

US 20140275666A1

(19) **United States**

(12) **Patent Application Publication**  
**Bauer et al.**

(10) **Pub. No.: US 2014/0275666 A1**

(43) **Pub. Date: Sep. 18, 2014**

(54) **TWO STAGE PROCESS FOR PRODUCING  
RENEWABLE BIOFUELS**

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(21) Appl. No.: **13/829,473**

(22) Filed: **Mar. 14, 2013**

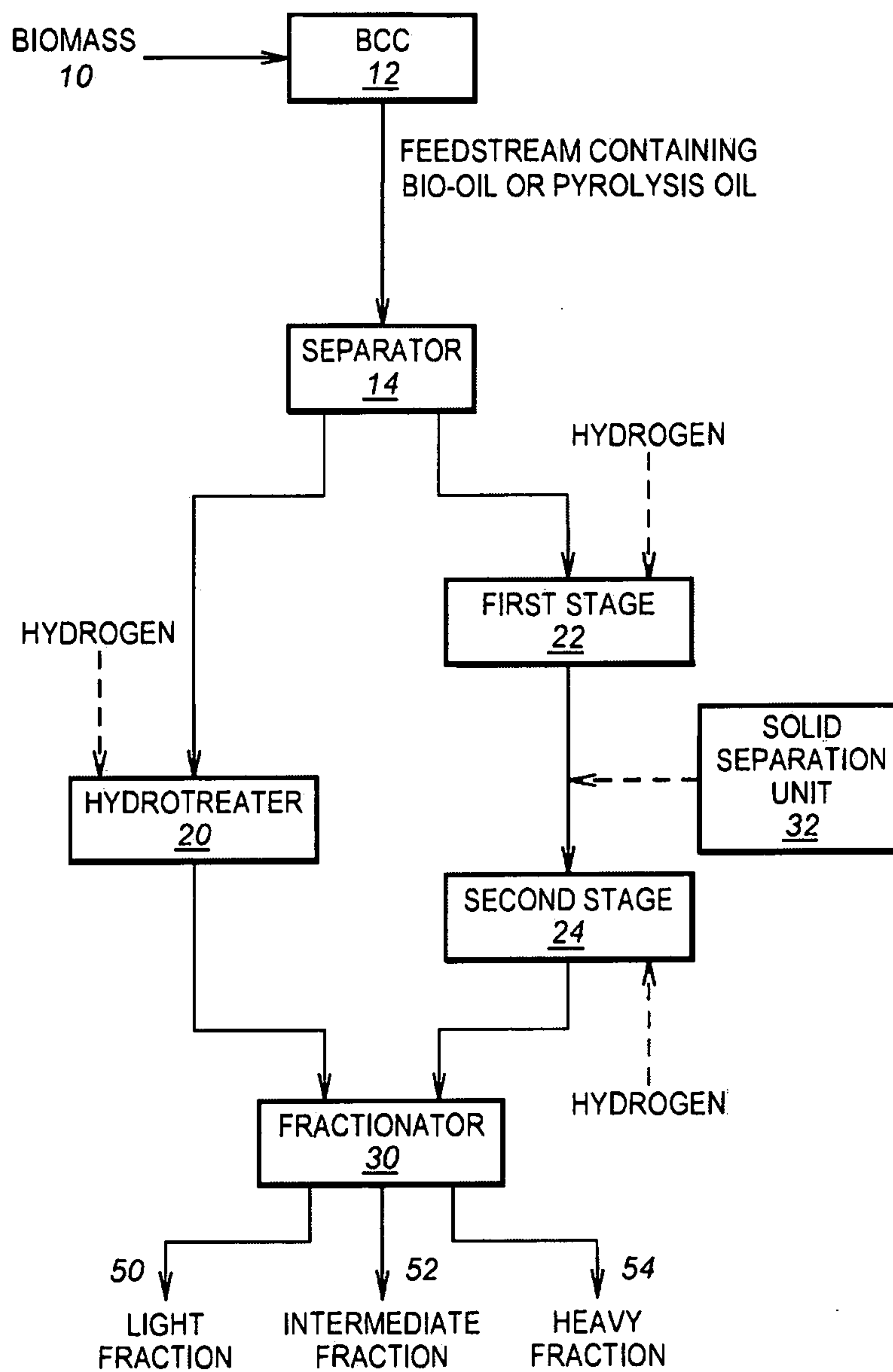
**Publication Classification**

(51) **Int. Cl.**  
**C10G 1/00** (2006.01)

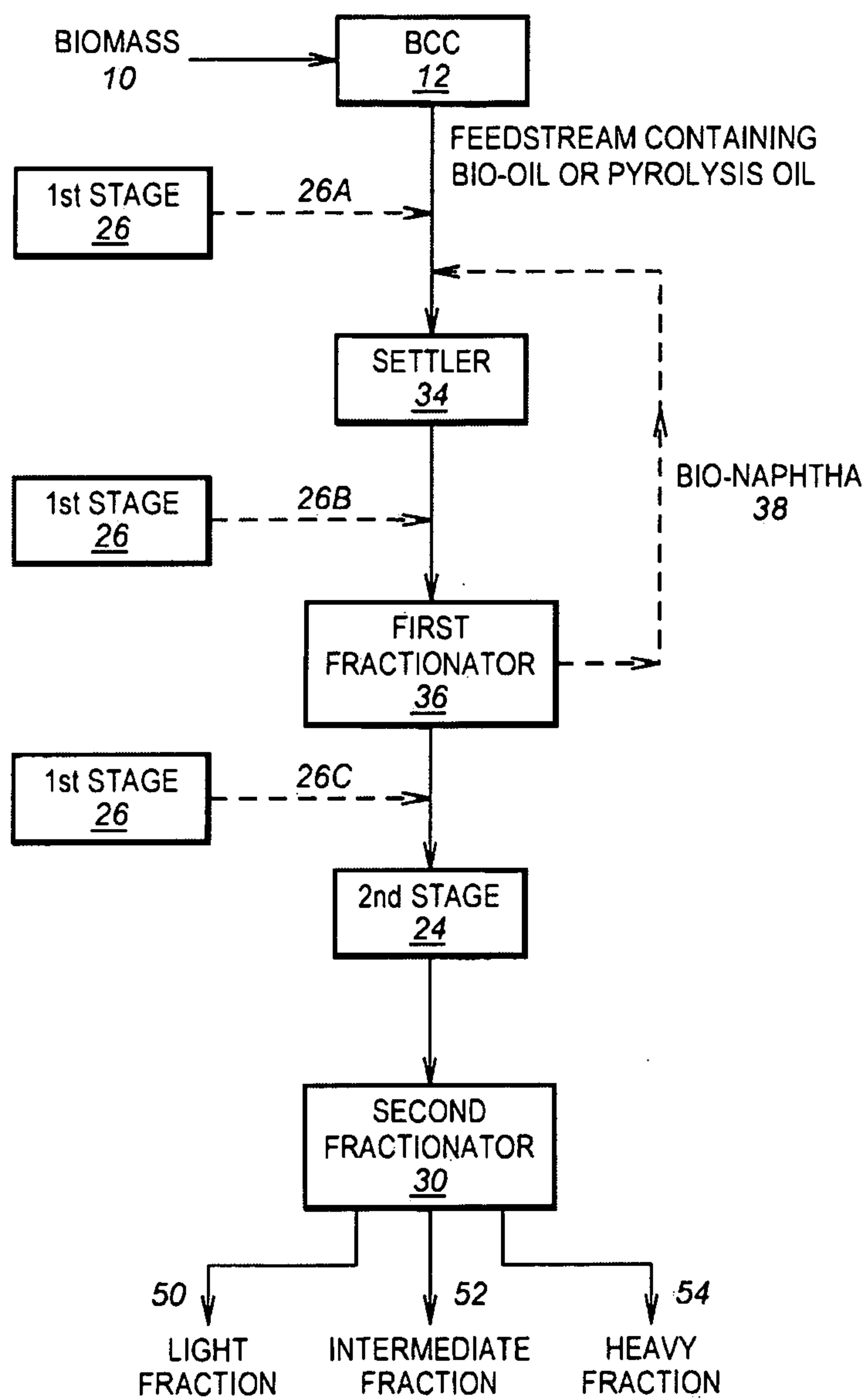
(52) **U.S. Cl.**  
CPC ..... **C10G 1/002** (2013.01)  
USPC ..... **585/240**

(57) **ABSTRACT**

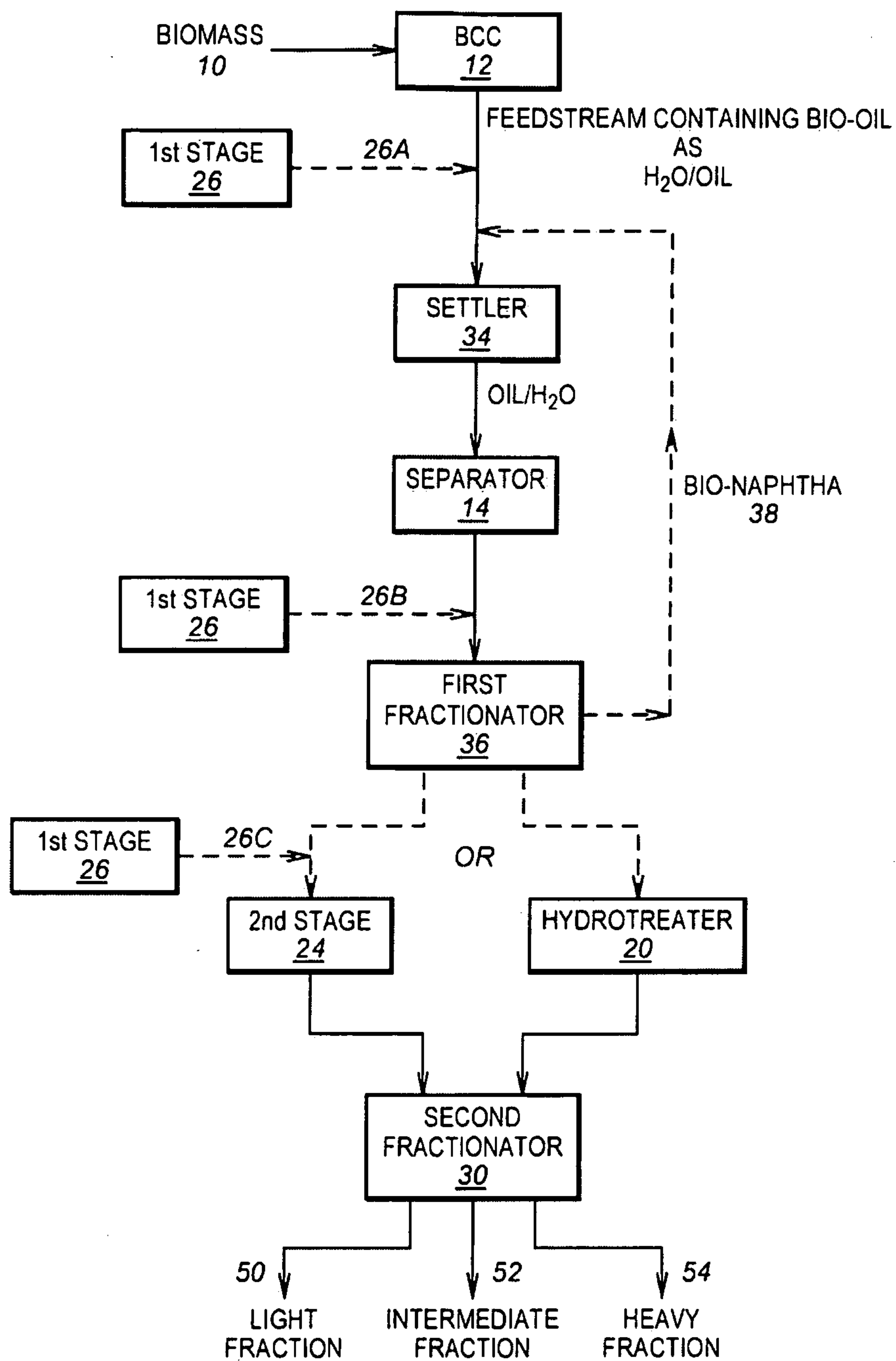
A process for treating bio-oil or pyrolysis oil used to produce renewable biofuel. In a first stage, solids and/or organic reactive molecules within the feedstream are reduced without substantially deoxygenating the organic reactive molecules in the feedstream. The resulting feedstream is then introduced into a second hydrotreatment stage to produce deoxygenated bio-oil or pyrolysis oil.



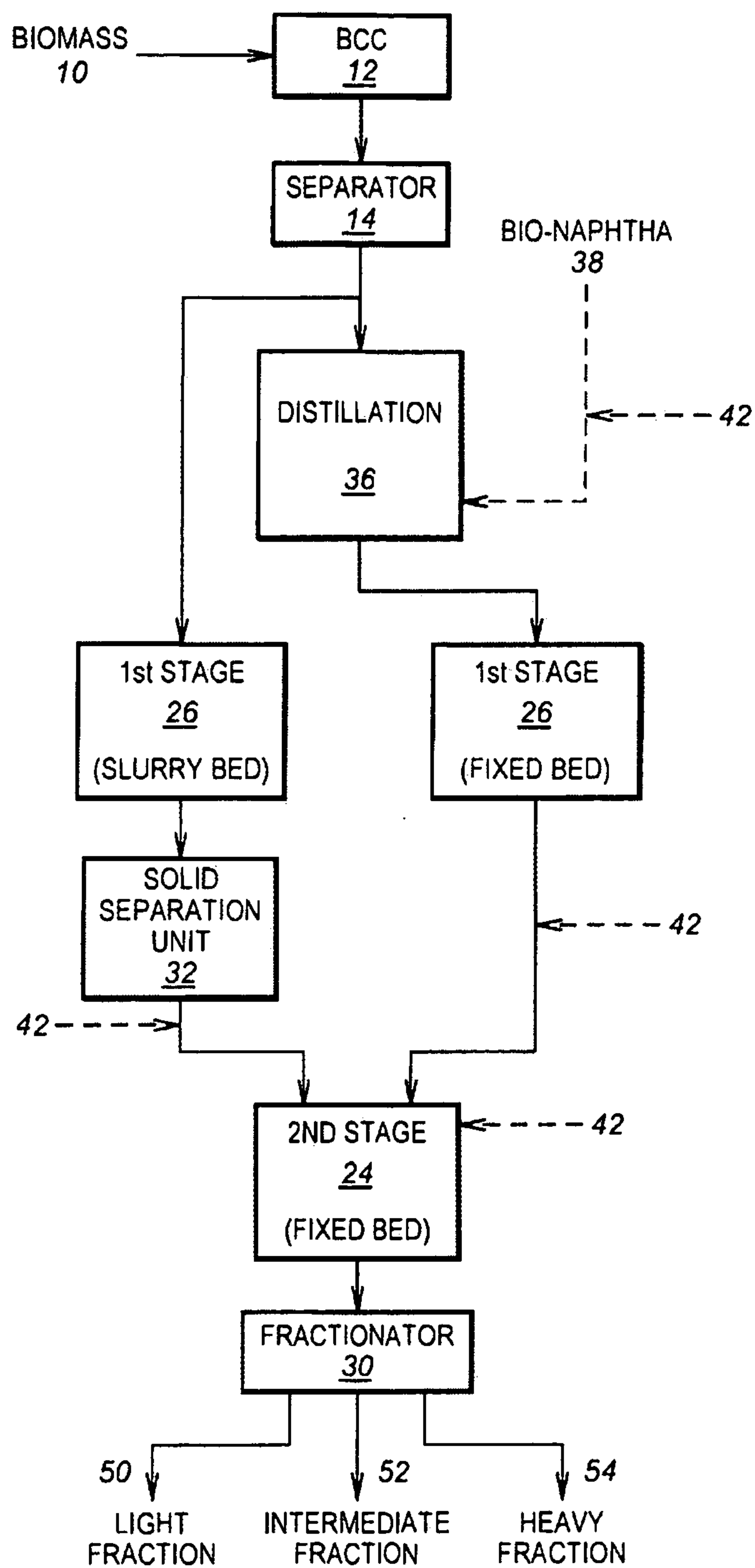
**FIG. 1**



**FIG. 2**



**FIG. 3**



**FIG. 4**



## TWO STAGE PROCESS FOR PRODUCING RENEWABLE BIOFUELS

### FIELD OF THE DISCLOSURE

[0001] The disclosure relates to a method of producing a renewable biofuel by treating a feedstream containing bio-oil or pyrolysis oil in two stages.

### BACKGROUND OF THE DISCLOSURE

[0002] Renewable energy sources, such as biofuels, provide a substitute for fossil fuels and a means of reducing dependence on petroleum oil. In light of its low cost and wide availability, biomass is often used as a feedstock to produce liquid products as biofuels.

[0003] In the conversion of biomass to liquid products, the product stream can contain both an oil phase and a water phase. Existing biomass conversion processes include, for example, slow pyrolysis, fast pyrolysis, liquefaction and enzymatic conversion.

[0004] Pyrolysis oil is the resultant of thermal non-catalytic treatment of biomass in an oxygen-poor or oxygen-free atmosphere. Where solid biomass is used as the feedstock of a pyrolysis process, the process produces gaseous, liquid and solid products. Pyrolysis oil is relatively soluble in water, as water is in pyrolysis oil.

[0005] The thermocatalytic treatment of biomass renders a liquid product that easily separates into an aqueous phase and an organic phase. Bio-oil consists of the organic phase, though bio-oil retains a small amount of water.

[0006] While thermolysis processes and other conversion processes produce high yields of such oils, much of the pyrolysis oil and bio-oil produced is of low quality due to the presence of high levels of reactive organic molecules as well as solids including char, inorganics from biomass, scale from processing equipment and fines from heat transfer agents and catalysts. Also, the amount of dissolved metal in bio-oil greatly exceeds that of typical fossil fuels. This is likely attributable to the acidic nature of bio-oil which is capable of leaching and solubilizing cationic species.

[0007] The most potentially reactive species in bio-oil is comprised of such organic materials as aliphatic olefins, aromatic hydrocarbons, unsaturated ketones, furans, aldehydes and phenols. Such oils thus require secondary upgrading.

[0008] A known method for converting those heteroatomic reactive species into hydrocarbons is hydrotreating wherein the stream is contacted with hydrogen under pressure and at moderate temperatures, generally less than 850° F., over a fixed bed reactor. Hydroprocessing of thermo-chemically produced bio-oil and pyrolysis oil has, however, been limited by the formation of solids, solid contaminants, dissolved impurities and poor stability. A wide variety of chemical reactions occur on heating to the temperatures required to start hydrogenation. These reactions produce heavier compounds, solids and gums that can cause fouling in hydrotreaters. The reactive species can also react rapidly with hydrogen at high pressure and relatively low temperatures and release a significant amount of additional heat that makes control of the reactor temperature profile difficult.

[0009] It should be understood that the above-described discussion is provided for illustrative purposes only and is not intended to limit the scope or subject matter of the appended claims or those of any related patent application or patent. Thus, none of the appended claims or claims of any related

application or patent should be limited by the above discussion or construed to address, include or exclude each or any of the above-cited features or disadvantages merely because of the mention thereof herein.

[0010] Accordingly, there exists a need for improved compositions, systems, apparatus and methods which minimizes fouling within hydrotreaters of solid contaminants and dissolved impurities and which enhances the production of thermally converted oil into liquid hydrocarbons having one or more of the attributes or capabilities described or shown in, or as may be apparent from, the other portions of this patent.

### SUMMARY OF THE DISCLOSURE

[0011] In various embodiments, the present disclosure involves a process for treating bio-oil or pyrolysis oil used to produce renewable biofuel by:

[0012] (a) introducing a feedstream containing bio-oil or pyrolysis oil to a first stage and reducing solids and/or organic reactive molecules within the feedstream in the first stage without substantially deoxygenating the organic molecules in the feedstream;

[0013] (b) introducing the feedstream having reduced solids and/or reduced organic reactive molecules to a second stage, which is a hydrotreatment stage, wherein the temperature in the second stage is greater than the temperature in the first stage and the pressure in the first stage is less than or equal to the pressure in the second stage; and

[0014] (c) producing deoxygenated bio-oil or pyrolysis oil in the second stage.

[0015] In some embodiments, the present disclosure involves a process for producing renewable biofuel from bio-oil or pyrolysis oil by:

[0016] (a) introducing a feedstream containing bio-oil or pyrolysis oil and containing solids and organic reactive materials into a first stage wherein the temperature at the entrance is from about 120° F. to about 350° F.;

[0017] (b) reducing the amount of solids and/or reactive species in the bio-oil or pyrolysis oil without substantially deoxygenating the organic reactive molecules at elevated temperature and pressure in the first stage, wherein the temperature at the entry port of the first stage does not exceed 450° F.;

[0018] (c) introducing the bio-oil or pyrolysis oil having reduced solids into a hydrotreatment second stage and deoxygenating the bio-oil or pyrolysis oil within the second stage, the temperatures and pressure in the second stage being sufficient to produce a deoxygenated bio-oil or pyrolysis oil; and

[0019] (d) producing renewable biofuels from the deoxygenated bio-oil or pyrolysis oil.

[0020] In other embodiments, the present disclosure involves a process for producing renewable biofuels from bio-oil or pyrolysis oil by:

[0021] (a) reducing solids in the bio-oil or pyrolysis oil in a first stage while minimizing hydrogenation of organic reactive molecules in the bio-oil or pyrolysis oil, wherein the temperature in the first stage at the port of entry is from about 120° F. to about 350° F., the temperature at the exit port of the first stage does not exceed 450° F., the pressure is less than about 1,000 psig; the space velocity within the first stage is from about 0.2 to about 6; and the amount of organic reactive molecules in the first stage is less than 5 percent; and



**[0022]** (b) deoxygenating the resulting product in a hydrotreatment second stage to render deoxygenated bio-oil or pyrolysis oil, wherein the temperature at the exit port of the hydrotreatment second stage is from about 650° F. to about 850° F., the pressure is between from about 500 to about 2,000 psig, the space velocity is less than 2; and

**[0023]** (c) generating renewable biofuels from the deoxygenated product.

**[0024]** Accordingly, the present disclosure includes features and advantages which are believed to enable it to enhance the production of thermally converted oil into liquid hydrocarbons. Characteristics and advantages of the present disclosure described above and additional features and benefits will be readily apparent to those skilled in the art upon consideration of the following detailed description of various embodiments and referring to the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0025]** The following figures are part of the present specification, included to demonstrate certain aspects of various embodiments of this disclosure and referenced in the detailed description herein:

**[0026]** FIG. 1 illustrates a representative flow path wherein the first stage and the hydrotreatment second stage are either within a single reactor or two distinct reactors.

**[0027]** FIG. 2 illustrates a representative flow path wherein the first stage and second stage are in distinct reactors and further illustrates various alternatives for placement of the first reactor in relation to the hydrotreater second reactor.

**[0028]** FIG. 3 illustrates a representative flow path for the treatment of a bio-oil containing feedstream in multiple reactors when the aqueous phase of the bio-oil containing feedstream has been subjected to various modifications.

**[0029]** FIG. 4 illustrates a representative flow path wherein the feedstream is subjected to controlled pre-heating prior to subjecting the feedstream to the first stage.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0030]** Characteristics and advantages of the present disclosure and additional features and benefits will be readily apparent to those skilled in the art upon consideration of the following detailed description of exemplary embodiments of the present disclosure and referring to the accompanying figures. It should be understood that the description herein and appended drawings, being of example embodiments, are not intended to limit the claims of this patent or any patent or patent application claiming priority hereto. On the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the claims. Many changes may be made to the particular embodiments and details disclosed herein without departing from such spirit and scope.

**[0031]** In showing and describing preferred embodiments in the appended figures, common or similar elements are referenced with like or identical reference numerals or are apparent from the figures and/or the description herein. The figures are not necessarily to scale and certain features and certain views of the figures may be shown exaggerated in scale or in schematic in the interest of clarity and conciseness.

**[0032]** Certain terms are used herein and in the appended claims to refer to particular components or steps of a process.

As one skilled in the art will appreciate, different persons may refer to a component or process steps by different names. This document does not intend to distinguish between components or process steps that differ in name but not function. Also, the terms “including” and “comprising” are used herein and in the appended claims in an open-ended fashion, and thus should be interpreted to mean “including, but not limited to . . .” Further, reference herein and in the appended claims to components and aspects in a singular tense does not necessarily limit the present disclosure or appended claims to only one such component or process step, but should be interpreted generally to mean one or more, as may be suitable and desirable in each particular instance.

**[0033]** The disclosure relates to the use of two stages for treating a feedstream. It is understood that reference to a “second stage” refers to a stage which succeeds a “first stage.” The second stage may immediately succeed a first stage. Other treatment stage(s) may occur between the first stage and the second stage. Further, either the bio-oil containing feedstream or the pyrolysis oil containing feedstream may be subjected to any number of conventional treatments prior to or subsequent to being introduced into the first stage. For instance, solids in the feedstream may be separated from the liquid phase of the bio-oil or pyrolysis oil in a solids separator. Further, other treatment stage(s) may occur after the second stage.

**[0034]** The feedstream of the process originates from biomass and contains bio-oil or pyrolysis oil. The feedstream containing pyrolysis oil or bio-oil may originate from the treatment of biomass in a biomass conversion reactor. The pyrolysis oil referred in this application results from the thermal non-catalytic treatment of biomass. Typically, such treatment of biomass occurs at temperatures in excess of 450° C. Bio-oil results from the thermocatalytic treatment of the biomass. The use of catalysts permits operation of the biomass conversion reaction at lower temperatures than those required in non-catalytic pyrolysis.

**[0035]** The biomass may be in the form of solid particles. The biomass particles can be fibrous biomass materials such as cellulose. Examples of suitable cellulose-containing materials include algae, paper waste, and/or cotton linters. In one embodiment, the biomass particles can comprise a lignocellulosic material. Examples of suitable lignocellulosic materials include forestry waste such as wood chips, wood slag, saw dust, pulping waste, bark, and tree branches; agricultural waste such as corn stover, wheat straw, and bagasse; and/or energy crops such as eucalyptus, switch grass, and coppice; as well as municipal waste, such as yard waste, paper and cardboard. The biomass may also be lignins or hemicelluloses. The biomass may be in a solid or finely divided form or may be a liquid. Typically, the water soluble content of the biomass is no greater than about 7 volume percent.

**[0036]** In the first stage, the feedstream may or may not be subjected to hydrotreatment. In those instances where the feedstream is subjected to hydrotreatment in the first stage, the first stage and the second stage may occur in the same hydrotreater reactor. Alternatively, the first stage and the second stage may be conducted in separate reactors.

**[0037]** The conditions in the first stage are such as to reduce the amount of solids, dissolved metals and organic reactive materials in the feedstream. Organic reactive materials may be reduced in the first stream by hydrogenation of reactive functional groups. Alternatively, reactive species may be converted by condensation reactions or any other exothermic



reaction, as well. The temperature of the pyrolysis oil or bio-oil will increase in the first stage, and consumption of reactive species would result in a more stable oil. Conversion in this first stage is defined by the desired feed temperature for the second stage.

**[0038]** The conditions in the first stage are controlled such that no substantial deoxygenation of the organic reactive materials in the feedstream occurs. Typically, less than 10 percent, more typically less than 5 percent, of organic reactive materials are deoxygenated in the first stage, more typically less than 3 percent. In a preferred embodiment, the amount of organic reactive molecules deoxygenated in the first stage is less than 0.1 percent.

**[0039]** Catalysts used in the first stage are well known in the prior art and are commercially available. Typically, catalysts consist of metal loaded on supports such as alumina, silica, zirconia, carbon, etc. Active metals include transition metal sulfides, like NiMo, sulfided NiMo, CoMo, sulfided CoMo, NiW; reduced metals, such as reduced Ni; and noble metal catalysts, such as Ru, Pt, and Pd.

**[0040]** Catalysts with an acid functionality such as a silica-alumina, sulfated oxides, support phosphoric acids could also be used.

**[0041]** In certain embodiments, sulfide transition metal oxides, such as sulfided oxides of NiMo and NiW on supports, such as alumina, are preferred since lower temperatures and pressures within the hydrotreatment stage are needed compared to when noble metal catalysts are used. Further, transition metal sulfides may be prepared using hydrogen sulfide from hydrogen recycled from the hydrotreatment stage.

**[0042]** The feedstream from the first stage is substantially deoxygenated in the hydrotreatment second stage to render deoxygenated bio-oil or pyrolysis oil. Typically, greater than 95 vol. % of the stream exiting the hydrotreatment second stage has been deoxygenated. In most instances, greater than 98 vol. % of the stream exiting the second stage has been deoxygenated. Normally, all of the stream exiting the second stage has been deoxygenated.

**[0043]** The entire liquid and gaseous effluent from the first stage may be passed through to the second stage.

**[0044]** When the first stage is a hydrotreatment stage, the first stage and the second stage may be conducted in a single hydrotreater reactor. In this instance, the hydrotreatment stages are typically over a fixed bed of catalyst.

**[0045]** When two reactors are used, the first stage may be conducted over a fixed bed of catalyst, an ebullated bed or a slurry bed. Deoxygenation of the feedstream in the hydrotreatment stage is typically conducted over a fixed catalytic hydrotreating bed.

**[0046]** The efficiency of hydrogenation in the hydrotreater reactor of the second stage may be improved by a stage between the first stage and the second stage for removing solid particulates. This is especially the case where a first hydrotreatment stage is conducted in a slurry bed. Solid particles may be removed from the stream entering the hydrotreater reactor of the second stage by any well known solid/liquid separation method, such as settling, filtration, decanting, centrifuging, etc.

**[0047]** When the first stage is a hydrotreatment stage and where both the first stage and the hydrotreatment stage are conducted in the same reactor, the pressure in the two stages is the same. Typically, the pressure in the hydrotreatment reactor is from about 1,500 to about 2,000 psig.

**[0048]** Where the first stage and the second stage are conducted in different reactors, the pressure in the hydrotreater reactor of the second stage is higher than the pressure in the first reactor. The pressure in the first reactor is typically less than 1,000 psig and may be less than about 500 psig. The pressure in the hydrotreater of the second stage is normally in excess of 500 psig and may be as high as about 2,500 psig. Typically, the pressure in the hydrotreater reactor of the second stage is from about 1,500 psig to about 2,000 psig.

**[0049]** The space velocity in the first stage and the hydrotreatment stage are typically different. Normally, the space velocity within the first stage is from about 0.2 to about 10 and the space velocity within the second hydrotreatment stage is less than 5.

**[0050]** The temperature in the first stage at the port of entry is typically from about 120° F. to about 400° F. The temperature of the stream entering the hydrotreatment stage typically does not exceed 450° F.

**[0051]** The temperature at the exit of the second stage is generally in excess of 650° F. Typically, the temperature at the exit of the second stage is between from about 650° F. to about 800° F.

**[0052]** In those instances where two reactors are employed, the temperature of the feedstream exiting the first reactor may be dramatically reduced by the time the feedstream enters the hydrotreater reactor of the second stage. While condensation reactions may occur at low temperatures, even at room temperature, such reactions may occur quickly when the temperature within the reactor is rapidly increased. Heat generated by the exothermic nature of the condensation reactions further may provide uncontrolled acceleration of such reactions especially at the top of the hydrotreater reactor of the second stage with the sudden rise in temperature of the entering stream. Products generated during condensation tend to foul or plug the reactor if carried into the catalytic bed within the reactor. Condensation reactions are a source of instability to the bio-oil, which is heat sensitive. Condensation reactions may cause the formation of gums and solid deposits. Further, condensation reactions between organic reactive materials (not reduced in the first reactor) may compete with deoxygenation of the feedstream in the hydrotreater reactor of the second stage. This in turn decreases the efficiency of the hydrotreatment stage.

**[0053]** In an embodiment, the feedstream may be exposed to a controlled pre-heat source prior to introduction of the feedstream into the first reactor. Controlled pre-heating of the feedstream may occur in a fractionator. Controlled pre-heating reduces the heat of reaction once the feedstream is brought into contact with the catalyst in the first stage. Reduction of the heat of reaction by use of a pre-heater controls the otherwise rapid temperature rise which may occur once the feedstream is brought into contact with the catalyst in the first stage. The use of a pre-heat source advantageously minimizes the sudden acceleration of heat within the hydrotreater reactor, and consequently the likelihood of the hydrotreater being plugged by condensation reaction products and less reactive/heavier refractory compounds may therefore be decreased. The temperature of the heat source is generally between from about 150° C. to about 450° C.

**[0054]** In an embodiment, the heat of the stream entering the frontal section of the hydrotreater reactor of the second stage may be controlled by a heat source within the hydrotreater as well as by a heat source located in front of the



hydrotreater. The heat source may also be externally applied to the frontal section of the reactor.

**[0055]** The heat source may be a heat chamber such as a pre-heater or a guard reactor wherein the temperature of the feedstream is elevated prior to the feedstream being fed into the first reactor. In an embodiment, a mild exothermic chemical reaction may be generated in the heat chamber prior to entry of the feedstream into the hydrotreater reactor of the second stage. A suitable chemical reaction may be generated by exposing the feedstream to hydrogen. Any other exothermic chemical reaction may be chosen to occur in the heat chamber to generate the desired temperature.

**[0056]** Alternatively, the feedstream may be pre-heated by providing hydrogen to the reactor of the first stage or the frontal section of the hydrotreater of the second stage in the presence of a suitable catalyst and in an amount sufficient to deoxygenate a small portion of the stream entering into the hydrotreater. Heat is generated by the exothermic reaction between the stream and hydrogen. The amount of hydrogen added is an amount sufficient to provide a temperature increase from the exothermic reaction. Typically, less than about 2% of the stream entering the hydrotreater of the second stage may be deoxygenated within the first reactor or the frontal section of the hydrotreater of the second stage. The amount of deoxygenation of the stream occurring in reactor of the first stage or the frontal section of the hydrotreater of the second stage is only that amount needed to provide the requisite amount of heat to prevent a temperature spike within the reactor.

**[0057]** FIGS. 1, 2, 3, and 4 are flow diagrams illustrating alternative embodiments for hydrotreating a feedstream originating from biomass. The hydrotreated feedstream may be used in the production of a renewable biofuel.

**[0058]** In each of the figures, biomass 10 is illustrated as entering into a biomass conversion reactor 12 where a pyrolysis oil containing feedstream or bio-oil containing feedstream is produced.

**[0059]** Separator 14 is shown which allows water and solid materials, such as tar, to be separated from the bio-oil containing feedstream or pyrolysis oil containing feedstream. The separator may be a conventional separator such as a coalescer, gravity phase separator, liquid hydrocyclone, electrostatic desalter, etc. Typically, from about 90 to 95 percent of the solids are removed from the mixture in the separator. Optionally, and preferably, the remaining solids in the mixture may be removed, such as by polishing filtration.

**[0060]** FIG. 1 illustrates two treatment stages, wherein the second treatment stage is a hydrotreatment stage and the first treatment may or may not be a hydrotreatment stage. For instance, FIG. 1 illustrates a reactor housed in a first stage 22 and a reactor housed in a second stage 24. The first stage 22 may or may not be a hydrotreatment stage. In the situation where both the first stage and the second stage are both hydrotreatment stages, the two stages can be conducted in a single hydrotreater reactor shown as stage 20.

**[0061]** Solids and organic reactive materials in the feedstream may be reduced by the presence of hydrogen in the first stage. The feedstream, however, in the first stage is not substantially deoxygenated. The stream is deoxygenated in the second stage.

**[0062]** The first stage and the second stage may both be conducted in fixed bed reactors.

**[0063]** To avoid difficulties which may arise by the fixed bed being plugged by solids, when two reactors are used, the

first stage may be conducted over a slurry bed. A slurry bed may be used in the first stage within the first reactor. Catalyst, composed of small particles, is dispersed in the slurry. Suitable catalysts include those conventionally used in the art such as cobalt aluminum, molybdenum, iron pyrite, iron sulfate, ammonium heptamolybdate, metal naphthenates, and multimetal catalysts including nickel, iron, molybdenum, manganese, cobalt and the like. The stability of the bio-oil may be improved by passing the dispersed catalyst through the slurry reactor (such as a tubular or bubble column type reactor). The bulk of the catalyst leaves the reactor with the treated product.

**[0064]** Where first reactor 22 is a slurry reactor, FIG. 1 illustrates a solid separation unit 32 between first reactor 22 and hydrotreater 24. Exemplary solid separation units include a settler, centrifuge or a filtration unit. Since reaction conditions coupled with the choice of catalyst may cause agglomeration of solids, the catalyst and agglomerated solids may be removed in 32. While not illustrated in FIG. 1, the collected solids and catalyst may be recycled to biomass conversion reactor 12 or to the front of the first reactor.

**[0065]** Following removal of solids and conversion of organic reactive molecules in the first stage and deoxygenation of the feedstream in the hydrotreatment stage, the deoxygenated stream may then be introduced into fractionator 30. In the fractionator, at least a portion of the material may be separated into light fraction stream 50, intermediate fraction stream 52 and heavy fraction stream 54 for use in renewable bio-fuels. The light fraction stream may have a boiling range below petroleum-derived gasoline and the intermediate fraction may have a boiling range comparable to petroleum-derived gasoline. The heavy fraction stream may have a boiling range comparable to diesel fuel. For instance, in an embodiment, the light fraction stream may have a boiling point less between from about 150° F. to about 180° F., the intermediate fraction may have a boiling point between from about 180° F. to about 420° F. and the heavy fraction may have a boiling point above 420° F.

**[0066]** In another embodiment where the feedstream is a bio-oil containing feedstream, bio-naphtha may be separated from the feedstream in a fractionator prior to the stream entering the hydrotreater. The bio-naphtha may then be introduced into the bio-oil fraction from the biomass conversion reactor. The bio-naphtha serves as a diluent by reducing the density of the bio-oil fraction. The density of the bio-oil fraction is lowered to less than 1 g/cc. The lowering of the density of the bio-oil by the diluent further facilitates particle settling. Conventional diluents may also be used in lieu of or in addition to bio-naphtha. Bio-naphtha is, however, preferred since it provides an inexpensive source of diluent.

**[0067]** FIG. 2 illustrates an embodiment where two reactors are used. As illustrated, the first stage 26 may be located in three separate areas —26A, 26B or 26C of the process. For instance, first stage 26A may be between separator 14 and second stage 24 housing the hydrotreater reactor.

**[0068]** FIG. 2 illustrates separation of bio-naphtha in first fractionator 36 from the feed containing bio-oil. At least a portion of bio-naphtha stream 38 may then be introduced into the pyrolysis oil containing feedstream or bio-oil containing feedstream exiting biomass conversion reactor 12. The greatest efficiency is noted where the introduction of bio-naphtha stream 38 occurs after the bio-oil or pyrolysis oil containing feedstream is subjected to the first stage. Typically, the temperature in the first fractionator is about 350° F.



[0069] Further, the first stage may, when first fractionator 36 is used, be between separator 14 and first fractionator 36, illustrated as 26B. The first stage may further be in between first fractionator 36 and hydrotreater 24, illustrated as 26C.

[0070] As illustrated in FIG. 3, first stage 26A may be between biomass conversion reactor 12 and settler 34. Settler 34 may also be a desalter or a separator. When first fractionator 36 is used, bio-naphtha 38 may be removed from the stream exiting first fractionator 36 and introduced into the feedstream containing the bio-oil or pyrolysis oil. In such cases, it is desired that the bio-naphtha stream 38 re-enter the feedstream after treatment of the feedstream in first reactor 26.

[0071] FIG. 3 further illustrates an embodiment wherein the solids content of the bio-oil containing feedstream or pyrolysis containing feedstream may be reduced prior to entry of the feedstream into separator 14. The water present in the aqueous phase of the feedstream may originate from the biomass prior to conversion of the biomass in biomass conversion reactor 12. The water in the feedstream may also be produced during conversion of the biomass in biomass conversion reactor 12. Since the oil phase has a higher specific gravity than the water phase, the oil phase settles to the bottom quickly and emulsions form between the oil and water phases. Further, solids present in the reaction products also settle in the oil phase. As such, the specific gravity of the oil phase to the aqueous phase is greater than 1. In settler 34, the specific gravity of either the oil phase or the aqueous phase or both the oil phase and the aqueous phase are modified in order to provide a mixture wherein the ratio of the specific gravities of the oil phase to the aqueous phase is less than 1. As such, the specific gravities of the stream exiting settler 34 are reversed such that the oil phase is the upper layer and the water phase is the lower layer. Methods for effectuating this reversal are set forth in U.S. patent application Ser. No. 13/212,861, filed Aug. 18, 2011, herein incorporated by reference.

[0072] FIG. 4 illustrates an embodiment of the disclosure wherein the stream exiting the first reactor is subjected to a controlled heat treatment in order to minimize plugging of the catalyst bed within the hydrotreater. Typically, the temperature of the first reactor product entering the hydrotreatment reactor is between from about 330° F. to about 350° F. The feed is then heated to approximately 450° F. prior to entering the hydrotreatment stage using hot recycled hydrogen. After treatment of the stream in first stage, the bio-oil is much more stable. It is therefore possible to heat the bio-oil stream to a higher temperature before it enters the hydrotreatment stage. Fouling or plugging of the reactor when the stream is carried over into the catalytic bed of the hydrotreatment stage is decreased.

[0073] In one embodiment, FIG. 4 illustrates three alternatives when the first stage and the hydrotreatment second stage are in separate reactors. The stream is heated prior to entry of the stream into the first reactor in order to minimize the rapid increase in temperature within the reactor. Such pre-heating of the feedstream typically occurs in the absence of a catalyst. Most typical, the pre-heating only involves application of heat to the stream, at very mild conditions.

[0074] In one embodiment illustrated in FIG. 4, where the first stage is housed in a slurry bed reactor, the stream exiting the reactor may be subjected to pre-heat treatment after the slurry has been subjected to solids removal in unit 32 and prior to entry of the feedstream into hydrotreater reactor 24.

[0075] In another embodiment, where the treatment stage in the first reactor is conducted over a fixed bed, the stream may be subjected to pre-heat treatment after the product exits first reactor 26 and prior to entry into hydrotreater reactor 24.

[0076] FIG. 4 also illustrates that the stream exiting first reactor 26 (either a slurry bed or fixed bed reactor) may be pre-heated at the front of hydrotreater reactor 24.

[0077] FIG. 4 further illustrates that the feedstream within first fractionator 36 may be pre-heated prior to entry into first reactor 26. Further, where the separated feedstream has been subjected to first fractionator 36, the feedstream may be pre-heated at the rear end of the unit.

[0078] FIG. 4 also illustrates the use of a pre-heater (typically to a temperature of from about 300 to about 350° F.) for heating of bio-naphtha stream 38 prior to admixing the bio-naphtha stream with the bio-oil containing feedstream 12 and prior to entry of feedstream 12 into separator 14.

[0079] All of the processing of the biomass as described herein may occur in the same plant or facility including the plant or facility where the renewable biofuel is prepared. In addition, the biomass may be treated in the same plant or facility where the processing of the biomass as described herein or a portion of the processing occurs. Alternatively, all or some of the processing described herein may occur in the same plant or facility where either the first stage, the hydrotreatment stage or both the first stage and the hydrotreatment stage occur.

[0080] Preferred embodiments of the present disclosure thus offer advantages over the prior art and are well adapted to carry out one or more of the objects of this disclosure. However, the disclosure does not require each of the components and acts described above and are in no way limited to the above-described embodiments or methods of operation. Any one or more of the above components, features and processes may be employed in any suitable configuration without inclusion of other such components, features and processes. Moreover, the present disclosure includes additional features, capabilities, functions, methods, uses and applications that have not been specifically addressed herein but are, or will become, apparent from the description herein, the appended drawings and claims.

[0081] The methods that may be described above or claimed herein and any other methods which may fall within the scope of the appended claims can be performed in any desired suitable order and are not necessarily limited to any sequence described herein or as may be listed in the appended claims. Further, the methods of the disclosure do not necessarily require use of the particular embodiments shown and described herein, but are equally applicable with any other suitable structure, form and configuration of components.

[0082] All percentages set forth in the Examples are given in terms of weight units except as may otherwise be indicated.

#### Examples

[0083] The feeds used in the experimental work were obtained from a biomass converter reactor and were produced using the same catalyst under similar but not identical experimental conditions in the reactor. The physical parameters of the bio-oil of the feeds are characterized in Table I.



TABLE I

| Product Properties   |         |                |               |               |
|----------------------|---------|----------------|---------------|---------------|
|                      | Feed    | Exp. A Product | Exp B Product | Exp C Product |
| Density, g/cc        | 1.1003  | 0.88           | 1.01          | 1.05          |
| Delta API            | 0       | 33             | 4             | 0.7           |
| Wt. % Oxygen         | 13.8    | 0.4            | 11            | 13.8          |
| TAN of Feed          | 19.5    | 0.25           | 20            | 19            |
| Hydrogen Consumption |         | 3900           | 600           | 125           |
| Filterable Solids    | 113 ppm | 1              | 70            | 62            |
| SimDis               |         |                |               |               |
| IBP-320F             | 15      | 16             | 14            | 14            |
| 320F-700F            | 66      | 70             | 68            | 68            |
| 700F-FBP             | 19      | 14             | 18            | 18            |

The feed was pretreated by reversing the specific gravity of the oil phase and water phase as set forth in U.S. patent application Ser. No. 13/212,861. The feed was subjected to a fixed bed hydrotreatment reactor under the conditions set forth in Table II:

TABLE II

| Experimental Conditions  |                             |                                    |                                   |
|--------------------------|-----------------------------|------------------------------------|-----------------------------------|
|                          | Experiment A                | Experiment B                       | Experiment C                      |
| Description              | High Severity Hydrotreating | Two-stage upgrading single reactor | First stage hydrogenation reactor |
| Catalyst                 | NiMo on Alumina             | NiMo on Alumina                    | NiMo on Alumina                   |
| Pressure                 | 1800 psig                   | 1800 psig                          | 500 psig                          |
| Space Velocity           | 1.5                         | 1.5                                | 1.5                               |
| Inlet Temp               | 275 degree F.               | 250 degree F.                      | 250 degree F.                     |
| Max Bed Temp             | 675 degree F.               | 460 degree F.                      | 300 degree F.                     |
| H2 Feed Rate             | 8000 standar cu ft/barrel   | 8000 standar cu ft/barrel          | 2000 standar cu ft/barrel         |
| Run Time before Plugging | 91 Hours                    | 520 Hours                          | 640 Hours                         |

As shown in Table II, the run time was greatest for the hydrotreatment stage run at low pressure and low temperature. Table III provides the NMR (proton) analysis of the treated feed and demonstrates the largest consumption of hydrogen resulting from the hydrotreatment stage run at high pressure and high temperature.

TABLE III

| NMR Analysis of Hydrogen Type (% H) |       |               |               |
|-------------------------------------|-------|---------------|---------------|
| Hydrogen Type                       | Feed  | Exp C Product | Exp A Product |
| —CHn                                | 7.82  | 11.31         | 42.34         |
| —C—CHn                              | 31.97 | 37.7          | 44.92         |
| Aromatics                           | 38.22 | 32.39         | 11.09         |
| Ethers and Alcohols                 | 8.26  | 10.15         | 1.22          |
| Esters                              | 0.15  | 0.06          | 0             |
| Double bonds                        | 5.99  | 3.62          | 0             |
| Phenols                             | 1.39  | 0.68          | 0.43          |
| Diols                               | 5.24  | 3.44          | 0             |
| Aldehydes                           | 0.85  | 0.49          | 0             |
| Acids                               | 0.11  | 0.15          | 0             |
| Sum                                 | 100   | 100           | 100           |

**[0084]** The methods that may be described above or claimed herein and any other methods which may fall within the scope of the appended claims can be performed in any desired suitable order and are not necessarily limited to any sequence described herein or as may be listed in the appended claims. Further, the methods described herein do not necessarily require use of the particular embodiments shown and described, but are equally applicable with any other suitable structure, form and configuration of components.

**[0085]** While exemplary embodiments have been shown and described in this disclosure, many variations, modifications and/or changes of the system, apparatus and methods, such as in the components, details of construction and operation, arrangement of parts and/or methods of use, are possible, contemplated by the patent applicant(s), within the scope of the appended claims, and may be made and used by one of ordinary skill in the art without departing from the spirit or teachings of the disclosure and scope of appended claims. Thus, all matter herein set forth or shown in the accompanying drawings should be interpreted as illustrative, and the scope of the disclosure and the appended claims should not be limited to the embodiments described and shown herein.

What is claimed is:

1. A process for treating bio-oil or pyrolysis oil used to produce renewable biofuel, the process comprising:

(a) introducing a feedstream containing bio-oil or pyrolysis oil to a first stage and reducing solids and/or organic reactive molecules within the feedstream in the first stage without substantially deoxygenating the organic reactive molecules in the feedstream;

(b) introducing the feedstream having reduced solids and/or reduced organic reactive molecules to a second stage, wherein the second stage is a hydrotreatment stage, and further wherein the temperature in the second stage is greater than the temperature in the first stage and the pressure in the first stage is less than or equal to the pressure in the second stage and producing deoxygenated bio-oil or pyrolysis oil in the second stage.

2. The process of claim 1, wherein the first stage is a hydrotreatment stage.

3. The process of claim 2, wherein the first stage and the second stage are housed within the same hydrotreater reactor.

4. The process of claim 1, in which the entire liquid and gaseous effluent from the first stage is passed through to the second stage.

5. The process of claim 3, wherein the pressure in the hydrotreater reactor is from about 1,500 psig to about 2,000 psig.

6. The process of claim 1, wherein the first stage and the second stage are housed in different reactors.

7. The process of claim 6, wherein the feedstream is heated by an exothermic reaction upon entry into the hydrotreater of the second stage.

8. The process of claim 2, wherein the feedstream prior to entry into the hydrotreater in the second stage is exposed to hydrogen to generate an exothermic reaction without substantially deoxygenating the reactive species in the feedstream.

9. The process in claim 1, where a reactive species is added to the feedstream and further wherein heat generated by the addition of the added reactive species causes at least part of the increase in temperature needed for the second stage.



**10.** The process of claim **9**, wherein the reactive species is an olefin or an alcohol.

**11.** The process of claim **2**, wherein the pressure in the hydrotreater reactor housing the first stage is between from about 500 to about 1,000 psig and the pressure in the hydrotreater reactor housing the second stage is between from about 500 psig to about 2,000 psig.

**12.** The process of claim **6**, wherein the feedstream introduced into the first stage or second stage is heated in a controlled pre-treatment heat exchanger.

**13.** The process of claim **1**, wherein the amount of organic reactive molecules deoxygenated in the first stage is less than 5 percent.

**14.** The process of claim **13**, wherein the amount of organic reactive molecules deoxygenated in the first stage is less than 3 percent.

**15.** The process of claim **14**, wherein the amount of organic reactive molecules deoxygenated in the first stage is less than 0.1 percent.

**16.** The process of claim **2**, wherein the temperature at the entry of the first stage is from about 120° F. to about 350° F.

**17.** The process of claim **1**, wherein the temperature of the feedstream entering the second stage does not exceed 500° F.

**18.** The process of claim **1**, wherein the space velocity within the first stage is from about 0.5 to about 6.

**19.** The process of claim **1**, wherein greater than 80 percent of oxygen has been removed from the feedstream exiting the second stage.

**20.** The process of claim **19**, wherein greater than 90 percent of oxygen has been removed from the feedstream exiting the second stage.

**21.** The process of claim **20**, wherein greater than 95 percent of oxygen has been removed from the feedstream exiting the second stage.

**22.** The process of claim **1**, wherein the temperature at the exit of the second stage is between from about 650° F. to about 850° F.

**23.** The process of claim **1**, wherein the space velocity within the second stage is less than 5.

**24.** The process of claim **1**, wherein the feedstream is a bio-oil containing feedstream.

**25.** The process of claim **24**, wherein the bio-oil containing feedstream is separated into bio-oil and an aqueous phase.

**26.** The process of claim **24**, wherein the bio-oil containing feedstream is separated into bio-oil and an aqueous phase prior to step (a).

**27.** The process of claim **6**, wherein step (a) occurs in a slurry bed reactor.

**28.** The process of claim **1**, wherein step (a) occurs in a fixed bed reactor.

**29.** The process of claim **4**, wherein step (b) occurs in a fixed bed reactor.

**30.** The process of claim **27**, wherein solids are separated from the slurry prior to step (b).

**31.** The process of claim **25**, wherein the bio-oil containing feedstream is separated into bio-oil and an aqueous phase between step (a) and step (b).

**32.** The process of claim **25**, wherein the ratio of the specific gravities of the oil phase to the aqueous bio-oil phase is less than 1.0.

**33.** The process of claim **25**, wherein at least a portion of the solids are removed from the bio-oil prior to step (a).

**34.** The process of claim **33**, wherein the removal of the at least a portion of the solids from the bio-oil occurs in a desalter, settler and/or separator.

**35.** The process of claim **25**, wherein the bio-oil is subjected to fractionation to produce bio-naphtha.

**36.** The process of claim **35**, wherein fractionation occurs prior to step (a).

**37.** The process of claim **35**, wherein at least a portion of the bio-naphtha is blended with the bio-oil containing feedstream.

**38.** The process of claim **2** wherein the first stage reactor contains a catalyst selected from the group consisting of NiMo, CoMo or NiW, sulfided transition metals, reduced metals and noble metals.

**39.** The process of claim **2** wherein the first stage reactor contains a catalyst having an acid functionality.

**40.** The process of claim **39**, wherein the catalyst is a silica-alumina, sulfated oxide, supported phosphoric acids or a mixture thereof.

**41.** The process of claim **38**, wherein the sulfided transition metals are selected from the group consisting of sulfided NiMo and sulfided CoMo.

**42.** The process of claim **1**, wherein at least a portion of the organic reactive molecules are subjected to a condensation reaction in step (a).

**43.** A process for producing renewable biofuel from bio-oil or pyrolysis oil comprising:

(a) introducing a feedstream containing bio-oil or pyrolysis oil and containing solids and organic reactive materials into a first stage wherein the temperature at the entrance is from about 120° F. to about 350° F.;

(b) reducing the amount of solids and/or reactive species in the bio-oil or pyrolysis oil without substantially deoxygenating the organic reactive molecules at elevated temperature and pressure in the first stage, wherein the temperature at the entry port of the first stage does not exceed 450° F.;

(c) introducing the bio-oil or pyrolysis oil having reduced solids into a second stage, wherein the second stage is a hydrotreatment stage, and deoxygenating the bio-oil or pyrolysis oil within the second stage, wherein the temperatures and pressure in the second stage is an amount sufficient to produce a deoxygenated bio-oil or pyrolysis oil; and

(d) producing renewable biofuels from the deoxygenated bio-oil or pyrolysis oil.

**44.** The process of claim **43**, wherein the first stage is a hydrotreatment stage.

**45.** The process of claim **44**, wherein the pressure in the first stage and the pressure in the second stage are the same and wherein the first stage and the second stage are housed in the same hydrotreater reactor.

**46.** The process of claim **44**, wherein the first stage and the second stage are housed in separate hydrotreater reactors.

**47.** The process of claim **44**, wherein the pressure in the first stage does not exceed 1,000 psig.

**48.** The process of claim **43**, wherein the space velocity within the first stage is from about 1 to about 6 and wherein the space velocity within the second hydrotreatment stage is less than 2.

**49.** The process of claim **43**, wherein the bio-oil or pyrolysis oil originates from a biomass converted feedstream.



**50.** The process of claim **49**, wherein the biomass converted feedstream is separated into bio-oil and an aqueous phase prior to introducing the bio-oil into the first stage.

**51.** The process of claim **43**, wherein the bio-oil is subjected to fractionation prior to step (a).

**52.** The process of claim **43**, wherein bio-naphtha is separated from the bio-oil during fractionation and further wherein at least a portion of the separated bio-naphtha is blended with the biomass converted feedstream.

**53.** The process of claim **43**, wherein at least a portion of the organic reactive molecules are subjected to a condensation reaction in step (a).

**54.** A process for producing renewable biofuels from bio-oil or pyrolysis oil comprising:

- (a) reducing solids in the bio-oil or pyrolysis oil in a first stage while minimizing hydrogenation of organic reactive molecules in the bio-oil or pyrolysis oil, wherein:
  - (i) the temperature in the first stage at the port of entry is from about 120° F. to about 350° F. and wherein the temperature at the exit port of the first stage does not exceed 450° F.;
  - (ii) the pressure in the first stage is less than about 1,000 psig;

- (iii) the space velocity within the first stage is from about 0.2 to about 6; and

- (iv) the amount of organic reactive molecules in the first stage is less than 5 percent; and

- (b) deoxygenating the product of step (a) in a second stage to render deoxygenated bio-oil or pyrolysis oil, wherein:

- (i) the temperature at the exit port of the second stage is from about 650° F. to about 850° F.;

- (ii) the pressure in the second stage is between from about 500 to about 2,000 psig;

- (iii) the space velocity within the second stage is less than 2; and

- (c) generating renewable biofuels from the deoxygenated product of step (b).

**55.** The process of claim **54**, wherein the first stage is a hydrotreatment stage.

**56.** The process of claim **55**, wherein the first stage and the second stage are housed in the same hydrotreater reactor.

**57.** The process of claim **55**, wherein the first stage and the second stage are housed in separate hydrotreater reactors.

**58.** The process of claim **54**, wherein at least a portion of the organic reactive molecules are subjected to a condensation reaction in step (a).

\* \* \* \* \*