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(54) **BIOMASS LIQUEFACTION TO PRODUCE REFINERY-READY BIO-OIL**

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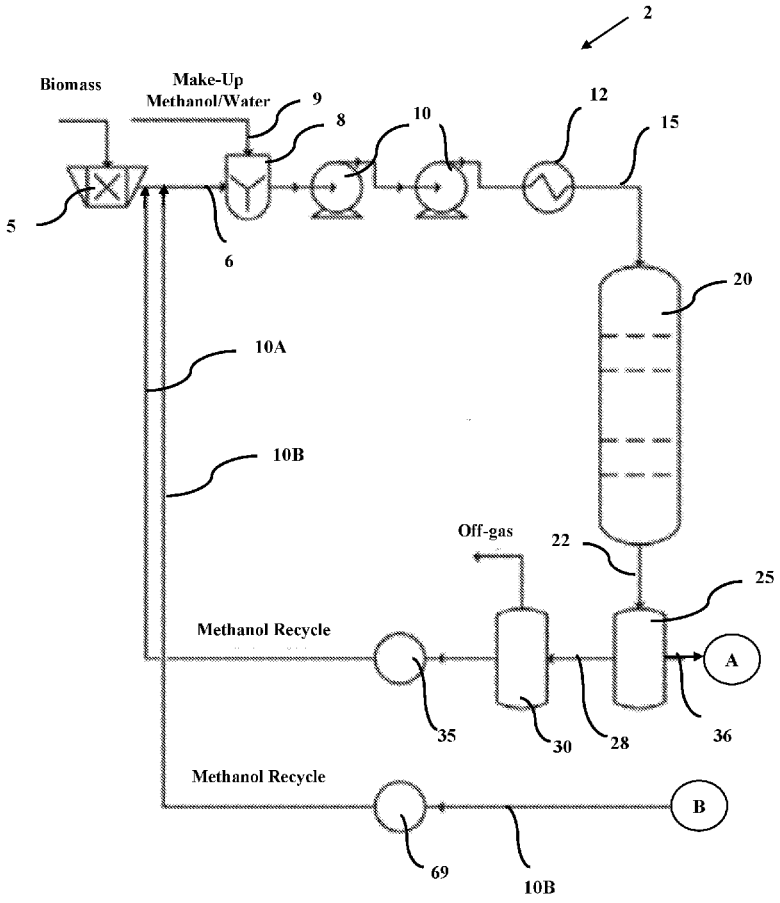
(57) **ABSTRACT**

A bio-oil product is produced from biomass material by subjecting the biomass material to a first stage liquefaction process, where the first stage liquefaction process includes combining the biomass material with a co-solvent including methanol and water to form a first slurry mixture, providing the slurry mixture within a first liquefaction reactor and maintaining the first slurry mixture at a sufficient temperature and pressure so as to convert a portion of the biomass material into a first liquefied bio-oil product as well as form a first aqueous product and a first solid product, and separating the first liquefied bio-oil product from the aqueous and solid products. The solid product obtained from the first stage liquefaction process is subjected to a second stage liquefaction process, where the second stage liquefaction process includes combining the first solid product with methane to form a second slurry mixture, and providing the second slurry mixture within a second liquefaction reactor and maintaining the second slurry mixture at a sufficient temperature and pressure so as to convert a portion of the first solid product to a second liquefied bio-oil product as well as form a second aqueous product and a second solid product.



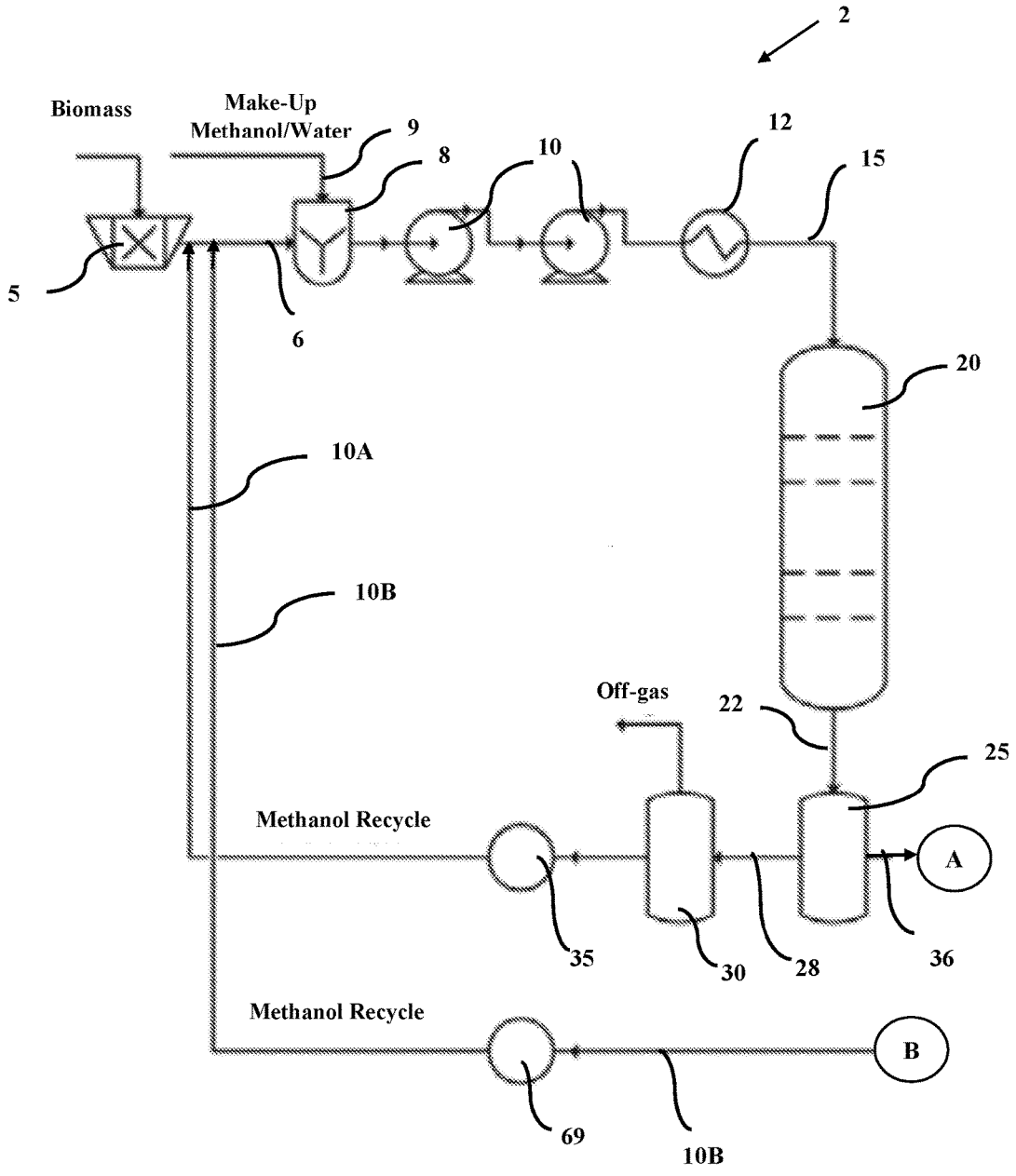
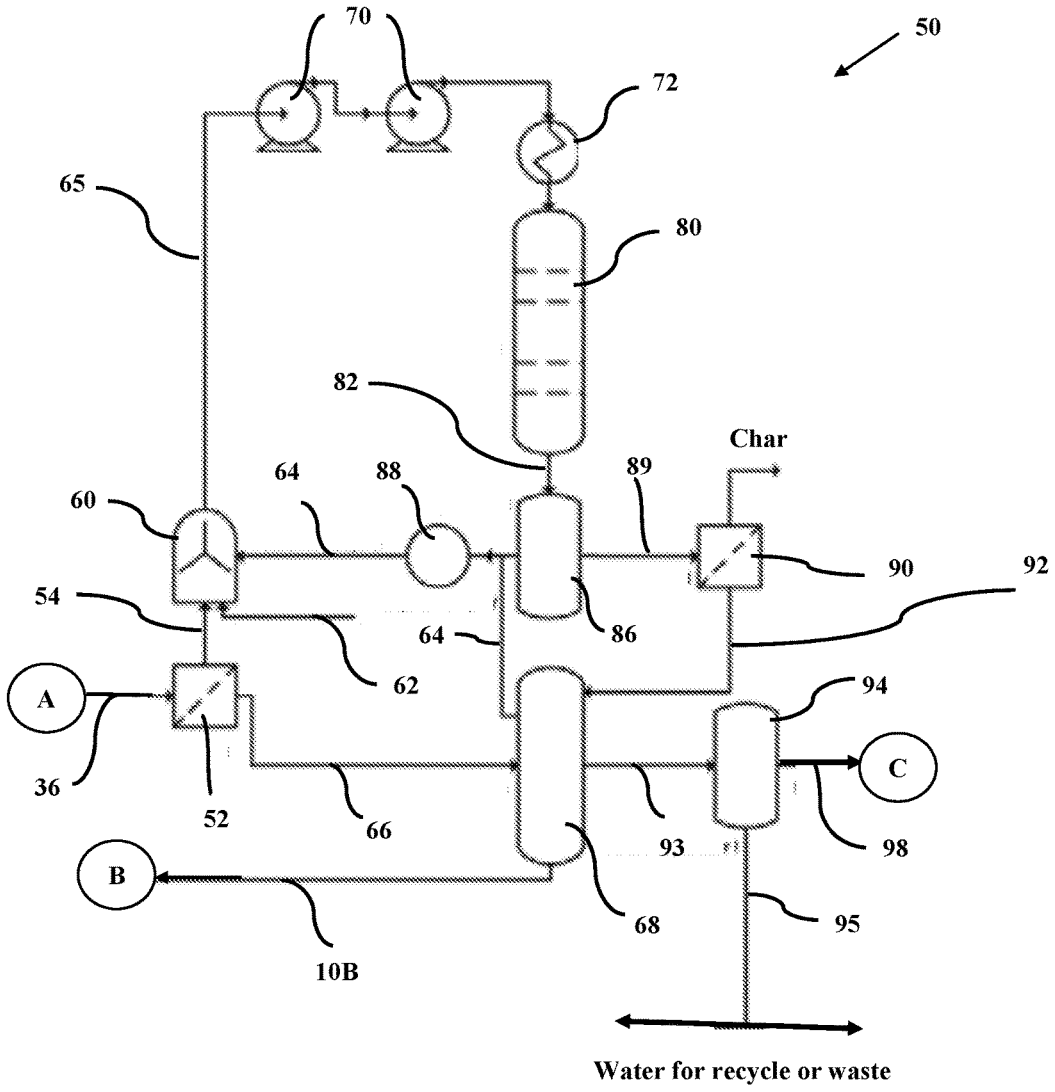

2
Biomass
Make-Up
Methanol/Water
9
8
10
12
15
5
6
20
10A
10B
Off-gas
22
25
Methanol Recycle
A
35
30
28
36
Methanol Recycle
B
69
10B

FIG. 1


70
50
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80
82
Char
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60
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54
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A
C
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52
66
93
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B
68
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10B
Water for recycle or waste

FIG. 2

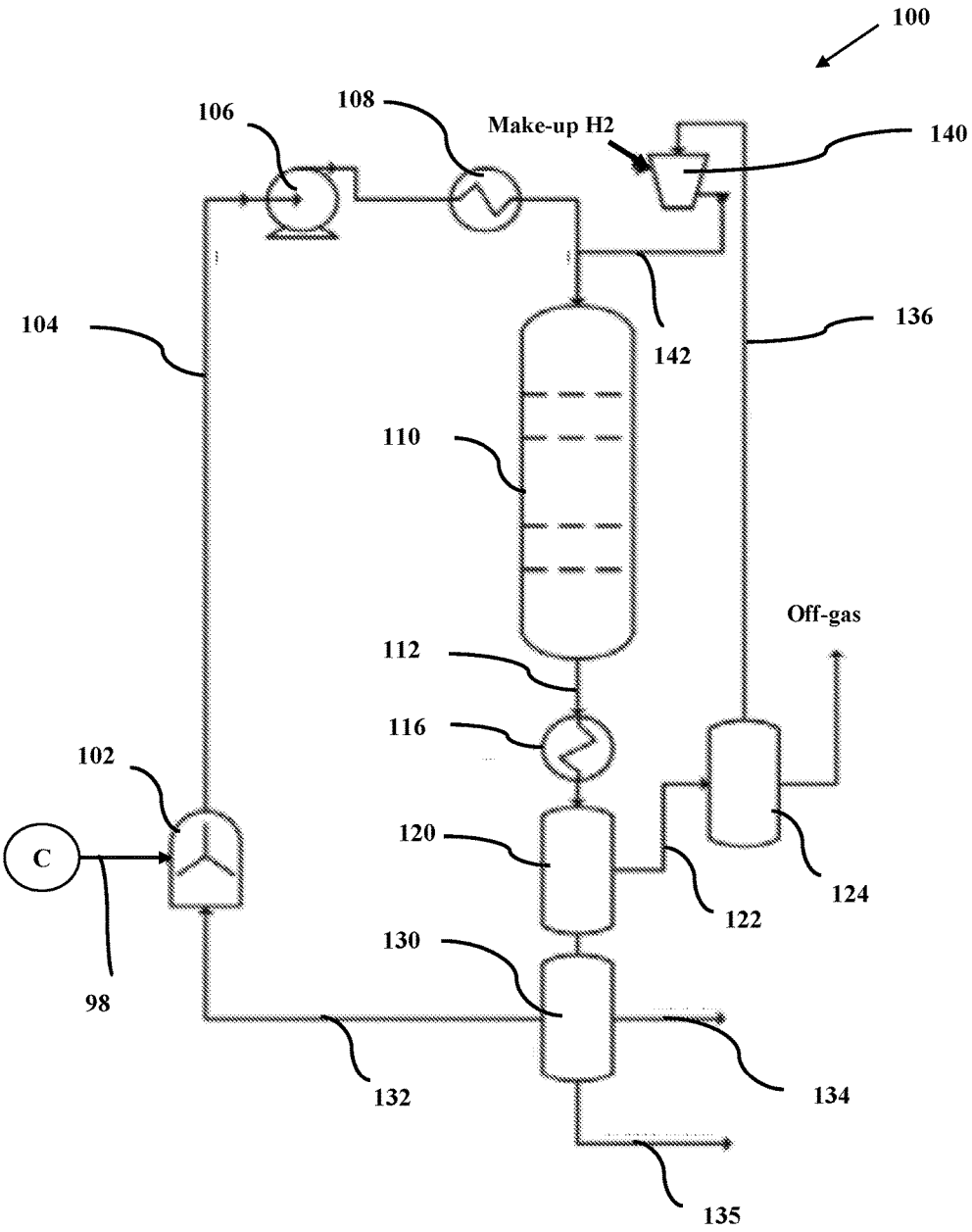
100
106
108
Make-up H2
140
104
142
136
110
Off-gas
112
116
102
C
120
122
124
130
98
132
134
135

FIG. 3

BIOMASS LIQUEFACTION TO PRODUCE REFINERY-READY BIO-OIL

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from U.S. Provisional Patent Application Ser. No. 62/483,130, entitled "Biomass Liquefaction Process for Refinery-Ready Bio-Oil Production", filed Apr. 7, 2017, the disclosure of which is incorporated herein by reference in its entirety.

GOVERNMENT LICENSE RIGHTS

[0002] This invention was made with government support under contract number DE—EE0006062 awarded by the U.S. Department of Energy. The government may have certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates to the production of bio-oil from a biomass liquefaction process.

[0004] BACKGROUND

[0005] Bio-oil obtained from fast pyrolysis of biomass is a green intermediate that can be further upgraded into a biofuel for blending in a petroleum refinery using a hydrodeoxygenation (HDO) process. Co-processing pyrolysis bio-oil in a petroleum refinery is an attractive approach to leverage the refinery's existing capital. However, the petroleum industry is reluctant to accept pyrolysis bio-oil because of a lack of a standard definition for an acceptable bio-oil feedstock in existing refinery processes. In addition, fast pyrolysis-based bio-fuel is determined to be non-competitive with petroleum-based transportation fuels.

[0006] Further, biomass material (such as woody biomass) is conventionally converted to bio-oil using a hydrothermal liquefaction process in which compressed and heated water is provided as a solvent to liquefy the biomass material. This process must be operated under very high temperatures (e.g., about 350° C. or greater) and also very high pressures (e.g., about 3000 psig (about 20.7 MPa) or greater) and further utilizes catalysts to enhance the liquefaction process. The severe (high temperature/high pressure) operating conditions required for liquefying biomass material can make it difficult for converting the biomass material into a useful form of bio-oil for use as transportation fuel.

[0007] It would be desirable to provide a cost-effective low-severity thermal liquefaction and hydrodeoxygenation (HDO) process to convert woody biomass to stabilized bio-oils (defined as bio-oils with low oxygen content, low water content and low total acidity number) that can be directly blended with hydrotreater input streams in a petroleum refinery for production of gasoline and/or diesel range hydrocarbons.

SUMMARY OF THE INVENTION

[0008] In example embodiments, a method of producing a bio-oil product from biomass material, the method comprising subjecting the biomass material to a first stage liquefaction process, the first stage liquefaction process comprising combining the biomass material with a co-solvent comprising methanol and water to form a first slurry mixture, and providing the slurry mixture within a first liquefaction reactor and maintaining the first slurry mixture at a temperature between 200° C. and 310° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to convert a portion of the biomass material into a first liquefied bio-oil product as well as form a first aqueous product and a first solid product. The first liquefied bio-oil product is separated from the aqueous and solid products, and the solid product obtained from the first stage liquefaction process is subjected to a second stage liquefaction process, the second stage liquefaction process comprising combining the first solid product with methanol to form a second slurry mixture, and providing the second slurry mixture within a second liquefaction reactor and maintaining the second slurry mixture at a temperature between 200° C. and 310° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to convert a portion of the first solid product to a second liquefied bio-oil product as well as form a second aqueous product and a second solid product.

[0009] The first liquefied bio-oil product can be combined with the second liquefied bio-oil product to form a combined liquefied bio-oil product, where the combined liquefied bio-oil product is further combined with hydrogen in a HDO reactor at a temperature between 200° C. and 300° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to remove oxygen from carbon-based compounds within the combined liquefied bio-oil product.

[0010] In further embodiments, a system is provided to perform the operations of the first and second stage liquefaction processes as described herein.

[0011] The systems and methods as described herein facilitate the formation of a bio-oil under less harsh conditions (e.g., at temperatures no greater than 310° C. and pressures less than 3000 psig (20.7 MPa)) than conventional biomass to bio-oil conversion processes (e.g., utilizing conventional hydrothermal liquefaction techniques), where a significant portion of the solvents used to liquefy biomass material can be recovered and recycled for re-use, and the liquefied bio-oil product has a low oxygen content (e.g., no greater than 25% by weight of the bio-oil product), a low water content (e.g., no greater than about 10% by weight of the bio-oil product, such as no greater than about 5% by weight of the bio-oil product) and further a total acid number (TAN) of less than 5 (e.g., a TAN of no greater than 3, such as a TAN from about 1-3). When the liquefied bio-oil product is further processed in an HDO reactor, the resultant HDO bio-oil product can be further reduced in oxygen content to no greater than about 10% by weight of the HDO bio-oil product. Further, the systems and methods described herein provide a yield of at least 60% (e.g., 69% or greater) of bio-oil based upon amount of input biomass to the process.

[0012] The above and still further features and advantages of embodiments of the present invention will become apparent upon consideration of the following detailed description thereof, particularly when taken in conjunction with the accompanying drawings wherein like reference numerals in the various figures are utilized to designate like components.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1** is a schematic view of a first stage liquefaction section for a system that converts biomass to bio-oil in accordance with an example embodiment of the present invention.

[0014] FIG. **2** is a schematic view of a second stage liquefaction section for the system located downstream from the first stage liquefaction section of FIG. **1**.

[0015] FIG. **3** is a schematic view of a bio-oil HDO section for the system located downstream from the second stage liquefaction section of FIG. **2**.

[0016] Like reference numerals have been used to identify like elements throughout this disclosure.

DETAILED DESCRIPTION

[0017] In accordance with the present invention, a liquefaction process and corresponding systems are described herein for enhanced biomass conversion, where the system and process include a two stage liquefaction process followed by a HDO process. The first stage liquefaction process utilizes water and methanol as co-solvents to liquefy biomass material, while the second stage liquefaction process utilized methanol as a solver to liquefy biomass material remaining from the first stage liquefaction process. The system and process described herein increases the yield and stability of resulting pyrolysis oil, also referred to herein as bio-oil, where the resultant bio-oil has a reduced oxygen content, and reduced water content (e.g., no greater than 5% by weight, or even as low as no greater than 1% by weight of water within the bio-oil), and a total acid number (TAN) that is lower in relation to other bio-oils formed utilizing known or conventional processes. Further, both the first and second stage liquefaction processes are free from any catalyst (i.e., the presence of a catalyst is not required in each of the first and second liquefaction stages). The solvents utilized in the liquefaction stages are also easily separated and can be recycled for re-use in the process.

[0018] Generally, the process comprises pumping a biomass slurry into a high pressure heated reactor. The product stream is de-pressurized in order to vaporize some of the excess solvent for recapture and recycle. The remaining stream is filtered and the solids (e.g., non-converted biomass material) and heavy oils adsorbed on the solid are recycled for further conversion. The remaining liquid reaction products are separated between organic and aqueous phases. After removal of the aqueous phase, the remaining organic phase is purified (e.g., via vacuum distillation) to yield a bio-oil product. The bio-oil product is subjected to HDO to yield an oil product lower in oxygen content. The separated aqueous phase can be treated to remove organic acids that are present while the remaining water and soluble sugars within the aqueous phase can be recycled to start of the liquefaction process to further increase biomass conversion and bio-oil yield (as well as minimizing water consumption).

[0019] An example embodiment of a system and process for conversion of biomass into bio-oil is now described with reference to FIGS. **1-3**. The biomass liquefaction process comprises a two-stage biomass liquefaction process using a co-solvent combination of supercritical methanol and subcritical water in the first stage liquefaction process and supercritical methanol in the second stage liquefaction process so as to maximize light bio-oil production. The produced bio-oil is then subjected to a bio-oil HDO process to produce a low-oxygen-content fuel intermediate (HDO oil). The HDO oil can be used, e.g., at a petroleum refinery where it is mixed with a petroleum feed for co-processing at the refinery to drop-in transportation fuels. All the liquefaction preheaters and reactors can be heated using a centralized hot oil heating system. Solvent methanol can be recovered for recycling using flash evaporation and distillation. The overall process can be divided into three operation blocks or sections, with each section depicted in FIG. **1**, FIG. **2** and FIG. **3**, where the biomass is subjected to a liquefaction process in a first stage **2** (FIG. **1**), followed be further liquefaction and solvent recovery in a second stage **50** (FIG. **2**) to produce a light bio-oil and a heavy bio-oil, with subsequent hydrodeoxygenation (HDO) of the light bio-oil at section **100** to produce refinery ready bio-oil (FIG. **3**).

[0020] The biomass utilized herein can be any suitable organic material, such as pulverized wood. Any suitable type of wood can be utilized. In example embodiments, the biomass utilized to synthesize bio-oil comprises pulverized southern pine wood that is pulverized to an average particle size in the micrometer range (e.g., average particle size of no greater than about 1000 μm, such as no greater than about 150 μm, or an average particle size in the range of about 100 μm). In example embodiments of the process, southern pine wood that has been pulverized has a chemical composition as follows:

TABLE 1

Elemental and Chemical Composition of Pulverized Southern Pine Wood Used in Process

	Weight Percentage (%)
Elemental Analysis (dry basis)	
Carbon	53.3
Hydrogen	6.3
Nitrogen	0.27
Oxygen	40.2
Sulfur	0.01
Chemical Composition	
Glucan	44.8
Xylan	3.0
Galactan	1.3
Arabinan	0.0
Mannan	11.4
Lignin	28.4
Extractives	3.3

[0021] The wood can be mixed with water and methanol to produce a biomass slurry that is heated in a liquefaction reactor in the initial stages of the bio-oil synthesis process. As described herein, the combination of water and methanol as co-solvents facilitates sufficient liquefaction (conversion of solid to liquid) of the biomass at lower temperatures (e.g., less than 350° C.) and under less harsh conditions (e.g., operating pressures under 2000 psig or 13.8 MPa) than required when using water or other aqueous solvents. Further, the time required to achieve suitable liquefaction in the reactors can be significantly reduced (e.g., 30 minutes or less) in comparison to other processes which convert biomass to bio fuel.

[0022] Referring to FIG. **1**, the solid biomass material is delivered to a grinding vessel or grinder **5** of the first stage liquefaction section **2** for the system, where it is sufficiently pulverized within the grinder prior to delivery (via conduit or line **6**, where the line **6** can comprise, e.g., a screw extruder) to a mixing unit or mixer **8**. The pulverized biomass material is combined and sufficiently mixed with a co-solvent comprising water and methanol. At initial system start-up, water and methanol are added to the mixer **8** via

conduit or line **9**. In addition, it is noted that a portion of the co-solvent (e.g., water, methanol or a combination of both) can also be added at a location directly downstream from the grinder **5** to assist in the flow of pulverized biomass material from the grinder **5** to the mixer **8**. The equipment of the system (e.g., various reaction vessels, pumps, heat exchangers, fluid conduits, and other vessels) can be configured and suitably scaled so as to process a suitable amount of wood biomass (e.g., about 1000 US ton per day, or about 907,185 kg per day) for conversion to bio-oil in a particular application. In the process, the mass ratio of water to methanol for making up the co-solvent is about 1:1 (i.e., about the same amount in weight for water and methanol, or about 50% by weight water and about 50% by weight methanol). Alternatively, one of the water or methanol can comprise slightly more than the other, such that each of the water and methanol can comprise from about 40% to about 60% by weight of the co-solvent. The amount by weight of pulverized woody biomass mass is much greater than co-solvent in the slurry mixture. For example, a mass ratio of pulverized woody biomass to co-solvent can be at least about 5:1, or at least about 8:1 (e.g., about 10:1).

[0023] The biomass/solvent mixture or slurry that exits the mixer **8** is pressurized and heated to a sufficient temperature and sufficient pressure that facilitates suitable conditions for liquefying the biomass material. In particular, the biomass/solvent slurry is directed through a series of pumps and a heat exchanger (e.g., two pumps **10** followed by a hot-oil heat exchanger **12** provided in series as depicted in FIG. **1**) to pressurize and heat the slurry prior to deliver through conduit or line **15** into a first liquefaction reactor **20**. The slurry can be pressurized (via pumps **10**) to a pressure ranging from about 1000 psig to about 2500 psig (e.g., from about 6.9 MPa to about 17.2 MPa), such as a pressure of about 1500 psig (about 10.3 MPa). The slurry is further heated (via heat exchanger **12**) to a temperature ranging from about 200° C. to about 310° C., where the temperature is preferably no greater than about 300° C. In example embodiments, the slurry is heated to about 200° C. prior to delivery to the liquefaction reactor **20**.

[0024] A substantially oxygen free environment is maintained within the liquefaction reactor **20**, the mixture is held within the reactor at a pressure ranging from about 1000 psig to about 2500 psig (e.g., from about 6.9 MPa to about 17.2 MPa) and a temperature ranging from about 200° C. to about 310° C., where the temperature is preferably no greater than about 300° C. In an example embodiment, the operating conditions within the reactor **20** are maintained within a range from about 280° C. to 290° C. and about 1500 psig (about 10.3 MPa). The mixture is further maintained within the reactor vessel at these operating conditions until such time as sufficient liquefaction of the biomass material has occurred. In example embodiments, the residence time within the liquefaction reactor **20** can range from about 10 minutes to about 30 minutes. Under these conditions, the solvent mixture comprises methanol in a supercritical state and water in a subcritical state. These conditions within the reactor **20** are less harsh (with lower temperatures and lower pressures, e.g., temperatures no greater than about 300° C. and pressures no greater than about 2500 psig (about 17.2 MPa)) than conventional processes for breakdown and conversion of the biomass to bio-oil (e.g., conventional processes typically require temperatures much greater than 310° C. and pressures of about 3000 psig (20.7 MPa) or greater).

[0025] When operating at such conditions, at least about 80% (e.g., about 90% or more) by weight of the biomass material can be liquefied or converted to non-solid/liquid products and other products within the reactor **20** of the first stage liquefaction section **2**. In other words, the term "liquefied", as used herein, refers to conversion of a solid material to a liquid material (i.e., conversion of a solid biomass material into a liquid bio-oil product). The first stage liquefaction process further does not require any catalyst to achieve such conversion (i.e., the first liquefaction reactor **20** is free from any catalyst).

[0026] The products exiting the reactor **20** include the following: a light bio-oil material in a liquid state (which is soluble in methanol); a solid product that includes unconverted biomass material and a heavy bio-oil material adsorbed on the solids, an aqueous liquid material (including water); and gaseous products (primarily CO_2). In example embodiments (Table 2), about 50% by weight or more of the products exiting the liquefaction reactor **20** comprise light bio-oil material, while less than 10% by weight of the products comprise a solid material (e.g., non-converted biomass solid material and heavy bio-oil material adsorbed on the solid material), about 30-40% (e.g., about 35% by weight) of the products comprise aqueous organic product (e.g., water and liquefied biomass carbohydrates dissolved in water), and less than 10% by weight (e.g., no more than about 5% by weight) of the products are in gaseous form (e.g., CO_2). Further, the oxygen content within the liquefied light bio-oil product is less than 30% by weight (e.g., about 25% by weight). In an example embodiment under the conditions described herein and utilizing pulverized southern pine wood having a composition as previously described in Table 1, the mass distribution (weight percentage) and elemental distribution (percentage of elements) of products formed within the first stage liquefaction reactor are as follows:

TABLE 2

Mass and elemental distribution of products formed within first stage liquefaction reactor

	Light Bio-oil product	Aqueous organic product	Solid product (including heavy bio-oil)	Gas
Mass distribution (wt %)	50.8	35.7	9.3	4.2
Elemental distribution (%)				
Carbon	66.5	18.4	12.4	2.7
Oxygen	30.7	57.0	5.8	6.5
Hydrogen	61.3	28.9	9.0	0.8

[0027] Utilizing gas chromatography-mass spectrometry (GC-MS) analyzing techniques, the light bio-oil obtained from the first stage liquefaction has been characterized as including the following chemical compounds. It is noted that the bio-oil was found to contain complicated chemical compounds such that only about 60% of the total peaks recorded from the GC-MS analysis were identified (using a standard GC library).

TABLE 3

GC/MS Characterization of Light Bio-Oil Product from First Stage Liquefaction

Bio-Oil compound	Weight percentage
Methyl Alcohol	3.5%
Acetone	11.1%
Ethanone, 1-[4-(methyltelluro)phenyl]-	1.4%
Furan, tetrahydro-2-methyl-	1.6%
2-Propanone, 1-hydroxy-	2.0%
n-Propyl acetate	0.6%
Furan, tetrahydro-2,4-dimethyl-, trans-	0.9%
Butane, 1,1,3-trimethoxy-	1.0%
1-Propanol, 2-methoxy-	1.2%
Acetic acid, butyl ester	0.3%
Furfural	1.6%
2-Propanol, 1-ethoxy-	1.3%
2-Furancarboxaldehyde, 5-methyl-	0.8%
Pentanoic acid, 4-oxo-, methyl ester	0.7%
2-Furanmethanol, tetrahydro-	0.4%
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.7%
Acetic acid, heptyl ester	0.5%
Guaiacol	1.0%
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.4%
Hepta-2,4-dienoic acid, methyl ester	0.5%
Cyclopropanecarboxylic acid, 2-pentyl-, methyl ester	0.3%
Catechol	0.7%
5-Hydroxymethylfurfural	0.7%
2(3H)-Furanone, 5-hexyldihydro-4-methyl-, (4R-cis)-	0.1%
Phenol, 4-ethyl-2-methoxy-	1.1%
Vanillin	0.9%
trans-Isoeugenol	1.2%
Nonanedioic acid, dimethyl ester	0.9%
Methyl-(2-hydoxy-3-ethoxy-benzyl)ether	0.9%
5-(7a-Isopropenyl-4,5-dimethyl-octahydroinden-4-yl)-3-methyl-pent-2-en-1-ol	1.3%
Hexadecanoic acid, methyl ester	1.4%
Phenol, 4-[2,3-dihydro-7-methoxy-3-methyl-5-(1-propenyl)-2-benzofuranyl]-2-methoxy-	1.5%
6-Octadecenoic acid, methyl ester, (Z)-	9.9%
9,12-Octadecadienoic acid, methyl ester	1.5%
Methyl 5,11,14-eicosatrienoate	1.0%
5-Androstene-3.beta.,7.beta.-diol 3-isocaproate	1.9%
Total	56.8%

[0028] The liquefied light bio-oil further has an oxygen content of no greater than about 25% by weight of the light bio-oil (e.g., an oxygen content that is no greater than about 20% by weight of the light bio-oil), a water content that is no greater than about 10% by weight of the light bio-oil (e.g., a water content that is no greater than about 5% or even no greater than about 1% by weight of the bio-oil), and a TAN (total acid number, in mg KOH/g) that is less than 5 (e.g., a TAN that is no greater than 3, such as a TAN in the range of 1-3).

[0029] The liquefaction products exiting the reactor **20** (via conduit or line **22**) are provided to a flash evaporation unit or evaporator **25**, where the pressure is sufficiently reduced (e.g., to about 500 psig (about 3.4 MPa)) to evaporate a mixture of methanol and water (e.g., about 65% by weight methanol and about 45% by weight water) for separation along with the gaseous products from the other liquefied products. The evaporated and gaseous products mixture exiting the flash evaporator **25** are provided (via conduit or line **28**) at the reduced pressure and also a reduced temperature (e.g., between about 220° C. to about 240° C., such as from about 230° C. to about 235° C.) to a gas-liquid separator **30**. The gas-liquid separator **30** is maintained at sufficient reduced temperature and pressure conditions to condense the water and methanol mixture from the other gaseous products (e.g., CO_2), where the gaseous products are separated from the condensed water/methanol mixture as off gases. The methanol/water mixture exiting the separator **30** is then recycled (e.g., delivered via a recycle pump **35**) into recycle conduit or line **10**A for delivery to the mixer **8** (where it is combined with pulverized biomass material at the starting point of the system **2**). The other liquefied and solid liquefaction products, including light bio-oil, aqueous soluble organics and heavy bio-oil adsorbed solid material, exit the flash evaporator **25** for further processing at a secondary stage liquefaction section **50** as depicted in FIG. **2** (where point A represents a continuation in conduit or line **36** from the first stage liquefaction section **2** depicted in FIG. **1** to the second stage liquefaction section **50** depicted in FIG. **2**).

[0030] Referring to FIG. **2**, the liquefaction products from the first stage liquefaction process are delivered from the evaporator **25** (via line **36**) to a filtration unit or filter **52**, where the liquid phase (including light bio-oil and aqueous soluble organics dissolved in water/methanol mixture) is separated as filtrate from the solid product residue (e.g., any unconverted wood biomass and/or other solid material as well as heavy bio-oil adsorbed on the solid material). Any suitable one or more types of filters with suitable filter media (e.g., with any suitable filter media mesh sizes and/or other configurations) can be utilized to facilitate separation of liquid products (including liquefied light bio-oil) from solid products (including heavy bio-oil). In example embodiments, the filtration unit **52** can comprise a rotary drum filter including suitable filter media to facilitate separation of liquefied products from any solid product residue. The filtrate including light bio-oil and aqueous soluble organics is provided (via a conduit or line **66**) to a distillation unit **68**, where methanol is removed from the liquid mixture leading to a phase separation between light bio-oil (bottom phase) and aqueous organics (top phase) (e.g., via vacuum distillation at reduced pressure) as described herein.

[0031] The heavy bio-oil and solid product residue exiting the filter **52** is delivered (via conduit or line **54**) to a mixing

unit **60**, where the residue is combined with a solvent comprising substantially entirely methanol (e.g., the solvent comprises methanol in an amount of at least about 90% by weight of the solvent, such as at least 95% by weight of the solvent) prior to being subjected to further liquefaction treatment in section **50**. Methanol can be provided from a make-up source (e.g., via conduit or line **62**) as well as from a recycle source (e.g., via recycle conduit or line **64**) obtained from further processing within section **50** as described herein. The heavy bio-oil/methanol mixture exiting the mixer **60** is provided (via conduit or line **65** to a series of pumps series of pumps and a heat exchanger (e.g., two high pressure slurry pumps **70** followed by a hot-oil heat exchanger **72** provided in series as depicted in FIG. **2**) to pressurize and heat the slurry mixture prior to deliver into a second liquefaction reactor **80** of the secondary stage liquefaction section **50**. Similar to the first stage liquefaction section **2**, the slurry can be pressurized (via pumps **70**) to a pressure ranging from about 1000 psig to about 2500 psig (e.g., from about 6.9 MPa to about 17.2 MPa), such as a pressure of about 1500 psig (about 10.3 MPa), and the slurry can also be heated (via heat exchanger **72**) to a temperature ranging from about 200° C. to about 310° C. In example embodiments, the slurry is heated to about 200° C. prior to delivery to the second liquefaction reactor **80**. Operating conditions within the second liquefaction reactor **80** can be maintained at about 250° C. and about 1500 psig (about 10.3 MPa). Under such temperature and pressure conditions, the residence time for liquefaction of heavy oil and/or solid biomass to light bio-oil within the second liquefaction reactor **80** can be similar to that for the first liquefaction reactor **20** (e.g., from about 10 minutes to about 30 minutes). Similar to the first stage liquefaction process, the stage liquefaction process also does not require any catalyst to achieve liquefaction of solids into bio-oil (i.e., the second liquefaction reactor **80** is free from any catalyst).

[0032] The liquefaction products exiting the second liquefaction reactor **80** (which comprise a liquefied product including light bio-oil material (where the light bio-oil material is the same or substantially similar in its properties as the light bio-material formed in the first stage liquefaction reactor **20**), solid material products, and gaseous products such as CO_2) are delivered (via conduit or line **82**) to a flash evaporation unit or evaporator **86**, where the pressure and temperature are sufficiently reduced, e.g., to a pressure of about 500 psig (about 3.4 MPa) and a temperature between about 220° C. to about 240° C. (e.g., from about 230° C. to about 235° C.), to evaporate methanol within the liquefied products for separation from the other liquefied products. For example, as much as about 90% of the methanol can be evaporated and separated from the liquefied products by the evaporator **86**. The evaporated methanol is pressurized (e.g., via pump **88**) and recycled via the recycle line **64** to the mixer **60** for combining with the heavy bio-oil and solid residue. The remaining liquefied products separated from methanol in the evaporator **86** are delivered (via conduit or line **89**) to a filtration unit or filter **90**. The filter **90** can be similar as filter **52** and provided with a suitable filter media and/or suitable configuration to facilitate separation of liquefied products as filtrate from any other solid product residue. The solid product residue separated from the filtrate can be burned for heat generation or processed in any suitable manner, e.g. as carbon-based sorbent, while the filtrate is delivered to the distillation unit **68** for further processing.

[0033] In the distillation unit **68**, the filtrate including light bio-oil obtained from liquefaction in the first liquefaction reactor **2** of the first stage liquefaction section **2** is combined with filtrate including the light bio-oil obtained from liquefaction in the second liquefaction reactor **80** of the second stage liquefaction section **50**. The distillation unit **68** operates at a reduced pressure, such as a pressure of about 150-500 psig (1.1-3.4 MPa) and also a temperature (150-200° C.) that is suitable to separate methanol as vapor from the remaining liquid products (including light bio-oil, aqueous soluble organics and water). The methanol separated within the distillation unit **68** is recycled (via conduit or line **10**B and recycle pump **69**) back to the grinder **5** and/or mixer **8** of the first stage liquefaction section **2** for combining with pulverized biomass feed (where point B represents a continuation in conduit or line **10**B from the second stage liquefaction section **50** depicted in FIG. **2** to the first stage liquefaction section **2** depicted in FIG. **1**).

[0034] The remaining liquid products (including light bio-oil) exiting the distillation unit **68** are directed (via conduit or line **93**) to a phase separation vessel **94**, where an aqueous phase including water is separated from a light bio-oil phase due to differences in hydrophobicity and density of the two phases (i.e., separation of oil from water). Operating conditions within the phase separator **94** can include a pressure of about 500 psig (about 3.4 MPa) and a temperature ranging from about 220° C. to about 240° C. (e.g., ranging from about 230° C. to about 235° C.). The aqueous phase separated within vessel **94** can be discarded or, preferentially, directed (via conduits or lines **95**, with one or more pumps provided along the one or more lines **95**) to recycle water for use by the first stage liquefaction section **2** (e.g., combining with methanol to form the co-solvent mixture for combining with pulverized biomass feed) and/or for use downstream in section **100**.

[0035] The various evaporators, gas and phase separators provided within the first and second stages **2** and **50** facilitate recovery of a significant portion of the water/methanol and methanol solvents for re-use during system operation. For example, about 90% of the separated aqueous phase (which includes water and methanol) formed from the first stage liquefaction process (i.e., within liquefaction reactor **20**) can be recycled back to the first stage liquefaction section **2** for re-use. In example embodiments, the biomass feed has a moisture content that accounts for about 10% of the aqueous phase, this amount can be maintained within the light bio-oil phase that is separated from the aqueous phase and emerges from the separation vessel **94**. The light bio-oil phase exiting the separation vessel **94** is directed to the bio-oil hydrodeoxygenation (HDO) section **100** via conduit or line **98** (where point B represents a continuation in line **98** from the second stage liquefaction section **50** depicted in FIG. **2** to the bio-oil HDO section **100** depicted in FIG. **3**).

[0036] Referring to FIG. **3**, the light bio-oil phase is provided (via line **98**) to a mixing unit or mixer **102** of bio-oil HDO section **100**. In the mixer **102**, the light bio-oil stream (entering the mixer via line **98**) is diluted with a recycled HDO oil stream which is output from an HDO reactor **110** as described herein. The light bio-oil phase is combined with the recycled HDO oil stream in a suitable ratio (e.g., at about a 1:4 weight ratio of light bio-oil to

recycled HDO oil stream) so as ensure suitable flow of the mixture emerging from the mixer **102** through the remaining portions of section **100**.

[0037] The mixture exiting the mixer **102** is provided via a conduit or line **104** to HDO reactor **110**. The mixer is pressurized and heated within line **104** via one or more high pressure pumps (e.g., pump **106**) and a heat exchanger **108**, such that the temperature of the mixed stream is between about 200° C. to about 250° C. (e.g., about 220° C.) and a pressure from about 1000 psig to about 2000 psig (from about 6.9 MPa to about 17.2 MPa), such as a pressure of about 1500 psig (about 10.3 MPa). The heat exchanger **108** for section **100** can be configured as a countercurrent heat exchanger in which heat is exchanged between the input stream in line **104** directed to the inlet of the HDO reactor **110** and an outlet stream in conduit or line **112** which exits the reactor **110** and is directed through heat exchanger **116** as shown in FIG. **3** (i.e., heat exchangers **108** and **116** are combined as a single heat countercurrent flow heat exchanger, in which heat exchange occurs between the fluids in the inlet flow line **104** and the outlet flow line **112**). Alternatively, any other suitable heat exchange system can be provided to heat the inlet stream in line **104** to a suitable temperature (as well as cool outlet stream in line **112** to a suitable temperature).

[0038] The pressurized and heated mixture in input line **104** is combined with compressed hydrogen feed provided in conduit or line **142**, where the hydrogen in line **142** has been compressed by a high pressure compressor **140** to a pressure that is similar to the pressure of the fluid in input line **104** (e.g., a pressure of about 1500 psig or about 10.3 MPa). As described herein, the hydrogen feed can be provided as a recycle feed from the output of the HDO reactor **110**. The ratio of hydrogen to liquid feed entering the HDO reactor **110** can be selected to enhance or maximize hydrogenolysis of and removal of oxygen from the bio-oil so as to increase the amount of hydrocarbon compounds within the light bio-oil feed stream. In example embodiments, hydrogen is provided in an amount of about 1500 NL/kg of the feed stream at an operating temperature of about 220° C. and an operating pressure of about 1500 psig (about 10.3 MPa) within the HDO reactor **110**.

[0039] Within the HDO reactor **110**, carbon-based compounds within the bio-oil liquid feed react with hydrogen to remove or cleave oxygen atoms from such compounds, resulting in a reduction in the oxygen content within the bio-oil emerging from the reactor **110**. The operating conditions within the HDO reactor **110** are maintained at a temperature ranging from about 200° C. to about 300° C. (e.g., about 280° C. or less, such as 250° C.) and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) (e.g., a pressure of about 1500 psig (about 10.3 MPa)). Any suitable one or combination of catalysts (e.g., catalysts including cobalt, molybdenum or combinations thereof) can be provided within the HDO reactor **110** to achieve or enhance a desired HDO reaction of the light bio-oil with hydrogen to form the HDO bio-oil. The HDO bio-oil (i.e., the light bio-oil processed within the HDO reactor) has an increase in hydrocarbon compounds and a reduction in oxygen content in relation to the input liquefied light bio-oil. For example, the oxygen content of the light bio-oil (at about 25% by weight or less) can be significantly reduced to no greater than about 10% by weight of the HDO bio-oil, such as no greater than about 5% by weight of the HDO bio-oil, or even as low as no greater than about 1% by weight of the HDO bio-oil. The HDO bio-oil further has a low TAN of 1-3 and even as low as a TAN less than 1.

[0040] The HDO products emerging from the reactor in exit conduit or line **112** include HDO oil, aqueous products and gases (e.g., hydrogen and methane). The HDO products are cooled in heat exchanger **116** from the HDO reaction temperature (e.g., the same heat exchanger **108** as previously described herein, where the HDO products are used to heat the input bio-oil stream to the HDO reactor **110**) of 200-280° C. to about 30° C. and then delivered to a gas/liquid separation unit or gas/liquid separator **120**. The cooled HDO products are separated within the gas/liquid separator **120** between gaseous products and liquid products. The gaseous products comprise substantially (e.g., 90% by weight or greater) hydrogen, but also include methane.

[0041] The gaseous products exiting the gas/liquid separator **120** (via conduit or line **122**) are provided to an inlet of a pressure swing adsorption (PSA) unit **124**, which operates at a pressure of about 300 psig (about 2.1 MPa) to separate some or all of the hydrogen from the remaining gases (e.g., where hydrogen is non-adsorbed or substantially non-adsorbed on a selected surface and therefore can be separated from the remaining adsorbed gases within the PSA unit) and exits the PSA unit **124** via recycle conduit or line **136**. The hydrogen in line **136** is provide to the compressor **140** where it is compressed to a suitable pressure and combined with the bio-oil stream in line **104** prior to input to the HDO reactor **110**.

[0042] The liquid products exiting the gas/liquid separator **120** are directed to a further phase separation unit or phase separator **130** to separate the aqueous phase (i.e., phase including water) from the HDO bio-oil phase based upon differences in their hydrophobicity. The separated aqueous phase exits the separator **130** via conduit or line **135**, where it can be discarded or further processed for a particular application. The separated HDO bio-oil phase exits the separator **130** via conduit or line **134**, where it can be utilized as a fuel in certain applications. A portion of the separated HDO bio-oil phase is also provided via line **132** to the mixer **102** for combining with the light oil feed of line **98** as previously described herein.

[0043] The system and process described herein and depicted in the figures results in the formation of a final (HDO) bio-oil product having a reduced water content and a reduced oxygen content in relation to other bio-oils formed from woody biomass. In particular, the system and methods as described herein facilitates the formation of bio-oils having a water content of no greater than about 5% by weight of the bio-oil (or even as little as no greater than 1% by weight of the bio-oil). Further, the bio-oils formed herein can have an oxygen content of no greater than about 10% by weight of the bio-oil, in particular no greater than about 5% by weight of the bio-oil (e.g., no greater than about 1% by weight of the bio-oil) and also a TAN (total acid number, as measured in mg KOH/g of oil) within the range of about 1 to about 3 (where the final HDO bio-oil can further have a TAN of less than 1). Bio-oils formed in accordance with the techniques described herein include hydrocarbons ranging from C_{10} to C_{24} carbon chains (where the bio-oils can also include hydrocarbons less than C_{10} and greater than C_{24}), which facilitate blending and solubility with diesel oil and/or other petroleum products.

[0044] The two stage liquefaction process (utilizing the solvents and operating conditions as described herein) combined with the HDO process can result in an overall biomass conversion rate that is significant. For example, the system and process described herein and depicted in the figures can result in a yield of at least 60% (e.g., 69% or greater) of bio-oil based upon amount of input biomass to the process. This is due, at least in part, to the conversion of biomass to light bio-oil in the first liquefaction reactor **20**, the selection of specific solvents and operating conditions at different processing stages, the further conversion of heavier oils and other solid product (e.g., unconverted biomass material from the first stage liquefaction process) to further light bio-oil in the second stage liquefaction reactor **80**, the recycle of solvents within the system, etc.

[0045] Thus, utilizing the system and methods described herein, a biomass material can be converted at high yield to a bio-oil that is low in oxygen and water content, has a low acid content (low TAN), and is suitable for direct blending with petroleum products for a variety of applications. The two stage liquefaction portion of the process utilizes solvents (methanol/water combination for the first stage and methanol for the second stage) that are readily recovered after liquefaction of the biomass and therefore available for recycling/reuse in the process, and the liquefaction is achieved in the absence of any catalyst (i.e., no catalyst present in either of the first and second stage liquefaction reactors). Further, the operating conditions required in the liquefaction stages are very mild, with much lower temperatures and pressures required to liquefy the woody biomass in comparison to conventional biomass liquefaction techniques.

[0046] Further reduction in oxygen content (and increase in amount of hydrocarbons) within the light bio-oil can further be achieved by subjecting the light bio-oil to an HDO process as described herein. While the process described herein and depicted in FIGS. **1-3** includes the two stages of liquefaction integrated with an HDO section for further processing of the light bio-oil, it is noted that a system and process can also be implemented that separates the two stage liquefaction from HDO processing. For example, the light bio-oil produced from the two stage liquefaction process (e.g., sections **2** and **50** as depicted in FIGS. **1** and **2**) can be utilized to produce a liquefied bio-oil product which is commercially sold for use in certain bio fuel applications and/or further processed at another location (e.g., a refinery) using an HDO process and/or other processes to yield a final bio-oil product.

[0047] While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. Thus, it is intended that the present invention covers modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed:

1. A method of producing a bio-oil product with a total acid number (TAN) less than 5 from biomass material, the method comprising:

subjecting the biomass material to a first stage liquefaction process, the first stage liquefaction process comprising:

combining the biomass material with a co-solvent comprising methanol and water to form a first slurry mixture; and

providing the slurry mixture within a first liquefaction reactor and maintaining the first slurry mixture at a temperature between 200° C. and 310° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to convert a portion of the biomass material into a first liquefied bio-oil product as well as form a first aqueous product and a first solid product;

separating the first liquefied bio-oil product from the aqueous and solid products; and

subjecting the solid product obtained from the first stage liquefaction process to a second stage liquefaction process, the second stage liquefaction process comprising:

combining the first solid product with methanol to form a second slurry mixture; and

providing the second slurry mixture within a second liquefaction reactor and maintaining the second slurry mixture at a temperature between 200° C. and 310° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to convert a portion of the first solid product to a second liquefied bio-oil product as well as form a second aqueous product and a second solid product.

2. The method of claim **1**, wherein the biomass material comprises pulverized wood.

3. The method of claim **2**, wherein the mass ratio of biomass material to co-solvent is at least about 1:5.

4. The method of claim **1**, wherein the co-solvent comprises each of methanol and water in a range of 40% to 60% of the co-solvent.

5. The method of claim **1**, wherein at least 80% by weight of the biomass material is converted to the first liquefied bio-oil product within the first liquefaction reactor.

6. The method of claim **1**, wherein one or both of the first and second liquefaction reactors is free of any catalyst.

7. The method of claim **1**, where each of the first and second liquefied bio-oil products has a total acid number (TAN) no greater than 3.

8. The method of claim **1**, wherein each of the first and second liquefied bio-oil products has an oxygen content of no greater than about 25% by weight of the liquefied bio-oil product.

9. The method of claim **8**, wherein the oxygen content is no greater than about 20% by weight of the liquefied bio-oil product.

10. The method of claim **1**, wherein each of the first and second liquefied bio-oil products has a water content of no greater than about 10% by weight of the liquefied bio-oil product.

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

separating water and/or methanol from one or more of the products obtained from the first liquefaction reactor and/or the second liquefaction reactor; and

recycling the separated water and/or methanol for use as at least a portion of the co-solvent combined with the biomass material that forms the first slurry mixture.

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

combining the first liquefied bio-oil product with the second liquefied bio-oil product to form a combined liquefied bio-oil product.

13. The method of claim **12**, further comprising:

combining the combined liquefied bio-oil product with hydrogen in a hydrodeoxygenation reactor at a temperature between 200° C. and 300° C. and a pressure between 1000 psig (6.9 MPa) and 2000 psig (17.2 MPa) so as to remove oxygen from carbon-based compounds within the combined liquefied bio-oil product to form a final bio-oil product.

14. The method of claim **13**, wherein the final bio-oil product has a total acid number (TAN) less than 1.

15. The method of claim **13**, wherein the final bio-oil product has an oxygen content of no greater than about 10% by weight of the final bio-oil product.

16. The method of claim **13**, wherein the final bio-oil product has a water content of no greater than about 5% by weight of the final bio-oil product.

17. The method of claim **13**, wherein the final bio-oil product includes hydrocarbons ranging from C_{10} to C_{24}.

18. A liquefied bio-oil product formed according to the method of claim **12**.

19. A liquefied bio-oil product derived from a biomass material comprising pulverized wood, wherein the liquefied bio-oil product has a total acid number (TAN) that is less than 5, and further has an oxygen content no greater than 25% by weight of the liquefied bio-oil product.

20. The liquefied bio-oil product of claim **20**, wherein the oxygen content is no greater than 10% by weight of the liquefied bio-oil product, and the bio-oil product further includes a plurality of carbon-containing compounds having carbon chains in the range of C_{10} to C_{24}.

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