amount of K in trial #3 was removed to below 6 ppm, which was still judged to be effective.

[00161] The minimal amount of sulfur-containing species removed in trial #3 compared to other inorganic atoms was thought to indicate that most sulfur-containing species contained sulfur covalently bonded in organic compounds, with a lesser amount of sulfur present in the form of ionic species. By contrast, the effective removal of inorganic elements such as Al,

Ca, Fe, K, Mg, Na, and Si was thought to indicate the presence of these elements in ionic species which were readily adsorbed on the ion exchange resin. Six liters of cleaned, reduced-inorganic bio-oil produced according to this **EXAMPLE** was collected and retained for use in subsequent **EXAMPLES** including stabilization and hydrogenation/cracking.

[00162] It was thought that if the sulfur was bound covalently, then it could potentially remain bound to the carbon under subsequent mild stabilization conditions, which could avoid sulfur poisoning of the stabilization catalyst in Zone I (**EXAMPLE 10**). It was further thought that such stabilized, but sulfur-containing bio-oil would still be a suitable substrate if a sulfided catalyst was used for subsequent hydrogenation and cracking in Zone II (**EXAMPLE 11**).

[00163] The fine-filtered bio-oil (before ion exchange treatment) and the reduced-inorganic bio-oil (after ion exchange treatment) were also examined by ^1H NMR. **FIGs. 18A** and **18B** illustrate ^1H NMR (proton nuclear magnetic resonance) spectroscopy data of the fine-filtered bio-oil and the reduced-inorganic bio-oil. **FIG. 18A** shows ^1H NMR overlay spectra from about 6 ppm to 13 ppm, wherein the bottom spectrum is the spectrum obtained from the fine-filtered bio-oil and the top spectrum is the spectrum obtained from the reduced-inorganic bio-oil. **FIG. 18B** shows ^1H NMR overlay spectra from 0 ppm to about 6 ppm, wherein the bottom spectrum is was obtained from the fine-filtered bio-oil and the top spectrum was obtained from the reduced-inorganic bio-oil. No changes were observed in the functional groups associated with the bio-oil in the ^1H NMR spectra. Thus, the ion exchange resin treatment at 40°C reduced inorganic contaminants as shown in **FIG. 10** without significant chemical modifications to the bio-oil.

EXAMPLE 10: Use of Reduced-Inorganic Bio-Oil in Production of Stabilized Bio-oil (Zone I) Leads to 1,000 Hour TOS with Improved Catalyst Life and Reduced Corrosion

[00164] Bio-oil hydrotreatment has been performed in a dual zone reactor, with stabilization in Zone I at about 150 to 300 °C and hydrogenation and cracking in Zone II at a higher temperature, e.g., 300 to 400 °C. Previous experiments have shown that in a small-scale dual zone reactor, significant axial heat transfer takes place from the higher temperature

Zone II to the lower temperature Zone I. This tends to cause undesirably high temperatures in Zone I and poor temperature control, which can lead to accelerated coking and catalyst deactivation. Also, operation of a continuous dual zone reactor does not readily permit sampling and analysis of the bio-oil between Zones I and II, which is desirable in these initial experiments. In addition, at the flow rates used in small-scale test reactors, sulfur from Zone II may contaminate the catalyst in Zone I. Accordingly, in these initial experiments, bio-oil stabilization in Zone I and hydrogenation/cracking in Zone II were conducted separately. Separation of Zone I and Zone II in these initial experiments allowed provided desired control of the operating conditions. Production scale operations may operate Zone I and Zone II directly in series while reducing thermal and sulfur backflow by using one or more of higher flow rates, baffles, separation between zones, heat exchangers or insulated conduits between zones, and the like. Moreover, at production scale, sampling and analysis may not be needed between Zone I and Zone II.

[00165] The objective of the Zone I stabilization/hydrotreatment was to reduce aldehydes and acids and to partially hydrogenate the bio-oil. Prior to hydrotreatment, the resin-treated bio-oil (38 wt% water; 1.1 g/cm³; pH = 2) was diluted with methanol (30 wt%) to achieve a homogeneous bio-oil composition (24 wt% water; 0.99 g/cm³; pH = 2.46) in order to prevent stratification in the delivery syringe pump, thus providing a uniform feed to the reactor. Zone I stabilization/hydrotreatment was conducted at high pressure in the presence of hydrogen. Hydrotreatment was conducted in three cycles using the same catalyst, Ru/TiO₂. The catalyst was regenerated twice during the three test cycles. The total TOS achieved was 1,000 h at a LHSV of 0.2 hr⁻¹. More than 3.5 liters of bio-oil produced was processed. The Zone I stabilization/hydrotreatment was conducted in three cycles. After each cycle, the reactor was carefully disassembled and a sample of catalyst was collected. The catalyst loading and flow rate for cycle 1 are presented in **FIG. 12**.

[00166] In cycle 1, the catalyst was subjected to reducing conditions in-situ at 300 °C with hydrogen. The run started at 170°C with a LHSV of 0.2 hr⁻¹ based on bio-oil. After 516 h TOS, an increase in differential pressure across the catalyst bed related to carbon deposition

on the catalyst was noted. The system was shut down and the catalyst was carefully removed. The spent catalyst was washed carefully with methanol to remove soft carbon, dried at 60 °C, and loaded in the reactor to perform cycle 2.

[00167] In cycle 2, the catalyst as washed with methanol in cycle 1 was subjected to reducing conditions in-situ at 400 °C with hydrogen to remove additional remaining carbon. Some of the catalyst was lost due to washing and repacking the catalyst. The flow of bio-oil was adjusted to reflect the loss of catalyst. The reaction was then resumed at 170°C with a LHSV of 0.2 hr⁻¹. After 440 h TOS (cycle 2), the reactor started plugging, at which point the reactor was shut down and the catalyst was carefully removed. The spent catalyst was washed carefully with methanol to remove soft carbon, dried at 60 °C, and loaded in the reactor to perform cycle 2.

[00168] In cycle 3, the catalyst as washed with methanol in cycle 2 was subjected to reducing conditions in-situ at 400 °C with hydrogen to remove additional remaining carbon. Some of the catalyst was lost due to washing and repacking the catalyst. The flow of bio-oil was adjusted to reflect the loss of catalyst. The flow of bio-oil was adjusted to reflect these changes. The reaction was resumed at 170 °C and a LHSV of 0.2 hr⁻¹. After 260 h TOS, the reaction was stopped as planned.

[00169] In some runs, the reduced-inorganic bio-oil of **EXAMPLE 9** was diluted with methanol to improve homogeneity of the bio-oil and improve loading into the stabilization reactor with the available vertically-oriented benchtop syringe pumps. The run described in **FIG. 12**, with a LHSV of 0.2 hr⁻¹, was conducted in the absence of methanol.

[00170] In each cycle, the liquid yield (stabilized bio-oil product / reduced-inorganic bio-oil feed) was approximately 100%. Two phases were obtained during all cycles, a light phase (95% wt) with a density of approximately 0.97 g/cm³ and a heavy phase (5% wt) with a density of 1.07 (g/cm³). It was easier to discern two phases in the stabilized bio-oil during the first 400 h TOS. After 400 h TOS, the stabilized bio-oil had the appearance of a single phase. Since the yield of the heavy phase was only about 5%, no measurement was made on

the heavy phase after 400 h TOS. **FIG. 13** graphs liquid and dry yield ratios of (stabilized bio-oil product / cleaned bio-oil feed). Dry yield is the total yield excluding water.

[00171] **FIG. 14** is a graph of the pH of the stabilized bio-oil product versus TOS. The pH of the liquid product increased from 2.4 (in the reduced-inorganic bio-oil feed) to 3.7 after treatment in Zone I.

[00172] **FIG. 15** is a graph of water content in the liquid phase as determined by the Karl Fisher method. Water content increased slightly in the light phase to approximately 35% after cycle 1 relative to the water content of the reduced-inorganic bio-oil feed (approximately 25%). Without wishing to be bound by theory, it is believed that this can be explained by esterification reactions and interactions with aldehydes with other functional groups such as acids, ketones and olefins as well as etherification reactions which may occur during Zone I stabilization.

[00173] The reduced-inorganic bio-oil (before Zone I) and the stabilized bio-oil (after Zone I) were also examined by ^1H NMR. **FIGs. 19A** and **19B** illustrate ^1H NMR spectroscopy data of the reduced-inorganic bio-oil and the stabilized bio-oil from 0-324 h TOS. **FIG. 19A** shows ^1H NMR overlay spectra from about 6 ppm to 13 ppm. The spectrum at TOS = 0 h was obtained from the reduced-inorganic bio-oil. The overlay spectra at TOS = 55-60 h, 106-112 h, 242-252 h, and 312-324 h were obtained from the stabilized bio-oil at the corresponding TOS. **FIG. 19B** shows ^1H NMR overlay spectra from 0 ppm to about 6 ppm. The spectrum at TOS = 0 h was obtained from the reduced-inorganic bio-oil. The overlay spectra at TOS = 55-60 h, 106-112 h, 242-252 h, and 312-324 h were obtained from the stabilized bio-oil at the corresponding TOS.

[00174] **FIGs. 20A** and **20B** illustrate data of the stabilized bio-oil from 466-478 h TOS with respect to the reduced inorganic bio-oil at TOS = 0 h. **FIG. 20A** shows ^1H NMR overlay spectra from about 6 ppm to 13 ppm. The spectrum at TOS = 0 h was obtained from the reduced-inorganic bio-oil. The overlay spectra at TOS = 466-478 h, 502-514 h, 676-700 h, 773-797 h, 820-844 h, 916-940 h, and 964-1010 h were obtained from the stabilized bio-oil at the corresponding TOS. **FIG. 20B** shows ^1H NMR overlay spectra from 0 ppm to about 6

ppm. The spectrum at TOS = 0 h was obtained from the reduced-inorganic bio-oil. The overlay spectra at TOS = 466-478 h, 502-514 h, 676-700 h, 773-797 h, 820-844 h, 916-940 h, and 964-1010 h were obtained from the stabilized bio-oil at the corresponding TOS. The ^1H NMR spectra indicated that Zone I treatment caused led to reduction of significant amounts of aldehyde and acid functional groups, partial hydrogenation of aromatics and olefins, and the appearance of new aliphatic compounds. These results indicate that esterification, etherification, and partial hydrogenation reactions were taking place during the Zone I stabilization/hydrotreatment. These reactions were more pronounced in the first 500 h and then decreased as TOS progressed. The disappearance in carboxylic acid resonances suggested that esterification reactions had occurred during Zone I treatment, though later reappearance of carboxylic acid resonances suggested that saponification of the esters may have occurred.

[00175] **FIG. 16A** displays the molar hydrogen/carbon ratio (H/C) of the stabilized bio-oil as function of TOS. The H/C ratio is corrected for the presence of methanol and water. The H/C ratio was higher than that of the reduced-inorganic bio-oil feed (1.1) but decreased with TOS suggesting continued catalyst deactivation. Even after 1,000 h TOS, the H/C ratio was at 1.4, significantly higher than that of the feed, indicating that the catalyst was still active.

[00176] **FIG. 16B** displays the Total Acidity Number, TAN (mg KOH/ gram of sample). The TAN was less than the feed stock even after 1,000 h TOS. However, the TAN increased with TOS reflecting deactivation of catalyst. The TAN of the stabilized bio-oil was still lower than that of the feed after 1,000 h TOS.

[00177] The results of this **EXAMPLE** indicate that Zone I processing effectively reduced aldehydes during over the 1,000 h TOS hydrotreatment operation. **FIG. 16A** shows that significant hydrogenation continued to occur, increasing the H/C ratio from 1.1 to 1.4, even at 1,000 h TOS. Moreover, **FIG. 14** shows that the pH of the stabilized bio-oil was fairly constant at about 3.5, relative to the pH of 2.4 for the reduced-inorganic bio-oil feed. **FIG. 16B** shows that the TAN of the product is still lower than the TAN of the feed. Although there is some indication of deactivation of the catalyst, these results show that the catalyst

was still effective at reducing the aldehydes in the reduced-inorganic bio-oil feed, in hydrogenation, and in reducing organic acids. The stabilized bio-oil produced in this **EXAMPLE** was collected and reserved for further use.

EXAMPLE 11: Production of Hydrocarbon Products by Hydrotreating Stabilized Bio-oil

[00178] The stabilized bio-oil produced in **EXAMPLE 10** was then treated in a second stage, Zone II hydrotreatment/cracking process hydrotreating using a sulfided CoMo catalyst. This **EXAMPLE** was conducted at about 310 °C under about 1,500 PSI of hydrogen. Further runs are contemplated in a temperature range of 280-340 °C under about 1160-1740 PSI of hydrogen.

[00179] In an initial run, the Zone II process was run for 200 h TOS was successfully finished in this quarter. **FIG. 17A** is a graph of the density of the hydrocarbon product of Zone II versus TOS. **FIG. 17A** shows that the density of the hydrocarbon product of Zone II increased during the first 60 h TOS and then was relatively constant from 60-200 h TOS. **FIG. 17B** shows that H₂ consumption was also constant during the run. Further runs using this same catalyst and another stabilized bio-oil sample effectively demonstrated about 1,400 h TOS.

[00180] To the extent that the term “includes” or “including” is used in the specification or the claims, it is intended to be inclusive in a manner similar to the term “comprising” as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term “or” is employed (e.g., A or B) it is intended to mean “A or B or both.” When the applicants intend to indicate “only A or B but not both” then the term “only A or B but not both” will be employed. Thus, use of the term “or” herein is the inclusive, and not the exclusive use. See Bryan A. Garner, *A Dictionary of Modern Legal Usage* 624 (2d. Ed. 1995). Also, to the extent that the terms “in” or “into” are used in the specification or the claims, it is intended to additionally mean “on” or “onto.” To the extent that the term “selectively” is used in the specification or the claims, it is intended to refer to a condition of a component wherein a user of the apparatus may activate or deactivate the feature or

function of the component as is necessary or desired in use of the apparatus. To the extent that the terms “operatively coupled” or “operatively connected” are used in the specification or the claims, it is intended to mean that the identified components are connected in a way to perform a designated function. To the extent that the term “substantially” is used in the specification or the claims, it is intended to mean that the identified components have the relation or qualities indicated with degree of error as would be acceptable in the subject industry.

[00181] As used in the specification and the claims, the singular forms “a,” “an,” and “the” include the plural unless the singular is expressly specified. For example, reference to “a compound” may include a mixture of two or more compounds, as well as a single compound.

[00182] As used herein, the term “about” in conjunction with a number is intended to include $\pm 10\%$ of the number. In other words, “about 10” may mean from 9 to 11.

[00183] As used herein, the terms “optional” and “optionally” mean that the subsequently described circumstance may or may not occur, so that the description includes instances where the circumstance occurs and instances where it does not.

[00184] As stated above, while the present application has been illustrated by the description of embodiments thereof, and while the embodiments have been described in considerable detail, it is not the intention of the applicants to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art, having the benefit of the present application. Therefore, the application, in its broader aspects, is not limited to the specific details, illustrative examples shown, or any apparatus referred to. Departures may be made from such details, examples, and apparatuses without departing from the spirit or scope of the general inventive concept.

[00185] The various aspects and embodiments disclosed herein are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.

CLAIMS

1. A method **200** for forming a stabilized bio-oil suitable for subsequent hydrotreatment, comprising:
 - 202** providing the bio-oil;
 - 204** filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers;
 - 206** treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil; and
 - 208** catalytically stabilizing the bio-oil,thereby providing the stabilized bio-oil suitable for subsequent hydrotreatment.
2. The method of claim 1, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil.
3. The method of claim 2, further comprising preparing the biomass prior to the pyrolyzing by selecting the biomass in a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters.
4. The method of claim 1, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil, the biomass being characterized by a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters.
5. The method of claim 1, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil at a temperature in °C of between about one or more of: 400 to 600, 400 to 550, and 450 to 500.
6. The method of claim 1, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil in a downflow reactor.
7. The method of claim 1:
 - providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor; and

filtering the bio-oil comprising in-line filtering the bio-oil vapor produced by the pyrolysis effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

8. The method of claim 1:

providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor and condensing the bio-oil vapor to provide the bio-oil in condensed form; and

filtering the bio-oil comprising in-line filtering the bio-oil in condensed form effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

9. The method of claim 1, filtering the bio-oil comprising removing at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

10. The method of claim 1, filtering the bio-oil comprising a first filtering process effective to remove at least a portion of the particles having an effective particulate diameter greater than about 10 micrometers.

11. The method of claim 10, filtering the bio-oil comprising a second filtering process effective to remove at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

12. The method of claim 10, filtering the bio-oil comprising a second filtering process conducted on the bio-oil offline from a pyrolysis process used to provide the bio-oil.

13. The method of claim 10, filtering the bio-oil comprising a second filtering process conducted using a pressure differential in pounds per square inch of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200.

14. The method of claim 10, filtering the bio-oil comprising a second filtering process conducted at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100.

15. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin.
16. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin in a fixed-bed column reactor or a slurry bed reactor.
17. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20.
18. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40.
19. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to one or more of: an ion exchange resin, a zeolite, and activated carbon.
20. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin comprising one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid).
21. The method of claim 1, the inorganic species comprising one or more of: Al, Ca, Na, K, Mg, Fe, P, Si, S, and Zn.
22. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising reducing the amount of one or more inorganic species in the bio-oil to a concentration in parts per million of less than one or more of about: 25, 20, 15, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1.
23. The method of claim 1, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising reducing a content or amount of each of Al, Ca,

Na, K, Mg, and Fe in the bio-oil to a corresponding concentration in parts per million of less than one or more of about: 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1.

24. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a metal dispersed on a solid support.

25. The method of claim 24, the metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

26. The method of claim 24, the solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

27. The method of claim 24, further comprising contacting the bio-oil to a diluting medium to form a diluted bio-oil, and catalytically stabilizing the bio-oil comprising contacting the diluted bio-oil to the stabilizing catalyst.

28. The method of claim 27, the diluting medium comprising one or more of: an organic solvent, a petroleum fuel, water, and a portion of the stabilized bio-oil.

29. The method of claim 28, the portion of the stabilized bio-oil comprising one or more of: a light phase of the stabilized bio-oil comprising water and a heavy phase of the stabilized bio-oil comprising the bio-oil.

30. The method of claim 28, further comprising removing at least a portion of the solvent comprising one or more of: the organic solvent, the petroleum fuel, and the water from the diluted bio-oil after catalytically stabilizing the diluted bio-oil.

31. The method of claim 28, the organic solvent comprising a protic organic solvent.

32. The method of claim 28, the organic solvent comprising one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, diethyl ether, acetonitrile, dimethyl formamide, and dimethylsulfoxide.

33. The method of claim 28, the petroleum fuel comprising one or more of: diesel, gasoline, kerosene, jet fuel, fuel oil, naphtha, fractions thereof, and combinations thereof.

34. The method of claim 27, contacting the bio-oil to the diluting medium comprising diluting the bio-oil to a percentage by weight of the diluting medium of about one or more of: 5 to 50, 10 to 45, 15 to 40, 20 to 35, 25 to 35, and 30.
35. The method of claim 27, comprising contacting the bio-oil to the diluting medium to form the diluted bio-oil using a positive pressure differential in pounds per square inch compared to atmospheric pressure of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 500, 1000, 1500, 1800, and 2000.
36. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a zeolite.
37. The method of claim 36, the zeolite comprising one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.
38. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising Ru/TiO₂.
39. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, and 170.
40. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.
41. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst in the presence of hydrogen.
42. The method of claim 41, catalytically stabilizing the bio-oil comprising providing a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500.
43. The method of claim 1, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹.

44. The method of claim 1, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst for a Time On Stream (TOS) in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.
45. The method of claim 1, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising rinsing the stabilizing catalyst with an organic solvent.
46. The method of claim 45, the organic solvent comprising a protic organic solvent.
47. The method of claim 45, the organic solvent comprising one or more of methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, acetonitrile, and dimethyl formamide.
48. The method of claim 1, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising contacting the stabilizing catalyst with hydrogen at a temperature in °C of about one or more of: 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400.
49. The method of claim 1, the stabilized bio-oil being characterized compared to the bio-oil by one or more of:
- a decreased content of aldehydes and free carboxylic acids;
 - an increase in pH of at least one or more of about: 0.25, 0.5, 0.75, 1, 1.25, and 1.5;
- and
- a percent increase in dry hydrogen:carbon ratio of one or more of about: 5, 10, 15, 20, and 25.
50. The method of claim 1, the bio-oil being characterized by one or more of: a density of about 1 to 1.2 grams per milliliter, a dry hydrogen:carbon ratio of about 1.4:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 30% to 45%.

51. The method of claim 1, the stabilized bio-oil being characterized by one or more of: a density of about 1 to 1.1 grams per milliliter, a dry hydrogen:carbon ratio of about 1.2:1 to 1.8:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 20% to 35%.

52. The method of claim 1, comprising one or more of: cooling the stabilized bio-oil prior to the subsequent hydrotreatment, insulating the stabilizing catalyst from heat of the subsequent hydrotreatment, and cooling the stabilizing catalyst against heat of the subsequent hydrotreatment.

53. The method of claim 1, comprising conveying the stabilized bio-oil directly from the catalytically stabilizing to the subsequent hydrotreatment.

54. The method of claim 1, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding at least the heavy phase directly from the catalytically stabilizing to the subsequent hydrotreatment.

55. The method of claim 1, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding the light phase and the heavy phase in parallel to the subsequent hydrotreatment.

56. The method of claim 55, further comprising controlling a ratio between the light phase and the heavy phase while feeding in parallel to the subsequent hydrotreatment, the ratio of light phase:heavy phase being between about 1:20 and 20:1.

57. The method of claim 1, further comprising conducting at least a portion of the method under an inert atmosphere.

58. The method of claim 1, further comprising conducting at least a portion of the method under an atmosphere comprising one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis.

59. A method **300** for forming a hydrocarbon product from a stabilized bio-oil, comprising:

302 providing the stabilized bio-oil, the stabilized bio-oil being characterized by one or more of: a total acid number (TAN) value less than 100 mg KOH/g; a water content

of at least about 17 wt.%; a hydrogen to carbon ratio greater than 1.4:1; and an average percentage of aldehyde and ketone groups of less than about 5%; and

304 hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the hydrocarbon product.

60. The method of claim 59, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen at a temperature in °C of about one or more of: 200 to 420, 220 to 400, 240 to 380, 260 to 360, 280 to 340, 300 to 320, and 310.

61. The method of claim 59, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

62. The method of claim 59, the hydrotreatment catalyst comprising one or more of: an active metal catalyst and a sulfided catalyst.

63. The method of claim 62 the sulfided catalyst comprising one or more of: sulfided: Ni, Nb, Mo, Co, W, NiMo, and CoMo.

64. The method of claim 62, the active metal catalyst comprising:

a solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, silica, a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, a Chabazite zeolite, and carbon; and

a metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

65. The method of claim 62, the active metal catalyst comprising one or more of Ru/TiO₂, Ru/TiO₂-ZSM5, Pd/C, Pd/SiO₂-Al₂O₃, Pd/Nb/Al₂O₃, Pd/Nb/TiO₂-SiO₂, Pt/ZrO₂-Al₂O₃, and Pd/Mg/Al₂O₃.

66. The method of claim 59, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of a substantial excess of

hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500.

67. The method of claim 59, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr^{-1} to 1 hr^{-1} .

68. The method of claim 59, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen for a Time On Stream (TOS) in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

69. The method of claim 59, the hydrocarbon product comprising a liquid fraction characterized compared to the stabilized bio-oil at 25°C and 1 atmosphere by one or more of:

one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% $\text{nC}_5\text{-C}_6$ alkanes, and about 2.4% olefins; and

one or more of: a density in grams/mL of 0.78-0.85; a total sulfur weight percent of less than 0.08%; a pour point in $^\circ\text{C}$ of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 2.1:1; and an energy value in mega Joules per kilogram of about 40 to 45..

70. The method of claim 59, the hydrocarbon product comprising a $\text{C}_1\text{-C}_4$ gas fraction.

71. The method of claim 59, the hydrocarbon product being characterized by one or more of: a density of about 0.8 to about 0.86 grams per milliliter, a hydrogen:carbon ratio of about 1.5:1 to about 2.2:1, a dry oxygen weight percentage of about 0% to about 5%, and a water weight percentage of about 0% to about 5%.

72. The method of claim 59, further comprising conducting at least a portion of the method under an inert atmosphere.

73. The method of claim 59, further comprising conducting at least a portion of the method under an atmosphere comprising one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis.

74. The method of claim 59, providing the stabilized bio-oil comprising:
providing a bio-oil;
filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers;
treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil; and
catalytically stabilizing the bio-oil,
thereby providing the stabilized bio-oil.
75. The method of claim 74, comprising one or more of: cooling the stabilized bio-oil prior to hydrotreating the stabilized bio-oil, insulating the stabilizing catalyst from heat of hydrotreating the stabilized bio-oil, and cooling the stabilizing catalyst against heat of hydrotreating the stabilized bio-oil.
76. The method of claim 74, comprising conveying the stabilized bio-oil directly from the catalytically stabilizing to the hydrotreating.
77. The method of claim 74, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding at least the heavy phase directly from the catalytically stabilizing to the hydrotreating.
78. The method of claim 74, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding the light phase and the heavy phase in parallel to the hydrotreating.
79. The method of claim 78, further comprising controlling a ratio between the light phase and the heavy phase while feeding in parallel to the hydrotreating, the ratio of light phase:heavy phase being between about 1:20 and 20:1.
80. The method of claim 74, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil.
81. The method of claim 74, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil, the biomass being characterized by a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters.

82. The method of claim 74, providing the bio-oil comprising pyrolyzing biomass in a downflow reactor to produce the bio-oil at a temperature in °C of between about one or more of: 400 to 600, 400 to 550, and 450 to 500.

83. The method of claim 74:

providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor; and

filtering the bio-oil comprising in-line filtering the bio-oil vapor produced by the pyrolysis effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

84. The method of claim 74:

providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor and condensing the bio-oil vapor to provide the bio-oil in condensed form; and

filtering the bio-oil comprising in-line filtering the bio-oil in condensed form effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

85. The method of claim 74, filtering the bio-oil comprising removing at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

86. The method of claim 74, filtering the bio-oil comprising:

a first filtering process effective to remove at least a portion of the particles having an effective particulate diameter greater than about 10 micrometers; and

a second filtering process effective to remove at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

87. The method of claim 86, the second filtering process conducted on the bio-oil offline from a pyrolysis process used to provide the bio-oil.

88. The method of claim 86, the second filtering process being conducted using a pressure differential in pounds per square inch of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200.
89. The method of claim 86, the second filtering process being conducted at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100.
90. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin.
91. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin in a fixed-bed column reactor or a slurry bed reactor.
92. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20.
93. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40.
94. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to one or more of: an ion exchange resin, a zeolite, and activated carbon.
95. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin comprising one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid).
96. The method of claim 74, the inorganic species comprising one or more of: Al, Ca, Na, K, Mg, Fe, P, Si, S, and Zn.
97. The method of claim 74, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising reducing the amount of one or more inorganic

species in the bio-oil to a concentration in parts per million of less than one or more of about: 25, 20, 15, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1.

98. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a metal dispersed on a solid support.

99. The method of claim 98, the metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

100. The method of claim 98, the solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

101. The method of claim 98, further comprising contacting the bio-oil to a diluting medium to form a diluted bio-oil, and catalytically stabilizing the bio-oil comprising contacting the diluted bio-oil to the stabilizing catalyst.

102. The method of claim 101, the diluting medium comprising one or more of: an organic solvent, a petroleum fuel, water, and a portion of the stabilized bio-oil.

103. The method of claim 102, the portion of the stabilized bio-oil comprising one or more of: a light phase of the stabilized bio-oil comprising water and a heavy phase of the stabilized bio-oil comprising the bio-oil.

104. The method of claim 102, the organic solvent comprising a protic organic solvent.

105. The method of claim 102, further comprising removing at least a portion of the one or more of: the organic solvent, the petroleum fuel, and the water from the diluted bio-oil after catalytically stabilizing the diluted bio-oil.

106. The method of claim 102, the organic solvent comprising one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, diethyl ether, acetonitrile, dimethyl formamide, and dimethylsulfoxide.

107. The method of claim 102, the petroleum fuel comprising one or more of: diesel, gasoline, kerosene, jet fuel, fuel oil, naptha, fractions thereof, and combinations thereof.

108. The method of claim 102, comprising contacting the bio-oil to the diluting medium comprising diluting the bio-oil to a percentage by weight of the diluting medium of about one or more of: 5 to 50, 10 to 45, 15 to 40, 20 to 35, 25 to 35, and 30.

109. The method of claim 101, comprising contacting the bio-oil to the diluting medium to form the diluted bio-oil using a positive pressure differential in pounds per square inch compared to atmospheric pressure of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 500, 1000, 1500, 1800, and 2000.

110. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a zeolite.

111. The method of claim 110, the zeolite comprising one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

112. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising Ru/TiO₂.

113. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, and 170.

114. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

115. The method of claim 4, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst in the presence of hydrogen.

116. The method of claim 115, catalytically stabilizing the bio-oil comprising providing a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500.

117. The method of claim 74, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹.

118. The method of claim 74, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

119. The method of claim 74, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising rinsing the stabilizing catalyst with an organic solvent.

120. The method of claim 119, the organic solvent comprising a protic organic solvent.

121. The method of claim 119, the organic solvent comprising one or more of methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, acetonitrile, and dimethyl formamide.

122. The method of claim 74, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising contacting the stabilizing catalyst with hydrogen at a temperature in °C of about one or more of: 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400.

123. The method of claim 74, the stabilized bio-oil being characterized compared to the bio-oil by one or more of:

a decreased content of aldehydes and free carboxylic acids;

an increase in pH of at least one or more of about: 0.25, 0.5, 0.75, 1, 1.25, and 1.5;

and

a percent increase in dry hydrogen:carbon ratio of one or more of about: 5, 10, 15, 20, and 25.

124. The method of claim 74, the bio-oil being characterized by one or more of: a density of about 1 to 1.2 grams per milliliter, a dry hydrogen:carbon ratio of about 1.4:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 30% to 45%.

125. The method of claim 59, the stabilized bio-oil being characterized by one or more of: a density of about 1 to 1.1 grams per milliliter, a dry hydrogen:carbon ratio of about 1.2:1 to 1.8:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 20% to 35%.

126. A method **350** for forming a hydrocarbon product from a bio-oil, comprising:

352 providing the bio-oil;

354 filtering the bio-oil effective to remove at least a portion of particles having an effective particulate diameter greater than about 10 micrometers;

356 treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil;

358 catalytically stabilizing the bio-oil to provide a stabilized bio-oil; and

360 hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of hydrogen, thereby providing the hydrocarbon product.

127. The method of claim 126, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen at a temperature in °C of about one or more of: 200 to 420, 220 to 400, 240 to 380, 260 to 360, 280 to 340, 300 to 320, and 310.

128. The method of claim 126, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

129. The method of claim 126, the hydrotreatment catalyst comprising one or more of: an active metal catalyst and a sulfided catalyst.

130. The method of claim 129 the sulfided catalyst comprising one or more of sulfided: Ni, Nb, Mo, Co, W, NiMo, and CoMo.

131. The method of claim 129, the active metal catalyst comprising:

a solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid,

molybdic acid, carbon, silica, a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, a Chabazite zeolite, and carbon; and

a metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

132. The method of claim 129, the active metal catalyst comprising one or more of Ru/TiO₂, Ru/TiO₂-ZSM5, Pd/C, Pd/SiO₂-Al₂O₃, Pd/Nb/Al₂O₃, Pd/Nb/TiO₂-SiO₂, Pt/ZrO₂-Al₂O₃, and Pd/Mg/Al₂O₃.

133. The method of claim 126, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to a hydrotreatment catalyst in the presence of a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500.

134. The method of claim 126, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹.

135. The method of claim 126, hydrotreating the stabilized bio-oil comprising contacting the stabilized bio-oil to the hydrotreatment catalyst in the presence of hydrogen for a Time On Stream (TOS) in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

136. The method of claim 126, the hydrocarbon product comprising a liquid fraction characterized compared to the stabilized bio-oil at 25 °C and 1 atmosphere by one or more of:

one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% nC₅-C₆ alkanes, and about 2.4% olefins; and

one or more of: a density in grams/mL of 0.78-0.85; a total sulfur weight percent of less than 0.08%; a pour point in °C of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 2.1:1; and an energy value in mega Joules per kilogram of about 40 to 45..

137. The method of claim 126, the hydrocarbon product comprising a C₁-C₄ gas fraction.

138. The method of claim 126, the hydrocarbon product being characterized by one or more of: a density of about 0.8 to about 0.86 grams per milliliter, a hydrogen:carbon ratio of about 1.5:1 to about 2.2:1, a dry oxygen weight percentage of about 0% to about 5%, and a water weight percentage of about 0% to about 5%..

139. The method of claim 126, further comprising conducting at least a portion of the method under an inert atmosphere.

140. The method of claim 126, further comprising conducting at least a portion of the method under an atmosphere comprising one or more of: nitrogen, carbon dioxide, and a non-condensable gas product of biomass pyrolysis.

141. The method of claim 126, comprising one or more of: cooling the stabilized bio-oil prior to hydrotreating the stabilized bio-oil, insulating the stabilizing catalyst from heat of hydrotreating the stabilized bio-oil, and cooling the stabilizing catalyst against heat of hydrotreating the stabilized bio-oil.

142. The method of claim 126, comprising conveying the stabilized bio-oil directly from the catalytically stabilizing to the hydrotreating.

143. The method of claim 126, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding at least the heavy phase directly from the catalytically stabilizing to the hydrotreating.

144. The method of claim 126, the stabilized bio-oil comprising one or more of a light phase and a heavy phase, further comprising feeding the light phase and the heavy phase in parallel to the hydrotreating.

145. The method of claim 144, further comprising controlling a ratio between the light phase and the heavy phase while feeding in parallel to the hydrotreating, the ratio of light phase:heavy phase being between about 1:20 and 20:1.

146. The method of claim 126, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil.

147. The method of claim 126, providing the bio-oil comprising pyrolyzing biomass to produce the bio-oil, the biomass being characterized by a particulate diameter distribution of between about 0.5 millimeters and about 5 millimeters.

148. The method of claim 126, providing the bio-oil comprising pyrolyzing biomass in a downflow reactor to produce the bio-oil at a temperature in °C of between about one or more of: 400 to 600, 400 to 550, and 450 to 500.

149. The method of claim 126:

providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor; and

filtering the bio-oil comprising in-line filtering the bio-oil vapor produced by the pyrolysis effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

150. The method of claim 126:

providing the bio-oil comprising pyrolyzing the biomass in a downflow reactor to produce a bio-oil vapor and condensing the bio-oil vapor to provide the bio-oil in condensed form; and

filtering the bio-oil comprising in-line filtering the bio-oil in condensed form effective to remove at least a portion of the particles having the effective particulate diameter greater than about 10 micrometers.

151. The method of claim 126, filtering the bio-oil comprising removing at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

152. The method of claim 126, filtering the bio-oil comprising:

a first filtering process effective to remove at least a portion of the particles having an effective particulate diameter greater than about 10 micrometers; and

a second filtering process effective to remove at least a portion of the particles having an effective particulate diameter in micrometers greater than one or more of about: 5, 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

153. The method of claim 152, the second filtering process conducted on the bio-oil offline from a pyrolysis process used to provide the bio-oil.

154. The method of claim 152, the second filtering process being conducted using a pressure differential in pounds per square inch of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200.

155. The method of claim 152, the second filtering process being conducted at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100.

156. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin.

157. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin in a fixed-bed column reactor or a slurry bed reactor.

158. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20.

159. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40.

160. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to one or more of: an ion exchange resin, a zeolite, and activated carbon.

161. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising contacting the bio-oil to an ion exchange resin comprising one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid).

162. The method of claim 126, the inorganic species comprising one or more of: Al, Ca, Na, K, Mg, Fe, P, Si, S, and Zn.

163. The method of claim 126, treating the bio-oil effective to remove at least a portion of inorganic species from the bio-oil comprising reducing one or more inorganic species in the bio-oil to a concentration in parts per million of less than one or more of about: 25, 20, 15, 10, 9, 8, 7, 6, 5, 4, 3, 2, and 1.

164. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a metal dispersed on a solid support.

165. The method of claim 164, the metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

166. The method of claim 164, the solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica.

167. The method of claim 164, further comprising contacting the bio-oil to a diluting medium to form a diluted bio-oil, and catalytically stabilizing the bio-oil comprising contacting the diluted bio-oil to the stabilizing catalyst.

168. The method of claim 167, the diluting medium comprising one or more of: an organic solvent, a petroleum fuel, water, and a portion of the stabilized bio-oil.

169. The method of claim 168, the portion of the stabilized bio-oil comprising one or more of: a light phase of the stabilized bio-oil comprising water and a heavy phase of the stabilized bio-oil comprising the bio-oil.

170. The method of claim 168, the organic solvent comprising a protic organic solvent.

171. The method of claim 168, further comprising removing at least a portion of one or more of: the organic solvent, the petroleum fuel, and the water from the diluted bio-oil after catalytically stabilizing the diluted bio-oil.

172. The method of claim 168, the organic solvent comprising one or more of: methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, diethyl ether, acetonitrile, dimethyl formamide, and dimethylsulfoxide.

173. The method of claim 168, the petroleum fuel comprising one or more of: diesel, gasoline, kerosene, jet fuel, fuel oil, naphtha, fractions thereof, and combinations thereof.

174. The method of claim 168, comprising contacting the bio-oil to the diluting medium comprising diluting the bio-oil to a percentage by weight of the diluting medium of about one or more of: 5 to 50, 10 to 45, 15 to 40, 20 to 35, 25 to 35, and 30.

175. The method of claim 167, comprising contacting the bio-oil to the diluting medium to form the diluted bio-oil using a positive pressure differential in pounds per square inch compared to atmospheric pressure of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 500, 1000, 1500, 1800, and 2000.

176. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising a zeolite.

177. The method of claim 176, the zeolite comprising one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.

178. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst comprising Ru/TiO₂.

179. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, and 170.

180. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

181. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst in the presence of hydrogen.

182. The method of claim 181, catalytically stabilizing the bio-oil comprising providing a substantial excess of hydrogen at a pressure in pounds per square inch gauge of one or more of: 100 to 2000, 500 to 1800, and 1000 to 1500.

183. The method of claim 126, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst at a liquid hourly space velocity (LHSV) of between about 0.05 hr^{-1} to 1 hr^{-1} .

184. The method of claim 126, catalytically stabilizing the bio-oil comprising contacting the bio-oil to a stabilizing catalyst for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

185. The method of claim 126, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising: rinsing the stabilizing catalyst with an organic solvent.

186. The method of claim 126, the organic solvent comprising a protic organic solvent.

187. The method of claim 186, the organic solvent comprising one or more of methanol, ethanol, 2-propanol, n-butanol, sec-butanol, *tert*-butanol, pentanol, hexanol, methyl cyclohexanol, acetone, methyl ethyl ketone, butanone, ethyl acetate, tetrahydrofuran, methyl *tert*-butyl ether, acetonitrile, and dimethyl formamide.

188. The method of claim 126, catalytically stabilizing the bio-oil comprising flowing the bio-oil past a stabilizing catalyst, the method further comprising regenerating the stabilizing catalyst comprising contacting the stabilizing catalyst with hydrogen at a temperature in °C of about one or more of: 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400.

189. The method of claim 126, the stabilized bio-oil being characterized compared to the bio-oil by one or more of:

a decreased content of aldehydes and free carboxylic acids;

an increase in pH of at least one or more of about: 0.25, 0.5, 0.75, 1, 1.25, and 1.5;

and

a percent increase in dry hydrogen:carbon ratio of one or more of about: 5, 10, 15, 20, and 25.

190. The method of claim 126, the bio-oil being characterized by one or more of: a density of about 1 to 1.2 grams per milliliter, a dry hydrogen:carbon ratio of about 1.4:1, a dry

oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 30% to 45%.

191. The method of claim 126, the stabilized bio-oil being characterized by one or more of: a density of about 1 to 1.1 grams per milliliter, a dry hydrogen:carbon ratio of about 1.2:1 to 1.8:1, a dry oxygen weight percentage of about 20% to 35%, and a water weight percentage of about 20% to 35%.

192. A system **400** for forming a hydrocarbon product from biomass, comprising:

a pyrolysis reactor **402** configured to pyrolyze a biomass input and provide a bio-oil output;

an inline filter **404** operatively coupled to receive the bio-oil output and configured to remove at least a portion of particles having an effective diameter greater than about 10 micrometers from the bio-oil output to provide a coarse-filtered bio-oil output;

a fine filtration module **406** configured to receive the coarse-filtered bio-oil output and remove at least a portion of particles having an effective diameter greater than about 5 micrometers to provide a fine-filtered bio-oil output;

a bed **408** effective to receive the fine-filtered bio-oil, and remove at least a portion of inorganic species from the fine filtered bio-oil to produce a reduced-inorganic bio-oil output, the bed **408** being configured to contain one or more of: an ion exchange resin, a zeolite, and activated carbon;

a first catalytic unit **410** configured to contain a stabilizing catalyst effective to receive the reduced-inorganic bio-oil, and to stabilize the reduced-inorganic bio-oil to produce a stabilized bio-oil output;

a second catalytic unit **412** configured to contain a hydrotreatment catalyst effective to receive the stabilized bio-oil, and to hydrotreat the stabilized bio-oil to provide a hydrocarbon output; and

a hydrogen source **414** operatively coupled to provide hydrogen to one or more of the first catalytic unit **410** and the second catalytic unit **412**.

193. The system of claim 192, the pyrolysis reactor **402** comprising a downflow pyrolysis reactor.
194. The system of claim 192, the pyrolysis reactor **402** being configured to heat to a temperature in °C of at least about one or more of: 400 to 600, 400 to 550, and 450 to 500.
195. The system of claim 192, further comprising a condenser module **416**.
196. The system of claim 195, the condenser module **416** comprising a three-stage condenser.
197. The system of claim 195, the condenser module **416** comprising an electrostatic precipitator.
198. The system of claim 195, the condenser module **416** being operatively coupled between the pyrolysis reactor **402** and the inline filter **404** such that the inline filter **404** is configured to receive the bio-oil output in condensed form from the condenser module **416**.
199. The system of claim 192, the inline filter **404** being directly coupled to the pyrolysis reactor **402** such that the inline filter **404** is configured to receive the bio-oil output in vapor form from the pyrolysis reactor **402**.
200. The system of claim 192, the inline filter **404** comprising one or more of: a bag filter element, a metal mesh filter element, and a ceramic filter element.
201. The system of claim 192, the inline filter **404** being configured to remove at least a portion of particles having a diameter in micrometers greater than one or more of about: 10, 9, 8, 7, 6, 5, 4, and 2.
202. The system of claim 192, the fine filtration module **406** being a stand-alone unit.
203. The system of claim 192, the fine filtration module **406** operatively coupling the inline filter **404** and the bed **408** such that the fine filtration module **406** is configured for inline operation.
204. The system of claim 192, the fine filtration module **406** being configured to remove at least a portion of particles having a diameter in micrometers greater than one or more of about: 4, 3, 2.5, 2, 1.5, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1.

205. The system of claim 192, the fine filtration module **406** comprising one or more of: a bag filter element, a metal mesh filter element, and a ceramic filter element.
206. The system of claim 192, the fine filtration module **406** being operatively coupled to a pressure source **406A** configured to operate the fine filtration module **406** using a pressure differential in pounds per square inch of at least about one or more of: 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, and 200.
207. The system of claim 192, the fine filtration module **406** being operatively coupled to a heat source **406B** configured to operate the fine filtration module **406** at a temperature in °C of at least about one or more of: 30, 40, 50, 60, 70, 80, 90, and 100.
208. The system of claim 192, the bed **408** being configured in the form of a fixed-bed column reactor or a slurry bed reactor.
209. The system of claim 192, the bed **408** comprising the ion exchange resin.
210. The system of claim 192, the bed **408** being operatively coupled to a pressure source **408A** configured to operate the bed **408** at a pressure in pounds per square inch gauge (PSIG) of about one or more of: 0 to 100, 10 to 100, 10 to 75, 10 to 50, 10 to 25, and 10 to 20.
211. The system of claim 192, the bed **408** being operatively coupled to a heat source **408B** configured to operate the bed **408** at a temperature in °C of about one or more of: 25 to 100, 25 to 75, 30 to 50, 35 to 45, and 40.
212. The system of claim 192, the bed **408** comprising the ion exchange resin comprising one or more of: a poly(styrene sulfonic acid), a poly(styrene carboxylic acid), and a poly(2-acrylamido-2-methyl-1-propanesulfonic acid).
213. The system of claim 192, the first catalytic unit **410** comprising the stabilizing catalyst comprising a metal dispersed on a solid support.
214. The system of claim 213, the metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.
215. The system of claim 213, the solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, and silica

216. The system of claim 192, the first catalytic unit **410** comprising the stabilizing catalyst comprising a zeolite.
217. The system of claim 216, the zeolite comprising one or more of: a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, and a Chabazite zeolite.
218. The system of claim 192, the first catalytic unit **410** comprising the stabilizing catalyst comprising Ru/TiO₂.
219. The system of claim 192, the first catalytic unit **410** being operatively coupled to a pressure source **410A** configured to operate the first catalytic unit **410** at a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.
220. The system of claim 192, the first catalytic unit **410** being operatively coupled to a heat source **410B** configured to operate the first catalytic unit **410** at a temperature in °C of about one or more of: 40 to 300, 100 to 280, 120 to 270, 130 to 250, 140 to 225, 150 to 200, 160 to 180, 170, 250 to 550, 300 to 500, 325 to 475, 350 to 450, 375 to 425, and 400.
221. The system of claim 192, the first catalytic unit **410** being configured to operate at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹.
222. The system of claim 192, the first catalytic unit **410** being configured to operate for a Time On Stream (TOS) in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.
223. The system of claim 192, the first catalytic unit **410** being operatively coupled to an organic solvent source **410C**.
224. The system of claim 192, further comprising a heat exchanger **418** operatively coupled between the first catalytic unit **410** and the second catalytic unit **412**, the heat exchanger **418** being configured to actively or passively limit heating of the first catalytic unit **410** by heat from the second catalytic unit **412**.

225. The system of claim 192, the hydrotreatment catalyst comprising one or more of: an active metal catalyst and a sulfided catalyst.

226. The system of claim 225, the sulfided catalyst comprising one or more of sulfided: Ni, Nb, Mo, Co, W, NiMo, and CoMo.

227. The system of claim 225, the active metal catalyst comprising:

a solid support comprising one or more of: titania, ceria, magnesium oxide, niobium oxide, alumina, amorphous silica alumina, zirconia, zinc oxide, niobic acid, tungstic acid, molybdic acid, carbon, silica, a Y zeolite, a Beta zeolite, a ZSM-5 zeolite, a Mordenite zeolite, a Ferrierite zeolite, a Al-MCM-41 zeolite, a MCM-48 zeolite, a MCM-22 zeolite, a SAPO-34 zeolite, a Chabazite zeolite, and carbon; and

a metal comprising one or more of: Ru, Rh, Re, Pt, Pd, Ir, Au, Fe, Ni, Nb, and Os.

228. The system of claim 225, the active metal catalyst comprising one or more of Ru/TiO₂, Ru/TiO₂-ZSM5, Pd/C, Pd/SiO₂-Al₂O₃, Pd/Nb/Al₂O₃, Pd/Nb/TiO₂-SiO₂, Pt/ZrO₂-Al₂O₃, and Pd/Mg/Al₂O₃.

229. The system of claim 192, the second catalytic unit **412** comprising a pressure source **412A** configured to pressurize the second catalytic unit **412** to a pressure in PSI of about one or more of: 500 to 2500, 750 to 2250, 1000 to 2000, 1250 to 1750, 1400 to 1600, and 1500.

230. The system of claim 192, the second catalytic unit **412** comprising a heat source **412B** configured to heat the second catalytic unit **412** to a temperature in °C of about one or more of: 200 to 420, 220 to 400, 240 to 380, 260 to 360, 280 to 340, 300 to 320, and 310.

231. The system of claim 192, the second catalytic unit **412** being configured to operate at a liquid hourly space velocity (LHSV) of between about 0.05 hr⁻¹ to 1 hr⁻¹.

232. The system of claim 192, the second catalytic unit **412** being configured to operate for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

233. The system of claim 192, further comprising an inert gas source **420** operatively coupled to provide an inert atmosphere to at least a portion of system **400**.

234. The system of claim 192, the pyrolysis reactor **402**, the inline filter **404**, the fine filtration module **406**, the bed **408**, the first catalytic unit **410**, and the second catalytic unit **412** being operatively coupled to provide a continuous process for converting the biomass input to the hydrocarbon output.

235. The system of claim 234, being configured to operate for a TOS in hours of at least about one or more of: 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,750, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 12,000, and 16,000.

236. A stabilized bio-oil, characterized by one or more of: a total acid number (TAN) value less than 100 mg KOH/g; a water content of at least about 17 wt.%; a hydrogen to carbon ratio greater than 1.4:1; and an average percentage of aldehyde and ketone groups of less than about 5%.

237. A stabilized bio-oil, prepared according to any of claims 1-58.

238. A hydrocarbon product derived from bio-oil, characterized by one or more of:

one or more percentages by weight of: about 24% paraffin, about 5.6% aromatics, about 8.6% naphthalenes, about 59% nC₅-C₆ alkanes, and about 2.4% olefins; and

one or more of: a density in grams/mL of 0.78-0.86; a total sulfur weight percent of less than 0.08%; a pour point in °C of less than about 20; a viscosity in cPs of less than 2; a hydrogen:carbon atomic ratio of about 1.5:1 to about 2.2:1; and an energy value in mega Joules per kilogram of about 40 to 45.

239. The hydrocarbon product of claim 238, the hydrocarbon product being characterized by one or more of: a density of about 0.8 to about 0.86 grams per milliliter, a hydrogen:carbon ratio of about 1.5:1 to about 2.2:1, a dry oxygen weight percentage of about 0% to about 5%, and a water weight percentage of about 0% to about 5%.

240. A hydrocarbon product derived from bio-oil, prepared according to any of claims 59-191.

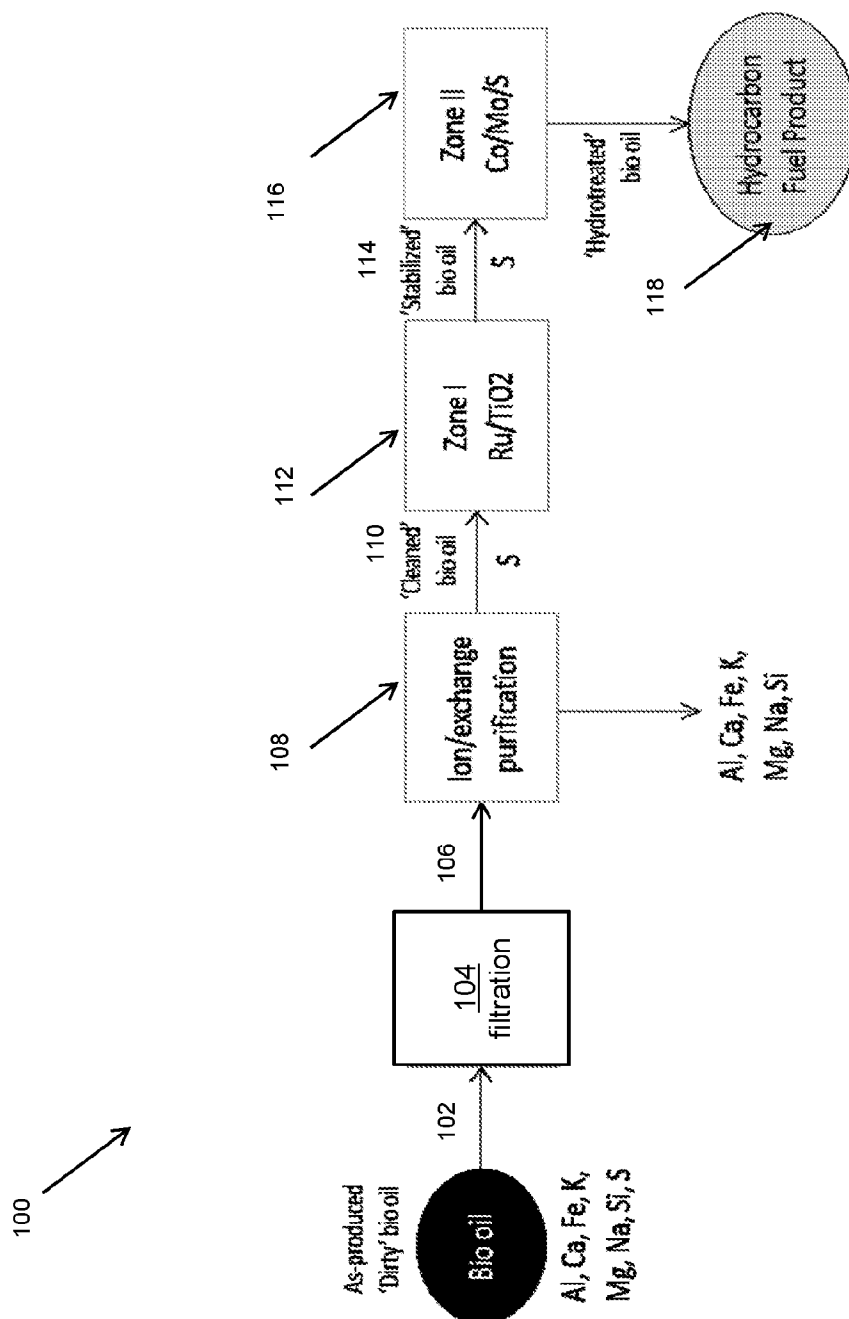
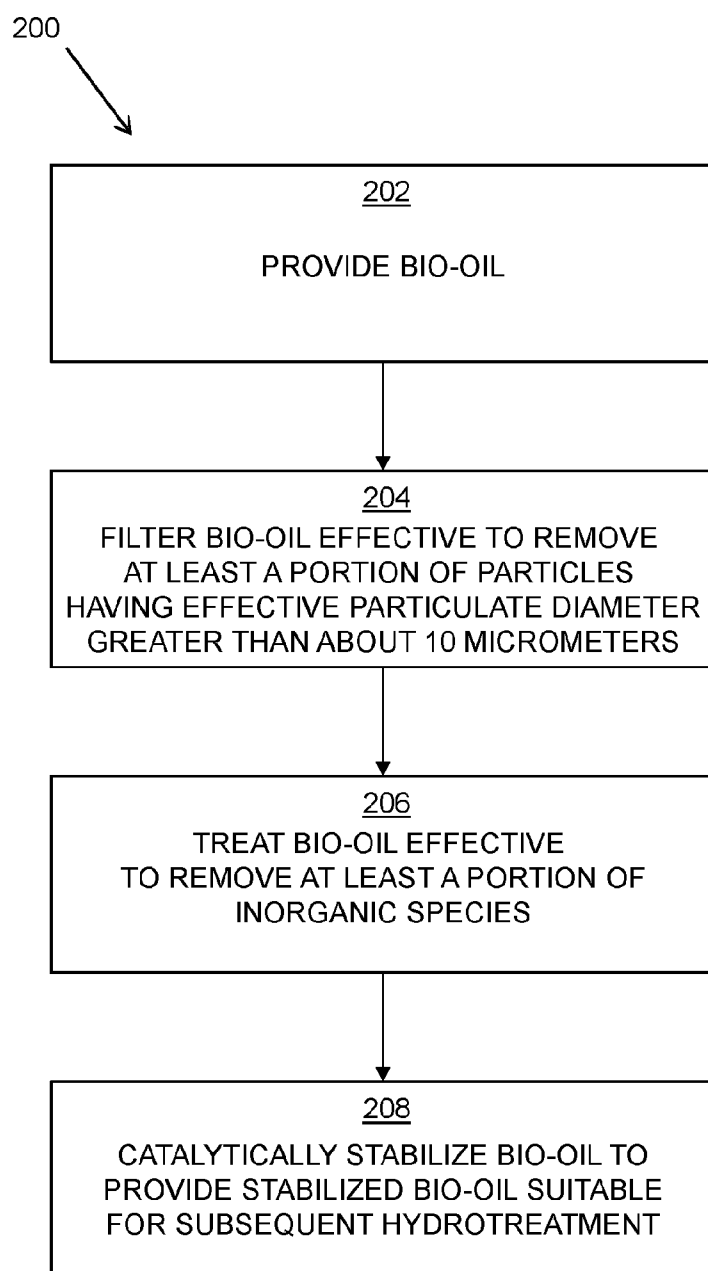
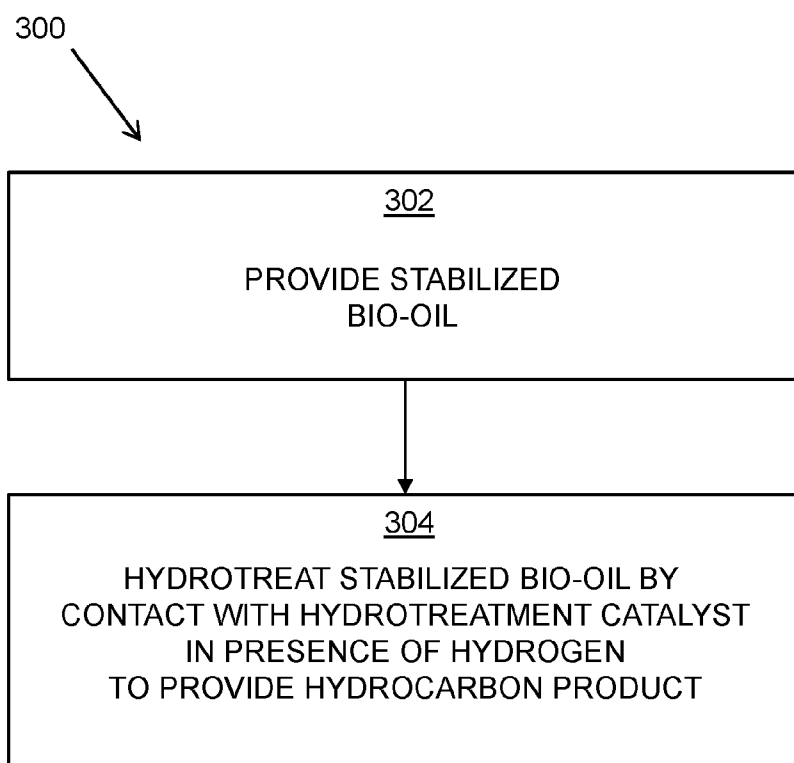


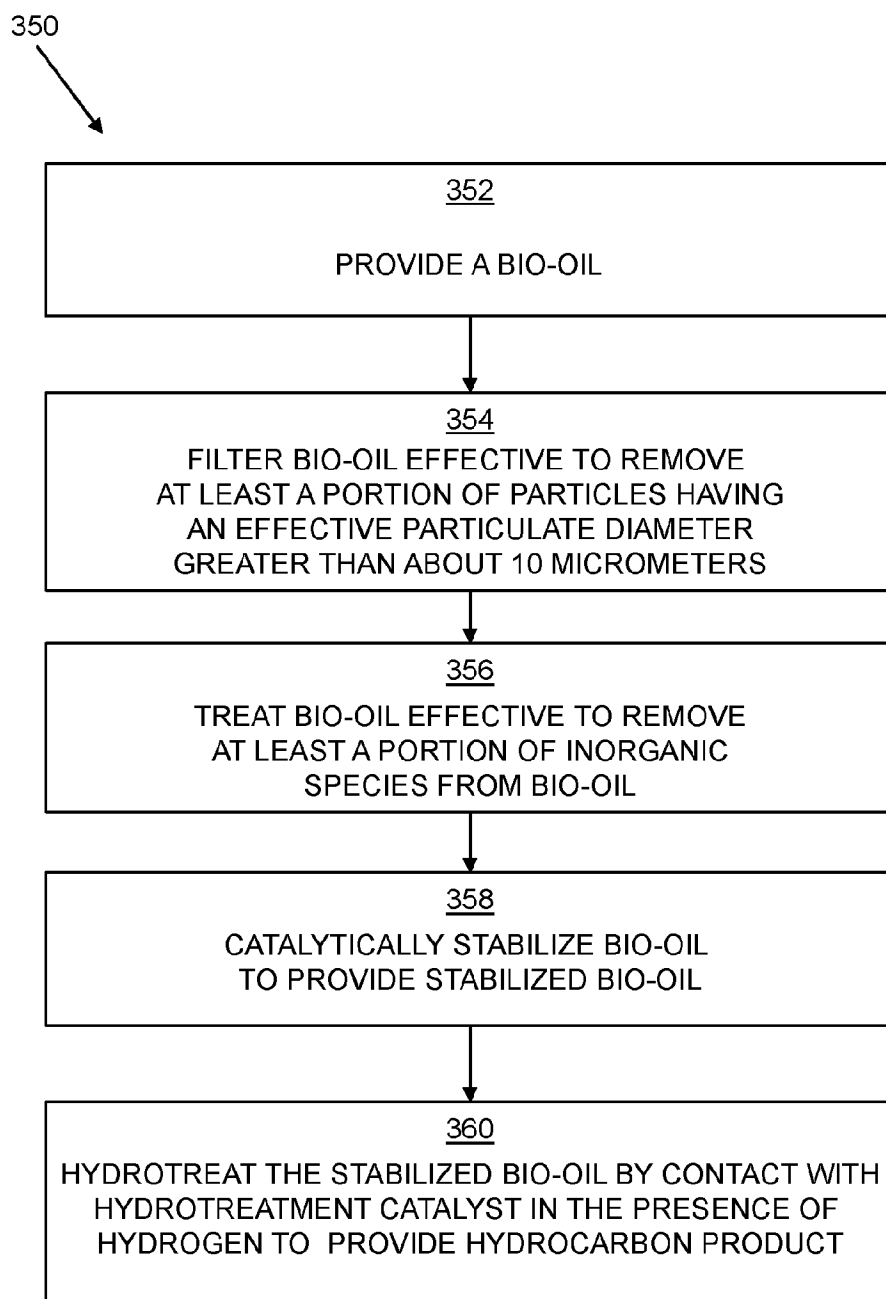
FIG. 1

**FIG. 2**

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**FIG. 3A**

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**FIG. 3B**

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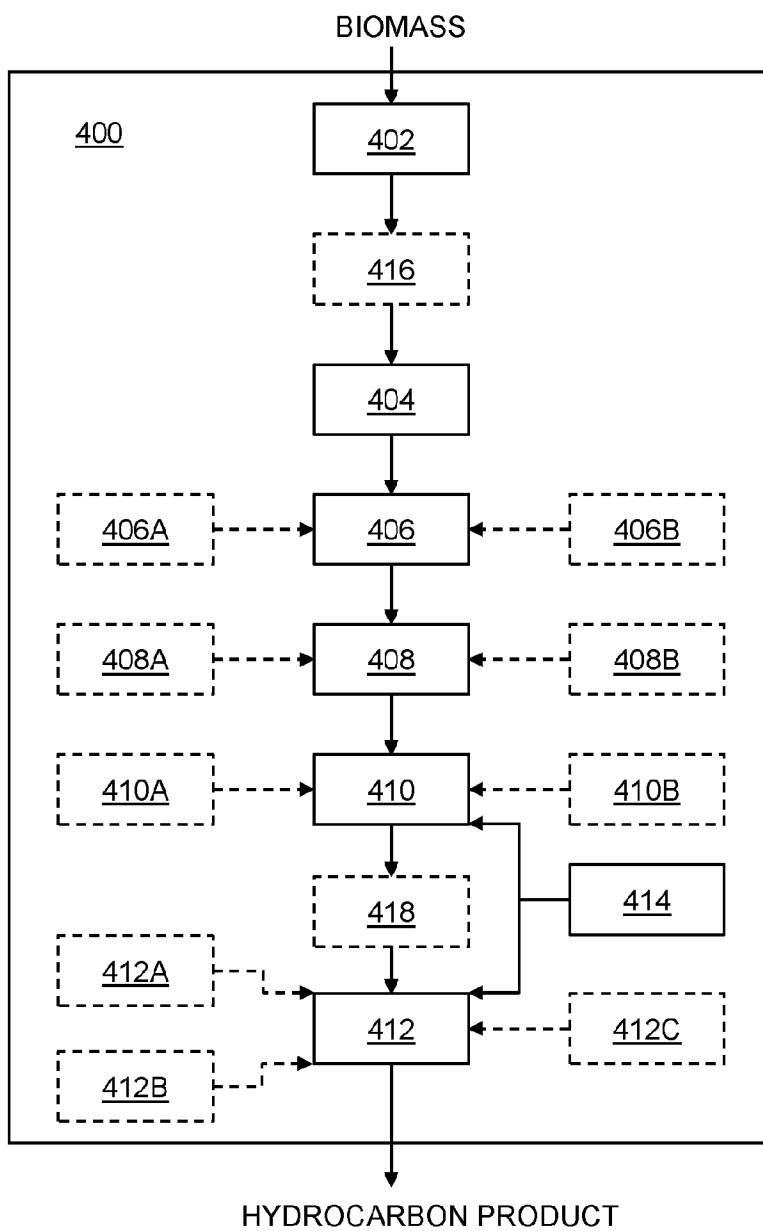


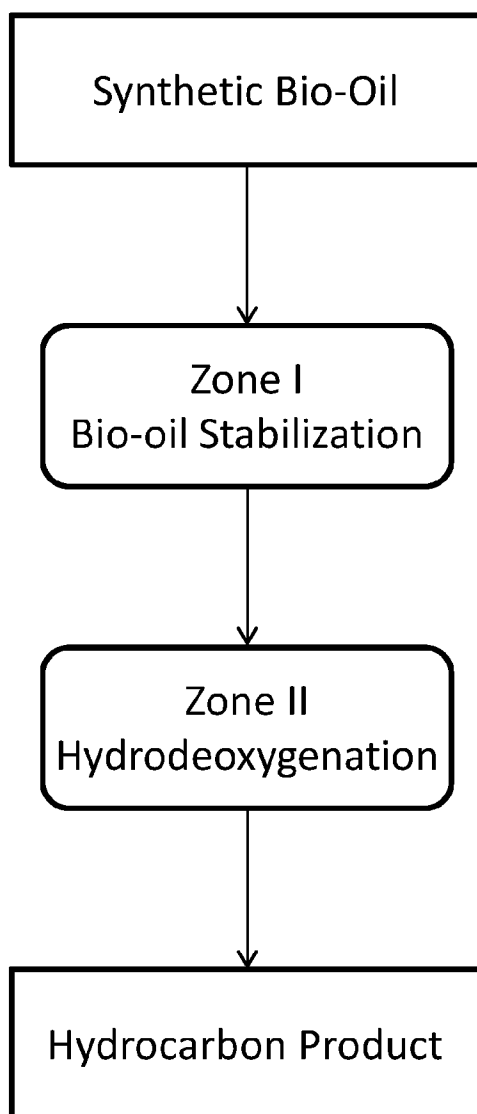
FIG. 4

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	ASTM D6349	ASTM D5185	Preparation
	Pyrolysis bio-oil (ppm)	Synthetic bio-oil (ppm)	Synthetic bio-oil (ppm)
Aluminum	161	186	101
Antimony	<3		
Arsenic	<5		
Barium	<1		
Beryllium	<1		
Cadmium			
Calcium	84	113	52
Chromium	27		
Cobalt	<1		
Copper	4		
Iron	130	117	49
Lead	<5		
Lithium	<3		
Magnesium	17	101	49
Manganese	6		
Molybdenum	<3		
Nickel	14		
Phosphorus	48	72	99
Potassium	29	103	148
Selenium	<3		
Silicon	699		
Sodium	13	63	287
Strontium	<1		
Tin	3		
Titanium	6		
Vanadium	<1		
Zinc	18	58	50
Zirconium	<3		
Sulfur	50	6	50
Total	1309	819	855

FIG. 5

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**FIG. 6A**

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Parameter	Conditions
Catalyst Zone I	Ru/TiO ₂
Temperature Zone I	100-280 °C
Catalyst Zone II	Ru/TiO ₂ – ZSM5
Temperature Zone II	100-280 °C
Catalyst Volume	approx. 15 mL
Bio-oil LHSV	0.2-0.4 h ⁻¹
H ₂ :Bio-oil volume ratio	4000
Total Pressure	1200 psig
Sample Collection	Every 4-8 h
Product Analysis	H ₂ O content, density, pH

FIG. 6B

Entry	TOS (h)	Zone I Temp (°C)	Zone II Temp (°C)	H ₂ flow (mL/min)	LHSV (h ⁻¹)	Organic Phase Yield (% wt)	Water in aq. Phase (%)
1	0-40	150	280	400	0.2	<1	(%)
2	40-48	150	280	600	0.4	<1	96
3	48-60	150	150	600	0.4	<1	32
4	60-170	200	200	600	0.4	58	94

FIG. 6C

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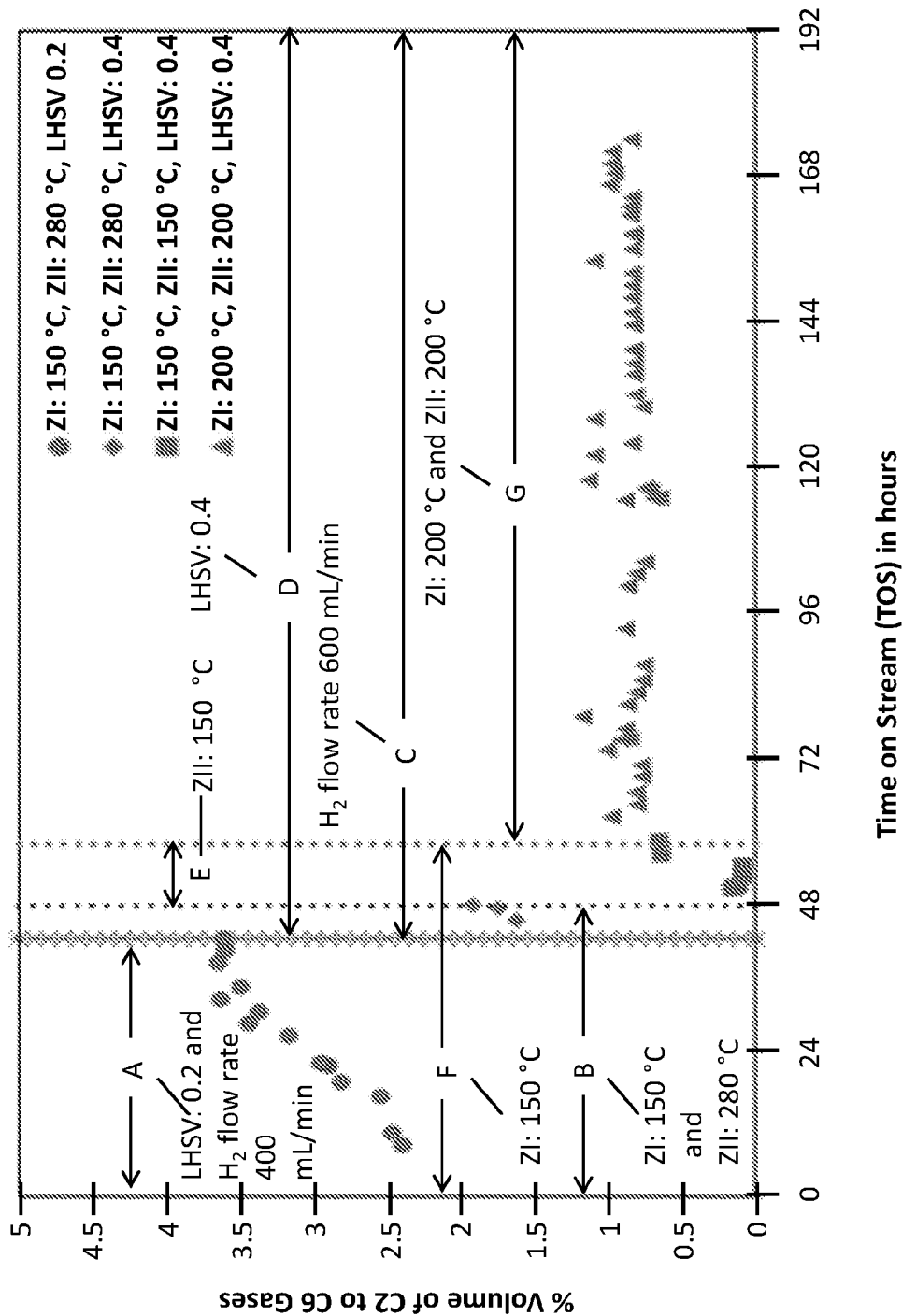


FIG. 6D

SUBSTITUTE SHEET (RULE 26)

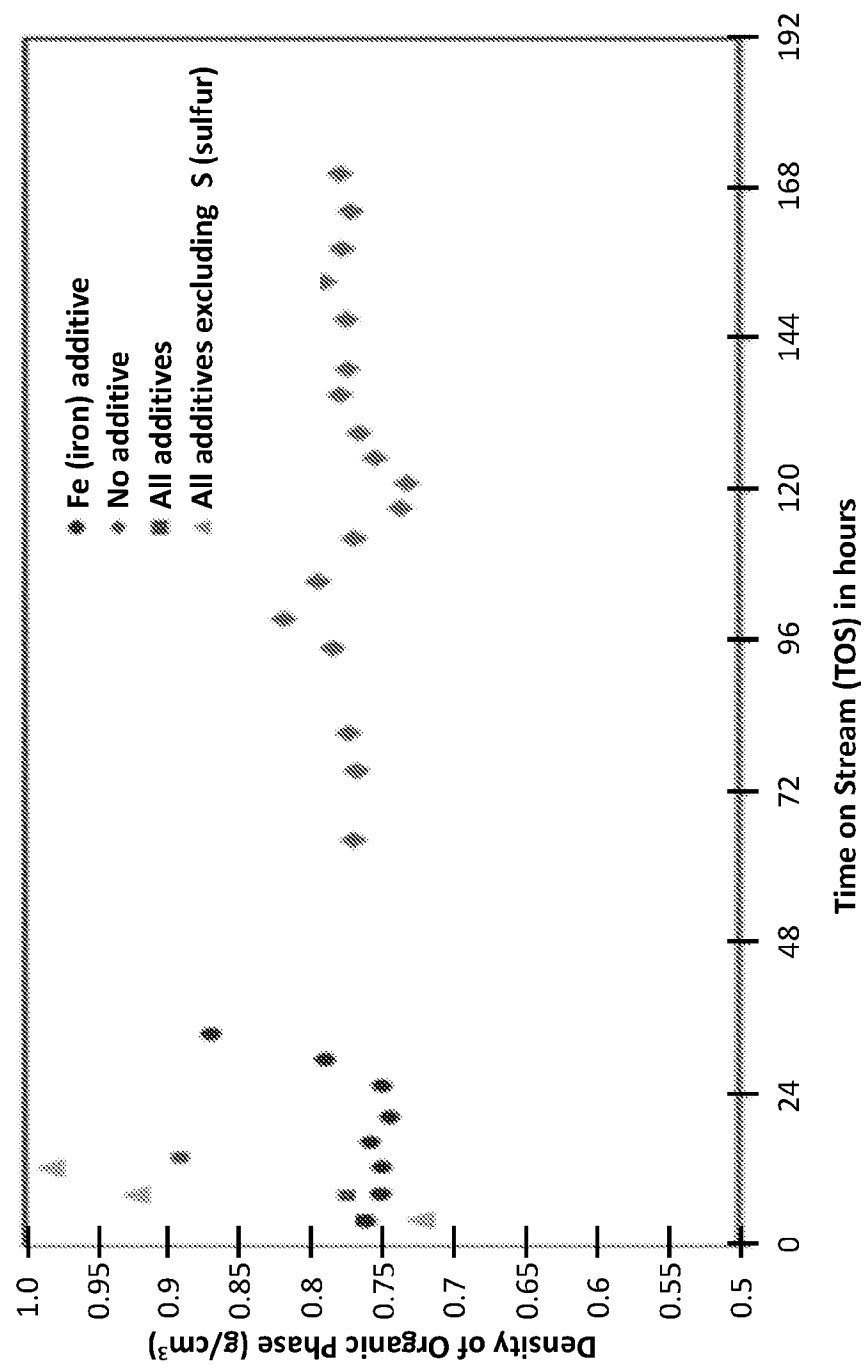


FIG. 6E

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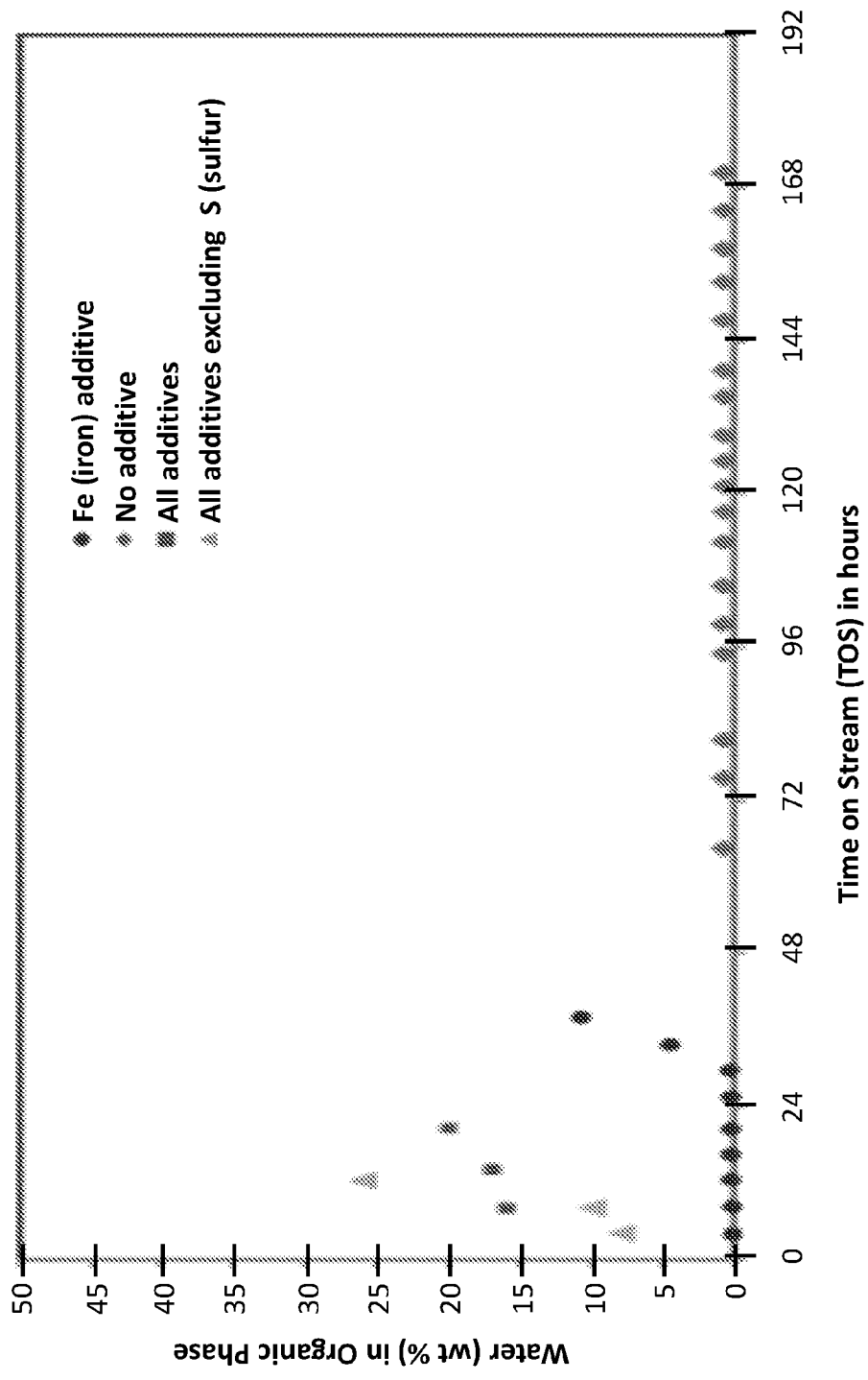


FIG. 6F

SUBSTITUTE SHEET (RULE 26)

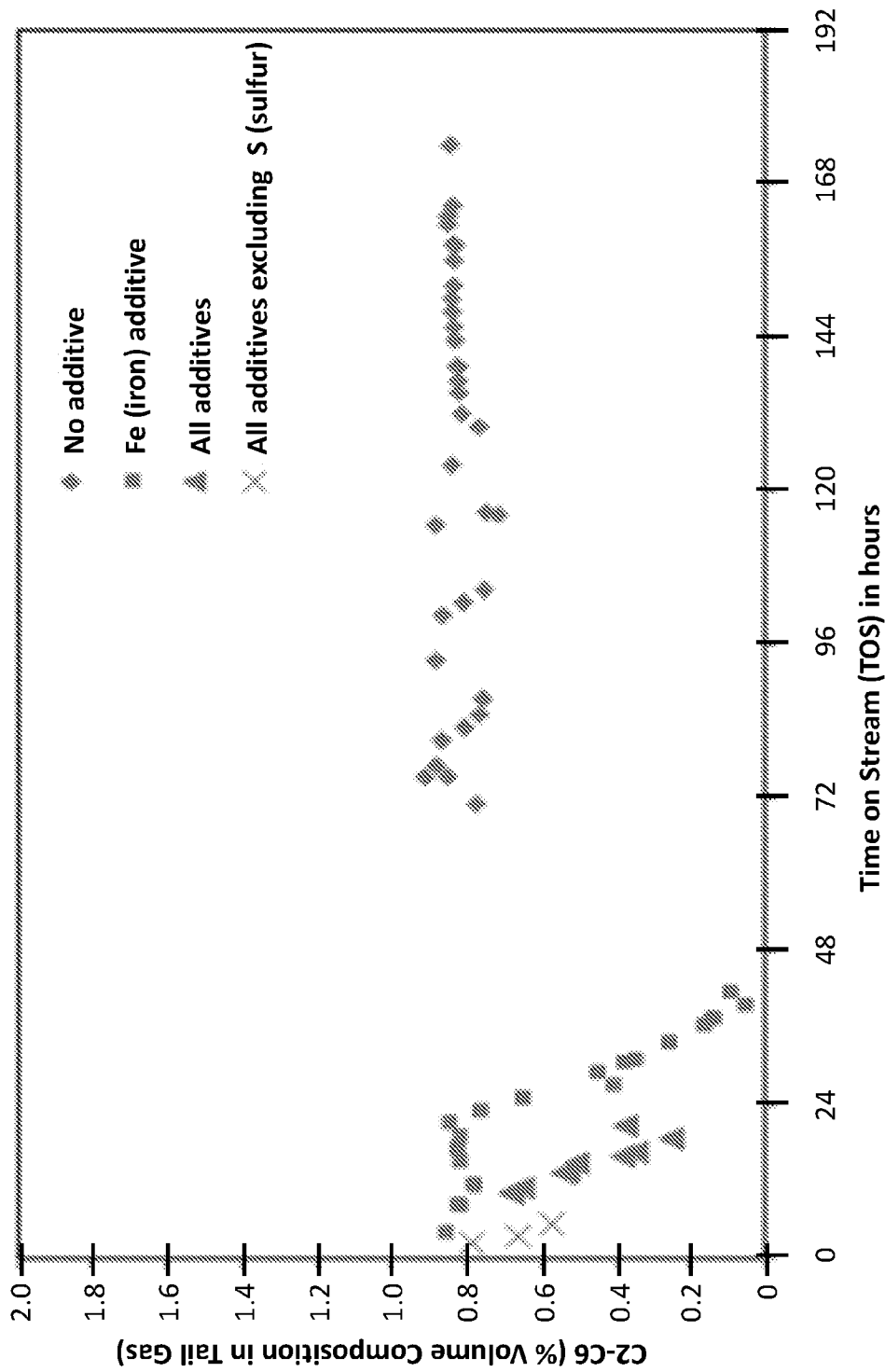
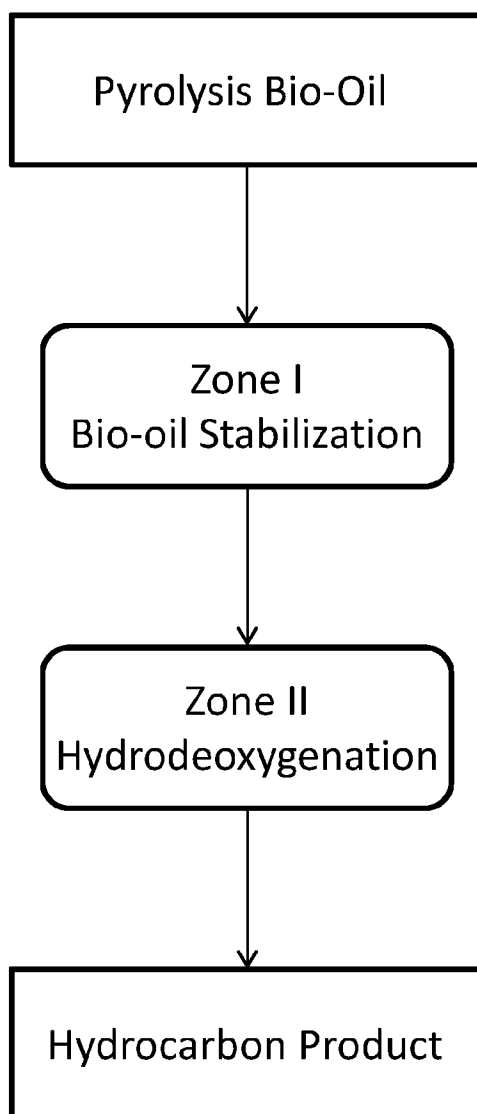


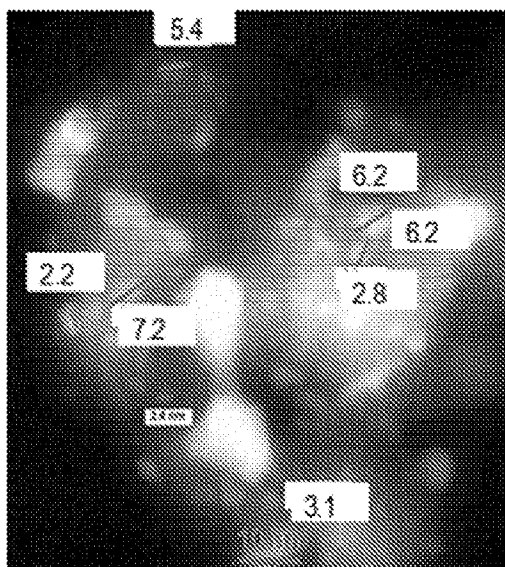
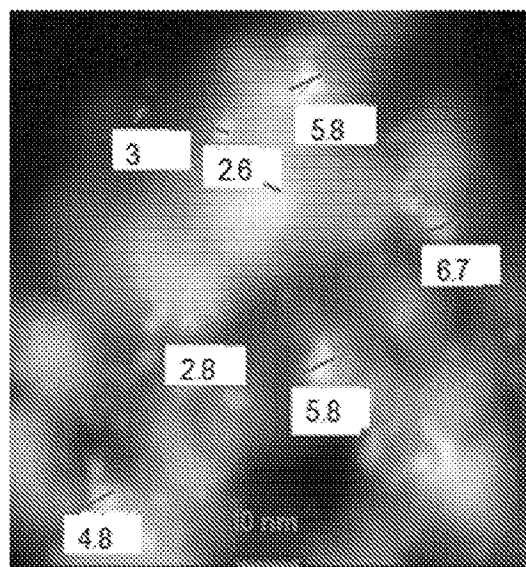
FIG. 6G

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**FIG. 7**

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Catalyst	T, °C	% wt loss from 120-700 °C in air	% wt carbon removed by H ₂
Fresh	400	1.5	0
Spent after 500 h TOS	Not reduced	25	0
	400	3.9	90
	450	3.1	93
	500	2.6	95

FIG. 8**FIG. 9A****FIG. 9B**

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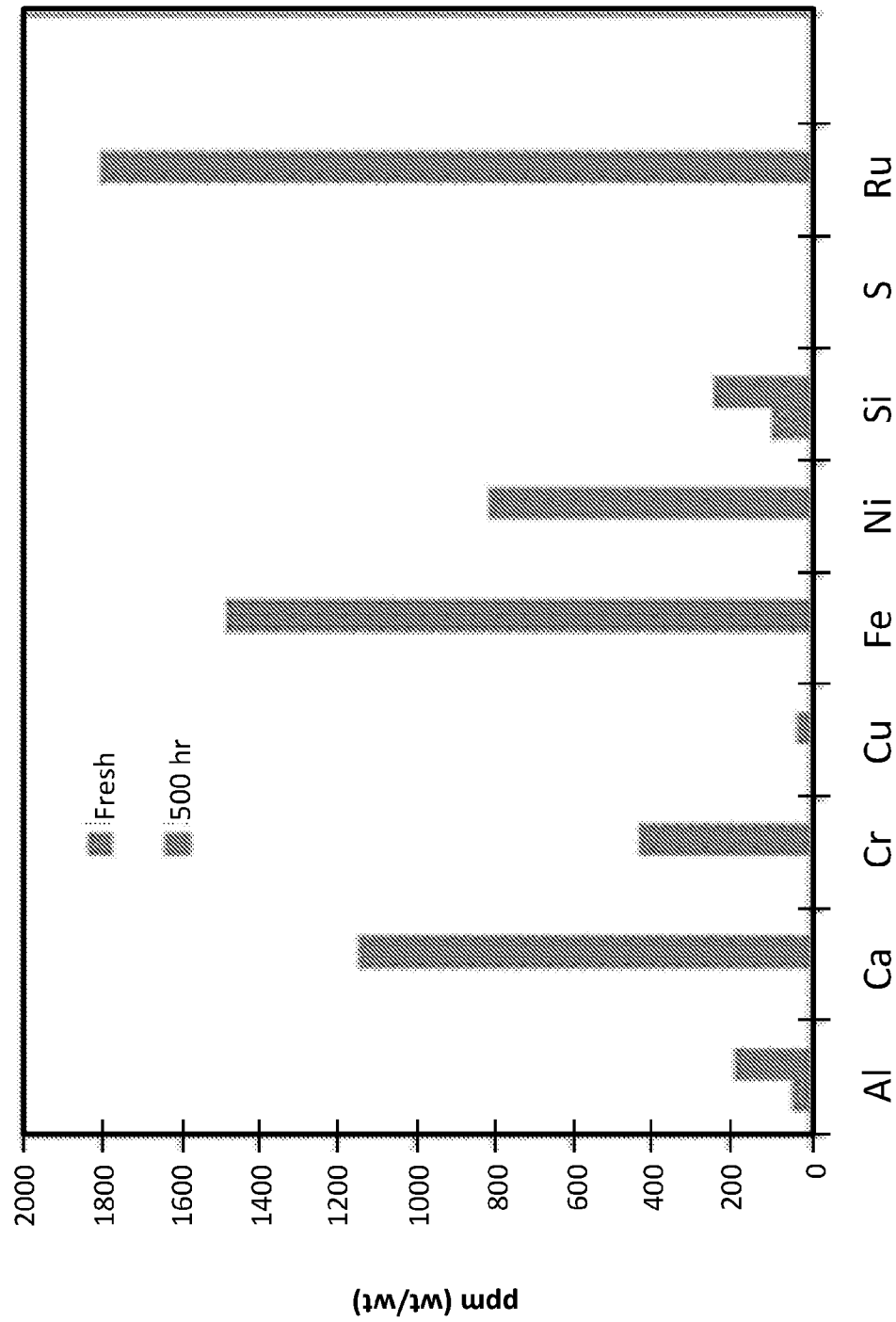


FIG. 10

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Element (conc. in ppm)	Trial #1, fixed bed flow reactor		Trial #2, slurry bed batch reactor		Trial #3, slurry bed batch reactor	
	Before	After	Before	After	Before	After
Al					5.11	<3
Ca	9	<3.0	24.7	<6.0	17.98	<3
Fe	19.6	<3.0	56.1	<6.0	15.76	<3
K	16.8	<3.0	33.6	<6.0	57.24	6.02
Mg	2	<3.0	14.8	<6.0	5.05	<3
Na	<3.0	<3.0	<6.0	<6.0	3.83	2.8
Si	16.1	17.1	6	8	10.62	0.84
S					10.16	8.92

FIG. 11

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Catalyst	Ru/TiO ₂ 17.8 mL (20.3 g) Diameter 350-800 mm
Temperature	170 °C
Total pressure	1,500 psi
LHSV	0.2 hr ⁻¹ , excluding methanol
Activation	H ₂ at 300°C , 3 h
Bio-oil	Reduced-inorganic bio-oil
co-solvent	30% methanol (wt)
total bio-oil feed	0.1 (mL/min)
H ₂ flow rate	400 mL/min
H ₂ /bio-oil volume ratio	4,000

FIG. 12

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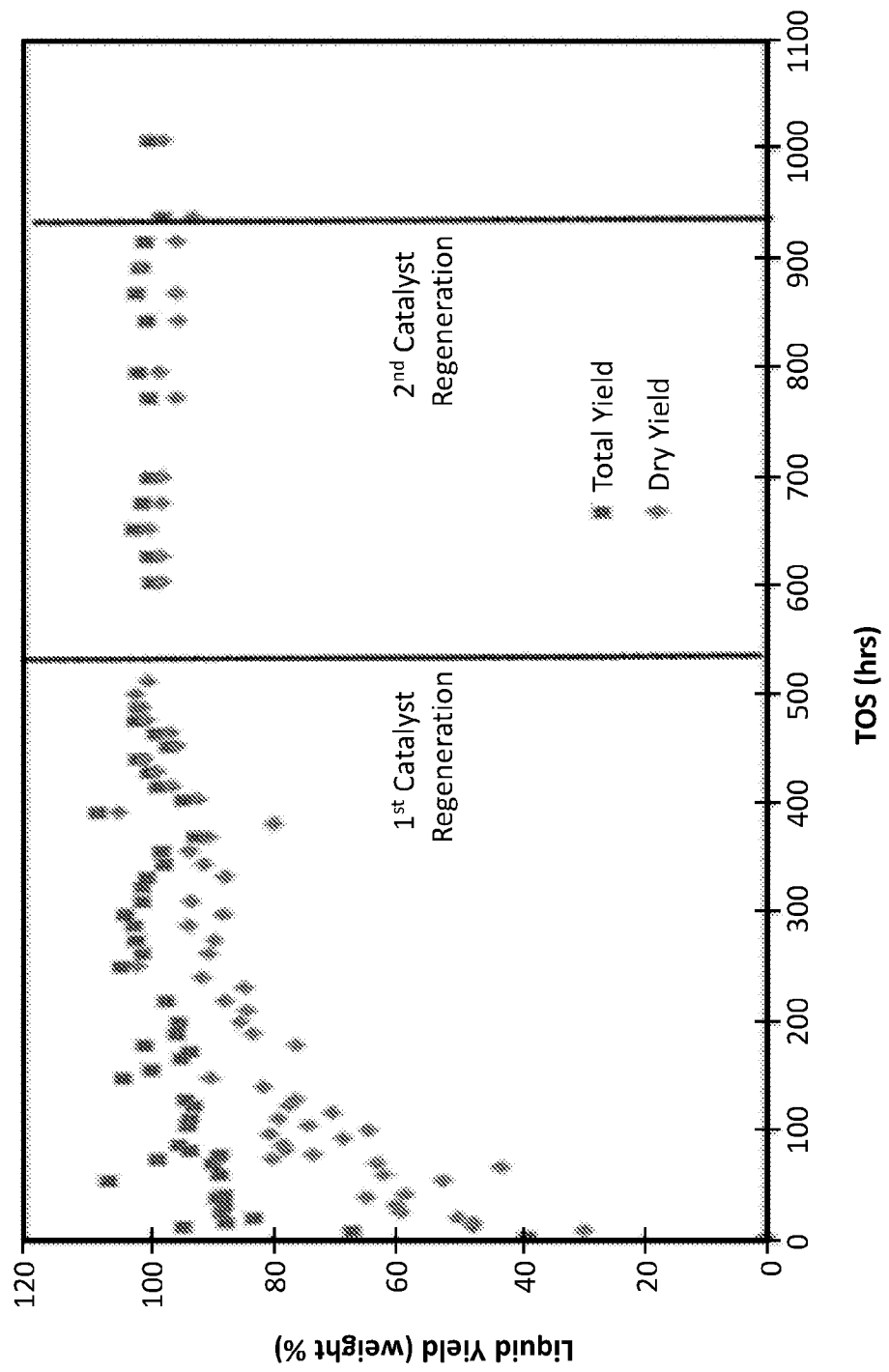


FIG. 13

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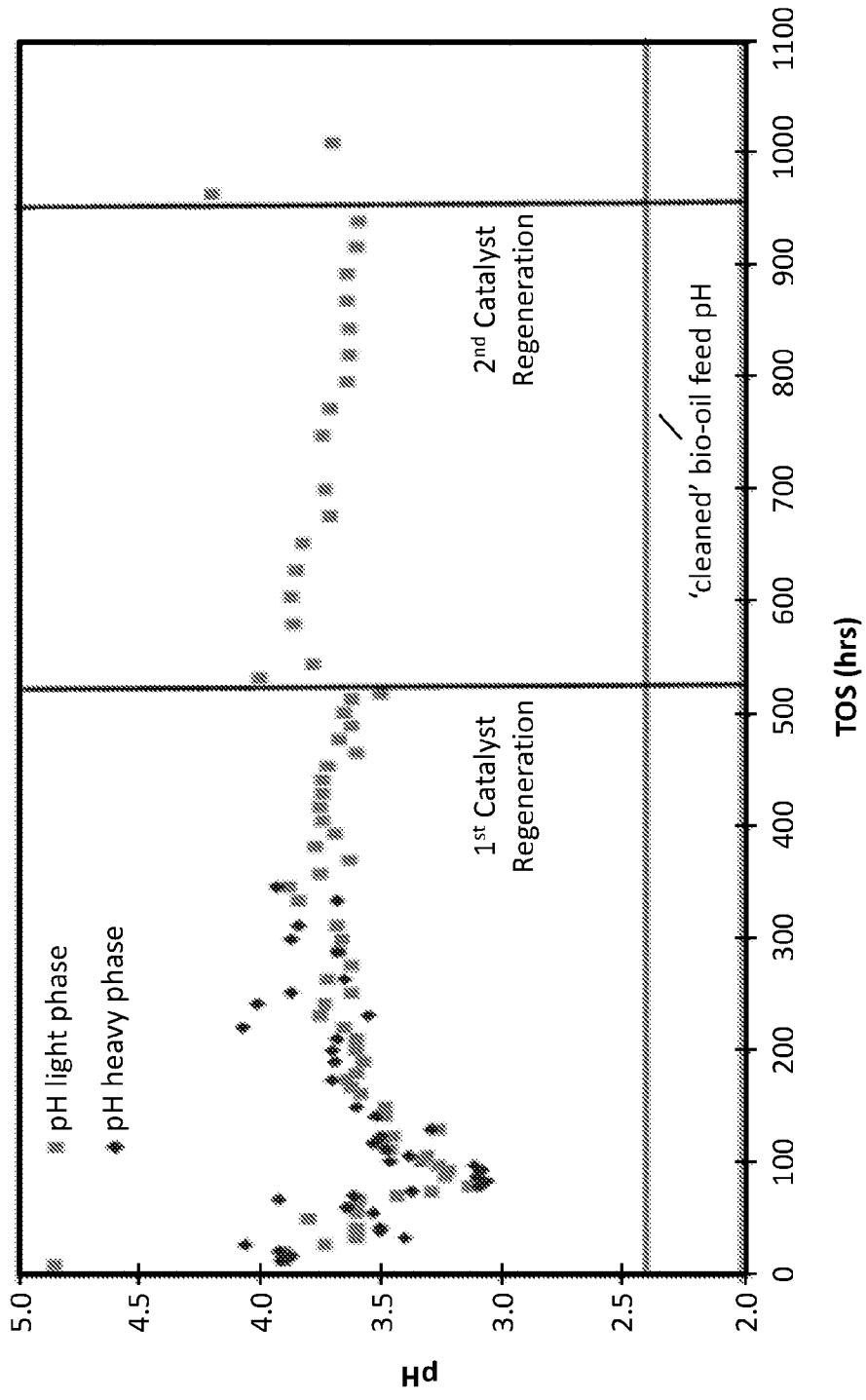


FIG. 14

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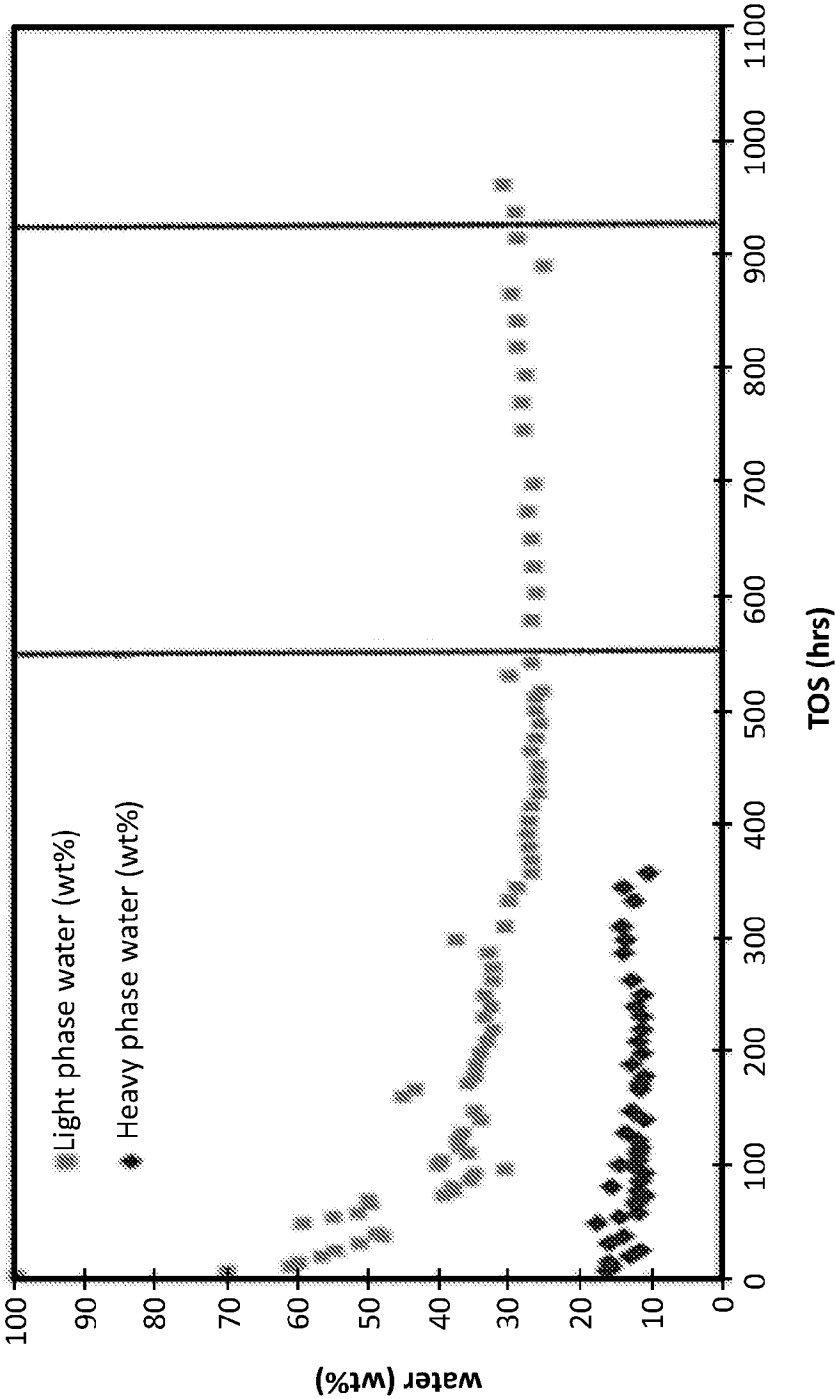
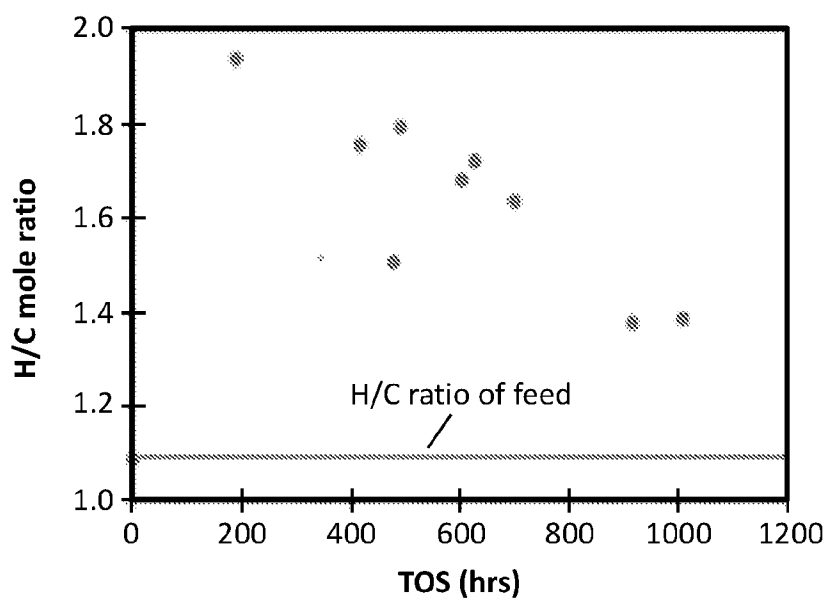
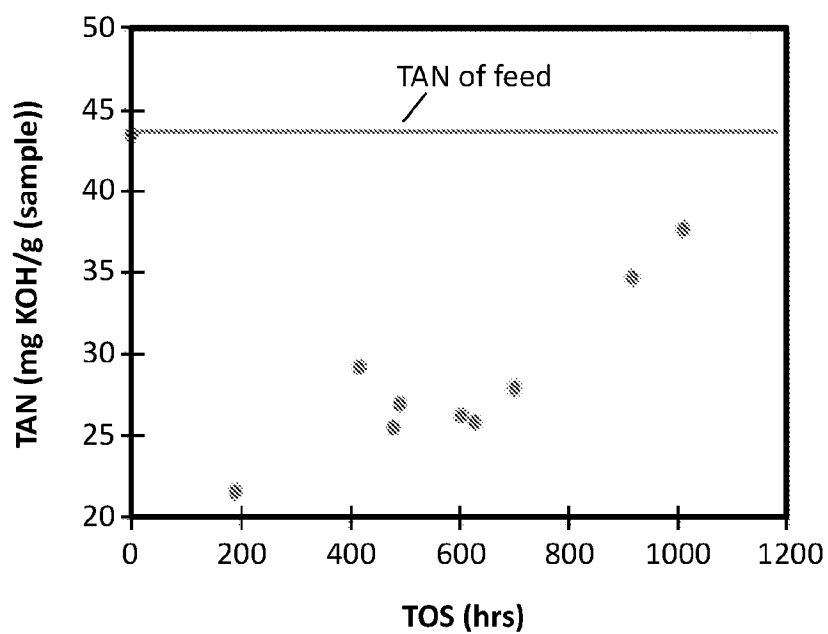
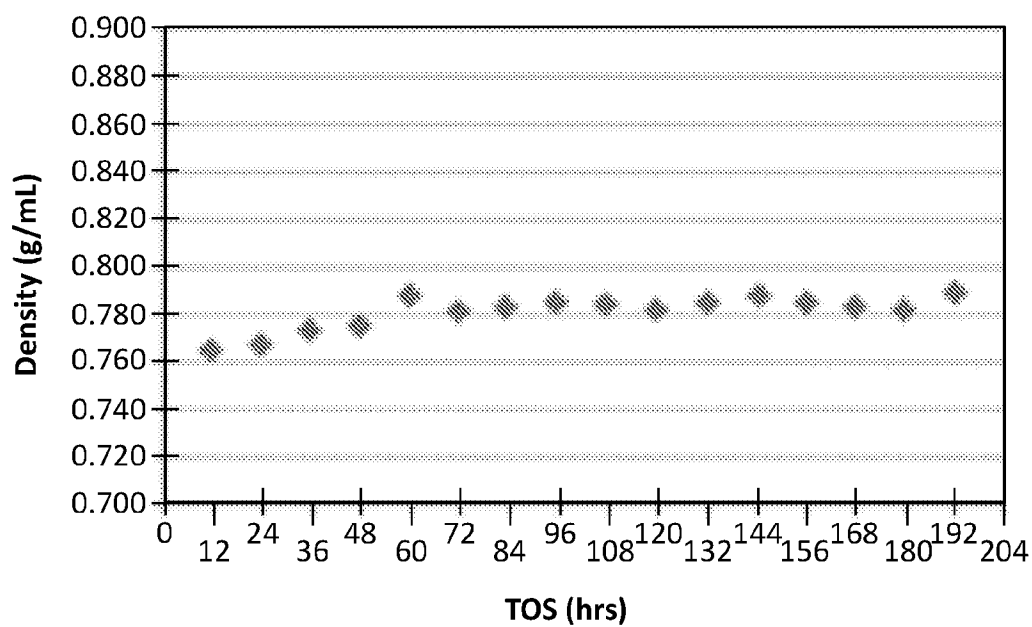
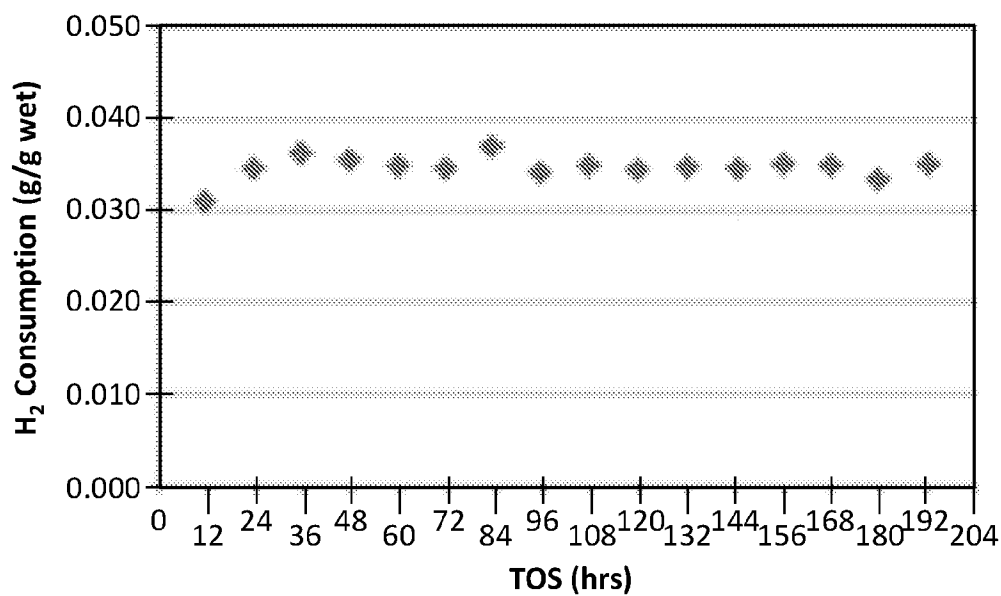


FIG. 15

**FIG. 16A****FIG. 16B**

**FIG. 17A****FIG. 17B**

SUBSTITUTE SHEET (RULE 26)

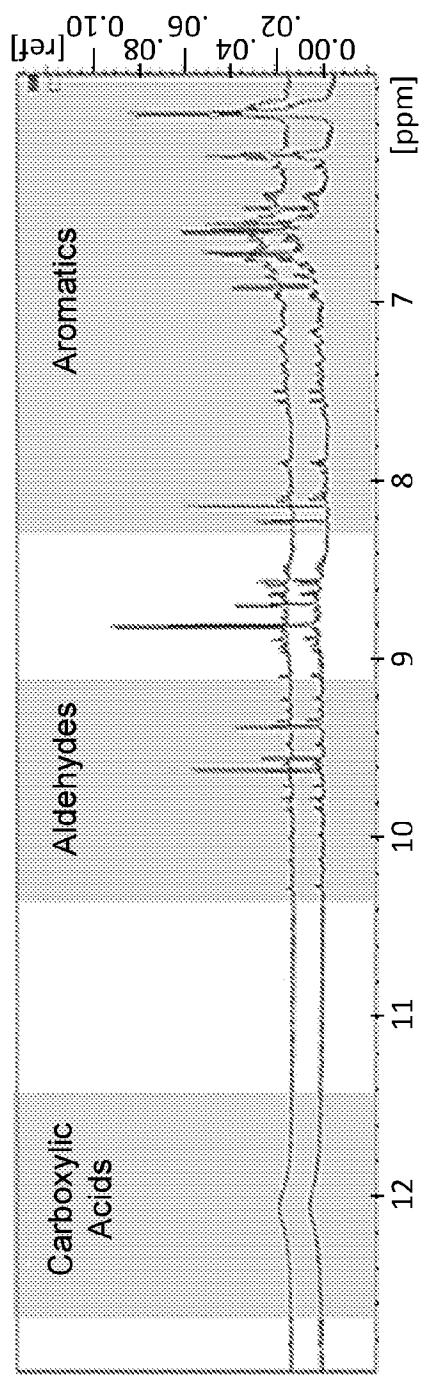


FIG. 18A

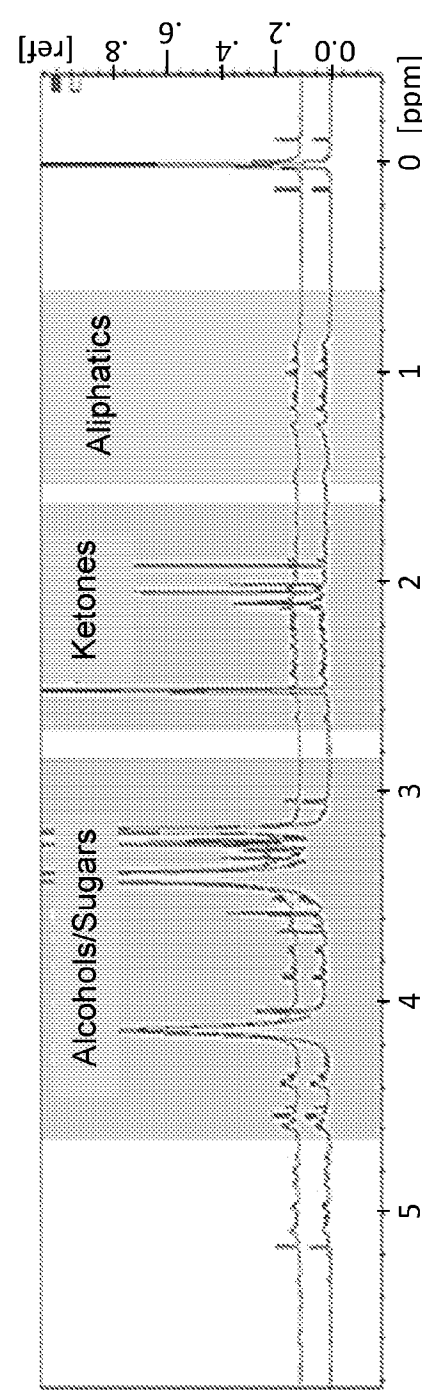


FIG. 18B

SUBSTITUTE SHEET (RULE 26)

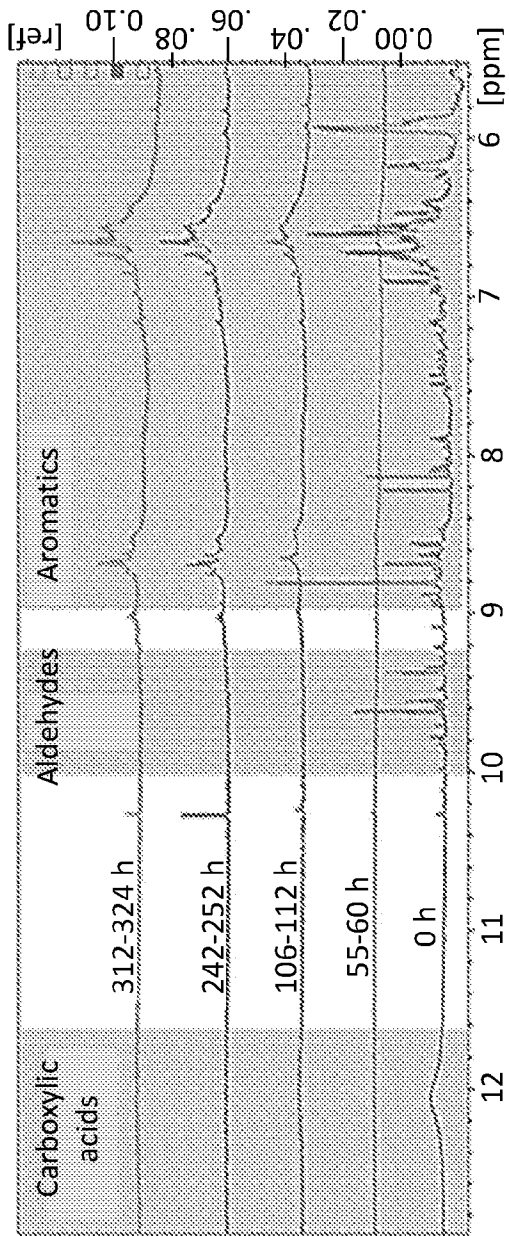


FIG. 19A

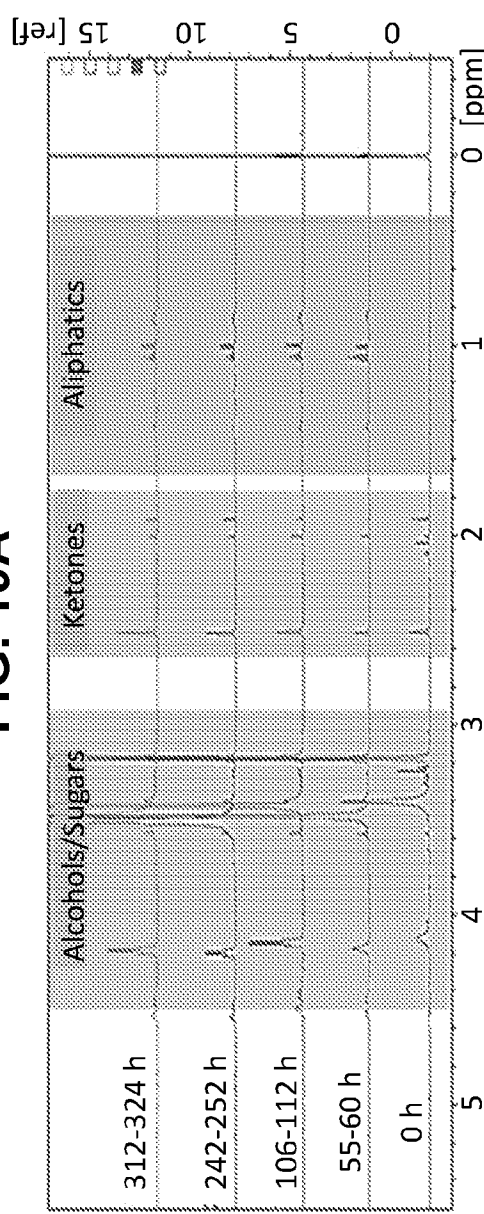


FIG. 19B

SUBSTITUTE SHEET (RULE 26)

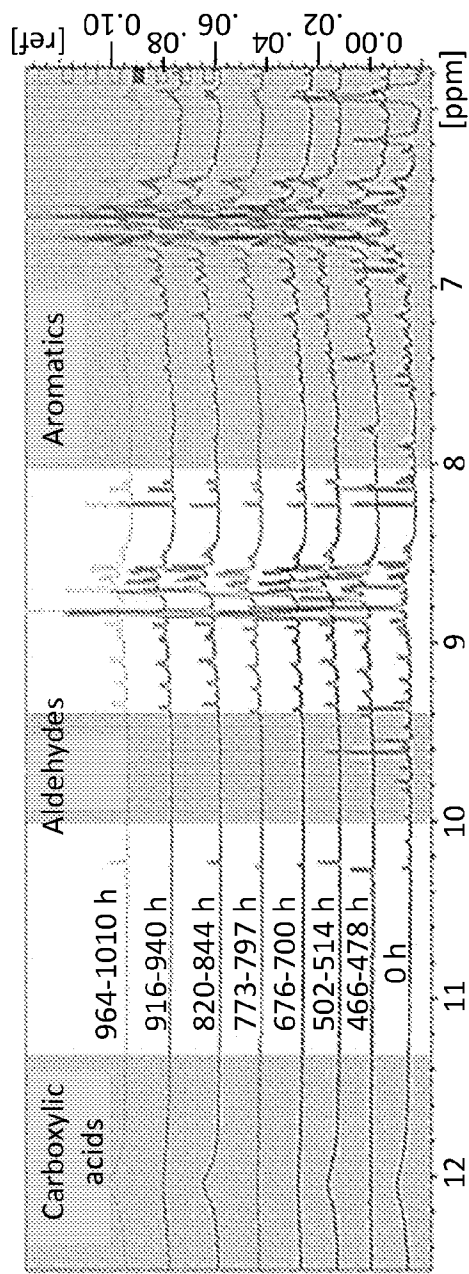


FIG. 20A

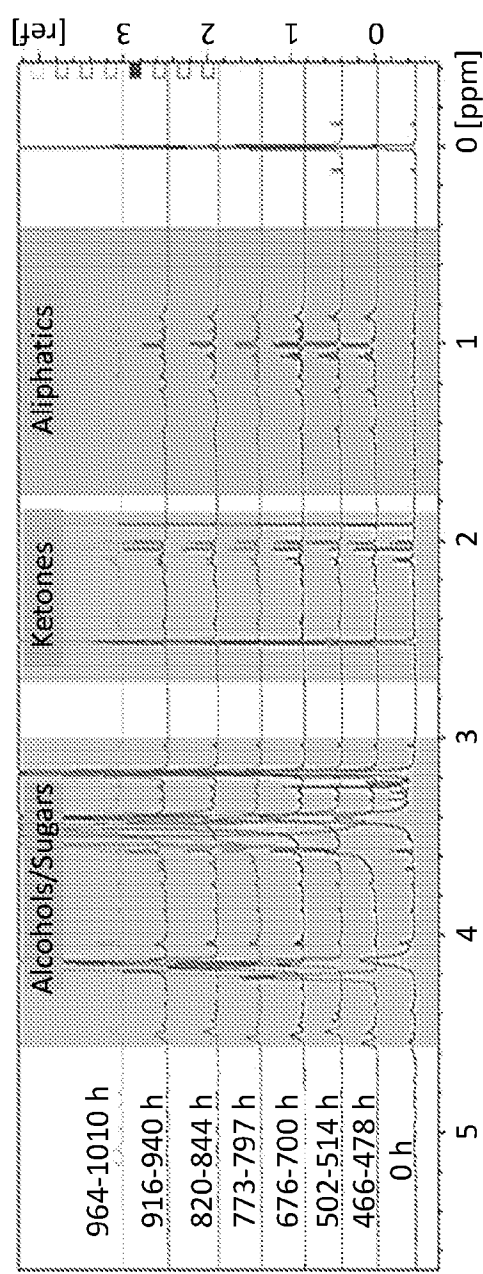


FIG. 20B

SUBSTITUTE SHEET (RULE 26)