METHODS AND SYSTEMS FOR DEOXYGENATING BIOMASS-DERIVED PYROLYSIS OIL WITH A RECYCLE COLUMN

Abstract: Methods and systems for deoxygenating a biomass-derived pyrolysis oil are provided. An exemplary method includes combining a biomass-derived pyrolysis oil stream with a heated low-molecular weight fraction low-oxygen-pyroil diluent recycle stream to form a heated diluted pyoil feed stream, which is contacted with a first deoxygenating catalyst in the presence of hydrogen at first hydropyrolysis conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent. A low-molecular weight fraction low-oxygen-pyroil diluent recycle stream is formed by contacting the low-oxygen biomass-derived pyrolysis oil effluent with a fractionation column to separate a low molecular weight fraction low-oxygen-pyroil diluent recycle stream at a cutpoint of 225°C or less. The low-molecular weight fraction low-oxygen-pyroil diluent recycle stream is then heated prior to combination with the biomass-derived pyrolysis oil stream.
METHODS AND SYSTEMS FOR DEOXYGENATING BIOMASS-DERIVED PYROLYSIS OIL WITH A RECYCLE COLUMN

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 14/101,842 which was filed December 10, 2013, the contents of which are hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with Government support under DE-EE0002879 awarded by the U.S. Department of Energy. The Government has certain rights in this invention.

TECHNICAL FIELD

[0003] The technical field generally relates to methods and systems for producing biofuels, and more particularly relates to methods and systems for producing low-oxygen biomass-derived pyrolysis oil from the catalytic deoxygenation of biomass-derived pyrolysis oil.

BACKGROUND

[0004] Fast pyrolysis is a process during which organic carbonaceous biomass feedstock, i.e., "biomass", such as wood waste, agricultural waste, algae, etc., is rapidly heated to between 300°C to 900°C in the absence of air using a pyrolysis reactor. Under these conditions, solid products, liquid products, and gaseous pyrolysis products are produced. A condensable portion (vapors) of the gaseous pyrolysis products is condensed into biomass-derived pyrolysis oil (commonly referred to as "pyoil"). Biomass-derived pyrolysis oil can be burned directly as fuel for certain boiler and furnace applications, and can also serve as a potential feedstock in catalytic processes for the production of fuels in petroleum refineries. Biomass-derived pyrolysis oil has the potential to replace up to 60% of transportation fuels, thereby reducing the dependency on conventional petroleum and reducing its environmental impact.
However, biomass-derived pyrolysis oil is a complex, highly oxygenated organic liquid having properties that currently limit its utilization as a biofuel. For example, biomass-derived pyrolysis oil has high acidity and a low energy density attributable in large part to oxygenated hydrocarbons in the oil, which can undergo secondary reactions during storage particularly if the oil is stored at elevated temperatures. As used herein, "oxygenated hydrocarbons" or "oxygenates" are organic compounds containing hydrogen, carbon, and oxygen. Such oxygenated hydrocarbons in the biomass-derived pyrolysis oil include carboxylic acids, phenols, cresols, alcohols, aldehydes, etc. Conventional biomass-derived pyrolysis oil comprises 30% or greater by weight oxygen from these oxygenated hydrocarbons. Conversion of biomass-derived pyrolysis oil into biofuels and chemicals requires full or partial deoxygenation of the biomass-derived pyrolysis oil. Such deoxygenation may proceed via two main routes, namely the elimination of either water or CO₂. Unfortunately, deoxygenating biomass-derived pyrolysis oil leads to rapid plugging or fouling of the processing catalyst in a hydroprocessing reactor caused by the formation of solids from the biomass-derived pyrolysis oil. Components in the pyrolysis oil form on the processing catalysts causing catalytic bed fouling, reducing activity of the catalyst, and causing build up in the hydroprocessing reactor. It is believed that this plugging is due to an acid catalyzed polymerization of the various components of the biomass-derived pyrolysis oil, e.g., second order reactions in which the various components of the oil polymerize with themselves, that create either a glassy brown polymer or powdery brown char that limits run duration and processability of the biomass-derived pyrolysis oil. So far, improvements in reactor design and processing methods (such as those described, e.g., in U.S. Pub. No. 2013/0152424) have delayed but not eliminated eventual plugging or fouling the processing catalyst.

Accordingly, it is desirable to provide methods for producing a low-oxygen biomass-derived pyrolysis oil without plugging, or at least with further reduced plugging, of the catalyst, thereby increasing run duration and improving processability of the biomass-derived pyrolysis oil. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.
BRIEF SUMMARY

[0007] Methods for deoxygenating biomass-derived pyrolysis oil are provided herein. In accordance with an exemplary embodiment, a method for deoxygenating a biomass-derived pyrolysis oil comprises the steps of: combining a biomass-derived pyrolysis oil stream with a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form a heated diluted pyoil feed stream that has a feed temperature of 150 °C or greater; contacting the heated diluted pyoil feed stream with a first deoxygenating catalyst in the presence of hydrogen at first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent; contacting the low-oxygen biomass-derived pyrolysis oil effluent with a fractionation column to separate a low molecular weight fraction low-oxygen-pyoil diluent recycle stream; and heating the low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream. In this embodiment, the low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated at a cutpoint of 225 °C or less.

[0008] Further, systems for deoxygenating a biomass-derived pyrolysis oil are provided herein. In an exemplary embodiment, a system comprises a first hydroprocessing reactor comprising a first hydroprocessing catalyst. The first hydroprocessing reactor is configured to receive a heated diluted pyoil feed stream and operated under first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent when the heated diluted pyoil feed stream contacts the first hydroprocessing catalyst in the presence of hydrogen, wherein the heated diluted pyoil feed stream comprises a combination of a biomass-derived pyrolysis oil and a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream combined at a predetermined ratio. The system further comprises a fractionation column configured to receive the low-oxygen biomass-derived pyrolysis oil effluent. The fractionation column is operated under conditions such that a low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of 225 °C or lower. The system further comprises a heater configured to receive and heat the low molecular weight fraction low-oxygen-pyoil diluent...
recycle stream to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream.

DETAILED DESCRIPTION OF THE DRAWINGS

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

[0010] FIG. 1 is a block diagram illustrating a system and method for deoxygenating a biomass-derived pyrolysis oil in accordance with a first exemplary embodiment.

[0011] FIG. 2 is a block diagram illustrating a system and method for deoxygenating a biomass-derived pyrolysis oil in accordance with a second exemplary embodiment.

[0012] FIG. 3 is a block diagram illustrating a system and method for deoxygenating a biomass-derived pyrolysis oil in accordance with a third exemplary embodiment.

[0013] FIG. 4 is a block diagram illustrating a system and method for deoxygenating a biomass-derived pyrolysis oil in accordance with a fourth exemplary embodiment.

DETAILED DESCRIPTION

[0014] The following detailed description is merely exemplary in nature and is not intended to limit the various embodiments or the application and uses thereof. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0015] Various embodiments contemplated herein relate to methods and systems for deoxygenating a biomass-derived pyrolysis oil. The exemplary embodiments taught herein produce a low-oxygen biomass-derived pyrolysis oil effluent by contacting a heated diluted pyoil feed stream with a deoxygenating catalyst in the presence of hydrogen at hydroprocessing conditions to partially deoxygenate the heated diluted pyoil feed stream. It should be appreciated that, while the deoxygenated oil produced according to exemplary embodiments are generally described herein as a "low-oxygen biomass-derived pyrolysis oil" or an "ultralow-oxygen biomass-derived pyrolysis oil," these terms generally include any pyoil produced having a lower oxygen concentration (i.e., a lower residual oxygen
content) than conventional biomass-derived pyrolysis oil. The term "low-oxygen biomass-derived pyrolysis oil" is pyoil having some oxygen, i.e., a biomass-derived pyrolysis oil in which a portion of the oxygenated hydrocarbons have been converted into hydrocarbons (i.e., a "hydrocarbon product"). In an exemplary embodiment, the low-oxygen biomass-derived pyrolysis oil comprises an organic phase (i.e. oil comprising primarily oxygenates and/or hydrocarbons) that comprises oxygen in an amount of from 5 to 25 weight percent (wt. %) of the organic phase. The term "ultralow-oxygen biomass-derived pyrolysis oil" is pyoil that has less oxygen than the low-oxygen biomass-derived pyrolysis oil and includes pyoil having substantially no oxygen, i.e., a biomass-derived pyrolysis oil in which substantially all the oxygenated hydrocarbons have been converted into hydrocarbons (i.e., a "hydrocarbon product"). In an exemplary embodiment, the ultralow-oxygen biomass-derived pyrolysis oil comprises an organic phase that comprises oxygen in an amount of from 0 to 2 wt. % of the organic phase. "Hydrocarbons" as used herein are organic compounds that contain principally only hydrogen and carbon, i.e., oxygen-free.

[0016] A heated diluted pyoil feed stream may be formed by combining a biomass-derived pyrolysis oil stream with a heated low-oxygen-pyoil diluent recycle stream. The heated low-oxygen-pyoil diluent recycle stream is formed from a portion of the low-oxygen biomass-derived pyrolysis oil effluent that has been recycled and heated. Therefore, the heated low-oxygen-pyoil diluent recycle stream has already been partially deoxygenated, which removes not only some of the oxygen but also significantly reduces the amount of pyoil reactant components that can undergo secondary polymerization reactions with various constituents of the biomass-derived pyrolysis oil stream.

[0017] The heated diluted pyoil feed stream is formed upstream from a hydroprocessing reactor that contains a deoxygenating catalyst in the presence of hydrogen and that is operating at hydroprocessing conditions. The heated diluted pyoil feed stream is introduced to the hydroprocessing reactor and contacts the deoxygenating catalyst to form the low-oxygen biomass-derived pyrolysis oil effluent.

[0018] While combining a heated portion of the low-oxygen pyoil diluent recycle stream with the biomass-derived pyrolysis oil stream is effective for reducing the
formation of secondary polymerization solids, it has been found that the recycled pyoil diluent stream can still react with the biomass-derived pyrolysis oil stream. In fact, over time the molecular weight and viscosity of the resulting low-oxygen biomass-derived pyrolysis oil effluent can increase to such an extent that the heated diluted pyoil feed stream can no longer be processed in a fixed bed reactor due to an increase in differential pressure across the reactor.

[0019] Without wishing to be bound by theory, it is believed that certain compounds in the low-oxygen pyoil diluent recycle stream may undergo secondary polymerization reactions in the biomass-derived pyrolysis oil stream resulting in a gradual increase in molecular weight and viscosity of the effluent, which ultimately limits the time on stream before a pressure differential across the reactor becomes too high. Described herein are methods, systems, and apparatus that reduce or eliminate these secondary polymerization reactions by removing or reducing higher molecular weight species from the low-oxygen pyoil diluent recycle stream prior to combination of the recycle stream with the biomass-derived pyrolysis oil stream.

[0020] As used herein, the phrase "low molecular weight species" as it relates to chemical species found in the low-oxygen pyoil diluent recycle stream refers to the chemical species that evaporate and are collected as vapor as a result of fractional distillation of the low-oxygen pyoil diluent recycle stream to a desired cutpoint. Conversely, the phrase "high molecular weight species" as it relates to chemical species found in the low-oxygen pyoil diluent recycle stream refers to the chemical species that remain liquid following this distillation. In some embodiments, the desired cutpoint is a temperature of 225 °C or less; such as between 190 to 225°C; such as between 200 to 220°C; such as 215°C.

[0021] Thus, in some embodiments, the low-oxygen pyoil diluent recycle stream is subjected to a distillation and the low molecular weight fraction collected to a cutpoint of between 190 to 225°C is routed for optional further processing prior to combination with a biomass-derived pyrolysis oil stream. The cutpoint is selected such that the remaining high molecular weight fraction has a liquid viscosity low enough to be processable, e.g., in a second hydroprocessing reactor.
Thus, in an exemplary embodiment a biomass-derived pyrolysis oil stream has an initial temperature of 100 °C or less, for example of ambient, prior to being combined with a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form a heated diluted pyoil feed stream. The low molecular weight fraction is heated to a recycle temperature of 200 to 450 °C before being combined with the biomass-derived pyrolysis oil stream at a predetermined recycle ratio of at least 2:1 diluent recycle stream:pyrolysis oil stream. In some embodiments, the biomass-derived pyrolysis oil stream is diluted at a ratio of between 2:1 to 20:1 diluent recycle stream:pyrolysis oil stream. By combining the biomass-derived pyrolysis oil stream with the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream, the biomass-derived pyrolysis oil stream is diluted by the low molecular weight fraction and is rapidly heated, for example, to a temperature that is suitable for hydropyrolysis. Moreover, diluting the biomass-derived pyrolysis oil stream with the mutually miscible heated diluent facilitates solubilizing any solids that may have formed during storage or that could otherwise form in the pyoil during subsequent hydropyrolysis (e.g. glassy brown polymers or powdery brown char).

Further, it has been found that limiting the conversion per pass across the first hydropyrolysis reactor to retain a portion of the initial oxygen in the low-oxygen biomass-derived pyrolysis oil effluent facilitates separation of the low and high molecular weight fractions, while still being sufficiently converted such that the portion of the effluent that is not recycled may still be fully deoxygenated by a second stage of hydropyrolysis, e.g., with a second hydropyrolysis reactor. As such, in some embodiments, the hydropyrolysis conditions utilized in the first reactor are such that the conversion per pass is limited so that between 10 to 25% residual oxygen, such as between 15 to 22 wt. % residual oxygen, such as 20 wt. % residual oxygen, is retained in the hydropyrolysed organic phase of the low-oxygen biomass-derived pyrolysis oil effluent.

It has further been found that the amount of residual water that remains in the low molecular weight fraction low-oxygen pyoil diluent recycle stream affects the extent of secondary polymerization reactions between components of the recycled diluent stream and components of the biomass-derived pyrolysis oil stream. Thus, in some embodiments, the amount of water in the low molecular weight fraction low-oxygen pyoil diluent recycle
stream may be modulated to further inhibit the secondary polymerization reactions. The amount of water in the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted by any suitable method, such as by incorporation of one or more optional sub-systems to the recycle system.

[0025] For instance, in some embodiments the low-oxygen pyoil diluent recycle stream may be subjected to phase separation prior to fractional distillation such that the low-oxygen pyoil diluent recycle stream is separated into a \( \frac{3}{4} \) gas containing stream, a water stream, and a water-depleted low-oxygen-pyoil stream. If phase separation is used, the \( \frac{3}{4} \) gas containing stream and water stream are diverted and collected, while the water-depleted low-oxygen-pyoil stream is subjected to fractional distillation to separate low molecular weight and high molecular weight fractions, as described above.

[0026] Before phase separation, the low-oxygen pyoil diluent recycle stream typically contains 10 wt. % water. However, the temperature at which the low-oxygen pyoil diluent recycle stream is subjected to phase separation affects the solubility of water in the low-oxygen pyoil diluent recycle stream, and thus the amount of residual water that remains in the water-depleted low-oxygen-pyoil stream after phase separation. Thus, in some embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted (e.g. cooled by any suitable means, such as with a condenser) after exiting the first hydroprocessing reactor and before phase separation.

[0027] In some embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted so that the amount of residual water that remains in the water-depleted low-oxygen-pyoil stream after phase separation is minimized. In such embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted so that phase separation is conducted within the temperature range of 0 to 60 °C, such as between 30 to 60 °C.

[0028] In some alternative embodiments, the temperature of the of the low-oxygen pyoil diluent recycle stream may be adjusted so that the amount of residual water that remains in the water-depleted low-oxygen-pyoil stream after phase separation is maximized. That is, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted such that water and organic phases of the low-oxygen pyoil diluent recycle
stream are fully miscible as the recycle stream enters the separator. In these embodiments, only two streams will result from phase separation: a ¾ gas containing stream, and a ¼ gas depleted low-oxygen-pyoil liquid stream. In such embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted so that phase separation is conducted within the temperature range of 140 to 200 °C.

[0029] In yet further alternative embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted so that the amount of residual water that remains in the water-depleted low-oxygen-pyoil stream after phase separation is at an amount between the minimum and maximum possible amounts. In such embodiments, the temperature of the low-oxygen pyoil diluent recycle stream may be adjusted so that phase separation is conducted within the temperature range of 60 to 140 °C.

[0030] In addition or in the alternative, the amount of water in the low-oxygen pyoil diluent recycle stream may be adjusted after fractional distillation and prior to combination with the biomass-derived pyrolysis oil stream. As described above with respect to the low-oxygen pyoil diluent recycle stream, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream affects the saturation point of water vapor, and thus, the amount of residual water that remains in the low molecular weight fraction low-oxygen pyoil diluent recycle stream after distillation. Thus, in some embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted (e.g. cooled by any suitable means, such as with a condenser) after distillation to form aqueous and organic phases. In such embodiments, the aqueous phase may then be separated, e.g., with a phase separator, and the organic phase routed for combination with the biomass-derived pyrolysis oil stream.

[0031] For instance, in some embodiments the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted so as create an aqueous phase and an organic phase with a minimum amount of residual water. The aqueous phase may then be separated, e.g., with a phase separator, and the organic phase routed for combination with the biomass-derived pyrolysis oil stream. In such embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil
diluent recycle stream may be adjusted so that phase separation is conducted within the temperature range of 0 to 60 °C, such as between 10 to 50 °C.

[0032] In some alternate embodiments, the temperature of the low molecular weight fraction of the low-oxygen pyoil diluent recycle stream may be adjusted so that the amount of residual water that remains in the low molecular weight fraction low-oxygen pyoil diluent recycle stream is maximized. In such embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted such that the residual water in the low molecular weight fraction low-oxygen pyoil diluent recycle stream after distillation is completely miscible. That is, in these embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream after distillation may be adjusted such that the low molecular weight fraction low-oxygen pyoil diluent recycle stream is a single phase. In these embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream after distillation may be adjusted to be within the range of 140 to 200 °C after distillation but prior to combination with the biomass-derived pyrolysis oil stream. In such embodiments, the low molecular weight fraction low-oxygen pyoil diluent recycle stream may not be subjected to a phase separation prior to combination with the biomass-derived pyrolysis oil stream.

[0033] In yet further alternative embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted so that the amount of residual water that remains in the low molecular weight fraction low-oxygen pyoil diluent recycle stream is at an amount between the minimum and maximum possible amounts. The aqueous phase may then be separated, e.g., with a phase separator, and the organic phase routed for combination with the biomass-derived pyrolysis oil stream. In such embodiments, the temperature of the low molecular weight fraction low-oxygen pyoil diluent recycle stream may be adjusted so that phase separation is conducted within the temperature range of 60 to 150 °C, such as between 60 to 140 °C.

[0034] Four specific exemplary embodiments are described below with reference to Figures 1-4. Discussion of these embodiments is not intended to be limiting, but rather
merely illustrative of systems and apparatus that can be used to achieve the process features described above.

[0035] Referring to FIG. 1, a schematic depiction of a system 10 for deoxygenating a biomass-derived pyrolysis oil in accordance with an exemplary embodiment is provided. As illustrated, a biomass-derived pyrolysis oil stream 12 is introduced to the apparatus 10. The biomass-derived pyrolysis oil found in the biomass-derived pyrolysis oil stream 12 may be produced, such as, for example, from pyrolysis of biomass in a pyrolysis reactor. Virtually any form of biomass can be used for pyrolysis to produce the biomass-derived pyrolysis oil. The biomass-derived pyrolysis oil may be derived from biomass material, such as, wood, agricultural waste, nuts and seeds, algae, forestry residues, and the like. The biomass-derived pyrolysis oil may be obtained by different modes of pyrolysis, such as, for example, fast pyrolysis, vacuum pyrolysis, catalytic pyrolysis, and slow pyrolysis or carbonization, and the like.

[0036] The composition of the biomass-derived pyrolysis oil can vary considerably and depends on the feedstock and processing variables. Examples of biomass-derived pyrolysis oil "as-produced" can contain up to 1,000 to 30,000 ppm total metals, 20 to 33 weight percent (wt. %) of water that can have high acidity (e.g. total acid number (TAN)>150), and a solids content of from 0.1 wt. % to 5 wt. %. The biomass-derived pyrolysis oil may be untreated (e.g. "as produced"). However, if needed the biomass-derived pyrolysis oil can be selectively treated to reduce any or all of the above to a desired level. In an exemplary embodiment, the biomass-derived pyrolysis oil comprises an organic phase (i.e., oil comprising primarily oxygenates and/or hydrocarbons along with any dissolved water) that has a residual oxygen content of 10 wt. % or greater, for example of 30 wt. % or greater, for example from 30 to 50 wt. %, such as from 35 to 45 wt. % of the organic phase.

[0037] The biomass-derived pyrolysis oil may be thermally unstable and may be stored and/or handled so as to reduce its exposure to higher temperatures, thus minimizing secondary polymerization reactions between various components in the biomass-derived pyrolysis oil prior to hydroprocessing. In an exemplary embodiment, the biomass-derived pyrolysis oil stream 12 has as an initial temperature (e.g. storage temperature) of 100 °C or
less, for example from 15 °C to 100 °C, for example from 15 °C to 50 °C, such as ambient, to inhibit secondary polymerization reactions.

[0038] Upstream from a first hydroprocessing reactor 18, the biomass-derived pyrolysis oil stream 12 is combined and diluted with a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream 14 to form a heated diluted pyoil feed stream 16. The heated low-molecular weight fraction 14 can be introduced to the biomass-derived pyrolysis oil stream 12 in a single stream together with a H2-containing gas stream 33, as illustrated and discussed in further detail below, or alternatively, the heated low-molecular weight fraction 14 can be introduced to the biomass-derived pyrolysis oil stream 12 in a single or in multiple separate streams that do not include the H2-containing gas stream 33. For example, the H2-containing gas stream 33 can be introduced directly to the heated diluted pyoil feed stream 16 and/or directly to the first hydroprocessing reactor 18, and the heated low-molecular weight fraction 14 can be introduced to the biomass-derived pyrolysis oil stream 12 absent the hydrogen-containing gas stream 33.

[0039] As will be discussed in further detail below, the heated low-molecular weight fraction 14 is a low-molecular weight fraction of a pyoil stream that has been previously partially deoxygenated, recycled, and heated. As such, the heated low-molecular weight fraction 14 has less pyoil reactant components that can undergo secondary polymerization reactions (which result in formation of solids or a viscosity increase of the heated diluted pyoil feed stream 16), and contains some oxygen but less oxygen than the biomass-derived pyrolysis oil stream 12. By having some oxygen in the heated low-molecular weight fraction 14, the biomass-derived pyrolysis oil stream 12 and the heated low-molecular weight fraction 14 are mutually miscible. Moreover, it has been found that incomplete conversion (i.e., leaving some oxygen in the low-oxygen biomass-derived pyrolysis oil effluent) facilitates separation of the low and high molecular weight fractions, while still being sufficiently converted such that the portion of the effluent that is not recycled may still be fully deoxygenated by a second stage of hydroprocessing, e.g., with a second hydroprocessing reactor.
In an exemplary embodiment, the hydroprocessing conditions utilized in the first reactor are such that the conversion per pass is limited so that between 10 to 25 wt. % oxygen, such as between 15 to 22 wt. % oxygen, such as 20 wt. % oxygen, is retained in the low-oxygen biomass-derived pyrolysis oil effluent. In one example, the hydroprocessed organic phase comprises oxygenates such as phenols, alkyl phenols, alcohols, ethers, and/or the like that are similar to and/or easily solubilize the oxygenates contained in the biomass-derived pyrolysis oil stream 12.

In an exemplary embodiment, the heated low-molecular weight fraction 14 has a temperature of from 200 to 450 °C, for example from 300 to 450 °C, such as from 325 to 425 °C. In an exemplary embodiment, the biomass-derived pyrolysis oil stream 12 and the heated low-molecular weight fraction 14 are combined at a predetermined recycle ratio that is defined by a mass flow rate of the heated low-molecular weight fraction 14 to a mass flow rate of the biomass-derived pyrolysis oil stream 12 to form the heated diluted pyoil feed stream 16 that has a feed temperature of 150 °C or greater, for example from 150 to 400 °C, such as from 200 to 350 °C. In an exemplary embodiment, the biomass-derived pyrolysis oil stream 12 is combined with the heated low-molecular weight fraction 14 at the predetermined recycle ratio of from 2:1 to 20:1.

The heated diluted pyoil feed stream 16 is introduced to the first hydroprocessing reactor 18. The first hydroprocessing reactor 18 can be a continuous flow reactor, such as a fixed-bed reactor, a continuous stirred tank reactor (CSTR), a trickle bed reactor, an ebulliating bed reactor, a slurry reactor, or any other reactor known to those skilled in the art for hydroprocessing.

The first hydroprocessing reactor 18 contains a deoxygenating catalyst in the presence of hydrogen. In an exemplary embodiment, the deoxygenating catalyst comprises a metal or a combination of metals, such as a base metal(s), a refractory metal(s), and/or a noble metal(s), such as platinum, palladium, ruthenium, nickel, molybdenum, tungsten, and/or cobalt. The metal(s) may be on a support, such as a carbon support, a silica support, an alumina support, a silica-alumina support (amorphous or zeolite), a gamma alumina support, a zirconia support, and/or a titanium support. Other hydroprocessing catalysts known to those skilled in the art may also be used.
The first hydroprocessing reactor 18 is operating at hydroprocessing conditions. In an exemplary embodiment, the hydroprocessing conditions include a reactor temperature of from 150 to 400 °C, such as from 200 to 350 °C, a reactor pressure of from 2 to 20 MPa gauge, a liquid hourly space velocity on a basis of weight of the biomass-derived pyrolysis oil/weight of catalyst/hour (hr⁻¹) of from 0.10 to 1 hr⁻¹, and a hydrogen-containing gas treat rate of from 1,000 to 15,000 standard cubic feet per barrel (SCF/B).

In an exemplary embodiment, the heated diluted pyoil feed stream 16 is formed just upstream of the first hydroprocessing reactor 18 and the feed temperature of the heated diluted pyoil feed stream 16 is at the reactor temperature to facilitate rapid catalytic deoxygenation of the heated diluted pyoil feed stream 16 with a short or minimal residence time. The term "residence time" as used herein is the amount of time from when the biomass-derived pyrolysis oil stream 12 is combined with the heated low-molecular weight fraction 14 to when the heated diluted pyoil feed stream 16 initially contacts the deoxygenating catalyst. By having a relatively short residence time, less secondary polymerization reactions can occur in the heated diluted pyoil feed stream 16 at elevated temperatures before hydroprocessing begins. In an exemplary embodiment, the residence time is 60 seconds or less, for example 20 seconds or less, for example 10 second or less, such as from 10 seconds to 1 second.

The heated diluted pyoil feed stream 16 contacts the deoxygenating catalyst at the hydroprocessing conditions in the presence of hydrogen and forms a low-oxygen biomass-derived pyrolysis oil effluent 20 by converting a portion of the oxygenated hydrocarbons in the biomass-derived pyrolysis oil into hydrocarbons (i.e., partial deoxygenation). In particular, hydrogen from a make-up hydrogen stream 31 is optionally combined with hydrogen 30 recovered from the low-oxygen biomass-derived pyrolysis oil effluent 20 to form a hydrogen-containing gas stream 33. The hydrogen-containing gas stream 33 removes oxygen from the biomass-derived pyrolysis oil as water to produce the low-oxygen biomass-derived pyrolysis oil effluent 20 that comprises an aqueous phase and a hydroprocessed organic phase. The hydroprocessed organic phase comprises oil that is partially deoxygenated with some residual oxygenated hydrocarbons. In an exemplary embodiment, the hydroprocessed organic phase of the low-oxygen biomass-derived
pyrolysis oil effluent 20 has a residual oxygen content of from 5 to 30 wt. %, for example from 10 to 25 wt. %, such as from 15 to 25 wt. % of the hydroprocessed organic phase.

[0047] It is believed that the benefits of catalytically deoxygenating the biomass-derived pyrolysis oil that is diluted with the heated low-molecular weight fraction 14, may result in increasing hydrogen solubility, immolating the exotherm by dilution of the reactive species in the biomass-derived pyrolysis oil stream 12, and reducing the reaction rate of bimolecular reactants that lead to secondary polymerization reactions. As such, simple reactions of the biomass-derived pyrolysis oil with hydrogen to form a lower-oxygen biomass-derived pyrolysis oil dominate while secondary polymerization reactions of biomass-derived pyrolysis oil components with themselves are reduced or minimized, thereby reducing or minimizing the formation of glassy brown polymers or powdery brown char on the deoxygenating catalyst, as well as reducing or minimizing viscosity increases in the heated diluted pyoil feed stream 16 resulting from continued recycling of the low-oxygen biomass-derived pyrolysis oil effluent 20.

[0048] In an exemplary embodiment, the low-oxygen biomass-derived pyrolysis oil effluent 20 is removed from the first hydroprocessing reactor 18, passed through a chiller 22, and subjected to a first phase separation. In an exemplary embodiment, the chiller 22 cools the low-oxygen biomass-derived pyrolysis oil effluent 20 to a temperature of from 30 to 60 °C. The first phase separation removes light volatiles, water, light liquids, and solids (if present) from the low-oxygen biomass-derived pyrolysis oil effluent 20 using one or more separation vessels, fractionation columns, heaters, condensers exchangers, pipes, pumps, compressors, controllers, and/or the like. In an exemplary embodiment and as illustrated, the first phase separation is conducted with a high pressure three-phase separator 24. The low-oxygen biomass-derived pyrolysis oil effluent 20 is introduced to the high pressure three-phase separator 24 and is separated into a water-containing (i.e., aqueous) stream 26, a H₂ gas-containing stream 30, and a water-depleted low-oxygen-pyoil stream 36. The aqueous stream 26 is passed along to an aqueous-organic separation zone. The H₂ gas-containing stream 30 may be removed from the apparatus 10, or optionally a portion or all of the H₂ gas-containing stream 30 is combined with a hydrogen from a make-up hydrogen stream 31 and diverted to a compressor 32, which generates the
H₂-containing gas stream 33 that may be introduced to the heated diluted pyoil feed stream 16 and/or directly to the first hydroprocessing reactor 18, as described above.

[0049] The water-depleted low-oxygen-pyoil stream 36 is then directed to a recycle column 38, where the water-depleted low-oxygen-pyoil stream 36 is separated into low-molecular weight and high-molecular weight fractions. In an exemplary embodiment, the recycle column 38 is a fractionation column wherein a low-molecular weight fraction 40 and a high-molecular weight fraction 42 are separated at a cutpoint temperature of 225 °C or less, such as between 190 to 225 °C; such as between 200 to 220 °C; such as 215 °C.

[0050] The low-molecular weight fraction 40 is passed through a chiller 44, and delivered to a phase separator 46, which separates an organic volatile gas stream 48, an aqueous stream 50, and a low-molecular weight fraction organic liquid phase 52. In one embodiment, the organic volatile gas stream 48 and aqueous stream 50 are diverted and collected, while the low-molecular weight fraction organic liquid phase 52 is passed through a pump 56 and sent to a heater 34 to generate the heated low-molecular weight fraction 14 discussed above. As indicated above, the heated low-molecular weight fraction 14 is combined with the biomass-derived pyrolysis oil stream 12, and is thus recycled through the first hydroprocessing reactor 18. In some embodiments, a portion of the low-molecular weight fraction organic liquid phase 52 is diverted prior to entering the heater 34 and instead directed to be combined with the high-molecular weight fraction 42. In these embodiments, the combination may then be directed to a second hydroprocessing reactor system 28, as discussed below.

[0051] The high-molecular weight fraction 42 from the recycle column 38 is passed through a pump 60 and is sent to a second hydroprocessing reactor system 28 for further processing. The second hydroprocessing reactor system 28 may be any suitable hydroprocessing reactor system known in the art, and may include, for instance, a batch reactor or continuous flow reactor, such as a fixed-bed reactor, a continuous stirred tank reactor (CSTR), a trickle bed reactor, an ebulliating bed reactor, a slurry reactor, or any other reactor known to those skilled in the art for hydroprocessing. The second hydroprocessing reactor system 28 contains a second hydroprocessing reactor that utilizes a deoxygenating catalyst in the presence of hydrogen as discussed above with respect to
the deoxygenating catalyst in the first hydroprocessing reactor 18. The second hydroprocessing reactor is operated at hydroprocessing conditions. In an exemplary embodiment, the hydroprocessing conditions include a second hydroprocessing reactor temperature of from 150 to 500 °C, such as from 300 to 450 °C, a reactor pressure of from 2 to 20 MPa gauge, a liquid hourly space velocity on a basis of weight of the biomass-derived pyrolysis oil/water of catalyst/hour (hr⁻¹) of from 0.1 to 1.5 hr⁻¹, and a hydrogen-containing gas treatment rate of from 1,000 to 15,000 standard cubic feet per barrel (SCF/B). The deoxygenating catalyst in the second hydroprocessing reactor system 28 can be the same as or different from the deoxygenating catalyst in the first hydroprocessing reactor 18.

[0052] The second hydroprocessing reactor system 28 removes oxygen from the net organic liquid product from the first stage hydroprocessing reactor system (comprising the heavy and optionally a portion of the light molecular weight fractions of the low-oxygen biomass-derived pyrolysis oil) to produce ultralow-oxygen biomass-derived pyrolysis oil effluent. The oil contained in the ultralow-oxygen biomass-derived pyrolysis oil effluent may be partially deoxygenated with some residual oxygenated hydrocarbons, or may be substantially fully deoxygenated where substantially all of the oxygenated hydrocarbons are converted into hydrocarbons. In an exemplary embodiment, the ultralow-oxygen biomass-derived pyrolysis oil effluent comprises a hydroprocessed organic phase that has a residual oxygen content of 2 wt. % or less, for example from 1 to 0 wt. %, such as 0.1 to 0 wt. % of the hydroprocessed organic phase.

[0053] In other embodiments, the system 10 described above may contain one or more additional optional elements at least for the manipulation of temperature and/or water content in various pyoil streams throughout the process.

[0054] For instance, in a second exemplary embodiment, the system 10 is as described above, but is further configured to provide improved control of the temperature of the low-oxygen biomass-derived pyrolysis effluent 20 when it is introduced to the high pressure three-phase separator 24. An example of such an embodiment is seen in FIG. 2.

[0055] Specifically, the outlet temperature of the chiller 22 may be monitored with a temperature controller 64 and the temperature and/or flow rate of coolant through the
chiller 22 adjusted to achieve a desired temperature of the chilled low-oxygen biomass-derived pyrolysis oil effluent 20. Alternatively or in addition, a portion of the low-oxygen biomass-derived pyrolysis oil effluent 20 may be diverted around the chiller 22 to achieve a desired temperature of the chilled low-oxygen biomass-derived pyrolysis oil effluent 20. In this way, the temperature of the low-oxygen biomass-derived pyrolysis oil effluent 20 can be modulated to a greater extend prior to introducing the low-oxygen biomass-derived pyrolysis oil effluent 20 into the high pressure three-phase separator 24. This modulation provides a degree of control of the amount of water that remains miscible in the low-oxygen biomass-derived pyrolysis oil effluent 20 as it enters the high pressure separator 24.

[0056] In a third exemplary embodiment, the system 10 is as initially described, but is further configured to provide improved control of the amount of residual water in the heated low-molecular weight fraction 14 when it is combined with the biomass-derived pyrolysis oil stream 12 and fed to the first hydroprocessing reactor 18. An example of such an embodiment is seen in FIG. 3.

[0057] Specifically, the low-molecular weight fraction 40 exiting the recycle column 38 is passed through the chiller 44 and the phase separator 46 under conditions such that water content of the reflux 70 is minimized. Net water and organic portions 50 exiting the phase separator 46 are directed to a pump 56 and passed through a heater 66 where the temperature is increased such that an additional portion or, in some cases, all of a separate water phase present in the low-molecular weight fraction becomes miscible. Specifically, the outlet temperature of the heater 66 may be monitored with a temperature controller 68 and the temperature of the heater 66 adjusted to achieve a desired temperature prior to entering phase separator 72. Thus, in these embodiments, the phase separator 46 separates the low-molecular weight fraction 40 into an organic volatile gas stream 48, a low-molecular weight fraction organic reflux liquid phase 70, and an organic/aqueous stream 50. The organic volatile gas stream 48 is handled as described above and the organic/aqueous phases in stream 50 are separated (if desired) in phase separator 72.

[0058] Like the low-molecular weight fraction organic liquid phase 52 in the embodiments described above, the low-molecular weight fraction organic/aqueous liquid
phase 50 is then sent to a heater 34 to generate the heated low-molecular weight fraction
14 discussed above. In some embodiments, a portion of the low-molecular weight fraction
organic/aqueous liquid phase 50 is diverted prior to entering the heater 34 and instead
directed to be combined with the high-molecular weight fraction 42, with the combination
directed to a second hydroprocessing reactor system 28, as previously discussed.

[0059] In a fourth exemplary embodiment, the system 10 is as initially described, but
is further configured to provide improved control of the temperature of the low-oxygen
biomass-derived pyrolysis oil effluent 20 as described in the second exemplary
embodiment, and provide improved control of the amount of residual water in the heated
low-molecular weight fraction 14 as described in the third exemplary embodiment. An
example of a fourth exemplary embodiment is shown in FIG. 4. As seen in FIG. 4, the
system 10 is as initially described but further includes temperature controller 64 located
downstream of the chiller 22 (as described in detail in the second exemplary embodiment),
and a heater 66, a temperature controller 68, and a phase separator 72 (as described in
detail in the third exemplary embodiment).

[0060] Accordingly, methods for deoxygenating a biomass-derived pyrolysis oil have
been described. Unlike the prior art, the exemplary embodiments taught herein produce a
low-oxygen biomass-derived pyrolysis oil effluent by contacting a heated diluted pyoil
feed stream with a deoxygenating catalyst in the presence of hydrogen at hydroprocessing
conditions. In particular, the heated diluted pyoil feed stream is formed by combining a
biomass-derived pyrolysis oil stream with a heated low-molecular weight fraction of a
low-oxygen-pyoil diluent recycle stream. The heated low-molecular weight fraction is
formed from a portion of the low-oxygen biomass-derived pyrolysis oil effluent that has
been separated into at least low and high molecular weight fractions, with at least a
portion of the low molecular weight fraction recycled and heated. The heated diluted
pyoil feed stream is introduced to a hydroprocessing reactor and contacts the
ddeoxygenating catalyst to partially deoxygenate the heated diluted pyoil feed stream to
form the low-oxygen biomass-derived pyrolysis oil effluent. By contacting the
ddeoxygenating catalyst with the heated diluted pyoil feed stream in the presence of
hydrogen at the hydroprocessing conditions, the amount of glassy brown polymer or
powdery brown char formed on the deoxygenating catalyst is substantially reduced or
minimized relative to conventional methods. Further, separation and recycling of only the low molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent further inhibits secondary polymerization reactions that otherwise result in increased viscosity and eventual pressure differential elevation across the deoxygenating catalyst. Therefore, a low-oxygen biomass-derived pyrolysis oil can be produced in the hydroprocessing reactor without plugging the deoxygenating catalyst, thereby increasing run duration and improving processability of the biomass-derived pyrolysis oil.

SPECIFIC EMBODIMENTS

[0061] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0062] A first embodiment of the invention is a method for deoxygenating a biomass-derived pyrolysis oil, the method comprising the steps of combining a biomass-derived pyrolysis oil stream with a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form a heated diluted pyoil feed stream that has a feed temperature of 150 °C or greater; contacting the heated diluted pyoil feed stream with a first deoxygenating catalyst in the presence of hydrogen at first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent; separating the low-oxygen biomass-derived pyrolysis oil effluent to produce a low molecular weight fraction low-oxygen-pyoil diluent recycle stream, wherein the low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of 225 °C or less; and heating the low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of between 190 to 225 °C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the first hydroprocessing
conditions include a reaction temperature of the feed temperature. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein heating the low molecular weight fraction low-oxygen-pyoil diluent recycle stream comprises heating to a temperature of from 200 to 450 °C. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the biomass-derived pyrolysis oil stream is combined with the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream at a predetermined recycle ratio of at least 21; wherein the predetermined recycle ratio is defined by a recycle mass flow rate of the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream to a pyoil mass flow rate of the biomass-derived pyrolysis oil stream. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein contacting the heated diluted pyoil feed stream with the first deoxygenating catalyst comprises partially deoxygenating the heated diluted pyoil feed stream, and wherein the low-oxygen biomass-derived pyrolysis oil effluent comprises a hydroprocessed organic phase that has a residual oxygen content of from 15 to 25 wt. % of the hydroprocessed organic phase. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising subjecting the low-oxygen biomass-derived pyrolysis oil effluent to a phase separation to at least reduce an amount of water in the low-oxygen biomass-derived pyrolysis oil effluent prior to separation of the low molecular weight fraction low-oxygen-pyoil diluent recycle stream. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the low-oxygen biomass-derived pyrolysis oil effluent is subjected to the phase separation at a temperature of 0 to 60 °C. An embodiment of the invention is one, any or all of the prior embodiments in this paragraph up through the first embodiment in this paragraph, further comprising subjecting the low molecular weight fraction low-oxygen-pyoil diluent recycle stream to a phase separation to at least reduce an amount of water in the low molecular weight fraction low-oxygen-pyoil diluent recycle stream prior to heating and combining with the biomass-derived...
pyrolysis oil stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the low molecular weight fraction low-oxygen-pyoil diluent recycle stream is subjected to the phase separation at a temperature of 60 to 140 °C.

[0063] A second embodiment of the invention is a method for deoxygenating a biomass-derived pyrolysis oil, the method comprising the steps of combining a biomass-derived pyrolysis oil stream with a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form a heated diluted pyoil feed stream that has a feed temperature of 150 °C or greater; contacting the heated diluted pyoil feed stream with a first deoxygenating catalyst in the presence of hydrogen at first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent; contacting the low-oxygen biomass-derived pyrolysis oil effluent with a fractionation column to separate the low-oxygen biomass-derived pyrolysis oil effluent into a low molecular weight fraction and a high molecular weight fraction, wherein the low molecular weight fraction and high molecular weight fraction are separated at a cutpoint of 225 °C or less, and wherein at least a portion of the a low molecular weight fraction is routed for use as a low molecular weight fraction low-oxygen-pyoil diluent recycle stream; separating the low-oxygen biomass-derived pyrolysis oil effluent to produce a low molecular weight fraction low-oxygen-pyoil diluent recycle stream and a high molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent, wherein the low molecular weight fraction low-oxygen-pyoil diluent recycle stream and high molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent are separated at a cutpoint of 225 °C or less; heating the low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream; and contacting the high molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent with a second deoxygenating catalyst in the presence of hydrogen at second hydroprocessing conditions effective to form an ultralow-oxygen biomass-derived pyrolysis oil effluent. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of between 190 to 225 °C. An
embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the first hydroprocessing conditions include a reaction temperature of the feed temperature. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein heating the low molecular weight fraction low-oxygen-pyroil diluent recycle stream comprises heating to a temperature of from 200 to 450 °C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the biomass-derived pyrolysis oil stream is combined with the heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream at a predetermined recycle ratio of at least 21; wherein the predetermined recycle ratio is defined by a recycle mass flow rate of the heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream to a pyoil mass flow rate of the biomass-derived pyrolysis oil stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein contacting the heated diluted pyoil feed stream with the first deoxygenating catalyst comprises partially deoxygenating the heated diluted pyoil feed stream, and wherein the low-oxygen biomass-derived pyrolysis oil effluent comprises a hydroprocessed organic phase that has a residual oxygen content of from 15 to 25 wt. % of the hydroprocessed organic phase. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising subjecting the low-oxygen biomass-derived pyrolysis oil effluent to a phase separation to at least reduce an amount of water in the low-oxygen biomass-derived pyrolysis oil effluent prior to separation of the low molecular weight fraction low-oxygen-pyroil diluent recycle stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising subjecting the low molecular weight fraction low-oxygen-pyroil diluent recycle stream to a phase separation to at least reduce an amount of water in the low molecular weight fraction low-oxygen-pyroil diluent recycle stream prior to heating and combining with the biomass-derived pyrolysis oil stream.

A third embodiment of the invention is a system for deoxygenating a biomass-derived pyrolysis oil, the system comprising a first hydroprocessing reactor configured to contain a first hydroprocessing catalyst, the first hydroprocessing reactor
configured to receive a heated diluted pyoil feed stream and contact the heated diluted pyoil feed stream with the first hydroprocessing catalyst in the presence of hydrogen under first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent, wherein the heated diluted pyoil feed stream comprises a combination of a biomass-derived pyrolysis oil stream and a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream combined at a predetermined ratio; a fractionation column configured to receive the low-oxygen biomass-derived pyrolysis oil effluent and operate under conditions such that a low molecular weight fraction low-oxygen-pyoil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of 225 °C or lower; and a heater configured to receive and heat the low molecular weight fraction low-oxygen-pyoil diluent recycle stream to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream.

[0065] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.
CLAIMS

1. A method for deoxygenating a biomass-derived pyrolysis oil, the method comprising the steps of:

   combining a biomass-derived pyrolysis oil stream with a heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream to form a heated diluted pyroil feed stream that has a feed temperature of 150 °C or greater;

   contacting the heated diluted pyroil feed stream with a first deoxygenating catalyst in the presence of hydrogen at first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent;

   separating the low-oxygen biomass-derived pyrolysis oil effluent to produce a low molecular weight fraction low-oxygen-pyroil diluent recycle stream, wherein the low molecular weight fraction low-oxygen-pyroil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of 225 °C or less; and

   heating the low molecular weight fraction low-oxygen-pyroil diluent recycle stream to form the heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream.

2. The method of claim 1, wherein separating the low-oxygen biomass-derived pyrolysis oil effluent further comprises producing a high molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent, and the method further comprises contacting the high molecular weight fraction of the low-oxygen biomass-derived pyrolysis oil effluent with a second deoxygenating catalyst in the presence of hydrogen at second hydroprocessing conditions effective to form an ultralow-oxygen biomass-derived pyrolysis oil effluent.

3. The method of claim 1 or 2, wherein the low molecular weight fraction low-oxygen-pyroil diluent recycle stream is separated from the low-oxygen biomass-derived pyrolysis oil effluent at a cutpoint of between 190 to 225 °C.
4. The method of claim 1 or 2, wherein the first hydroprocessing conditions include a reaction temperature of the feed temperature.

5. The method of claim 1 or 2, wherein heating the low molecular weight fraction low-oxygen-pyroil diluent recycle stream comprises heating to a temperature of from 200 to 450 °C.

6. The method of claim 1 or 2, wherein the biomass-derived pyrolysis oil stream is combined with the heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream at a predetermined recycle ratio of at least 2:1; wherein the predetermined recycle ratio is defined by a recycle mass flow rate of the heated low molecular weight fraction low-oxygen-pyroil diluent recycle stream to a pyoil mass flow rate of the biomass-derived pyrolysis oil stream.

7. The method of claim 1 or 2, wherein contacting the heated diluted pyoil feed stream with the first deoxygenating catalyst comprises partially deoxygenating the heated diluted pyoil feed stream, and wherein the low-oxygen biomass-derived pyrolysis oil effluent comprises a hydroprocessed organic phase that has a residual oxygen content of from 15 to 25 wt. % of the hydroprocessed organic phase.

8. The method of claim 1 or 2, further comprising subjecting the low-oxygen biomass-derived pyrolysis oil effluent to a phase separation to at least reduce an amount of water in the low-oxygen biomass-derived pyrolysis oil effluent prior to separation of the low molecular weight fraction low-oxygen-pyroil diluent recycle stream.

9. The method of claim 1 or 2, further comprising subjecting the low molecular weight fraction low-oxygen-pyroil diluent recycle stream to a phase separation to at least reduce an amount of water in the low molecular weight fraction low-oxygen-pyroil diluent recycle stream prior to heating and combining with the biomass-derived pyrolysis oil stream.

10. A system for deoxygenating a biomass-derived pyrolysis oil, the system comprising:
a first hydroprocessing reactor 18 configured to contain a first hydroprocessing catalyst, the first hydroprocessing reactor 18 configured to receive a heated diluted pyoil feed stream 16 and contact the heated diluted pyoil feed stream 16 with the first hydroprocessing catalyst in the presence of hydrogen under first hydroprocessing conditions effective to form a low-oxygen biomass-derived pyrolysis oil effluent 20, wherein the heated diluted pyoil feed stream 16 comprises a combination of a biomass-derived pyrolysis oil stream 12 and a heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream 14 combined at a predetermined ratio;

a fractionation column 38 configured to receive the low-oxygen biomass-derived pyrolysis oil effluent 20 and operate under conditions such that a low molecular weight fraction low-oxygen-pyoil diluent recycle stream 40 is separated from the low-oxygen biomass-derived pyrolysis oil effluent 20 at a cutpoint of 225 °C or lower; and

a heater 34 configured to receive and heat the low molecular weight fraction low-oxygen-pyoil diluent recycle stream 40 to form the heated low molecular weight fraction low-oxygen-pyoil diluent recycle stream 14.
# INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/US2014/047388

### A. CLASSIFICATION OF SUBJECT MATTER

CIOL 1/02(2006.01)i, CIOG 47/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOL 1/02; CIOB 53/02; CIOL 1/04; CIOG 45/00; CIOL 1/19; CIOG 4700

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS/KIPO internal & keywords: deoxygenation, biomass-derived pyrolysis oil, low-oxygen-pyroil diluent, low molecular weight fraction, hydroprocessing, fractionation, heat

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

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**Date of the actual completion of the international search**

27 October 2014 (27. 10.2014)

**Date of mailing of the international search report**

03 November 2014 (03.11.2014)

**Name and mailing address of the ISA/KR**

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