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(54) **METHOD FOR UPGRADING BIO-OIL USING SUPERCRITICAL ALCOHOLS AND UPGRADED BIO-OIL BY THE METHOD**

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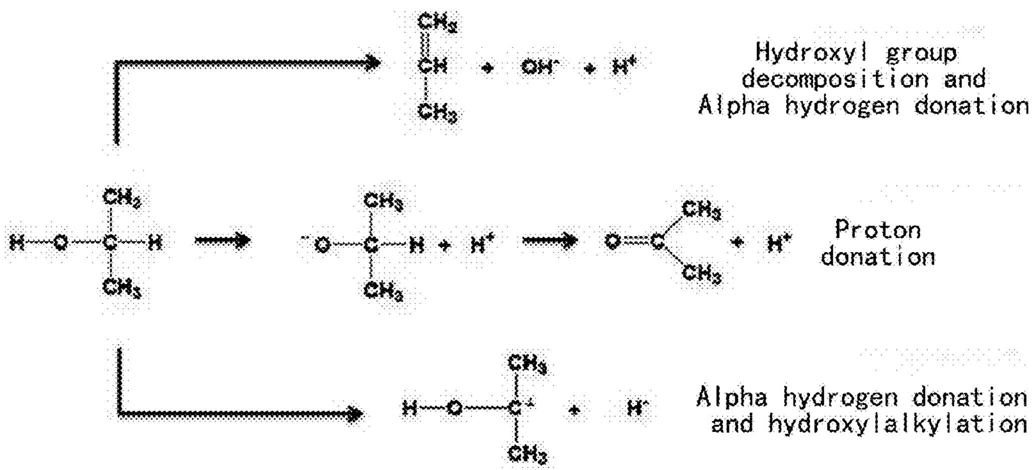
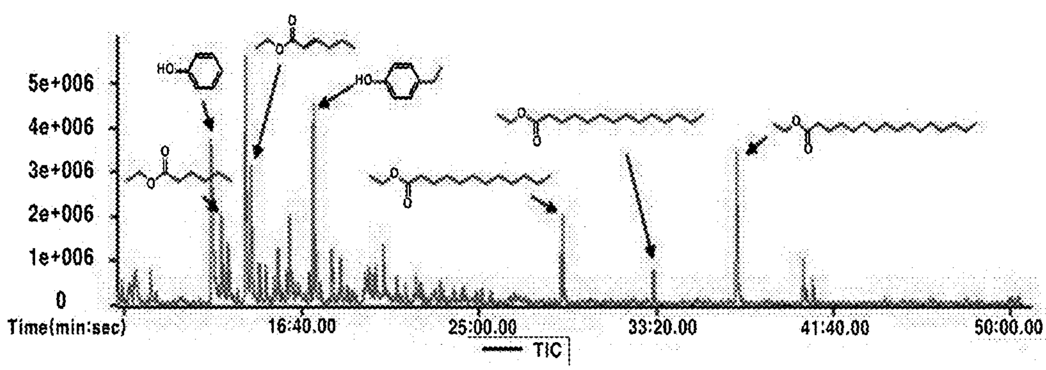
(57) **ABSTRACT**

Provided herein is a method for upgrading a bio-oil using a supercritical alcohol, and the bio-oil upgraded by the method, the method including removing oxygen existing in the molecule of the bio-oil using the supercritical state alcohol as a solvent and reacting the bio-oil and the alcohol solvent at supercritical state so as to increase the energy content, removing organic acids that increase the acidity of the bio-oil including formic acid and acetic acid or converting the organic acids to other materials so as to reduce the acidity, and converting hydrophilic materials in the bio-oil to hydrophobic materials so as to reduce the moisture content, and increasing the pH of the bio-oil to reduce the corrosiveness, thereby providing the effectiveness in upgrading a bio-oil.

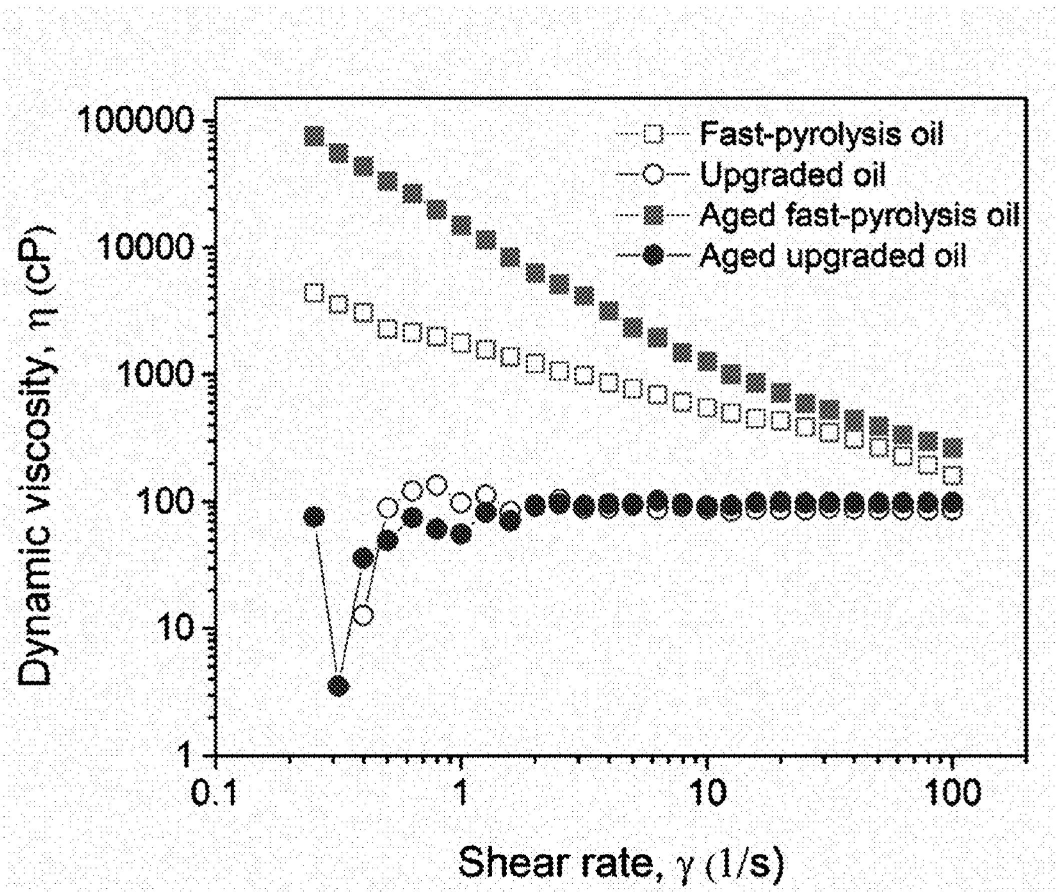
[FIG. 1]


Hydroxyl group
decomposition and
Alpha hydrogen donation
Proton
donation
Alpha hydrogen donation
and hydroxylalkylation

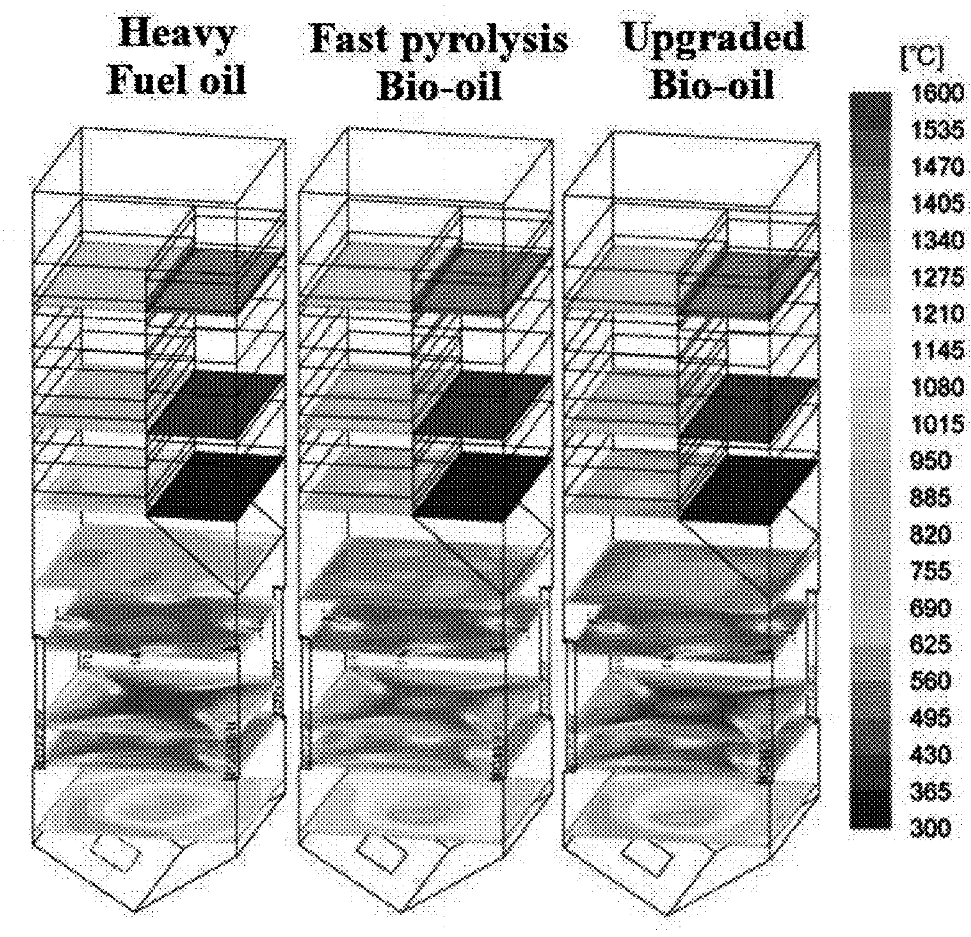
[FIG. 2]


5e+006
4e+006
3e+006
2e+006
1e+006
0
Time(min:sec)
16:40.00
25:00.00
33:20.00
41:40.00
50:00.00
TIC

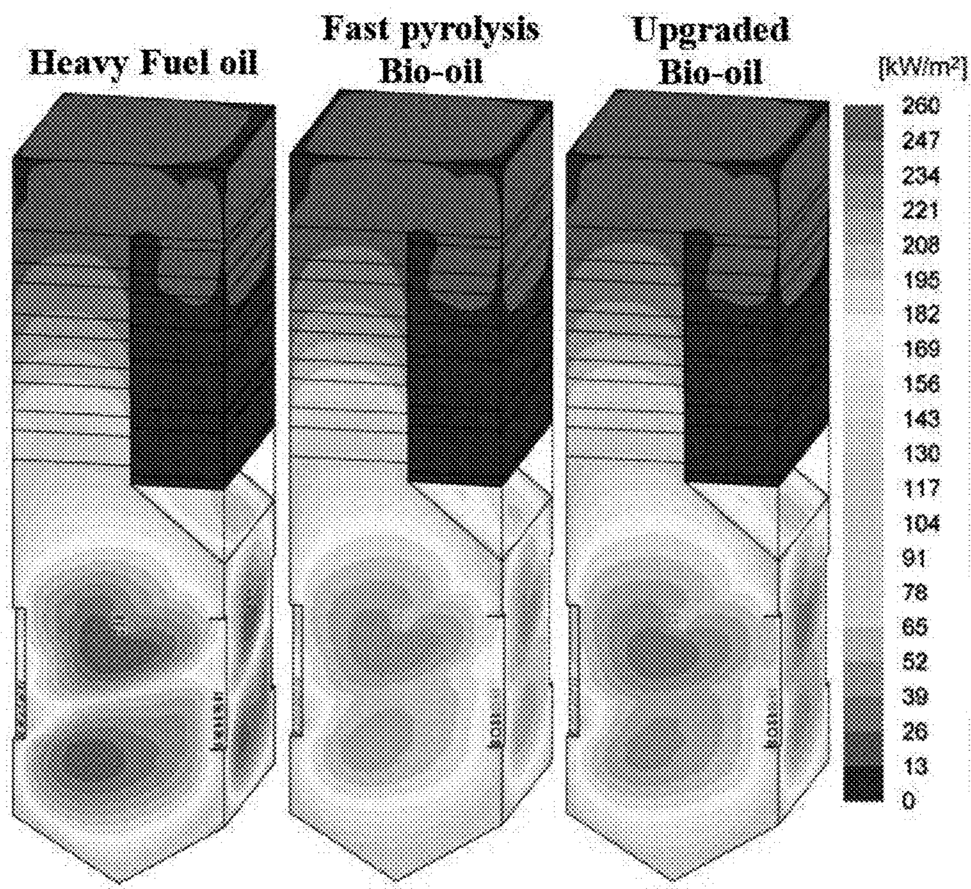
[FIG. 3]


Fast-pyrolysis oil
Upgraded oil
Aged fast-pyrolysis oil
Aged upgraded oil
Dynamic viscosity, η (cP)
100000
10000
1000
100
10
1
0.1
1
10
100
Shear rate, γ (1/s)

[FIG. 4]


Heavy Fuel oil
Fast pyrolysis Bio-oil
Upgraded Bio-oil
[°C]
1600
1535
1470
1405
1340
1275
1210
1145
1080
1015
950
885
820
755
690
625
560
495
430
365
300

[FIG. 5]


Heavy Fuel oil
Fast pyrolysis Bio-oil
Upgraded Bio-oil
[kW/m²]
260
247
234
221
208
195
182
169
156
143
130
117
104
91
78
65
52
39
26
13
0

METHOD FOR UPGRADING BIO-OIL USING SUPERCRITICAL ALCOHOLS AND UPGRADED BIO-OIL BY THE METHOD

BACKGROUND

[0001] 1. Field

[0002] The present invention relates to a method for upgrading a bio-oil using a supercritical alcohol and the bio-oil upgraded by the method, and more particularly, to a method for using a supercritical alcohol to upgrade a bio-oil prepared by a thermochemical process using biomass as raw material, thereby converting the bio-oil into a biofuel with improved stability, reduced oxygen content, and increased energy content, so as to be utilized as a fuel for power generation and transportation.

[0003] 2. Background

[0004] As concerns are growing over depletion of energy resources and environmental pollution due to the recent excessive use of fossil fuels, there is a surge of interest in preparing a non-fossil fuel and chemical material that are renewable, sustainable and environmentally friendly. Biomass that is generated on land or oceans is a renewable energy source with carbon-neutral characteristics of absorbing the carbon dioxide generated once used, unlike fossil fuels. Thus, biomass is gathering a lot of attention worldwide.

[0005] Among the biofuels, bioethanol that is prepared from saccharide raw materials such as corn, sugar cane and the like, and biodiesel that is prepared from vegetable oils such as palm oil, soybean oil and the like are being produced commercially, but these first generation biofuels have original limitations of competition with food resources, and contain oxygen in their molecules, and thus they have a disadvantage of low energy content when compared to gasoline, jet fuel, and diesel that are produced from conventional fossil fuels. Therefore, a lot of interest is concentrated on preparing a biofuel ("drop-in" biofuel) that does not compete with food resources, contain less or even no oxygen in its molecule.

[0006] Of the various thermochemical conversion processes for non-food biomass, fast pyrolysis that is a technology closest to commercialization is a method of using various types of biomass such as lignocellulosic biomass, herbaceous biomass, large algae and fine algae and the like as raw material to decompose it under a reaction temperature of 400-600° C. for a few seconds without oxygen, and then condensing the generated gas thereby preparing a liquid-phase material. The liquid-phase material prepared is generally called "bio-oil" or "bio-crude". Besides the fast pyrolysis, other methods for preparing bio-oil include a method of liquefying biomass by a reaction at high temperature and high pressure under the presence of water or organic solvent.

[0007] The bio-oil prepared in fast pyrolysis or liquefaction process may be utilized as a renewable fuel for transportation, a hydrocarbon chemical material or an expensive chemical material and the like, and have various environmentally friendly advantages such as NO_x reduction, SO_x reduction, carbon neutrality and the like. However, the bio-oil prepared by the conventional thermochemical conversion processes still has various disadvantages and thus it is still not being directly utilized as fuel for transportation or for power generation.

[0008] More specifically, bio-oil is disadvantageous in that it (1) has very poor thermo-stability and long-term storability due to its high oxygen content of 35-40 weight %, (2) has a low energy due to a high oxygen content (a higher heating value (HHV)=16-19 MJ/Kg), (3) contains a very high water content of 15-30 weight % and hydrophilic compounds that is soluble in water included in the bio-oil and thus has a very low miscibility with conventional hydrophobic fossil fuels, (4) contains a very high content of carboxylic acid of high acidity such as formic acid, acetic acid and the like and water, and thus an extremely low pH of 2 to 3, causing corrosion in processing apparatuses, and (5) generates a high molecular material by a reaction of a pyrolized lignin and bio-oil when stored for a long period of time, thereby increasing its viscosity and leading to a phenomenon such as phase separation and the like (Mohan et al., Energy & Fuels, 2006, 20, 848-889). These problems of bio-oil cause various technical difficulties when treating, transferring, storing and using bio-oil, and these disadvantages of bio-oil become reasons to increase the processing costs for preparing renewable fuels or chemical materials therefrom.

[0009] Most of the aforementioned problems of bio-oil come from oxygen that exists in the molecule of the bio-oil. For the bio-oil to be utilized as a renewable fuel and chemical material, it is necessary to develop a method for removing oxygen by upgrading the bio-oil. Examples of methods for stabilizing and upgrading bio-oil by removing the oxygen existing in the molecule of the bio-oil include hydrotreating or hydroprocessing represented by hydrodeoxygenation that mostly uses heterogeneous catalyst and hydrogen; and catalytic cracking that uses heterogeneous catalyst alone without using hydrogen.

[0010] The hydrotreating is a method of removing oxygen existing in the bio-oil under a hydrogen atmosphere of high temperature and high pressure using a heterogeneous catalyst containing a relatively expensive metal such as Co—Mo, Ni—Mo, Pd, Ni, Ru and the like. (Elliot et al., Energy & Fuels, 2007, 21, 1792-1815). The hydrotreating is a technology where a reaction should be proceeded at a very high pressure of 150-300 bar and a very high reaction temperature of 300° C. or above using very expensive hydrogen, and since hydrogen of high temperature and high pressure must be maintained in a reaction device, the device expenses and process operation expenses are very high, which is a big disadvantage. Furthermore, bio-oil is usually prepared in inland and mountainous regions where lignocellulosic or herbaceous biomass is abundant, but most of the hydrogen currently being used is from petrochemical refineries installed in coastal areas, and thus since it is necessary to build infrastructure for transferring hydrogen from the petrochemical refineries in the coastal areas to biorefineries in the mountainous areas or develop a new hydrogen production process in inland or mountainous regions, the processing expenses for preparing bio-oil have increased, thereby worsening the economic feasibility. Furthermore, while the reaction temperature of hydrotreating for upgrading bio-oil effectively is 300° C. or above, due to the high molecular materials that are generated rapidly in the bio-oil at 150° C. or below as the temperature rises, coking of the heterogeneous catalyst or blocking of pipes for transferring bio-oil may occur, causing difficulties in continuously operating the process for a long time.

[0011] Meanwhile, the catalytic cracking is a method for removing oxygen in the bio-oil using a zeolite catalyst such as ZSM-5 and the like. It has an advantage of not using expensive hydrogen, but it causes serious coking of the catalyst, and has limited capabilities for removing oxygen, and thus it cannot effectively upgrade the bio-oil.

[0012] Therefore, there is an urgent need to develop a method for upgrading bio-oil that could effectively remove oxygen existing in the bio-oil without using heterogeneous catalyst and hydrogen so as to increase the energy content and stability of the bio-oil, reduce the acidity of bio-oil and increase its pH so as to decrease the corrosiveness, and reduce the water content in the bio-oil so as to effectively prevent phase separation.

SUMMARY

[0013] A purpose of the present invention is to provide a method for upgrading a bio-oil using a supercritical alcohol, wherein the method uses a supercritical state alcohol as a solvent in order to remove oxygen existing in the molecule of the bio-oil so as to increase the energy content, and remove organic acids that increase the acidity of the bio-oil including formic acid and acetic acid or convert the organic acids to other stable materials so as to reduce the acidity, and convert hydrophilic materials in the bio-oil to hydrophobic material so as to reduce the moisture content, and increase the pH of the bio-oil to reduce the corrosiveness.

[0014] Another purpose of the present invention is to provide an upgraded bio-oil that has improved stability, reduced oxygen content, and high energy content by effectively upgrading the bio-oil using a supercritical state alcohol without using an expensive hydrogen or heterogeneous catalyst provided from outside.

[0015] According to an embodiment of the present invention, there is provided a method for upgrading a bio-oil using a supercritical alcohol, the method including mixing the bio-oil and an alcohol solvent; and upgrading the bio-oil by reacting the bio-oil and alcohol solvent at a supercritical state of the alcohol solvent.

[0016] The method may further include separating and collecting a product of reaction, after the upgrading.

[0017] The mixing may include additionally mixing an additive.

[0018] The additive may include at least one of LiOH, NaOH, KOH, RbOH, Li_2CO_3, Na_2CO_3, K_2CO_3, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $MgCO_3$, $CaCO_3$, $SrCO_3$, HCl, HNO_3, H_3PO_4, H_2SO_4, H_3BO_3, HF, H_2CO_3, HCOOH, CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH_2COOH$, $C_2H_4OHCOOH$, and C_6H_5COOH.

[0019] A raw material of the bio-oil may include at least one of lignocellulosic biomass, herbaceous biomass, microalgae, and macroalgae. And the bio-oil may be in a liquid phase form produced by a thermochemical conversion process.

[0020] The bio-oil may have a moisture content of 2 to 40 weight %.

[0021] The alcohol solvent may include at least one of methanol, ethanol, propanol, isopropylalcohol, butanol, isobutanol, 2-butanol, tert-butanol, n-pentanol, isopentyl alcohol, 2-methyl-1-butanol, neopentyl alcohol, diethyl carbinol, methyl propyl carbinol, methyl isopropyl carbinol, dimethyl ethyl carbinol, 1-hexanol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 4-methyl-1-pentanol, 2-methyl-2-pentanol, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 2,2-dimethyl-1-butanol, 2,3-dimethyl-1-butanol, 2,3-dimethyl-2-butanol, 3,3-dimethyl-1-butanol, 2-ethyl-1-butanol, 1-heptanol, 2-heptanol, 3-heptanol, and 4-heptanol.

[0022] The mixing may include mixing 0.1 to 60 weight % of bio-oil, based on a total sum of the alcohol solvent and the bio-oil.

[0023] The upgrading may involve upgrading the bio-oil at a reaction temperature of 250 to 600° C., and a reaction pressure of 30 to 700 bar.

[0024] The alcohol solvent may comprise at least one of methanol (critical temperature=239° C.; critical pressure=81 bar), ethanol (critical temperature=241° C.; critical pressure=63 bar), propanol (critical temperature=264° C.; critical pressure=52 bar), isopropylalcohol (critical temperature=307° C.; critical pressure=41 bar), butanol (critical temperature=289° C.; critical pressure=45 bar), isobutanol (critical temperature=275° C.; critical pressure=45 bar), 2-butanol (critical temperature=263° C.; critical pressure=42 bar), tert-butanol (critical temperature=233° C.; critical pressure=40 bar), n-pentanol (critical temperature=307° C.; critical pressure=39 bar), isopentyl alcohol (critical temperature=306° C.; critical pressure=39 bar), 2-methyl-1-butanol (critical temperature=302° C.; critical pressure =39 bar), neopentyl alcohol (critical temperature=276° C.; critical pressure=40 bar), diethyl carbinol (critical temperature=286° C.; critical pressure=39 bar), methyl propyl carbinol (critical temperature=287° C.; critical pressure=37 bar), methyl isopropyl carbinol (critical temperature =283° C.; critical pressure=39 bar), dimethyl ethyl carbinol (critical temperature=271° C.; critical pressure=37 bar), 1-hexanol (critical temperature=337° C.; critical pressure=34 bar), 2-hexanol (critical temperature=310° C.; critical pressure=33 bar), 3-hexanol (critical temperature=309° C.; critical pressure=34 bar), 2-methyl-1-pentanol (critical temperature=331° C.; critical pressure=35 bar), 3-methyl-1-pentanol (critical temperature=387° C.; critical pressure=30 bar), 4-methyl-1-pentanol (critical temperature=330° C.; critical pressure=30bar), 2-methyl-2-pentanol (critical temperature=286° C.; critical pressure =36 bar), 3-methyl-2-pentanol (critical temperature=333° C.; critical pressure=36 bar), 4-methyl-2-pentanol (critical temperature=301° C.; critical pressure=35 bar), 2-methyl-3-pentanol (critical temperature=303° C.; critical pressure=35 bar), 3-methyl-3-pentanol (critical temperature=302° C.; critical pressure=35 bar), 2,2-dimethyl-1-butanol (critical temperature=301° C.; critical pressure=35 bar), 2,3-dimethyl-1-butanol (critical temperature=331° C.; critical pressure=35 bar), 2,3-dimethyl-2-butanol (critical temperature=331° C., critical pressure=35bar), 3,3-dimethyl-1-butanol (critical temperature=331° C.; critical pressure=35 bar), 2-ethyl-1-butanol (critical temperature=307° C.; critical pressure=34 bar), 1-heptanol (critical temperature=360° C.; critical pressure=31 bar), 2-heptanol (critical temperature=335° C.; critical pressure=30 bar), 3-heptanol (critical temperature=332° C.; critical pressure=30 bar), and 4-heptanol (critical temperature=329° C.; critical pressure=30 bar), or a combination thereof.

[0025] According to another embodiment of the present invention, a bio-oil upgraded by the aforementioned method is provided.

[0026] The upgraded bio-oil may have an oxygen content of 10 to 15 weight %, and the O/C (oxygen/carbon) molar ratio may be 0.10 to 0.16.

[0027] The higher heating value (HHV) of the upgraded bio-oil may be 30 to 40 MJ/kg, according to Equation 4 below:

$$\text{Higher Heating Value}(HHV, \text{MJ/Kg}) = \frac{34C + 124.3H + 6.3N + 19.3S - 9.8O}{100}. \quad \text{[Equation 4]}$$

[0028] (In the Equation 4, each of C, H, N, S, and O represents mass ratios of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively, based on the total mass of all elements existing in the bio-oil).

[0029] The moisture content of the upgraded bio-oil may be 0.5 to 6 weight %, and the Total Acid Number (TAN) according to ASTM D664 of the upgraded bio-oil, which is the amount of KOH needed to neutralize acids included in 1g of bio-oil, may be 1 to 35mg, and pH of the upgraded bio-oil may be 6 to 7.5.

[0030] According to another embodiment of the present invention, there is provided a fuel for power generation comprising the upgraded bio-oil as aforementioned.

[0031] According to another embodiment of the present invention, there is provided a fuel for transportation comprising the upgraded bio-oil as aforementioned.

[0032] The method for upgrading bio-oil using a supercritical alcohol according to the present invention is capable of effectively removing the oxygen existing in the bio-oil without using an expensive hydrogen or heterogeneous catalyst provided from outside thereby increasing the energy content, and is also capable of removing formic acid, acetic acid, and organic acid that increases the acidity of the bio-oil or converting them to other stabilized materials thereby reducing the acidity of the bio-oil, and is also capable of converting hydrophilic materials in the bio-oil to hydrophobic materials thereby reducing the moisture content, and also increasing the pH of the bio-oil, thereby reducing the corrosiveness.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] FIG. **1** shows a hydrogen generation mechanism of a supercritical propanol.

[0034] FIG. **2** shows results of analyzing an upgraded bio-oil prepared by upgrading with a supercritical ethanol according to Example 1 of the present invention and a bio-oil prepared by fast pyrolysis, by a gas chromatography-mass spectrometer.

[0035] FIG. **3** shows results of measurements viscosity of before and after aging a bio-oil prepared by fast pyrolysis and a bio-oil upgraded using a supercritical ethanol.

[0036] FIG. **4** shows results of CFD (Computational Fluid Dynamics) analysis by analyzing combustion characteristics of a heavy oil generated in a petroleum refining process, a bio-oil prepared by fast pyrolysis, and a bio-oil upgraded according to Example 1 the present invention, in a heavy oil boiler.

[0037] FIG. **5** shows results of CFD analysis based on heat transfer distribution in a heavy oil boiler by analyzing the combustion characteristics of heavy oil generated in a petroleum refining process, a bio-oil prepared by fast pyrolysis, and a bio-oil upgraded according to Example 1 of the present invention.

DETAILED DESCRIPTION

[0038] The advantages and characteristics of the present invention, and methods for achieving those advantages and characteristics will become apparent with reference to the embodiments explained herein below. However, the present invention is not limited to those embodiments, but rather, the embodiments are provided to assist the reader in gaining a comprehensive understanding of the present invention. Accordingly, various changes, modifications, and equivalents of the embodiments described herein will be suggested to those of ordinary skill in the art, and thus the present invention is merely defined by the scope of the claims.

[0039] Unless defined otherwise, all terms (including technical and scientific terms) in the present invention will be used to refer to meanings that may be commonly understood by those skilled in the art. Furthermore, the terms defined in generally used dictionaries will not be interpreted overly or ideally unless specifically defined otherwise.

[0040] The present invention relates to a method for upgrading bio-oil using a supercritical alcohol and the bio-oil upgraded by the same method, and particularly, to a method for upgrading a bio-oil prepared by a thermochemical process using a supercritical alcohol.

[0041] The method for upgrading a bio-oil of the present invention may include a step of mixing (S10), and a step of upgrading (S20).

[0042] Furthermore, the method for upgrading a bio-oil may further include a step of separating and collecting the reaction products (S30).

[0043] Hereinafter, each step of the method for upgrading a bio-oil according to an embodiment of the present invention will be explained in detail.

[0044] First of all, the step of mixing (S10) is a step of adding a bio-oil and an alcohol solvent in a reactor and mixing the bio-oil and the alcohol solvent. Examples of the bio-oil that may be used in the present invention include various types of liquid bio-oil prepared by various types of thermos-chemical conversion processes such as fast pyrolysis and liquefaction using lignocellulosic biomass, herbaceous biomass, microalgae, and macroalgae and the like as raw material, but without limitation.

[0045] Furthermore, the moisture content existing in the bio-oil may be 2 to 40 weight %, and desirably 5 to 30 weight %, but without limitation.

[0046] In the case where the moisture content is less than 2 weight extensive undesirable reactions between the bio-oil constituent can occur, and in the case where the moisture content exceeds 40 weight %, a deoxygenation reaction is not proceeded effectively in the supercritical alcohol.

[0047] Preferably, the alcohol solvent may be an alcohol solvent that includes a main chain of about 1 to about 10 carbon numbers and about 1 or more hydroxyl groups, more preferably, that includes a main chain of about 1 to about 7 carbon numbers and about 1 or more hydroxyl groups, but without limitation. The alcohol solvent may include at least one of methanol (critical temperature=239° C.; critical pressure =81 bar), ethanol (critical temperature=241° C.; critical pressure=63 bar), propanol (critical temperature=264° C.; critical pressure=52 bar), isopropylalcohol (critical temperature=307° C.; critical pressure=41 bar), butanol (critical temperature=289° C.; critical pressure=45 bar), isobutanol (critical temperature=275° C.; critical pressure=45 bar), 2-butanol (critical temperature=263° C.; critical pressure=42 bar), tert-butanol (critical temperature=233° C.;

critical pressure=40 bar), n-pentanol (critical temperature=307° C.; critical pressure=39 bar), isopentyl alcohol (critical temperature=306° C.; critical pressure=39 bar), 2-methyl-1-butanol (critical temperature=302° C.; critical pressure =39 bar), neopentyl alcohol (critical temperature=276° C.; critical pressure=40 bar), diethyl carbinol (critical temperature=286° C.; critical pressure=39 bar), methyl propyl carbinol (critical temperature=287° C.; critical pressure=37 bar), methyl isopropyl carbinol (critical temperature =283° C.; critical pressure=39 bar), dimethyl ethyl carbinol (critical temperature=271° C.; critical pressure=37 bar), 1-hexanol (critical temperature=337° C.; critical pressure=34 bar), 2-hexanol (critical temperature=310° C.; critical pressure=33 bar), 3-hexanol (critical temperature=309° C.; critical pressure=34 bar), 2-methyl-1-pentanol (critical temperature=331° C.; critical pressure=35 bar), 3-methyl-1-pentanol (critical temperature=387° C.; critical pressure=30 bar), 4-methyl-1-pentanol (critical temperature=330° C.; critical pressure=30 bar), 2-methyl-2-pentanol (critical temperature=286° C.; critical pressure =36 bar), 3-methyl-2-pentanol (critical temperature=333° C.; critical pressure=36 bar), 4-methyl-2-pentanol (critical temperature=301° C.; critical pressure=35 bar), 2-methyl-3-pentanol (critical temperature=303° C.; critical pressure=35 bar), 3-methyl-3-pentanol (critical temperature=302° C.; critical pressure=35 bar), 2,2-dimethyl-1-butanol (critical temperature=301° C.; critical pressure=35 bar), 2,3-dimethyl-1-butanol (critical temperature=331° C.; critical pressure=35 bar), 2,3-dimethyl-2-butanol (critical temperature=331° C., critical pressure=35 bar), 3,3-dimethyl-1-butanol (critical temperature=331° C.; critical pressure=35 bar), 2-ethyl-1-butanol (critical temperature=307° C.; critical pressure=34 bar), 1-heptanol (critical temperature=360° C.; critical pressure=31 bar), 2-heptanol (critical temperature=335° C.; critical pressure=30 bar), 3-heptanol (critical temperature=332° C.; critical pressure=30 bar), and 4-heptanol (critical temperature=329° C.; critical pressure=30 bar), or a combination thereof. Hereinabove, the supercritical conditions are above critical temperature and critical pressure of each alcohol.

[0048] There is no particular limitation to the configuration of a reactor used at the step of mixing (S10), but a batch type or continuous type reactor may be used.

[0049] Furthermore, at the step of mixing (S10), the amount of the bio-oil may be 0.1 to 60 weight %, and desirably 1 to 40 weight % based on the total sum (100 weight %) of the alcohol solvent and the bio-oil. If the amount of the bio-oil is less than 0.1 weight %, the concentration of the bio-oil is too low and thus the amount of the bio-oil being upgraded within unit time is too small thereby reducing economic feasibility, and if the amount of the bio-oil exceeds 60 weight %, the concentration of the bio-oil is too high and thus a deoxygenation reaction and acidity reduction reaction will not be performed effectively, and further, the uniformity of the upgraded bio-oil will be deteriorated thereby degrading the quality.

[0050] Furthermore, at the step of mixing (S10), an additive may be further mixed. The additive may include a material that promotes hydrogen generation from the supercritical alcohol or a material that promotes the reaction of removing the oxygen existing in the bio-oil. Examples of the additive include at least one of alkali metal hydroxides such as LiOH, NaOH, KOH, RbOH, and the like; alkali metal carbonates such as Li_2CO_3, Na_2CO_3, K_2CO_3, and the like; alkali earth metal hydroxides such as $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ and the like; alkali earth metal carbonates such as $MgCO_3$, $CaCO_3$, $SrCO_3$ and the like; inorganic acids such as HCl, HNO_3, H_3PO_4, H_2SO_4, H_3BO_3, and the like; and organic acids such as formic acid(HCOOH), acetic acid (CH_3COOH), propionic acid(CH_3CH_2COOH), butyric acid ($CH_3CH_2CH_2COOH$), lactic acid($C_2H_4OHCOOH$), and benzoic acid(C_6H_5COOH) and the like.

[0051] Furthermore, the amount of the additive may be 0.1 to 20 weight %, and desirably 0.5 to 10 weight % based on the total amount of reactants, but without limitation. When the amount of the additive is less than 0.1 weight %, an effect by the additive cannot be expected when upgrading the bio-oil, and when the amount of the additive exceeds 20 weight %, it exceeds the limit where the additive may be dissolved in the supercritical alcohol, thereby increasing the cost for separating the excessive additive after processing.

[0052] Then, the step of upgrading (S20) is a step of reacting the bio-oil in the alcohol solvent that is at a supercritical state, and more specifically, it is a step of increasing the temperature and pressure of the reactor above the critical temperature and critical pressure of the alcohol, and reacting the bio-oil at the supercritical alcohol state, thereby upgrading the bio-oil. An advantage of upgrading bio-oil using the supercritical alcohol is that the deoxygenation reaction and acidity reduction reaction may be made effectively without using hydrogen and a heterogeneous catalyst provided from outside. The supercritical alcohol may provide highly activated hydrogen that is generated according to the temperature and pressure. For example, a propanol at a supercritical state may provide highly activated hydrogen such as proton, hydride and the like by at least one of three mechanisms as in FIG. **1** (Nakagawa et al., Journal of Supercritical Fluids 2003, 27, 255-261; Ross et al., Fuel 1979, 58, 438-442; Brand et al., Energy, 2013, 59, 173-182).

[0053] For example, the highly activated hydrogen that is generated from the supercritical alcohol itself may effectively remove the oxygen contained in the bio-oil by reactions such as decarboxylation, decarbonylation, hydrodeoxygenation and the like, thereby reducing the molar ratio of O/C (oxygen/carbon) in the bio-oil and increasing an energy content. In addition, the reactive carboxylic acids existing in the bio-oil may be converted to other stabilized materials by the unique chemical reactions of supercritical alcohol such as esterification, alkylation, alkoxylation and the like, thereby reducing the acidity and increasing the pH. Furthermore, water soluble materials having hydrophilicity due to the high oxygen content of the bio-oil may be converted to hydrophobic materials, thereby reducing the solubility in water.

[0054] At the step of upgrading (S20), the reaction temperature may be 250 to 600° C., and desirably 300 to 500° C. When the reaction temperature is less than 250° C., the hydrogen generation reaction, deoxygenation reaction, acidity reduction reaction and the like may not be carried out effectively, and therefore, the bio-oil may not be upgraded effectively. When the reaction temperature exceeds 600° C., a cracking reaction may be performed actively, which may gasify the bio-oil, thereby deteriorating the yield of liquid phase by the upgrading of the bio-oil and thus reducing the economic feasibility.

[0055] The reaction pressure at the step of upgrading (S20) may be 30 to 700 bar, and desirably 100 to 500 bar.

When the reaction pressure is less than 30 bar, the capability of the supercritical alcohol for hydrogen generation reaction, deoxygenation reaction, and acidity reduction reaction may be reduced, thereby making it difficult to upgrade the bio-oil effectively. And when the reaction pressure exceeds 700 bar, the processing costs for maintaining a high pressure may increase.

[0056] Furthermore, at the step of upgrading (S20), the reaction time may be 10 seconds to 5 hours, and desirably 1 minute to 2 hours, but without limitation. When the reaction time is less than 10 seconds, it would be too short for the bio-oil to be upgraded and thus the bio-oil may not be upgraded effectively by the hydrogen generation reaction, deoxygenation reaction, and acidity reduction reaction of the supercritical alcohol, and when the reaction time exceeds 5 hours, the processing costs will increase in order to maintain the high temperature and high pressure for a long period of time.

[0057] Then, the step of separating and collecting (S30) is a step of separating the reaction products by reducing the temperature and pressure after the step of upgrading (S20). The reaction product may be discharged through a decompressing device located at an outlet of the reactor. The reaction products may include the gaseous materials such as carbon dioxide, carbon monoxide, methane, ethane, ethylene, propylene, propane, butane and the like, the liquid materials such as an upgraded bio-oil, alcohol solvent, organic compounds converted from the alcohol, and water which is a byproduct of the reaction, and solid residues such as char, tar, and inorganic material. Herein, separation of the gaseous products may be performed through gas-liquid separation by reducing the temperature and pressure, and separation of the solid residues may be performed through solid-liquid separation using a filter, or cyclone and the like. Separating the upgraded bio-oil which is at a liquid phase from other liquid phase products or liquid phase byproducts may be performed by a general separation method such as atmospheric distillation, vacuum distillation and the like.

[0058] The present invention may provide the bio-oil upgraded by the aforementioned method.

[0059] The bio-oil upgraded by the aforementioned method may have an oxygen content of 10 to 15 weight %, a molar ratio of 10 to 15 weight %, and an O/C (oxygen/carbon) molar ratio of 0.10 to 0.16.

[0060] Furthermore, a higher heating value (HHV) of the upgraded bio-oil may be 30 to 40 MJ/kg according to Equation 4 below:

$$\text{Higher Heating Value}(HHV, \text{MJ/Kg}) = \frac{34C + 124.3H + 6.3N + 19.3S - 9.8O}{100}. \quad \text{[Equation 4]}$$

[0061] (In the Equation 4, each of C, H, N, S, and O represents mass ratios of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively, based on the total mass of all elements existing in the bio-oil).

[0062] The moisture content of the upgraded bio-oil may be 0.5 to 6 weight %, and a Total Acid Number (TAN) according to ASTM D664 of the upgraded bio-oil, which is the amount of KOH needed to neutralize acids included in 1g of bio-oil, may be 1 to 35 mg and pH the upgraded bio-oil may be 6 to 7.5.

[0063] Then, the present invention may provide a fuel for power generation, the fuel including the upgraded bio-oil. The fuel for power generation may be utilized for a single firing use or co-firing use. More specifically, the upgraded bio-oil may be used for a single firing use, using 100% of the upgraded bio-oil, or for co-firing use, using a portion of the upgraded bio-oil, according to characteristics of the boiler used.

[0064] Furthermore, the present invention may provide a fuel for transportation use that comprises the upgraded bio-oil. The fuel for transportation may be prepared through fractional distillation of the upgraded bio-oil at a boiling point and then mixing the upgraded bio-oil with petroleum-based fuel for transportation. Examples of the petroleum-based fuel for transportation that may be used in the present invention may include at least one of gasoline, jet fuel, and diesel.

[0065] Hereinafter, the present invention will be explained in detail with reference to the Examples and Comparative Examples, which are for exemplary purpose only, without limitation to the scope of the claims attached hereto.

EXAMPLE—UPGRADING BIO-OIL USING SUPERCRITICAL ALCOHOL

Example 1

[0066] The bio-oil used in this Example was prepared by subjecting empty fruit bunch (EFB) that is a type of lignocellulosic biomass to fast pyrolysis for a few seconds at 500° C. Characteristics of the bio-oil are shown in Table 2. The bio-oil and ethanol of a concentration of 10 weight % was put into a batch type reactor and then the reactor was pressurized by nitrogen of 10 bar, and then the temperature was raised at a speed of about 20° C./min, and then the bio-oil was upgraded with the supercritical ethanol for 30 minutes at a reaction temperature of 400° C. When the temperature of the reactor reached 400° C., the reaction pressure was 347 bar, and then the reaction pressure increased to 378 bar after 30 minutes. This shows that gasification reactions including a reaction of removing oxygens existing in the bio-oil had proceeded. When the temperature of the reactor was reduced to atmospheric temperature after 30 minutes of reaction, the pressure of the gas phase was 24 bar. The gaseous products were collected using a Tedlar bag to analyze them, and the solid and liquid phase products were separated from each other using a filter. The bio-oil and ethanol were separated from the liquid phase by vacuum distillation. The characteristics of the upgraded bio-oil were evaluated and shown in Tables 1 to 3.

Example 2

[0067] The bio-oil was upgraded in the same manner as Example 1 except the reaction time was 60 minutes. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 3

[0068] The bio-oil was upgraded in the same manner as Example 1 except the reaction temperature was 300° C. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in

[0069] Tables 1 to 3.

Example 4

[0070] The bio-oil was upgraded in the same manner as Example 1 except the reaction temperature was 350° C. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 5

[0071] The bio-oil was upgraded in the same manner as Example 1 except 1 weight % of Na_2CO_3 was used as an additive. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 6

[0072] The bio-oil was upgraded in the same manner as Example 1 except 10 weight % of HCOOH was used as an additive. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 7

[0073] The bio-oil was upgraded in the same manner as Example 1 except 5 weight % of KOH was used as an additive. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 8

[0074] The bio-oil was upgraded in the same manner as Example 1 except 2 weight % of HCl was used as an additive. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 9

[0075] The bio-oil was upgraded in the same manner as Example 1 except methanol was used instead of ethanol. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 10

[0076] The bio-oil was upgraded in the same manner as Example 1 except isopropyl alcohol was used instead of ethanol. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

Example 11

[0077] The bio-oil was upgraded in the same manner as Example 1 except butanol was used instead of ethanol. The upgraded bio-oil was analyzed in the same manner as Example 1 and its results are shown in Tables 1 to 3.

[0078] <Analysis on Characteristics of Bio-Oil>

[0079] The yields of the upgraded bio-oil finally obtained in the abovementioned Examples were calculated based on the weights of each component according to Equations 1 to 4 below. In Equations 1 to 3, the bio-oil prepared by fast pyrolysis and used in the Examples contained 14 weight % of moisture, and thus the weight of the dried bio-oil was used to calculate the yields.

$$\text{Liquid phase yield(wt \%)} = \frac{\text{Weight of upgraded bio oil}}{\text{Weight of dried and ash-removed bio oil}} \times 100 \quad \text{[Equation 1]}$$

$$\text{Solid residue yield(wt \%)} = \frac{\text{Weight of solid residue}}{\text{Weight of dried bio oil}} \times 100 \quad \text{[Equation 2]}$$

$$\text{Gas phase yield(wt \%)} = \frac{\text{Weight of gas phase product}}{\text{Weight of dried and ash-removed bio oil}} \times 100 \quad \text{[Equation 3]}$$

$$\text{Higher Heating Value}(HHV, \text{MJ}/\text{Kg}) = \frac{34C + 124.3H + 6.3N + 19.3S - 9.8O}{100} \quad \text{[Equation 4]}$$

[0080] (In the Equation 4, each of C, H, N, S, and O represents mass ratios of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively, based on the total mass of all elements existing in the bio-oil).

[0081] The yields of the gas phase, liquid phase, and solid phase products after upgrading the bio-oil using the supercritical alcohol calculated according to the above Equations are shown in Table 1.

TABLE 1

Exam.	Supercritical alcohol	Reaction temperature (° C.)	Reaction pressure (bar)	Reaction time (min)	Additive	Liquid phase yield (wt %)	Solid residue yield (wt %)	Gas phase yield (wt %)	Total product yield (wt %)
1	Supercritical ethanol	400	347-378	30	—	83.0	8.9	17.6	109.4
2	Supercritical ethanol	400	341-382	60	—	73.9	14.5	7.8	96.3
3	Supercritical ethanol	300	273-282	30	—	57.6	31.4	0.5	89.4
4	Supercritical ethanol	350	254-263	30	—	82.4	23.0	2.4	107.8
5	Supercritical ethanol	400	351-381	30	Na_2CO_3	164	9.3	12.0	185.3
6	Supercritical ethanol	400	410-420	30	HCOOH	105	15.7	83.2	203.9
7	Supercritical ethanol	400	352-385	30	KOH	125	9.2	14.9	149.1

TABLE 1-continued

Exam.	Supercritical alcohol	Reaction temperature (° C.)	Reaction pressure (bar)	Reaction time (min)	Additive	Liquid phase yield (wt %)	Solid residue yield (wt %)	Gas phase yield (wt %)	Total product yield (wt %)
8	Supercritical ethanol	400	359-388	30	HCl	117	8.1	11.5	136.6
9	Supercritical methanol	400	340-372	30	—	75.0	10.2	10.7	95.9
10	Supercritical isopropyl alcohol	400	314-384	30	—	71.2	15.7	4.3	86.9
11	Supercritical butanol	400	302-315	30	—	71.2	12.5	4.2	87.7

[0082] As shown in Table 1 above, when the bio-oil prepared by fast pyrolysis was upgraded with the supercritical ethanol under a temperature condition of 400° C. and reaction time of 30 to 60 minutes in Examples 1 to 2, the yield of the upgraded liquid phase was 74 to 83 weight %, the yield of the solid residue was less than 15 weight %, and the yield of the gas phase was about 8 to 18 weight %, and thus the yield of the liquid phase was the highest. Meanwhile, in Example 3, when the reaction temperature was reduced to 300° C., the yield of the liquid phase was somewhat decreased, and the yield of the solid phase was increased, but in Example 4, when the reaction temperature was increased to 350° C., the yield of the liquid phase was 82.4%, that is the highest, and the yield of the solid phase was decreased to 23.0 weight %, showing that an effective upgrading had been performed. Meanwhile, when an additive was used in Examples 5 to 8, the yield of the upgraded liquid phase was 100 weight % or more, whereas the yield of the solid residue was low as much as about 8 to 16 weight %. This seems to be because the supercritical alcohol is capable of providing hydrogen effectively, thereby restricting the condensation or repolymerization reactions of generating solid residue materials, and since alkylation, alkoxylation, and the like are effectively proceeded without using a catalyst so as to stabilize the unstable intermediate materials that are generated during decomposition of organic compounds existing in the bio-oil, thereby increasing the yield of the liquid phase. Meanwhile, in the case of using a supercritical methanol, supercritical isopropyl alcohol, or supercritical butanol instead of the supercritical ethanol in Examples 9 to 11, the yield of the liquid phase is higher than those of the solid residue and the gas phase, which shows that the upgrading reaction has been made successfully.

[0083] Next, the characteristics of the bio-oil before and after upgrading are shown in Table 2, and the components of the gas phase products are shown in Table 3.

[0084] First of all, the total acid number (TAN) of the bio-oil before and after upgrading is the amount of KOH necessary for neutralizing acids included in 1 g of bio-oil. It was measured by the ASTM D664 method using Metrohm 848 Titrino plus. The content of moisture of the bio-oil before and after the upgrading was measured using the Metrohm KF 870 Titrino plus Karl Fischer Titrator.

[0085] Furthermore, qualitative and quantitative analyses on the gas phase products were performed using Gas chromatography, GC, Clarus 600 GC-Model Arne! 1115PPC Refinery Gas Analyzer (RGA) (PerkinElmer) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

TABLE 2

	C (wt %)	O (wt %)	H (wt %)	N (wt %)	S (wt %)	O/C Molar ratio	HHV (MJ/kg)	Moisture content (wt %)	TAN (mg KOH/g)	pH	Ash content (wt %)
Bio-oil	56.7	26.8	6.1	1.6	0.1	0.35	24.3	14.0	69.4	4.2	9.9
Example 1	76.9	12.9	7.5	1.9	1.4	0.12	34.3	1.6	4.84	6.9	0.0
Example 2	69.0	14.9	7.9	1.3	0.7	0.16	32.2	1.8	12.4	6.9	0.0
Example 3	70.2	18.8	5.3	1.8	0.8	0.20	28.5	0.2	12.6	6.7	0.5
Example 4	71.6	17.4	6.0	2.3	0.8	0.18	30.5	0.9	3.6	6.8	0.7
Example 5	76.1	11.7	8.4	0.9	0.59	0.12	35.4	5.4	1.80	6.9	0.0
Example 6	71.6	14.3	6.6	1.8	0.76	0.15	31.5	1.1	33.1	6.1	0.2
Example 7	76.5	11.2	8.8	1.1	0.62	0.11	36.1	2.8	10.6	6.5	0.1
Example 8	75.3	11.9	8.1	1.3	0.57	0.12	34.8	3.1	15.2	6.5	0.0
Example 9	71.2	12	7.1	0.9	0.68	0.13	32.2	3.9	19.8	6.2	0.4
Example 10	74.3	13.5	6.7	2.1	0	0.14	32.5	2.4	21.0	6.8	0.1
Example 11	74.1	13	8.6	1.8	0.6	0.13	35.0	2.1	20.8	6.7	0.2

TABLE 3

	CO_2 (mol %)	CO (mol %)	H_2 (mol %)	CH_4 (mol %)	$C_2H_4 + C_2H_6$ (mol %)	$C_3H_6 + C_3H_8$ (mol %)	C4+ (mol %)	Gas phase yield (wt %)
Example 1	36.2	48.2	8.2	2.4	4.6	0.3	0.1	17.6
Example 2	72.1	10.9	5.6	0.9	10.0	0.3	0.1	7.8

TABLE 3-continued

	CO_2 (mol %)	CO (mol %)	H_2 (mol %)	CH_4 (mol %)	$C_2H_4 + C_2H_6$ (mol %)	$C_3H_6 + C_3H_8$ (mol %)	C4+ (mol %)	Gas phase yield (wt %)
Example 3	60.9	6.8	11.1	6.4	12.9	1.8	0.1	0.5
Example 4	8.8	3.6	71.7	5.8	8.7	1.2	0.2	2.4
Example 5	37.3	13.9	26.9	5.9	14.5	1.2	0.3	12.0
Example 6	21.3	3.0	1.8	0.3	1.4	72.1	0.1	83.2
Example 7	48.9	29.1	15.2	3.2	2.5	0.8	0.2	14.9
Example 8	46.5	35.5	13.4	1.1	1.9	1.5	0.1	11.5
Example 9	65.2	10.9	8.0	10.2	5.2	0.3	0.1	10.7
Example 10	67.6	1.3	0.6	0	3.4	27.1	0	4.3
Example 11	59.4	5.3	4.2	0	4.8	20.3	5.9	4.2

[0086] As shown in Table 2, in the case of bio-oil prepared using fast pyrolysis, the carbon content is 56.7 weight % which is quite low, oxygen content is 26.8 weight %, which is high, and O/C (oxygen/carbon) molar ratio is 0.35, which is high, and thus the higher heating value (HHV) is 24.3 MJ/kg, that is, the energy content is very low. Furthermore, the moisture content is 14 weight %, which is high, TAN is 69.4 mg KOH/g, which is high, and pH is 4.2, which is low, showing that it has acidity.

[0087] In Examples 1 to 2, when the bio-oil was upgraded using a supercritical ethanol under the temperature condition of 400° C. and time condition of 30 to 60 minutes, the carbon content of liquid phase was increased and the oxygen content decreased, and the 0/C molar ratio was decreased from 0.35 to 0.12-0.16, showing the deoxygenation reaction was proceeded effectively, and HHV was increased significantly from 24.3 to 32.2-34.2 MJ/kg. Furthermore, the moisture content contained in the upgraded bio-oil was significantly decreased to 1.6 to 1.8 weight %, which seems to be because oxygen included in the bio-oil was removed and hydrophilic materials had converted to hydrophobic materials, thereby decreasing the moisture absorptiveness. After the bio-oil was upgraded, TAN of the bio-oil significantly increased from 4.84 to 12.4 mg KOH/g compared to that of the bio-oil before it was upgraded, and pH significantly increased from 4.2 to 6.9, showing that carboxylic acids having strong acidity such as the formic acid and acetic acid have mostly been removed.

[0088] As shown in Table 3, according to the results of analyzing the components of the gas phase product of Example 1, excessive amounts of CO_2 (36.2 mol %) and CO (48.2 mol %) were detected, which shows that the oxygen contained in the bio-oil has been removed by decarbonylation and decarboxylation reactions, and detection of H_2 (8.2 mol %) shows that even when hydrogen is not provided from outside, the supercritical state ethanol generated hydrogen, and therefore restricted recombination or condensation reactions that may occur in the upgrading reaction, resulting in a high yield of the upgraded liquid phase. Furthermore, the detection of small amount of CH_4 (2.4 mol %), C_2H_4+C_2H_6 (4.6 mol %) and C_3H_6+C_3H_8 (0.3 mol %) shows that the cracking reaction of ethanol and bio-oil have been restricted. When the reaction time was increased to 60 minutes in Example 2, CO_2 (72.1 mol %) was significantly increased, showing that active decarboxylation reaction was carried out, and C_2H_4+C_2H_6 (10.0 mol %) was increased, showing that the cracking reaction of ethanol and bio-oil were proceeded rather actively compared to the case of 30 minutes reaction time. In Example 3, when the reaction temperature was reduced to 300° C., excessive amounts of CO_2 (60.9 mol %) and CO (6.8 mol %) were detected, showing the oxygen included in the bio-oil has been removed by decarboxylation and decarbonylation. When the reaction temperature was increased to 350° C., the content of the hydrogen generated, 71.7 mol %, was very high, showing that the capability of the supercritical ethanol generating hydrogen was significantly increased.

[0089] Meanwhile, in the case of using Na_2CO_3 as an additive in Example 5, HHV increased to 35.4 MJ/kg, and TAN significantly decreased to 1.8 mg KOH/g compared to Example 1, showing that the deoxygenation reaction occurred more actively, and that the organic acids included in the bio-oil had been removed more effectively. According to the result of analyzing the gas phase, the hydrogen amount was 26.9 mol %, that is a significant increase compared to the hydrogen amount of Example 1, showing that deoxygenation reaction and reaction of removing organic acids had been effective.

[0090] It can be seen from Examples 6 to 8 where HCOOH, KOH, and HCl were used as an additive, the deoxygenation reaction and the reaction of removing organic acids in the bio-oil were effective.

[0091] Furthermore, in Examples 9 to 11 where a supercritical methanol, supercritical isopropyl alcohol, and supercritical butanol were used instead of a supercritical ethanol, respectively, the O/C molar ratio was decreased to 0.13 to 0.14, HHV was increased to 32.2 to 35.0 MJ/kg, and TAN was decreased to 19.8 to 21.0 mg KOH/g compared to the bio-oil before the upgrading, showing that the deoxygenation reaction and the reaction of removing organic acids of the bio-oil were effective.

[0092] Meanwhile, FIG. **2** shows results of analyzing the bio-oil upgraded using a supercritical ethanol by a gas chromatography-mass spectrometer.

[0093] From the fact that oxygen-removed alcohols (such as mono- and polyhydric aliphatic alcohols, alicyclic alcohols and unsaturated aliphatic alcohols), ketones, esters and hydrocarbon compounds have been generated, it can be seen that a stabilized bio-oil has been generated.

[0094] Meanwhile, FIG. **3** shows results of analyzing the viscosities of the bio-oil prepared by upgrading with a supercritical ethanol and the bio-oil prepared by fast pyrolysis in EFB before upgrading. Measuring the viscosities was performed at 50° C. using a Rheometer (TA Instruments) of AR G-2 model. In order to analyze the aging effects of the bio-oil, the bio-oil prepared by fast pyrolysis and the bio-oil upgraded using a supercritical ethanol were aged at 80° C. for 1 week, and then the viscosities of before and after the aging were measured. The viscosity of the bio-oil prepared by fast pyrolysis before aging was 161-550 cP at shear rate of 10-100 s^{-1}, which was increased significantly to 265-1270 cP after the aging, showing that the viscosity was increased due to recombination reaction between components of the bio-oil. On the other hand, in the case of the bio-oil upgraded in Example 1, the viscosity before aging was 88 cP, and the viscosity after aging was 98 cP, indicating a small increase, which means that the recombination reaction had been restricted after the upgrading. Furthermore, in the case of the upgraded bio-oil, the viscosity was decreased significantly compared to before the upgrading, showing that the high molecular components (for example, pyrolized lignin) of the components of the upgraded bio-oil prepared by fast pyrolysis had been converted to low molecular materials.

[0095] <Analysis on Combustion Characteristics of Bio-Oil>

[0096] In order to confirm the possibility of applying the upgraded bio-oil prepared in Example 1 to thermoelectric power plants, Computational Fluid Dynamics (CFD) analysis was conducted on a heavy oil boiler of South Jeju thermoelectric power plants. The size of the heavy oil boilers of South Jeju thermoelectric power plants was 8.8 m×7.7 m×29.2 m, the heat input capacity was 270 MW_{th}, and for turbine output, the counter flow method of 103 MW_e was used. The combustion characteristics of the upgraded bio-oil prepared according to Example 1 were analyzed in the heavy boiler of South Jeju thermoelectric power plants.

[0097] The Computational Fluid Dynamics (CFD) analysis on the heavy oil boiler of South Jeju thermoelectric power plants was conducted based on the single firing conditions of heavy oil that is generated from petrochemical refineries and on the single firing conditions of the bio-oil upgraded according Example 1, respectively, and then compared and analyzed the results.

[0098] In the case of the boilers of South Jeju thermoelectric power plants, on the bottom part, there is provided an inlet for recirculation gas. A portion of the gas emitted through the outlet of the boiler re-enters into this inlet. The top part of the boiler is divided by a central wall, and it is configured such that the gas passed through the combustion furnace may go up to the ceiling and then exit towards the outlet.

[0099] Table 4 below shows the CFD analysis conditions of the heavy oil boiler of South Jeju thermoelectric power plants.

TABLE 4

Operation conditions		Heavy oil	Bio-oil before upgrading	Bio-oil after upgrading (Example 1)
Heat input (MW_{th})		273	273	273
Turbine output (MW_e)		103	—	—
Fuel	Throughput	6.34	11.22	7.96
	Temperature (° C.)	110	60	60
	Water content (%)	0.3	0.04	0.04
	Volatile component (%)	94.8	94.66	99.26
	Fixed carbon (%)	5.0	0	0
	Ash (%)	0	5.3	0.7
	C (%)	86.2	56.73	76.84
	H (%)	12.5	6.06	7.48
	O (%)	0.5	26.76	12.9
	N (%)	0.3	1.63	1.89

TABLE 4-continued

Operation conditions		Heavy oil	Bio-oil before upgrading	Bio-oil after upgrading (Example 1)
	S (%)	0.5	0.13	1.40
	HHV (MJ/kg)	43.04	24.33	34.28
Sprayed steam	Flow rate (kg/s)	0.5622	0.5622	0.5622
	Temperature (° C.)	250	250	250
Air	Excess air (%)	1.898	2.45	2.45
	Flow rate (kg/s)	91.94	89.45	89.22
	Temperature (° C.)	283	286	286
Circulation gas	Flow rate (kg/s)	7.778	7.778	7.778
	Temperature (° C.)	365	364	364
	CO_2 (vol %)	12.85	12.72	12.72
	H_2O (vol %)	13.44	14.26	14.26
	O_2 (vol %)	0.91	1.09	1.09

[0100] Table 4 shows the CFD analysis results on temperature distribution according to conditions in the boiler. The temperature distribution near the bottom part of the boiler was the highest when the heavy oil was combusted, the lowest when the non-upgraded bio-oil was combusted, and when the upgraded bio-oil was combusted, the temperature distribution was somewhat higher than before the upgrading. The highest temperature in the boiler in the case of heavy oil was 1597° C. In the case of the non-upgraded bio-oil, the highest temperature in the boiler was rather low (1559° C.). In the case of the upgraded bio-oil, the highest temperature in the boiler was the highest (1599° C.)

[0101] Furthermore, in order to analyze the heat transfer characteristics inside the boiler, a CFD analysis was conducted. FIG. **5** and Table 5 show the results.

TABLE 5

Total heat (MW_{th}) of wall	Heavy oil	Bio-oil before upgrading	Bio-oil after upgrading (Example 1)
Radiation	97.85	93.41	97.64
Convection	20.91	23.56	24.17
Total	118.76	116.98	121.81

[0102] In the case of the single firing of the heavy oil, the total heat from the walls by radiation heat was higher than that of the upgraded bio-oil. This is considered to be because of the soot being generated as the heavy oil is combusted. Meanwhile, in the case of the total heat from the wall by convection, the upgraded bio-oil showed the highest level of 24.17 MW_{th}, and also in the case of the total heat of the entire walls, the upgraded bio-oil showed the highest level of 121.81 MW_{th}. Furthermore, the upgraded bio-oil showed more uniform heat transfer in the boiler walls than that of heavy oil combustion, and the peak temperature was also low. Overall, it has been proved that like as when combusting heavy oil, combustion of the upgraded bio-oil can also be applied to a commercial heavy oil boiler.

[0103] The configuration of the present invention has been proved to be excellent through the aforementioned embodiments, but without limitation. Thus, any substitution, change, or modification may be made within the scope of the technological concept of the present invention. Therefore, the above disclosure is not limited by the scope of the present invention determined by the limitations of the claims.

What is claimed is:

1. A method for upgrading a bio-oil using a supercritical alcohol, the method comprising:

mixing the bio-oil and an alcohol solvent; and

upgrading the bio-oil by reacting the bio-oil and the alcohol at a supercritical state of the alcohol.

2. The method according to claim **1**,

further comprising separating and collecting a product of the reaction, after the upgrading.

3. The method according to claim **1**,

wherein the mixing comprises additionally mixing an additive.

4. The method according to claim **1**,

wherein a raw material of the bio-oil include at least one of lignocellulosic biomass, herbaceous biomass, fine algae, and large algae.

5. The method according to claim **1**,

wherein the bio-oil is in a liquid phase form produced by thermos-chemical conversion process.

6. The method according to claim **1**,

wherein the bio-oil has a moisture content of 2 to 40 weight %.

7. The method according to claim **1**,

wherein the alcohol solvent includes at least one of methanol, ethanol, propanol, isopropylalcohol, butanol, isobutanol, 2-butanol, tert-butanol, n-pentanol, isopentyl alcohol, 2-methyl-1-butanol, neopentyl alcohol, diethyl carbinol, methyl propyl carbinol, methyl isopropyl carbinol, dimethyl ethyl carbinol, 1-hexanol, 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 4-methyl-1-pentanol, 2-methyl-2-pentanol, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 2,2-dimethyl-1-butanol, 2,3-dimethyl-1-butanol, 2,3-dimethyl-2-butanol, 3,3-dimethyl-1-butanol, 2-ethyl-1-butanol, 1-heptanol, 2-heptanol, 3-heptanol, and 4-heptanol.

8. The method according to claim **1**,

wherein the mixing includes mixing 0.1 to 60 weight % of the bio-oil, based on a total sum of the alcohol solvent and the bio-oil.

9. The method according to claim **3**,

wherein the additive includes at least one of LiOH, NaOH, KOH, RbOH, Li_2CO_3, Na_2CO_3, K_2CO_3, $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $MgCO_3$, $CaCO_3$, $SrCO_3$, HCl, HNO_3, H_3PO_4, H_2SO_4, H_3BO_3, HF, H_2CO_3, HCOOH, CH_3COOH, CH_3CH_2COOH, $CH_3CH_2CH_2COOH$, $C_2H_4OHCOOH$, and C_6H_5COOH.

10. The method according to claim **1**,

wherein the upgrading includes upgrading the bio-oil at a reaction temperature of 250 to 600° C., and a reaction pressure of 30 to 700 bar.

11. The method according to claim **1**,

wherein the alcohol solvents comprises methanol (critical temperature=239° C.; critical pressure=81 bar), ethanol (critical temperature=241° C.; critical pressure=63 bar), propanol (critical temperature=264 ° C.; critical pressure=52 bar), isopropylalcohol (critical temperature=307° C.; critical pressure=41 bar), butanol (critical temperature=289° C.; critical pressure=45 bar), isobutanol (critical temperature=275° C.; critical pressure=45 bar), 2-butanol (critical temperature=263° C.; critical pressure=42 bar), tert-butanol (critical temperature=233° C.; critical pressure=40 bar), n-pentanol (critical temperature=307° C.; critical pressure=39 bar), isopentyl alcohol (critical temperature=306° C.; critical pressure=39 bar), 2-methyl-1-butanol (critical temperature=302° C.; critical pressure=39 bar), neopentyl alcohol (critical temperature=276° C.; critical pressure=40 bar), diethyl carbinol (critical temperature=286° C.; critical pressure=39 bar), methyl propyl carbinol (critical temperature=287° C.; critical pressure=37 bar), methyl isopropyl carbinol (critical temperature=283° C.; critical pressure=39 bar), dimethyl ethyl carbinol (critical temperature=271° C.; critical pressure=37 bar), 1-hexanol (critical temperature=337° C.; critical pressure=34 bar), 2-hexanol (critical temperature=310° C.; critical pressure=33 bar), 3-hexanol (critical temperature=309° C.; critical pressure=34 bar), 2-methyl-1-pentanol (critical temperature=331° C.; critical pressure=35 bar), 3-methyl-1-pentanol (critical temperature=387° C.; critical pressure=30 bar), 4-methyl-1-pentanol (critical temperature=330° C.; critical pressure=30 bar), 2-methyl-2-pentanol (critical temperature =286° C.; critical pressure =36 bar), 3-methyl-2-pentanol (critical temperature=333° C.; critical pressure=36 bar), 4-methyl-2-pentanol (critical temperature=301° C.; critical pressure=35 bar), 2-methyl-3-pentanol (critical temperature=303° C.; critical pressure=35 bar), 3-methyl-3-pentanol (critical temperature=302° C.; critical pressure=35 bar), 2,2-dimethyl-1-butanol (critical temperature=301° C.; critical pressure=35 bar), 2,3-dimethyl-1-butanol (critical temperature=331° C.; critical pressure=35 bar), 2,3-dimethyl-2-butanol (critical temperature=331° C., critical pressure=35 bar), 3,3-dimethyl-1-butanol (critical temperature =331° C.; critical pressure=35 bar), 2-ethyl-1-butanol (critical temperature=307° C.; critical pressure=34 bar), 1-heptanol (critical temperature=360° C.; critical pressure=31 bar), 2-heptanol (critical temperature=335° C.; critical pressure=30 bar), 3-heptanol (critical temperature=332° C.; critical pressure=30 bar), and 4-heptanol (critical temperature=329° C.; critical pressure=30 bar), or a combination thereof.

12. A bio-oil upgraded by the method of claim **1**.

13. The upgraded bio-oil according to claim **12**,

wherein the upgraded bio-oil has an oxygen content of 10 to 15 weight %, and O/C (Oxygen/Carbon) molar ratio is 0.10 to 0.16.

14. The upgraded bio-oil according to claim **12**,

wherein a higher heating value (HHV) of the upgraded bio-oil is 30 to 40 MJ/kg according to Equation 4 below:

$$\text{Higher Heating Value}(HHV, \text{MJ/Kg}) = \frac{34\text{C} + 124.3\text{H} + 6.3\text{N} + 19.3\text{S} - 9.8\text{O}}{100} \quad \text{[Equation 4]}$$

(In the Equation 4, each of C, H, N, S, and O represents mass ratios of carbon, hydrogen, nitrogen, sulfur, and oxygen, respectively, based on the total mass of all elements existing in the bio-oil).

15. The upgraded bio-oil according to claim **12**,

wherein the upgraded bio-oil has a moisture content of 0.5 to 6 weight %.

16. The bio-oil according to claim **12**,

wherein the Total Acid Number (TAN) according to ASTM D664 of the upgraded bio-oil, which is the amount of KOH needed to neutralize acids included in 1 g of bio-oil, is 1 to 35 mg, and pH of the upgraded bio-oil is 6 to 7.5.

17. A fuel for power generation comprising the upgraded bio-oil of claim **12**.

18. A fuel for transportation comprising the upgraded bio-oil of claim **12**.

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