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(54) PROCESS FOR PRODUCING A REFINERY STREAM-COMPATIBLE BIO-OIL FROM A LIGNOCELLULOSIC FEEDSTOCK

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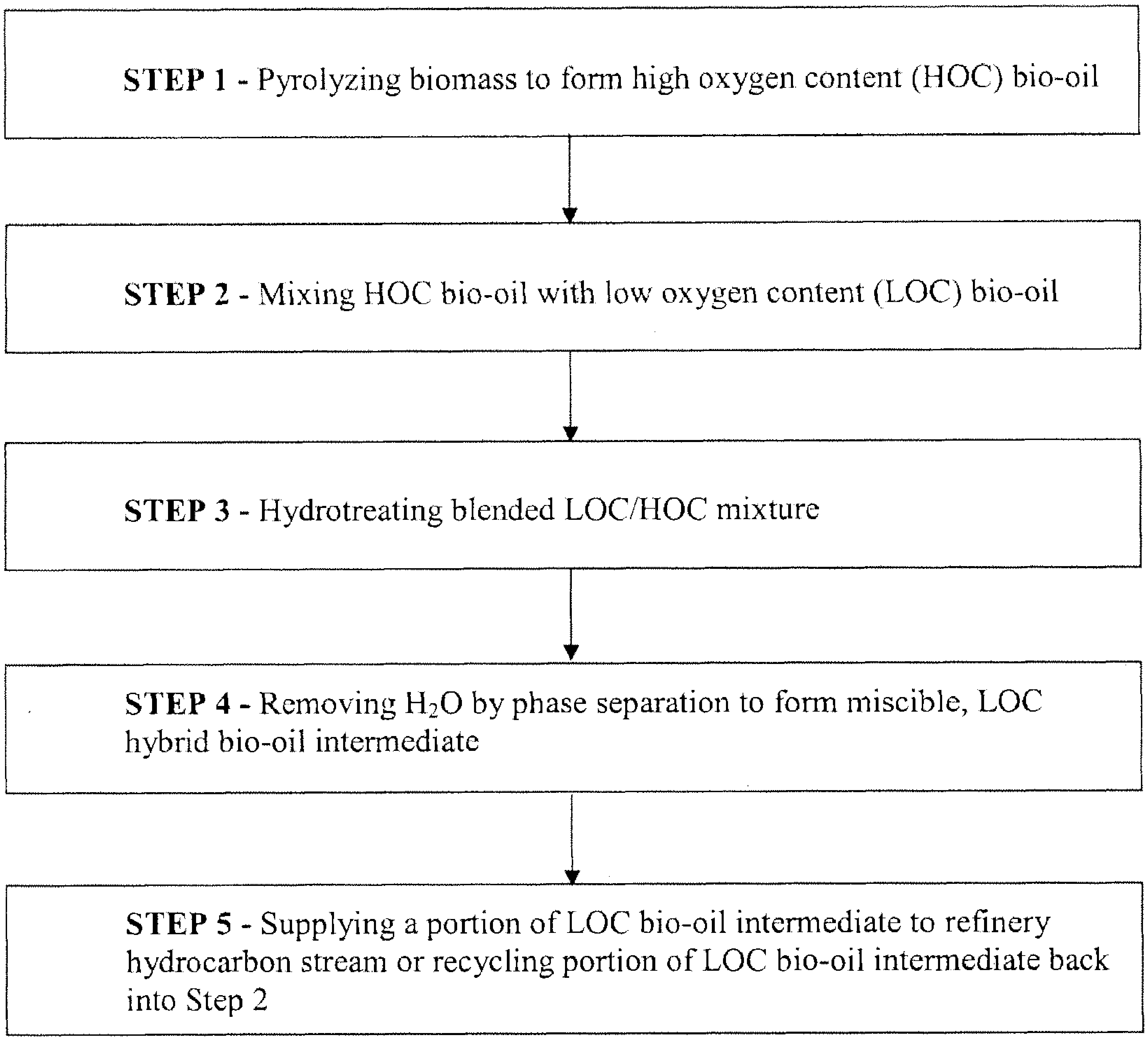
(57) ABSTRACT

In one aspect, a method for rendering biomass-derived pyrolysis oil miscible with refinery hydrocarbons comprises mixing a high oxygen content bio-oil having an oxygen content of at least about 10 wt. % with a low oxygen content bio-oil having an oxygen content of less than about 8 wt. % to produce a blended oil. The blended oil may be hydrotreated to produce a deoxygenated hydrotreated mixture from which water is removed using a separator, resulting in a low oxygen content hybrid bio-oil intermediate miscible in refinery process streams. A portion of the low oxygen content hybrid bio-oil intermediate may be recycled with the high oxygen content bio-oil or removed for use in a refinery process stream for further hydroprocessing.



STEP 1 - Pyrolyzing biomass to form high oxygen content (HOC) bio-oil

STEP 2 - Mixing HOC bio-oil with low oxygen content (LOC) bio-oil

STEP 3 - Hydrotreating blended LOC/HOC mixture

STEP 4 - Removing H_2O by phase separation to form miscible, LOC hybrid bio-oil intermediate

STEP 5 - Supplying a portion of LOC bio-oil intermediate to refinery hydrocarbon stream or recycling portion of LOC bio-oil intermediate back into Step 2

Fig. 1

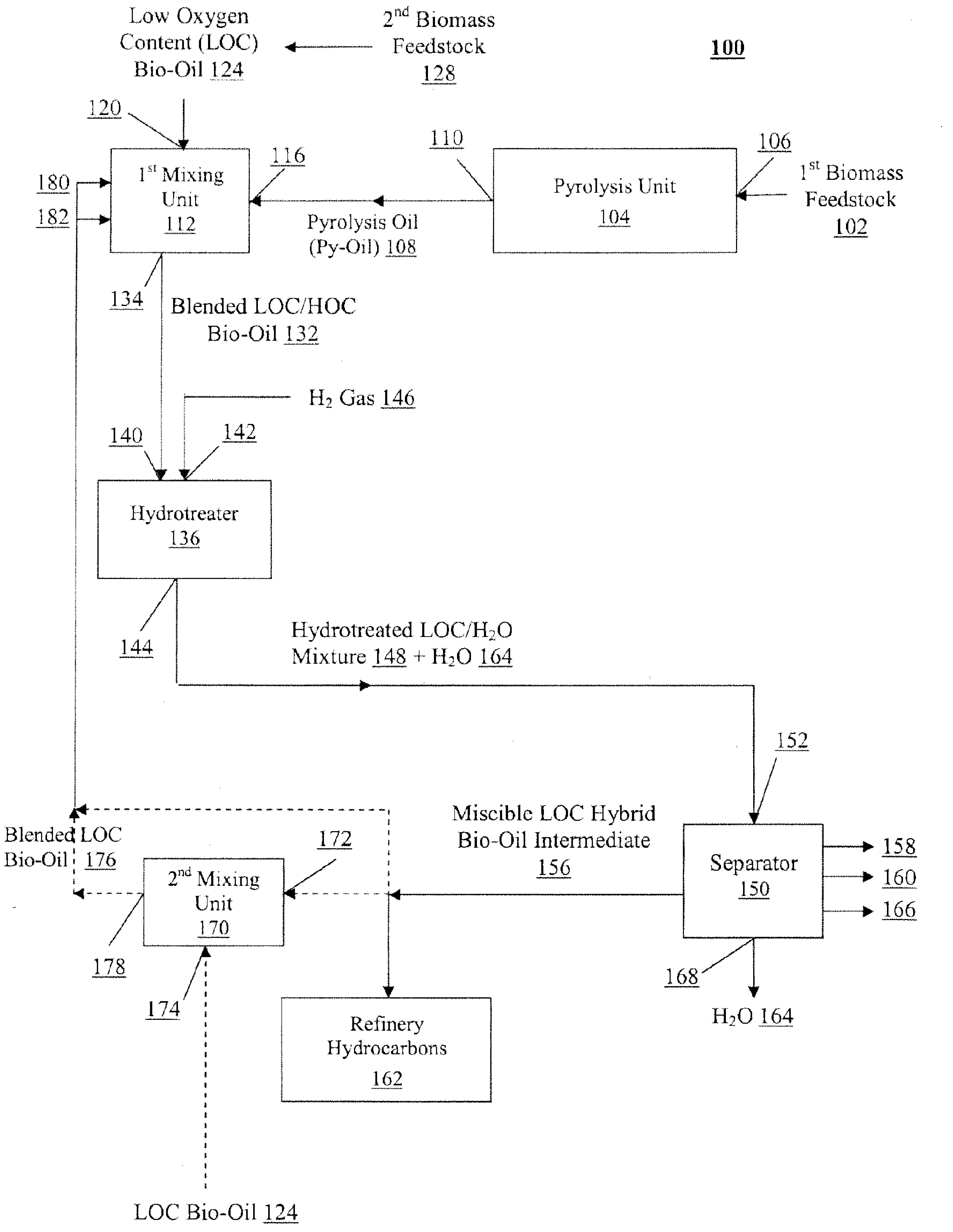

Low Oxygen Content (LOC) Bio-Oil 124
2nd Biomass Feedstock 128
100
120
1st Mixing Unit 112
116
110
Pyrolysis Unit 104
106
1st Biomass Feedstock 102
180
182
Pyrolysis Oil (Py-Oil) 108
134
Blended LOC/HOC Bio-Oil 132
H2 Gas 146
140
142
Hydrotreater 136
144
Hydrotreated LOC/H2O Mixture 148 + H2O 164
152
Miscible LOC Hybrid Bio-Oil Intermediate 156
Blended LOC Bio-Oil 176
2nd Mixing Unit 170
172
Separator 150
158
160
166
178
174
168
H2O 164
Refinery Hydrocarbons 162
LOC Bio-Oil 124

Fig. 2

PROCESS FOR PRODUCING A REFINERY STREAM-COMPATIBLE BIO-OIL FROM A LIGNOCELLULOSIC FEEDSTOCK

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119(e) to U.S. Application Ser. No. 61/542,083, filed Sep. 30, 2011, and which is included by reference in its entirety herein.

FIELD

[0002] The invention relates generally to compositions and methods for preparing biofuels, including lignocellulose-derived bio-oils compatible with refinery process streams.

BACKGROUND

[0003] A bio-oil produced from a lignocellulosic feedstock, typically has a high oxygen content, in the range of 10-25% O, or higher. In order for a bio-oil to be processed with a conventional refinery stream, the bio-oil needs to be miscible, or soluble, with the refinery stream. Incompatible liquids frequently will have flow or phase separation problems in flow lines, vessels or reactors.

[0004] Biomass liquefaction processes, such as wood pyrolysis or wood liquefaction with a donor solvent, are coarse transformations with minimal control on the chemical makeup of the product bio-oil. Specifically, the oxygen content and average molecular weight of the bio-oil has not been controlled sufficiently to make the oil compatible (miscible) with the refinery stream for further hydroprocessing. In addition, these coarse bio-oils may be highly reactive during catalytic hydrogenation with the result that they are prone to easy degradation and unwanted side reactions, such as charring.

[0005] There is a need in the art for systems enabling the use of lignocellulosic feedstock-derived bio-oils compatible with refinery process streams. The present disclosure addresses this need and more and describes: 1) compositions of processed bio-oil compatible with refinery streams; and, 2) processes and systems for converting a bio-oil precursor to a bio-oil compatible with refinery process streams.

SUMMARY OF THE INVENTION

[0006] In one aspect, compatibility of a bio-oil with a refinery process stream is achieved by using a previously hydrotreated bio-oil blend as a recycle oil in a process, whereby a coarse bio-oil is mixed with the recycled bio-oil in a controlled ratio to form a mixture from which oxygen and water are removed. The resultant bio-oil product in from this process has reduced oxygen content, lower molecular weight, and is suitably miscible for use in a refinery stream for further hydroprocessing, or it can be used as recycle oil for processing additional coarse bio-oil.

[0007] In one embodiment, a method for rendering biomass-derived pyrolysis oil miscible with refinery hydrocarbons comprises mixing a high oxygen content bio-oil having an oxygen content of at least about 10 wt. % with a low oxygen content bio-oil having an oxygen content of less than about 8 wt. % to produce a blended oil. The blended oil has an oxygen content for suitable miscibility.

[0008] In a further step, the blended oil is hydrotreated to yield a hydrotreated mixture comprising (i) low oxygen-content hydrotreated bio-oil and (ii) water, wherein the low oxygen-content hydrotreated bio-oil has an oxygen content of 10 wt. % or less.

[0009] In a further step, water is removed from the hydrotreated mixture via a phase separation between the low oxygen content hydrotreated bio-oil and the water to yield a low oxygen content hybrid bio-oil intermediate. Addition of a solvent may be unnecessary. The water may readily phase separate from the hydrotreated bio-oil, with the bio-oil floating on top of the water, so a typical water separator process may be used. Azeotropic distillation may be useful for determining the amount of water in a mixed bio-oil/water sample where good phase separation does not occur. One aspect of the claimed process is that it produces a bio-oil which readily phase separates from any associated water produced or carried into the process. A portion of the low oxygen content hybrid bio-oil intermediate may be recycled with the high oxygen content bio-oil according to the above described embodiments. Alternatively, a portion of the low oxygen content hybrid bio-oil intermediate may be removed for use in a refinery stream for further hydroprocessing.

[0010] In another aspect, a system for producing a bio-oil comprises a mixing unit, a hydrotreater, and a separator. The system may further comprise biomass conversion unit and a second mixing unit. The biomass conversion unit facilitates production of a high oxygen content bio-oil from a biomass feedstock. The mixing unit comprises a first inlet receiving the high oxygen content bio-oil from the conversion unit and a second inlet receiving a low oxygen content bio-oil from a bio-oil feedstock to form a blended oil. The hydrotreater comprises an inlet receiving the blended oil from the mixing unit to produce a hydrotreated bio-oil mixture. The separator separates and removes water from the hydrotreated bio-oil mixture to produce a low oxygen content hybrid bio-oil intermediate and includes an inlet receiving the hydrotreated bio-oil mixture from the hydrotreater, an outlet supplying at least at least a portion the low oxygen content hybrid bio-oil intermediate to the mixing unit, and optionally an outlet supplying at least another portion of the low oxygen content hybrid bio-oil intermediate to a source of refinery hydrocarbons.

[0011] In some embodiments, the system may further comprise a second mixing unit comprising a first inlet receiving the low oxygen content hybrid bio-oil intermediate from the separator, a second inlet receiving a low oxygen content bio-oil from a bio-oil feedstock to produce a low oxygen blended oil, and an outlet supplying the low oxygen blended oil formed in the second mixing unit to the first mixing unit. The separator further comprises an outlet supplying the low oxygen content hybrid bio-oil intermediate to the second mixing unit.

[0012] In another aspect, the present invention provides a blended oil composition that can be used in the above described system. In one embodiment, the blended oil composition comprises a high oxygen content bio-oil with an oxygen content of at least about 10 wt. % bio-oil blended with a low oxygen content bio-oil with an oxygen content of less than about 8 wt. %, wherein the ratio of the high oxygen content bio-oil to the low oxygen content bio-oil in the blended oil is at least about 5%, 10%, or 20% up to about 30%, 40%, 50%, and up to about 90%. An average molecular weight of the low oxygen content bio-oil may be about 100 g/mol, 125 g/mol, or 150 g/mol up to about 300 g/mol, 400 g/mol, or 500 g/mol. An average molecular weight of the high oxygen content bio-oil may be about 150 g/mol, 200 g/mol, or 250 g/mol up to about 800 g/mol, 900 g/mol, or 1000 g/mol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The accompanying drawings illustrate one or more embodiments of the invention and, together with the written description, serve to explain the principles of the invention. Wherever possible, the same reference numbers are used throughout the drawings to refer to the same or like elements of an embodiment.

[0014] FIG. **1** depicts, in stepwise fashion, a method for rendering biomass-derived bio-oil miscible with refinery hydrocarbons in accordance with some embodiments of the present invention.

[0015] FIG. **2** depicts a system for rendering biomass-derived bio-oil miscible with refinery hydrocarbons in accordance with some embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0016] Certain terms and phrases are defined throughout this description as they are first used, while certain other terms used in this description are defined below:

[0017] As used herein, the term "biomass" refers to any organic matter collected for use as a source of energy as further described herein.

[0018] The term "biofuel" refers to a fuel product at least partly derived from "biomass," the latter comprising a renewable resource of organic materials.

[0019] The term "bio-oil" refers to a liquid biofuel product comprising oxygen-containing organic compounds produced by thermochemical treatment of a solid biomass feedstock, such as by pyrolyis, or a natural oil, already present in the feedstock, and typically produced by mechanical and/or solvent extraction methods.

[0020] The terms "feed" or "feedstock" refer to a hydrocarbonaceous material fed into one or more of the systems or processes of the present invention in order to make a fuel, lubricant, or other commercial product. A biomass feedstock useful for the methods described herein can be a solid fuel, bio-oil, fluid fuel (e.g., a fuel that includes a liquid or a gas).

[0021] The term "pyrolysis" or "pyrolyzing" refer to the thermal processing and/or thermal decomposition of hydrocarbonaceous material, typically carried out in a non-oxidative environment.

[0022] The term "pyrolysis oil" refers to a liquid hydrocarbon product resulting from the pyrolyzing treatment of hydrocarbonaceous material.

[0023] The terms "hydroprocessing" or "hydrotreating" are used interchangeably herein with reference to processes or treatments that react a hydrocarbon-based material with hydrogen, typically under pressure and with a catalyst (hydroprocessing can be non-catalytic). Such processes include, but are not limited to, hydrodeoxygenation (of oxygenated species), hydrotreating, hydrocracking, hydroisomerization, and hydrodewaxing. For examples of such processes, see Cash et al., U.S. Pat. No. 6,630,066; and Elomari, U.S. Pat. No. 6,841,063.

[0024] The present invention provides a processed bio-oil composition compatible with refinery streams and a process for converting a bio-oil precursor to a bio-oil compatible with refinery streams. In one aspect, compatibility of a bio-oil with a refinery process stream is achieved by using a previously hydrotreated bio-oil blend as a recycle oil in a process, whereby a coarse bio-oil is mixed with the recycled bio-oil in a controlled ratio to form a mixture from which oxygen and water are removed. The resultant bio-oil product formed from this process has reduced oxygen content, lower molecular weight, and is suitably miscible for use in a refinery stream for further hydroprocessing, or it can be used as recycle oil for processing additional coarse bio-oil.

[0025] In one embodiment, exemplified in FIG. **1**, a method for rendering biomass-derived pyrolysis oil miscible with refinery hydrocarbons, comprises: (Step 1) pyrolyzing biomass to form a high oxygen content (HOC) bio-oil; (Step 2) mixing HOC bio-oil with low oxygen content (LOC) bio-oil; (Step 3) hydrotreating the blended LOC/HOC mixture; (Step 4) removing water by phase separation to form a miscible, LOC hybrid bio-oil intermediate; and (Step 5) supplying a portion of LOC hybrid bio-oil intermediate to refinery hydrocarbon stream or recycling a portion of the LOC hybrid bio-oil intermediate back into Step 2.

[0026] In one embodiment, a method for rendering biomass-derived pyrolysis oil miscible with refinery hydrocarbons comprises mixing a high oxygen content bio-oil having an oxygen content of at least about 10 wt. % with a low oxygen content bio-oil having an oxygen content of less than about 8 wt. % to produce a blended oil.

[0027] In a further embodiment, the blended oil is hydrotreated to yield a hydrotreated mixture comprising (i) low oxygen-content hydrotreated bio-oil and (ii) water, wherein the low oxygen-content hydrotreated bio-oil has an oxygen content of 10 wt. % or less. Hydrotreating processes in accordance with one or more embodiments disclosed herein are expected to reduce oxygen content to less than about 10%, reduce average molecular weight, and generally to "stabilize" the bio-oil so aging or phase stability may no longer be an issue or concern. Oxygen is removed by hydrotreatment via reaction with hydrogen over a suitable catalyst.

[0028] In a further step, water is removed from the hydrotreated mixture via a phase separation between the low oxygen content hydrotreated bio-oil and the water to yield a low oxygen content hybrid bio-oil intermediate. A portion of the low oxygen content hybrid bio-oil intermediate may be removed for use in a refinery stream or it may be combined and recycled with the high oxygen content bio-oil according to the above described embodiments.

[0029] In one embodiment, the high oxygen content bio-oil is produced in a biomass conversion unit by a conversion process comprising fast pyrolysis, slow pyrolysis, liquefaction, gasification, enzymatic conversion, cellulolysis, Fischer-Tropsch processing or combinations thereof. In a preferred embodiment, the high oxygen content bio-oil comprises a liquid hydrocarbon product resulting from pyrolysis of a lignocellulosic feedstock.

[0030] Bio-oils are a complex mixture of biomass compounds, including oxygenates, that are obtained from an organic matter collected for use as a source of energy. Any biomass source may be used as starting materials for the bio-oils of the present invention. Non-fossilized biomass includes plant biomass (defined below), animal biomass (any animal by-product, animal waste, etc.), and municipal waste biomass (residential and light commercial refuse with recyclables such as metal and glass removed). Biomass may also include any type of carbonaceous material from a fossilized source. Fossilized biomass, therefore, can further encompass various petroleum products, including, but not limited to petroleum and coal.

[0031] Plant biomass or lignocellulosic biomass includes virtually any plant-derived organic matter (woody or non-woody) available for energy on a sustainable basis. Exemplary plants include grasses, trees, and other sources of lignocellulosic material, including those derived from municipal waste, food processing wastes, forestry wastes and pulp and paper byproducts. "Plant-derived" necessarily includes both sexually reproductive plant parts involved in the production of seed (e.g., flower buds, flowers, fruit and seeds) and vegetative parts (e.g., leaves, roots, leaf buds and stems). Examples of such plants include, but are not limited to, corn, soybeans, cotton, wheat, rice, and algae. Plant biomass can include, but is not limited to, agricultural crop wastes and residues such as corn stover, wheat straw, rice straw, and sugar cane bagasse. Plant biomass can further include, but is not limited to, woody energy crops, wood wastes, and residues such as trees, softwood forest thinnings, barky wastes, sawdust, paper and pulp industry waste streams, and wood fiber. Examples of such trees, include, but are not limited to, hybrid poplar trees (e.g., Aspen). Additionally, any type of grasses, such as switch grass, for example, can be used as a plant biomass source. Typically, the plant biomass for use in the present invention includes starch, cellulose, hemicellulose, lignin, and combinations thereof.

[0032] Biomass starting materials may also include waste products from industry, agriculture, forestry, and households. Examples of such waste products that can be used as biomass include fermentation waste, straw, lumber, sewage, garbage, vegetable processing waste, yard waste, including grass clippings, tree clippings, leaves, and brush, and food leftovers.

[0033] Plant-derived starting materials typically include at least 5 wt. % water, in some embodiments at least 10% wt. % water, 20 wt. % water, or more. In some embodiments there may be 5 to 50 wt. % water, 10 to 40 wt. % water or up to about 35 wt. % water. The water may be present in a single phase with the oil, or primarily in a second phase (for an example an emulsion with the aqueous phase as either the major or minor component), or in mixture of phases. In some preferred embodiments, a second (primarily) water phase is formed during a hydrogenation reaction and is removed during or after the hydrogenation treatment.

[0034] The biomass starting materials may be thermally processed using any conventional process for preparing bio-oils therefrom, including fast pyrolysis, slow pyrolysis, liquefaction, gasification, enzymatic conversion, cellulolysis, Fischer-Tropsch processing, and combinations thereof. Bio-oils resulting therefrom represent a complex mixture of compounds, often derived from the thermal breakdown of solid biomass components, including cellulose, hemicellulose and lignin present in lignocellulosic biomass.

[0035] In a preferred embodiment, the biomass starting materials are thermally processed via fast pyrolysis. Fast pyrolysis is a high temperature process (350 to 800° C.) in which a biologically based feedstock, such as lignocellulosic biomass, is rapidly heated in the absence of air and vaporizes into a product gas stream. Fast pyrolysis of solid biomass causes the major part of its solid organic material to be instantaneously transformed into a vapor phase. This vapor phase contains both non-condensable gases (including methane, hydrogen, carbon monoxide, carbon dioxide and olefins) and condensable vapors. It is the condensable vapors that constitute the final liquid bio-oil.

[0036] The feedstocks of the present invention may be processed using a fast pyrolysis reactor, such as that disclosed in U.S. Pat. Nos. 5,961,780 and 5,792,340. Other known riser reactors with short residence times may also be employed, for example, but not limited to U.S. Pat. Nos. 4,427,539, 4,569, 753, 4,818,373, 4,243,514 (which are incorporated by reference). The reactor is preferably run at a temperature of from about 450° C. to about 600° C., more preferably from about 480° C. to about 550° C. The contact times between the heat carrier and feedstock is preferably from about 0.01 to about 20 sec, more preferably from about 0.1 to about 5 sec., most preferably, from about 0.5 to about 2 sec.

[0037] Preferably, the heat carrier used within the pyrolysis reactor is catalytically inert or exhibits low catalytic activity. Such a heat carrier may be a particulate solid, preferably sand, for example, silica sand. By silica sand it is meant any sand comprising greater than about 80% silica, preferably greater than about 95% silica, and more preferably greater than about 99% silica. It is to be understood that the above composition is an example of a silica sand that can be used as a heat carrier as described herein, however, variations within the proportions of these ingredients within other silica sands may exist and still be suitable for use as a heat carrier. Other known inert particulate heat carriers or contact materials, for example kaolin clays, rutile, low surface area alumina, oxides of magnesium and calcium are described in U.S. Pat. No. 4,818,373 or U.S. Pat. No. 4,243,514.

[0038] As used herein, the phrase "high oxygen content bio-oil" (HOC bio-oil) comprises an oxygen content of at least 15 wt % oxygen. In some embodiments, the high oxygen content bio-oil comprises at least 20 wt % oxygen, at least 25 wt % oxygen, at least 30 wt % oxygen, at least 35 wt % oxygen, 40 wt % oxygen, between 25 wt. % and 50 wt. %, and combinations or ranges therefrom.

[0039] The low oxygen content bio-oil comprises an oxygen content of about 8 wt. % or less. In some embodiments, the low oxygen bio-oil comprises an oxygen content between about 5 wt. % and about 8 wt % or less than 5 wt. %. In other embodiments, the low oxygen content bio-oil has a total acid number less than about 10 mg KOH/g.

[0040] The low oxygen content bio-oil may comprise a biomass feedstock produced by any convenient method, including, but not limited to, pyrolysis or catalytic pyrolysis, hydroliquefaction via catalytic hydrogenation or by hydrogen donor solvent liquefaction. Reduction may be by conventional hydrotreating using hydrogen, or with synthesis gas (CO/H2), or with aqueous reduction using water plus CO with suitable catalysts. In some embodiments, the low oxygen content bio-oil is produced from a hydrotreated lignocellulosic feedstock.

[0041] In one embodiment, the high oxygen content bio-oil is mixed with the low oxygen content bio-oil, wherein the ratio of the high oxygen content bio-oil to the low oxygen content bio-oil in the blended oil is less than or equal to 0.3. In some embodiments, the high oxygen content bio-oil and the low oxygen content bio-oil are mixed so that the low oxygen content bio-oil serves as a solvent for the high oxygen content bio-oil. In other embodiments, the high oxygen content bio-oil and the low oxygen content bio-oil are mixed so that the blended oil has a total acid number between about 50-100 mg

KOH/g. In yet other embodiments, a bio-oil is pretreated by hydrotreating the bio-oil prior to admixture in the blended oil.

[0042] In the present invention, the oxygenates present in the feed are removed by hydrotreating. "Hydrotreating" may be defined as a catalytic process, usually carried out in the presence of free hydrogen, in which the primary purpose when used to process conventional petroleum derived feed stocks is the removal of various contaminants, such as arsenic; heteroatoms, such as sulfur, oxygen, and nitrogen; and aromatics from the feed stock. In the present process, the primary purpose is to remove the oxygenates in the feed.

[0043] The method comprises hydrotreating the blended oil by passing the oil to a hydrotreating unit where the oil is contacted with a hydrotreating catalyst under a hydrogen atmosphere. The hydrotreating unit can also be a hydrocracking unit with a hydrocracking catalyst for breaking additional oxygenates out of the lignin compounds or any other unit known to remove oxygenates from a feed.

[0044] In one embodiment, the blended oil is passed to a hydrotreater where the blended oil is contacted with a hydrotreating catalyst under a hydrogen atmosphere. Alternatively, the hydrotreater can comprise a hydrocracking unit with a hydrocracking catalyst for breaking additional oxygenates out of e.g, the lignin compounds in the blended oil composition. When hydrotreating the blended oil, hydrogen is added separately or together with the blended oil in a reactor, thereby resulting in the production of low oxygen-content hydrotreated bio-oil and water. In a continuous process, hydrogen is added along the length of a reactor. The hydrogen is preferably added in excess of stoichiometry to maximize reaction rate by minimizing mass transfer limitations. Exemplary hydrogen flow rates may range between about 50 to about 5,000 standard cubic feet (SCF) of hydrogen per barrel (bbl) of oil feed. When milder hydrotreatment conditions are desired, the hydrogen between about 200 to about 2,000 SCF/bbl of oil feed, from about 400 to about 1,600 SCF/bbl, from about 600 to about 1,200 SCF/bbl, or combinations thereof.

[0045] Preferably, hydrogen is reacted with the blended oil feedstock at a level of at least 50 liter/liter, more preferably at least 100 liter/liter, and still more preferably at least 200 liter/liter, in some embodiments in the range of 100 to 300 liter/liter, and in some embodiments in the range of 100 to 175 liter/liter. Excess hydrogen may be recycled into a reactor.

[0046] The hydrotreater may comprise a metal-containing catalyst comprising Co—Mo, Ni—Mo, a transition metal, a noble metal, a metal oxide therefrom, a metal sulfide therefrom, or a combination thereof. Metal-containing catalysts useful for the methods described herein include, for example, a transition metal, a noble metal, or a combination thereof. The term "metal-containing catalyst" refers to a catalyst that includes a metal, a metal-containing compound, or a metal-containing composite. Exemplary metals include Ni, Co, Pd, Pt, Mo, W, Ru, Cu, Cr, Zn, and combinations thereof. In some embodiments, the metal-containing catalyst can optionally include a second metal, a second metal-containing compound, or a second metal-containing composite. The term "mixed-metal catalyst" refers to a catalyst that contains more than one metal, metal-containing compound, or metal-containing composite. Preferred catalysts include those comprising Ni, Co, Mo, W or combinations thereof, for example, one or more Group VIII metals and one or more Group VIB metals, for example comprising Ni and/or Co and W and/or Mo, preferably comprising a combination of Ni and Mo, or Co and Mo, or a ternary combination such as Ni, Co, and Mo or Ni, Mo, and W. Particular catalysts include ICR 181 and ICR511 (commercially available from Chevron Lummus Global), and Molyvan A (R.T. Vanderbilt Co., Norwalk, Conn.)

[0047] The hydrotreatment catalyst may be further supported on a suitable support material. In some embodiments, the support comprises alumina, especially gamma or eta alumina. Chromia and rare earth oxides may make take up at least part of the support. Other useful support oxides include titania, zirconia, hafnia, thoria, vanadia, urania, oxides of manganese, molybdenum and tungsten, and combined oxides and supports thereof. The support material typically has a pore volume over 0.2 cm^3/g and a surface area of at least 1.0, preferably over 15, especially in the range 50-200 m^2/g.

[0048] The catalyst can be present as a wall coating, fluidized bed, fixed bed of particles or pellets, etc. A fixed bed of catalyst particles has the advantage of ease of design and operation (clean-up and catalyst replacement). In some embodiments, fluidized bed reactors may be preferred, especially if the bio-oil is contaminated with inorganic material. In some embodiments, wall coated reactors, which have certain advantages for heat and mass transfer, may be preferred.

[0049] The hydrotreater may include any conventional hydrotreatment device or hydrotreatment process, including but not limited to hydrodeoxygenation (of oxygenated species), hydrotreating, hydrocracking, hydroisomerization, hydrodewaxing, and the like. The hydrotreater may include down flow reactor, autoclave batch reactor, fixed bed reactor, moving bed reactor, dynamic bed reactor, fluid bed reactor, slurry reactor, countercurrent free fall reactor, concurrent riser reactor, ebullated bed reactor, and reactors with continuous replacement or replenishment of the catalyst bed.

[0050] Preferably, the hydrotreatment is carried out relatively mild hydrotreating conditions. In one embodiment, hydrotreatment of the blended oil is carried out under a hydrogen atmosphere under a hydrogen partial pressure of about 15 pounds-force per square inch gauge (psig) to about 3,000 psig, from about 200 psig to about 2,000 psig, from about 400 psig to about 1,500 psig, from about 200 to about 1,000 psig, or combinations thereof.

[0051] In addition, the hydrotreatment may be carried out in a range of different temperature conditions. In one embodiment, the hydrotreatment is carried out at a temperatures between about 100° C. to about 500° C., between about 150° C. to about 350° C., below 300° C., or combinations thereof. In another embodiment, the hydrotreatment process employs a temperature gradient across a catalyst bed. In a specific embodiment, the temperature gradient comprises temperatures between about 100° C. to 200° C. at the lower temperature range up to about 300° C. or less at the upper temperature range.

[0052] In a further embodiment, water is removed from the hydrotreated mixture in a separator to form a low oxygen content hybrid bio-oil intermediate. In one embodiment, a portion of the low oxygen content hybrid bio-oil intermediate may be recycled with the high oxygen content bio-oil according to the above described embodiments. Alternatively, a portion of the low oxygen content hybrid bio-oil intermediate may be removed for use in a refinery stream for further hydroprocessing.

[0053] Generally, the separator will remove water by a phase separation process based on differences in volatility. Exemplary separators or separation methods include phase separation by decanting, distillation, or separation using membranes. Exemplary separator units include a phase separators, extractors, purifiers, distillation columns and the like.

[0054] In a preferred embodiment, water is separated by azeotropic distillation. Azeotrope selection is driven by the amount and cost of the azeotrope-forming liquids, the desired boiling temperature, and the compatibility of the azeotrope-forming liquid with the hydrotreated mixture. "Compatibility" as used herein means that the azeotrope-forming liquid is co-soluble with the hydrotreated mixture, i.e., there is no phase separation upon mixing of the hydrotreated mixture and the azeotrope-forming liquid(s). While certain azeotrope-forming liquids and azeotropes have been identified, the present invention is not so limited. Other azeotrope-forming liquids and azeotropes may be used if they form an azeotrope with water alone or with water in combination with other azeotrope-forming liquids.

[0055] Azeotropic distillation can be conducted using a Dean Stark trap or equivalent apparatus and the temperature is set to an elevated temperature in the range of about 130° C. to about 150° C., such as about 145° C., and it should be appreciated that distillation may start after a period of time to allow the reaction mixture to reach about 95° C. to 105° C. Once the distillation commences, the gas flow for the inert atmosphere (such as a blanket under N_2) can be increased to about 0.1 SCFH to about 1.0 SCFH, such as 0.5 SCFH as an example. The temperature is maintained at the selected elevated temperature for sufficient time, which may be about an additional 2 hours to about 2.5 hours.

[0056] Effective azeotrope-forming liquids for preparing low oxygen content hybrid bio-oil intermediate compositions include toluene, ethanol, acetone, 2-propanol, cyclohexane, 2-butanone, octane, benzene, ethyl acetate, and combinations thereof. Exemplary suitable azeotropes formed during process include binary azeotropes such as ethanol/water, toluene/water, acetone/water, 2-propanol/water, cyclohexane/water, 2-butanone/water, and octane/water and ternary azeotropes such as ethanol/toluene/water, 1-butanol/octane/water, benzene/2-propanol/water, ethanol/2-butanone/water, and ethanol/ethyl acetate/water

[0057] The low oxygen content hybrid bio-oil intermediate is preferably formed with a moderately low oxygen content, generally <10%, and has a total acid number (TAN) of <20 mg KOH/g. In one embodiment, the low oxygen content hybrid bio-oil intermediate has a total acid number less than or equal to 20 mg KOH/g. In other embodiments, the low oxygen content hybrid bio-oil intermediate has an average molecular weight between about 200-300 g/mol, with the highest molecular weight components not greater than 500-600 g/mol. The boiling point range low oxygen content hybrid bio-oil intermediate is generally no more than 500° C. with a typical midpoint of about 300° C., and may be as low as about 180° C., 200° C., or 220° C.

[0058] Preferably, the low oxygen content hybrid bio-oil intermediate is formed to be substantially miscible in a non-polar solvent. For example, suitable miscibility, as used herein, may refer to a low oxygen content hybrid bio-oil intermediate that may be greater than about 95% soluble when mixed with the non-polar solvent in a 10:90 ratio of bio-oil to solvent.

[0059] Where a portion of the low oxygen content hybrid bio-oil intermediate is combined and recycled with the high oxygen content bio-oil according to the above described embodiments, the low oxygen content hybrid bio-oil intermediate may be added to a second low oxygen content bio-oil in a second mixing unit to yield a second blended oil, wherein the second blended oil is added to the high oxygen content bio-oil in a first mixing unit.

[0060] In other embodiments, at least a portion of the low oxygen content hybrid bio-oil intermediate is directly applied for use in a refinery process stream. A suitable refinery process stream will have sufficiently high aromatic content, and will be compatible with the bio-oil and able to completely dissolve or be miscible with the bio-oil, without causing phase separation of the highest boiling or the highest oxygen content components.

[0061] In another aspect, the present invention provides a blended oil composition, comprising a high oxygen content bio-oil with an oxygen content of at least about 15 wt. % bio-oil blended with a low oxygen content bio-oil with an oxygen content of less than about 8 wt. %, wherein the blended oil has an oxygen content for suitable miscibility. The blended oil composition may be modified in accordance with the above method teachings.

[0062] In another aspect, a system for producing a bio-oil comprises a mixing unit, a hydrotreater, and a separator. The system may further comprise biomass conversion unit and a second mixing unit. With reference to FIG. **2**, in one embodiment of the present invention, an exemplary system **100** for producing a refinery stream compatible bio-oil comprises a mixing unit **112**, a hydrotreater **136**, and a separator **150**.

[0063] In one embodiment, the system **100** further comprises a biomass conversion unit **104** (depicted as a pyrolysis unit) producing a high oxygen content (HOC) bio-oil **108** or pyrolysis oil (Py-Oil) from a biomass feedstock **102**. In FIG. **2**, the biomass conversion unit **104** comprises an inlet **106** receiving the biomass feedstock **102** and an outlet **110** supplying the HOC bio-oil **108** or Py-Oil to a first mixing unit **112**.

[0064] The first mixing unit **112** comprises a first inlet **116** receiving the HOC bio-oil **108** from the conversion unit **104** and a second inlet **120** receiving a low oxygen content (LOC) bio-oil **124** from a second biomass feedstock **128** to form a blended LOC/HOC bio-oil **132**. The blended LOC/HOC bio-oil **132** exits from an outlet **134** in the first mixing unit **112** and is received in a hydrotreater **136**.

[0065] The hydrotreater **136** comprises a first inlet **140** receiving the blended LOC/HOC oil **132** from the first mixing unit **112** and a second inlet **142** receiving hydrogen gas **146**. The hydrotreater **136** produces a hydrotreated LOC/water mixture **148**, which exits from an outlet **144** and passes on to a separator **150**.

[0066] The separator **150** separates water **164** from the hydrotreated bio-oil mixture **148** to produce a miscible, LOC hybrid bio-oil intermediate **156** and water **164**. The separator **150** comprises an inlet **152** receiving the hydrotreated bio-oil mixture **148** from the hydrotreater **136** and may additionally include an outlet **158** supplying at least a portion of the LOC hybrid bio-oil intermediate **156** to the first mixing unit **112**, an outlet **160** supplying at least a portion of the LOC hybrid bio-oil intermediate **156** to a source of refinery hydrocarbons **162**, an outlet **166** supplying at least a portion of the LOC hybrid bio-oil intermediate **156** to a second mixing unit **170**, and an outlet **168** for water **164** to exit.

[0067] In some embodiments the system **100** comprises a second mixing unit **170** comprising an inlet **172** receiving the LOC hybrid bio-oil intermediate **156** from the separator **150** and an inlet **174** receiving a LOC bio-oil **124** from a bio-oil feedstock **128** to form a blended LOC oil **176** exiting from an outlet **178**, which supplies the blended LOC oil **176** formed in the second mixing unit **170** to the first mixing unit **112**. The first mixing unit **112** may further include an inlet **180** receiving the LOC hybrid oil intermediate **156** from the separator **150** and an inlet **182** receiving the blended LOC oil **176** from the second mixing unit **170**.

[0068] Each reactor vessel of the invention preferably includes an inlet and an outlet adapted to remove the product stream from the vessel or reactor. The vessels and reactors may include additional outlets to allow for the removal of portions of the reactant stream to help maximize the desired product formation, and allow for collection and recycling of byproducts for use in other portions of the system. Further, the apparatuses for conducting the inventive processes can be conducted batchwise or continuously.

[0069] In another aspect, the present invention provides a blended oil composition that can be used in the above described system. The blended oil composition may comprise any of the above described LOC/HOC bio-oil compositions. In one embodiment, the blended oil composition comprises a high oxygen content bio-oil with an oxygen content of at least about 15 wt. % bio-oil blended with a low oxygen content bio-oil with an oxygen content of less than about 8 wt. %.

[0070] The present invention is further illustrated by the following examples which should not be construed as limiting. The contents of all references, patents and published patent applications cited throughout this application, as well as the Figures and Tables are incorporated herein by reference to the extent that they are not inconsistent.

Example 1

Pyrolysis Oil

[0071] A pyrolysis oil was produced from pine sawdust by a fast pyrolysis method. Chemical analysis of the pyrolysis oil showed 21% water content, and elemental analyses of 48.72% carbon, 5.97% hydrogen, <0.05% nitrogen, and 44.64% oxygen (by difference) on a moisture and ash free basis (MAF). The total acid number (TAN) of the Pyrolysis Oil was 331 mg KOH/g.

[0072] This resulting Py-Oil was immiscible with n-dodecane. The low solubility of the Py-Oil in an aromatic solvent was demonstrated using toluene as a solvent. The Py-Oil was mixed with five-to-ten times the volume of toluene. The mixture was heated to boiling and the water removed by azeotropic distillation (Dean Stark method). The resulting Py-Oil/toluene mixture was allowed to cool and two phases resulted: a thin, light colored toluene rich phase and a thick, viscous Py-Oil phase immiscible in toluene. The toluene-insoluble Py-Oil accounted for 38% of the original Py-Oil.

[0073] The elemental composition of the toluene-insoluble Py-Oil phase was 59.3% C, 6.56% H, 0.1% N, and 34.5% **0** (by difference). As determined by vapor pressure osmometry, the number average molecular weight (Mn) was 730 g/mol. The high oxygen content and molecular weight of the toluene-insoluble Py-Oil is consistent with its low solubility in an aromatic solvent, such as toluene.

Example 2

Lignin Bio-Oil

[0074] A lignin bio-oil was produced by hydrotreating a purified pine Kraft lignin with hydrogen at 2000 psig and 420° C. and a suspended iron based catalyst. The chemical analysis of the resultant lignin oil showed <0.34% water content, and an elemental analyses of 83.47% carbon, 9.23% hydrogen, 1.19% nitrogen, 0.40% sulfur, and 5.71% oxygen (by difference). The TAN of lignin bio-oil was 7 mg KOH/g. The number average molecular weight of the lignin bio-oil was 229 g/mol.

[0075] The solubility of the lignin bio-oil in toluene was determined. The bio-oil was mixed with nine times the volume of toluene. The mixture was heated to reflux, and then allowed to cool to room temperature. A single organic phase resulted, with the lignin bio-oil being miscible with the toluene. The lignin bio-oil was miscible with the toluene due to its low oxygen content, molecular weight, and TAN value, as compared to the toluene-insoluble Py-Oil in Example 1.

Example 3

Mild Hydrotreating of Py-Oil+Lignin Oil

[0076] A Py-Oil, as described in Example 1, was blended in line with a lignin bio-oil, described in Example 2, to yield a 1:3 mixture and directly fed into a hydrotreating, down flow reactor containing a sulfided NiO/MoO_3 supported catalyst (ICR181). The process pressure was 800 psig of hydrogen. A temperature gradient was applied across the catalyst bed, with the inlet temperature at 140° C., and an outlet temperature of 245° C. The product bio-oil was homogeneous and the water phase could be separated. Chemical analysis of the bio-oil product was 80.93% carbon, 9.90% hydrogen, 1.11% nitrogen, and 8.07% oxygen (by difference). The TAN of the product bio-oil was 17 mg KOH/g. Simple dilution of the Py-Oil by the lignin oil produced a TAN value of 88 mg KOH/g.

[0077] The product bio-oil was mixed with about ten times the volume of toluene. The mixture was heated to boiling and residual water entrained in the oil was removed by azeotropic distillation (Dean Stark method). The resulting bio-oil/toluene mixture was then allowed to cool. A single organic phase resulted, with the product bio-oil being completely miscible with the toluene.

Example 4

Effect of Catalyst and Py-Oil Ratio on the Hydrotreated Py-Oil Product

[0078] Similar to Example 3, but the percent of Py-Oil to lignin bio-oil was varied at 25%, 37.5%, and 50% Py-Oil for three separate runs. A different sulfided NiO/MoO_3 supported catalyst (ICR511) was used for these runs. A similar temperature gradient for the catalyst bed was used as in Example 3, with the outlet temperature being about 265° C.

[0079] The product bio-oil from each condition was separated from the water phase. As shown in Table 1 below, determination of the percent toluene solubility showed that these products exhibited increasing toluene insolubility, consistent with higher molecular weight components.

TABLE 1

Py-Oil/Lignin Oil Ratio	% toluene-insoluble	% C	% H	% N	% O (by diff.)
25:75	1.4%	79.15	9.7	1.02	9.76
37.5:62.5	7.0%	—	—	—	—
50:50	10.3%	—	—	—	—

[0080] As in Example 3, the hydrotreated product bio-oil from the 25:75 ratio appeared to be homogeneous. The Total Acid Number (TAN) of this product bio-oil was 15 mg KOH/g.

[0081] The hydrotreated product bio-oils from the 37.5% and 50% ratio mixtures were non-uniform and each had two distinct organic phases. This is reflected in their higher toluene insoluble values.

Example 5

Effect of Hydrotreating Temperature

[0082] Similar to Example 3, but for these runs the reaction temperature was increased in the lower third of the catalyst bed to produce six separate run conditions with increasing reaction temperatures. Table 2 shows the effect of hydrotreating temperatures on product oil density, % O content, number average molecular weight, and toluene solubility.

TABLE 2

Reactor Outlet Temp ° C.	density	% O (by diff.)	Mol Wt	% toluene-insoluble
250	1.0291	9.28%	225	0.00%
260	1.0318	10.01%		0.02%
270	1.0216	8.38%	234	0.24%
280	1.0101	7.76%		0.15%
300	0.9967	6.04%	241	0.00%
320	0.9794	4.92%	231	0.00%

Example 6

Lignin Liquefaction in Tetralin Using a Catalyst

[0083] Approximately 2.97 g of Kraft lignin was slurried with 0.0029 g of MolyVan A and 29 mL of tetralin in a 300 mL Autoclave batch reactor. The reactor was purged and filled with H_2 to 800 psig. After 60 minutes at 400° C., the external heat was removed and the reactor was allowed to cool. The resulting product solution was removed from the reactor, collected, and filtered. The tetralin soluble phase was 21.6 g. The resulting solid was washed with acetone, and the acetone washings were combined and stripped to yield a polar phase (tetralin insoluble product, 2.27 g). The third phase was the residual solid (0.321 g) after the tetralin filtration and acetone washing steps. The analyses of the products are shown in Table 3 below.

TABLE 3

	Relative Amounts	% C	% H	% N	% S	% O (by difference)
Tetralin Soluble Phase	21.6 (89.3%)	89.07	9.41	0.0	0.10	1.52
Tetralin Insoluble Product	2.27 (9.4%)	89.82	9.75	0.0	—	0.43
Residual Solids	0.321 (1.3%)	61.00	3.11	0.3	0	20.1

[0084] Based on kraft lignin, the yield of Tetralin insoluble product was 76%.

Example 7

Lignin Liquefaction in Lignin Bio-Oil Using a Catalyst

[0085] Approximately 10.02 g of Kraft lignin was slurried with 0.1071 g of MolyVan A and 51.65 g of lignin bio-oil (from Example 2) in a 300 mL Autoclave batch reactor. The reactor was purged and filled with H_2 to 800 psig. After 60 minutes at 400° C., the external heat was removed and the reactor was allowed to cool. The resulting material was removed from the reactor and collected as described by the following. The lignin bio-oil soluble phase was collected by filtering the entire solution (≈39.47 g). The resulting solid was washed with acetone and stripped to collect the polar phase (6.53 g). The third phase was the residual solid after the lignin bio-oil filtration and acetone washing steps (1.518 g). The analyses of the products are shown in Table 4 below.

TABLE 4

	Relative Amounts	% C	% H	% N	% S	% O (by difference)
Lignin Bio-Oil Soluble Phase	39.47 (83.1%)	84.60	8.79	0.15	0.105	6.35
Lignin Bio-Oil Insoluble Product	6.53 (13.7%)	82.52	9.08	0	na	7.33
Residual Solids	1.52 (3.2%)					

[0086] Based on kraft lignin, the yield of lignin bio-oil insoluble product was 65%.

[0087] In both Examples 6 and 7, the solvent insoluble products are similar, as neither is soluble in the reaction solvent. The data indicates tetralin is a slightly poorer solvent than the lignin oil, because the amount of Tetralin insoluble product was higher than the amount of lignin bio-oil insoluble product.

[0088] The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention, which is defined by the following claims. The claims are intended to cover the claimed components and steps in any sequence which is effective to meet the objectives there intended, unless the context specifically indicates the contrary.

What is claimed is:

1. A method for rendering biomass-derived pyrolysis oil miscible with refinery hydrocarbons, the method comprising the steps of:

a) mixing (i) a high oxygen content bio-oil comprising an oxygen content of at least about 10 wt. % with (ii) a low oxygen content bio-oil an oxygen content of less than about 8 wt. % to yield a blended oil.

2. The method of claim **1**, further comprising:

b) hydrotreating the blended oil to yield a hydrotreated mixture comprising (i) low oxygen-content hydrotreated bio-oil and (ii) water, wherein the low oxygen-content hydrotreated bio-oil has an oxygen content of 10 wt. % or less.

3. The method of claim **2**, further comprising:

c) removing water from the hydrotreated mixture to yield a low oxygen content hybrid bio-oil intermediate, wherein water removal is effected via a phase separation between the low oxygen content hydrotreated bio-oil and the water.

4. The method of claim **3**, further comprising:

d) combining at least a portion of the low oxygen content hybrid bio-oil intermediate with the high oxygen content bio-oil in step (a), and

e) repeating steps (a) through (d).

5. The method of claim **1**, wherein the high oxygen content bio-oil is produced in a conversion reactor by a conversion process selected from the group consisting of fast pyrolysis, slow pyrolysis, liquefaction, gasification, or enzymatic conversion.

6. The method of claim **1**, wherein the high oxygen content bio-oil comprises an oxygen content between about 25 wt. % and 50 wt. %.

7. The method of claim **1**, wherein the low oxygen content bio-oil comprises a biomass feedstock produced by pyrolysis or catalytic pyrolysis, hydroliquefaction via catalytic hydrogenation, or by hydrogen donor solvent liquefaction.

8. The method of claim **1**, wherein the low oxygen content bio-oil is produced from a hydrotreated lignocellulosic feedstock.

9. The method of claim **1**, wherein the low oxygen content bio-oil comprises an oxygen content up to about 8 wt. %.

10. The method of claim **1**, wherein the low oxygen content bio-oil has a total acid number less than about 10 mg KOH/g.

11. The method of claim **1**, wherein upon mixing in the first mixing unit, the ratio of the high oxygen content bio-oil to the low oxygen content bio-oil in the blended oil is between about 0.1 and about 0.3.

12. The method of claim **1**, wherein the high oxygen content bio-oil and the low oxygen content bio-oil are mixed so that the blended oil has a total acid number between about 50-100 mg KOH/g.

13. The method of claim **4**, wherein the wherein the low oxygen content hybrid bio-oil intermediate is substantially miscible in a non-polar solvent.

14. The method of claim **4**, wherein the low oxygen content hybrid bio-oil intermediate has a total acid number less than or equal to 20 mg KOH/g.

15. The method of claim **4**, wherein the low oxygen content hybrid bio-oil intermediate has an average molecular weight between about 200-300 g/mol and a boiling point range below 500° C.

16. The method of claim **4**, wherein the wherein the low oxygen content hybrid bio-oil intermediate is added to a second low oxygen content bio-oil in a second mixing unit to yield a second blended oil, wherein the second blended oil is added to the high oxygen content bio-oil in the first mixing unit.

17. A system for producing a bio-oil comprising:

a biomass conversion unit facilitating production of a high oxygen content bio-oil from a biomass feedstock;

a first mixing unit comprising a first inlet receiving the high oxygen content bio-oil from the conversion unit and a second inlet receiving a low oxygen content bio-oil from a bio-oil feedstock to form a blended oil;

a hydrotreater comprising an inlet receiving the blended oil from the first mixing unit to produce a hydrotreated bio-oil mixture;

a separator for separating water from the hydrotreated bio-oil mixture to produce a low oxygen content hybrid bio-oil intermediate, the separator comprising a first inlet receiving the hydrotreated bio-oil mixture from the hydrotreater, an outlet supplying the low oxygen content hybrid bio-oil intermediate to the first mixing unit, and optionally an outlet supplying the low oxygen content hybrid bio-oil intermediate to a source of refinery hydrocarbons.

18. The system of claim **17**, further comprising a second mixing unit, wherein the second mixing unit comprises a first inlet receiving the low oxygen content hybrid bio-oil intermediate from the separator, a second inlet receiving a low oxygen content bio-oil from a bio-oil feedstock to produce a low oxygen blended oil, and an outlet supplying the low oxygen blended oil formed in the second mixing unit to the first mixing unit; and wherein the separator further comprises an outlet supplying the low oxygen content hybrid bio-oil intermediate to the second mixing unit.

19. The system of claim **17**, wherein the biomass conversion unit comprises a pyrolyis unit for forming a high oxygen content pyrolyis oil.

20. A blended oil composition, comprising a high oxygen content bio-oil with an oxygen content of at least about 10 wt. % bio-oil blended with a low oxygen content bio-oil with an oxygen content of less than about 8 wt. %.

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