

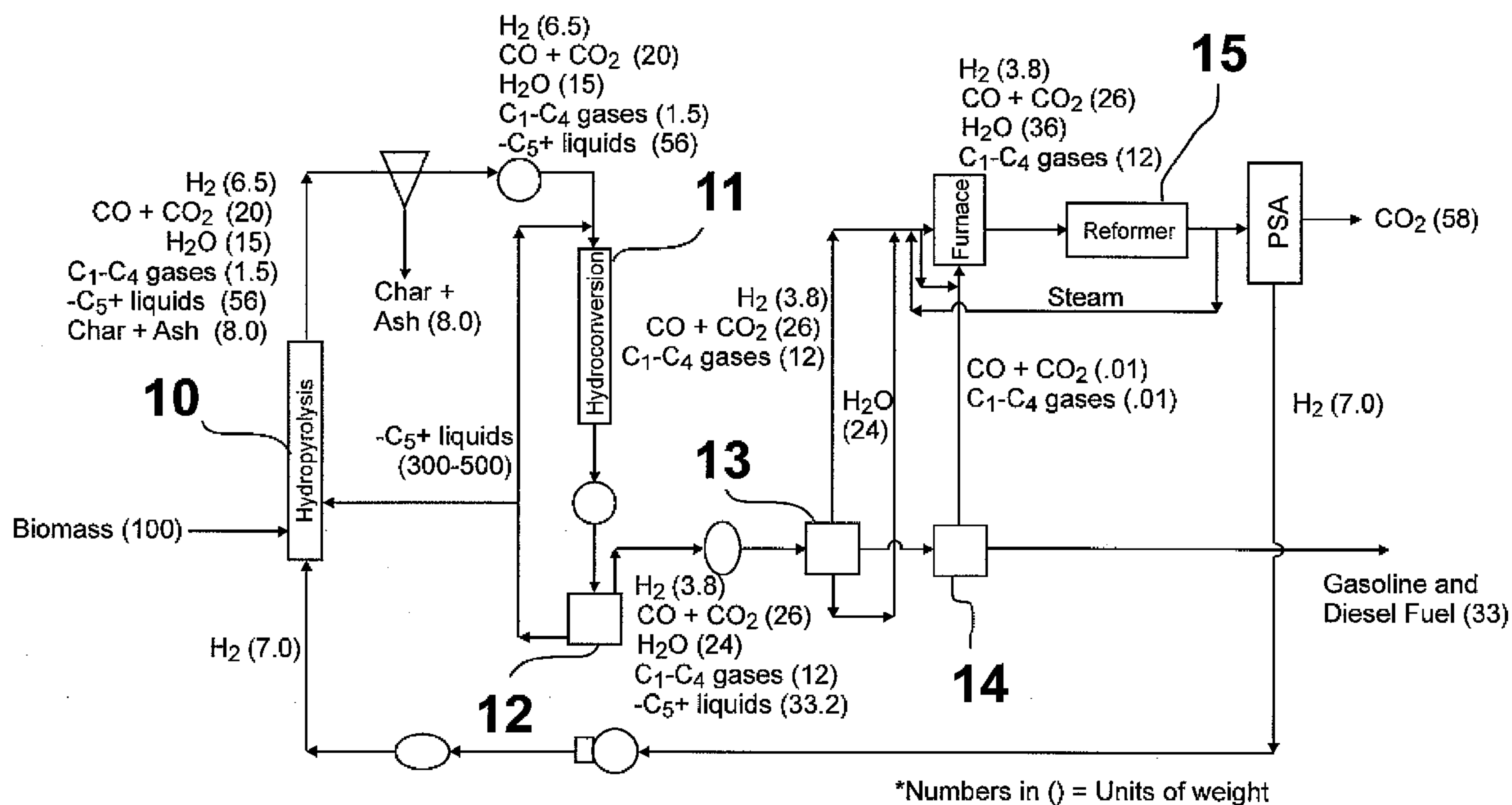
US 20100251600A1

(19) **United States**(12) **Patent Application Publication**  
**Marker et al.**(10) **Pub. No.: US 2010/0251600 A1**(43) **Pub. Date: Oct. 7, 2010**(54) **HYDROLYSIS OF BIOMASS FOR  
PRODUCING HIGH QUALITY LIQUID FUELS**(75) Inventors: **Terry L. Marker**, Palos Heights, IL  
(US); **Larry G. Felix**, Pelham, AL  
(US); **Martin B. Linck**, Mount  
Prospect, IL (US)

Correspondence Address:

**MARK E. FEJER****GAS TECHNOLOGY INSTITUTE****1700 SOUTH MOUNT PROSPECT ROAD  
DES PLAINES, IL 60018 (US)**(73) Assignee: **GAS TECHNOLOGY  
INSTITUTE**, Des Plaines, IL (US)(21) Appl. No.: **12/419,535**(22) Filed: **Apr. 7, 2009****Publication Classification**(51) **Int. Cl.**  
**C10L 1/18** (2006.01)(52) **U.S. Cl.** ..... **44/308**(57) **ABSTRACT**

A self-sustaining process for producing liquid fuels from biomass in which the biomass is hydrolyzed in a reactor vessel containing molecular hydrogen and a deoxygenating catalyst, producing a partially deoxygenated pyrolysis liquid, which is hydrogenated using a hydroconversion catalyst, producing a substantially fully deoxygenated pyrolysis liquid and a gaseous mixture comprising CO and light hydrocarbon gases (C<sub>1</sub>-C<sub>4</sub>). The gaseous mixture is reformed in a steam reformer, producing reformed molecular hydrogen, which is then introduced into the reactor vessel for hydrolyzing the biomass. The deoxygenated liquid product is further processed to produce diesel fuel and gasoline.



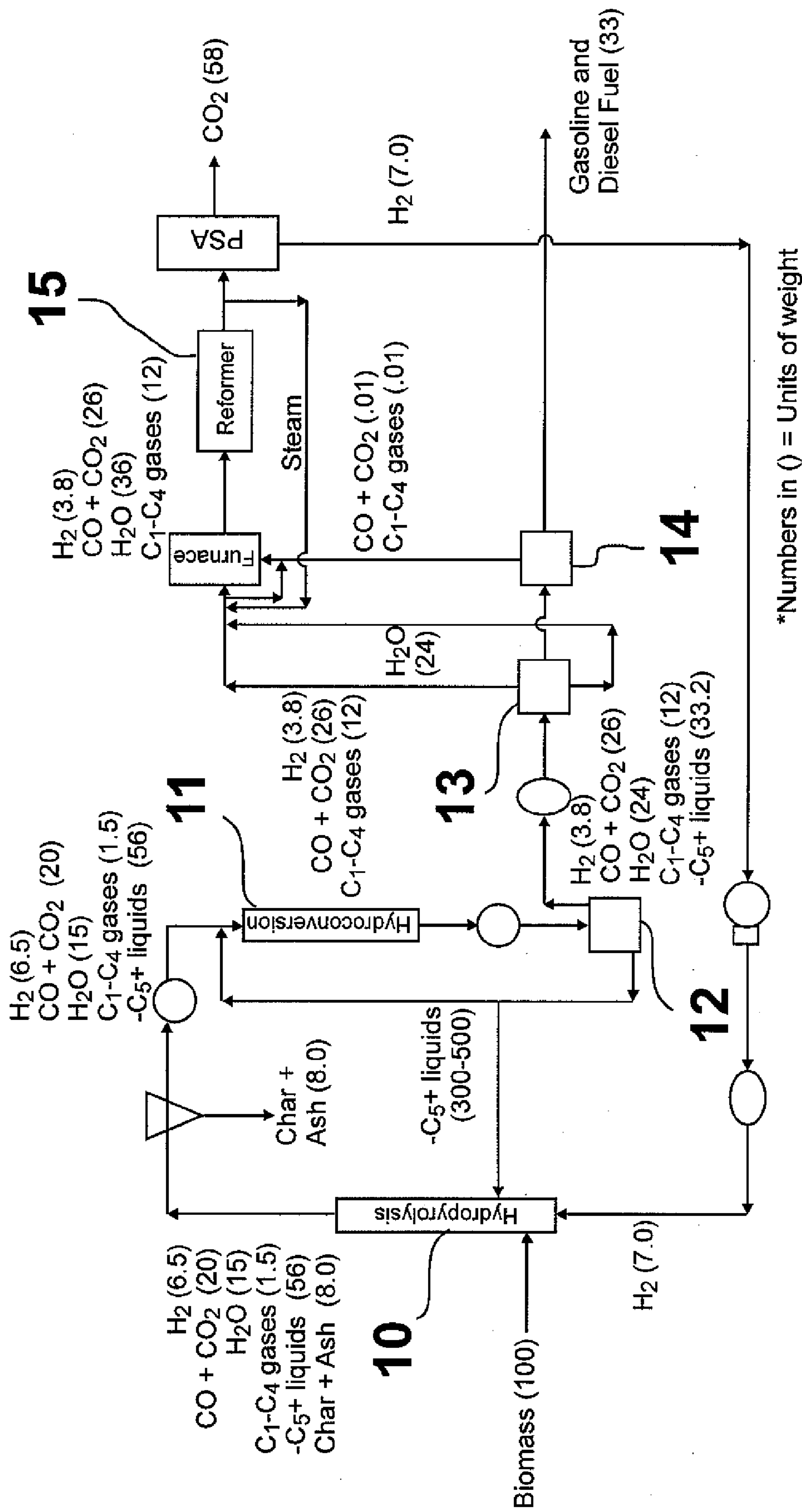


Fig. 1



## HYDROPYROLYSIS OF BIOMASS FOR PRODUCING HIGH QUALITY LIQUID FUELS

### BACKGROUND OF THE INVENTION

#### [0001] 1. Field of the Invention

[0002] This invention relates to an integrated process for thermochemically transforming biomass into high quality liquid fuels. In one aspect, this invention relates to a substantially self-sustaining process for creating high quality liquid fuels from biomass. In another aspect, this invention relates to a multi-stage hydrolysis process for creating high quality liquid fuels from biomass. In another aspect, this invention relates to a hydrolysis process for transforming biomass into high quality liquid fuels in which all of the process fluids are provided by the biomass. In another aspect, this invention relates to a hydrolysis process for transforming biomass into high quality liquid fuels in which the process outputs are substantially only liquid product and CO<sub>2</sub>.

#### [0003] 2. Description of Related Art

[0004] Conventional pyrolysis of biomass, typically fast pyrolysis, does not utilize or require H<sub>2</sub> or catalysts and produces a dense, acidic, reactive liquid product that contains water, oils, and char formed during the process. Because fast pyrolysis is most typically carried out in an inert atmosphere, much of the oxygen present in biomass is carried over into the oils produced in pyrolysis, which increases their chemical reactivity. The unstable liquids produced by conventional pyrolysis tend to thicken over time and can also react to a point where hydrophilic and hydrophobic phases form. Dilution of pyrolysis liquids with methanol or other alcohols has been shown to reduce the activity and viscosity of the oils, but this approach is not considered to be practical or economically viable, because large amounts of unrecoverable alcohol would be required to produce and transport large amounts of pyrolysis liquids.

[0005] In conventional pyrolysis carried out in an inert environment, the water miscible liquid product is highly oxygenated and reactive, with total acid numbers (TAN) in the range of 100-200, has low chemical stability for polymerization, is incompatible with petroleum hydrocarbons due to water miscibility and very high oxygen content, on the order of about 40% by weight, and has a low heating value. As a result, transport and utilization of this product are problematic and it is difficult to upgrade this product to a liquid fuel due to the retrograde reactions that typically occur in conventional pyrolysis and in conventional fast pyrolysis. In addition, the removal of char generated by conventional pyrolysis from the liquid pyrolysis product presents a technical challenge due to the large amounts of oxygen and free radicals in the pyrolysis vapors which remain highly reactive and form a pitch-like material when they come in intimate contact with char particles on the surface of a filter. Consequently, filters used to separate the char from the hot pyrolysis vapors blind quickly due to the reactions of char and oil that occur on and within the layer of char on the surface of the filter.

[0006] The upgrading of pyrolysis oils produced by conventional fast pyrolysis through hydroconversion consumes too much H<sub>2</sub>, and extreme process conditions make it uneconomical. The reactions are inherently out of balance due to the high pressures required, thereby creating too much water and consuming too much H<sub>2</sub>. In addition, hydroconversion reactors often plug due to coke precursors present in the pyrolysis oils or from coke product as a result of catalysis.

[0007] In general, hydrolysis is a catalytic pyrolysis process carried out in the presence of molecular hydrogen. Typically, the objective of conventional hydrolysis processes has been to maximize liquid yield in one step, and even in one known case in which a second stage reaction was added, the objective was to maximize yield while obtaining high oxygen removal. However, even this approach compromises economy, creates a system which requires an external source of H<sub>2</sub>, and must be carried out at excessive internal pressures. In addition to requiring a continuous input of hydrogen, such conventional hydrolysis processes produce excessive H<sub>2</sub>O which must then be disposed of.

### SUMMARY OF THE INVENTION

[0008] Accordingly, it is one object of this invention to provide a self-sustaining, balanced process for conversion of biomass to liquid product using hydrolysis. By self-sustaining, we mean that, once initiated, the process requires no input of additional reactants, heat, or energy from external sources.

[0009] It is another object of this invention to provide a process for conversion of biomass to a liquid product using hydrolysis wherein the total output of the overall process is substantially only liquid product and CO<sub>2</sub>. As used herein, the term "liquid product" refers to hydrocarbon products, typically C<sub>5</sub>+liquids, produced by the process of this invention.

[0010] These and other objects of this invention are addressed by a multi-stage, self-sustaining process for producing liquid products from biomass in which the biomass is hydrolyzed in a reactor vessel containing molecular hydrogen and a deoxygenating catalyst, producing a partially deoxygenated pyrolysis liquid, char, and first-stage process heat. The partially deoxygenated pyrolysis liquid is hydrogenated using a hydroconversion catalyst, producing a substantially fully deoxygenated pyrolysis liquid, a gaseous mixture comprising CO and light hydrocarbon gases (C<sub>1</sub>-C<sub>4</sub>), and second-stage process heat. The gaseous mixture is then reformed in a steam reformer, producing reformed molecular hydrogen. The reformed molecular hydrogen is then introduced into the reactor vessel for the hydrolysis of additional biomass.

[0011] To provide a self-sustaining, fully balanced process, the hydrolysis and hydroconversion steps are operated at conditions under which about 40-60% of oxygen in the biomass is converted to H<sub>2</sub>O and about 40-60% of the oxygen is converted to CO and CO<sub>2</sub>. That is, the ratio of oxygen in H<sub>2</sub>O produced therein to the oxygen in the CO and CO<sub>2</sub> produced therein equals about 1 (i.e. H<sub>2</sub>O/(CO+CO<sub>2</sub>)≈1). Preferably, process pressures for the hydrolysis and hydroconversion steps are in the range of about 300 psig to about 800 psig and are about the same for both steps. Pressures greater than about 800 psig result in a higher liquid product yield, which is the driving force behind the operating parameters employed by conventional processes for maximizing liquid product yield; however, such higher pressures also produce higher amounts of water, as a result of which the overall process is driven out of balance, requiring, for example, the introduction of additional hydrogen into the hydrolysis reactor vessel from an external source to complete the process. In addition, the excess water produced at the higher pressures must then



be purified and disposed of. Preferably, temperatures for the hydropyrolysis and hydroconversion steps are in the range of about 650° F. to about 900° F.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] These and other objects and features of this invention will be better understood from the following detailed description taken in conjunction with the drawings wherein:

[0013] FIG. 1 is a schematic flow diagram of the self-sustaining process for producing liquid fuels from biomass in accordance with one embodiment of this invention.

#### DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

[0014] The process of this invention, shown in FIG. 1, is a compact, balanced, integrated, multi-stage process for thermochemically transforming biomass into gasoline plus diesel liquid product suitable for use as a transportation fuel without the need for externally provided H<sub>2</sub>, CH<sub>4</sub>, or water. The first reaction stage of this process employs a pressurized, catalytically-enhanced, hydropyrolysis reactor vessel **10** to create a low-char, partially deoxygenated, hydropyrolysis liquid product from which the char is removed. The second reaction stage (subsequent to char removal) employs a hydroconversion reactor vessel **11** in which a hydroconversion process is carried out at substantially the same pressure as the first reaction stage. The product from the second reaction stage is then cooled and separated into liquid and gaseous fractions using high pressure separators **12**, **13** and low pressure separator **14**. CO plus C<sub>1</sub>-C<sub>4</sub> light gases produced in the two stages are then steam reformed in a steam reformer **15** to produce H<sub>2</sub> using water which is also produced in the process. A key aspect of this invention is that the heat energy required in the process is supplied by the heat of reaction of the deoxygenation reaction, which is exothermic, occurring in both the first and second stages. Another key aspect of this invention is that the biomass feed need not be severely dried and, in fact, the addition of water either in the feed or as a separate feed is advantageous to the process because it enhances in-situ H<sub>2</sub> formation through a water-gas-shift reaction.

[0015] The integrated, balanced process of this invention is carried out under conditions which balance the levels of decarboxylation, decarbonylation, and hydrodeoxygenation so that 40-60% of the oxygen present in the biomass is rejected as CO and CO<sub>2</sub> and the remaining 40-60% of the oxygen in the biomass is rejected as H<sub>2</sub>O at the end of the process where it is easily separated from the hydrophilic liquid products produced by the process for use in the reforming process. Overall, after reforming of the light gases produced by the first two stages of the process with water produced by the process, over 95% of the oxygen in the process is rejected as CO<sub>2</sub>.

[0016] The unique balancing of reactions is critical to the process of this invention and is achieved through the selection of appropriate catalysts and process conditions in each step. Although each step of the process of this invention can yield a variety of products depending on the catalyst, pressure, temperature, and time on stream employed, only when these processes are integrated in the specific series of steps and process conditions of this invention is it possible to provide a balanced process wherein all of the H<sub>2</sub>, CH<sub>4</sub>, and water

demands of the overall process are supplied by the biomass, which is critical for creating a fungible fuel that can be sold at a reasonable cost.

[0017] In the first step of the process of this invention shown in FIG. 1, biomass and molecular hydrogen are introduced into a reactor vessel **10** containing a deoxygenation catalyst in which vessel the biomass undergoes hydropyrolysis, producing an output comprising a low-char, partially deoxygenated, hydropyrolysis liquid product, pyrolysis vapors (C<sub>1</sub>-C<sub>4</sub> gases), H<sub>2</sub>O, CO, CO<sub>2</sub>, and H<sub>2</sub>. Although any reactor vessel suitable for hydropyrolysis may be employed, the preferred reactor vessel is a fluidized bed reactor. The hydropyrolysis process employs a rapid heat up of the biomass fuel such that the residence time of the pyrolysis vapors in the reactor vessel is less than about 5 minutes. In contrast thereto, the residence time of the char is relatively long because it is not removed through the bottom of the reactor vessel and, thus, must be reduced in particle size until the particles are sufficiently small to enable them to be carried out with the vapors exiting proximate the top of the reactor vessel.

[0018] Hydropyrolysis is carried out in the reactor vessel at a temperature in the range of about 800° F. to about 950° F. and a pressure in the range of about 300 psig to about 800 psig. In conventional hydropyrolysis processes as previously noted, the objective is to maximize liquid product yield, which requires operation at substantially higher pressures, e.g. 2000 psig. This is because decarboxylation is favored at lower pressures whereas hydrodeoxygenation is favored at higher operating pressures. By maintaining pressures in the process of this invention in the range of 300 to 800 psig, most preferably at about 500 psig, decarboxylation and hydrodeoxygenation are balanced, but liquid product yield is reduced. At higher pressures, hydrodeoxygenation is favored and the reactions become unbalanced.

[0019] As previously indicated, in the hydropyrolysis process of this invention, the solid biomass feed is rapidly heated, preferably in a hot fluidized bed, resulting in liquid product yields comparable to and possibly better than yields obtained with conventional fast pyrolysis. However, the pyrolysis vapors now are in the presence of a catalyst and a high partial pressure of H<sub>2</sub> within the fluidized bed, which provides hydrogenation activity and also some deoxygenation activity. Hydrogenation activity is very desirable for preventing reactive olefins from polymerizing, thereby reducing the formation of unstable free radicals. Similarly, deoxygenation activity is important so that the heat of reaction from pyrolysis is supplied by the exothermic deoxygenation reaction, thereby obviating the need for external heating. The advantage of hydropyrolysis over existing pyrolysis processes is that hydropyrolysis avoids the retrograde reactions of pyrolysis, which is usually carried out in an inert atmosphere, most certainly in the absence of H<sub>2</sub> and usually in the absence of a catalyst, thereby promoting the undesirable formation of polynuclear aromatics, free radicals and olefinic compounds that are not present in the original biomass.

[0020] The first stage hydropyrolysis process of this invention operates at a temperature hotter than is typical of a hydroconversion process, as a result of which the biomass is rapidly devolatilized. Thus, the process requires an active catalyst to stabilize the hydropyrolysis vapors, but not so active that it rapidly cokes. Although any deoxygenation catalyst suitable for use in the temperature range of this process



may be employed in the hydrolysis process, catalysts in accordance with preferred embodiments of this invention are as follows:

**[0021]** Glass-ceramic catalysts—Glass-ceramic catalysts are extremely strong and attrition resistant and can be prepared as thermally impregnated (i.e. supported) or as bulk catalysts. When employed as a sulfided NiMo, Ni/NiO, or Co-based glass-ceramic catalyst, the resulting catalyst is an attrition resistant version of a readily available, but soft, conventional NiMo, Ni/NiO, or Co-based catalyst. Glass-ceramic sulfided NiMo, Ni/NiO, or Co-based catalysts are particularly suitable for use in a hot fluidized bed because these materials can provide the catalytic effect of a conventional supported catalyst, but in a much more robust, attrition resistant form. In addition, due to the attrition resistance of the catalyst, the biomass and char are simultaneously ground into smaller particles as hydrolysis reactions proceed within the reaction vessel. Thus, the char that is ultimately recovered is substantially free of catalyst contaminants from the catalyst due to the extremely high strength and attrition resistance of the catalyst. The attrition rate of the catalyst will typically be less than about 2 weight % per hour, preferably less than 1 weight % per hour as determined in a standard, high velocity jet cup attrition test index test.

**[0022]** Nickel phosphide catalyst—Ni Phosphide catalysts do not require sulfur to work and therefore will be just as active in a sulfur-free environment as in an environment containing  $H_2S$ , COS and other sulfur-containing compounds. Therefore, this catalyst will be just as active for biomass which has little or no sulfur present as with biomass which does contain sulfur (e.g. corn stover). This catalyst may be impregnated on carbon as a separate catalyst or impregnated directly into the biomass feedstock itself.

**[0023]** Bauxite—Bauxite is an extremely cheap material and, thus, may be used as a disposable catalyst. Bauxite may also be impregnated with other materials such as Ni, Mo, or be sulfided as well.

**[0024]** Small size spray-dried silica-alumina catalyst impregnated with low amounts of NiMo or CoMo and sulfided to form a low activity hydroconversion catalyst—Commercially available NiMo or CoMo catalysts are normally provided as large size  $1/8$ - $1/16$  tablets for use in fixed or ebullated beds. In the instant case, NiMo is impregnated on spray dried silica alumina catalyst and used in a fluidized bed. This catalyst exhibits lower activity with lower NiMo loadings than a conventional NiMo catalyst but would be of the right size for use in a fluidized bed.

**[0025]** In between the hydrolysis and hydroconversion processes, char is removed from the pyrolysis liquid product. Char removal has been a major barrier in conventional fast pyrolysis because the char tends to coat filters and react with oxygenated pyrolysis vapors to form viscous coatings which can blind hot process filters. Char may be removed in accordance with the process of this invention by filtration from the vapor stream, or by way of filtering from a wash step—ebullated bed. Back pulsing may be employed in removing char from filters, as long as the hydrogen used in the process of this invention sufficiently reduces the reactivity of the pyrolysis vapors. Electrostatic precipitation or a virtual impact or separator may also be used to remove char and ash particles from the hot vapor stream before cooling and condensation of the liquid product.

**[0026]** In accordance with one embodiment of this invention, hot gas filtration may be used to remove the char. In this

case, because the hydrogen has stabilized the free radicals and saturated the olefins, the dust cake caught on the filters should be more easily cleaned than char removed in the hot filtration of the aerosols produced in conventional fast pyrolysis. In accordance with another embodiment of this invention, the char is removed by bubbling first stage product gas through a recirculating liquid. The recirculated liquid used is the high boiling point portion of the finished oil from this process and is thus a fully saturated (hydrogenated), stabilized oil having a boiling point above 650° F. Char or catalyst fines from the first reaction stage are captured in this liquid. A portion of the liquid may be filtered to remove the fines and a portion may be recirculated back to the first stage hydrolysis reactor. One advantage of using a recirculating liquid is that it provides a way to lower the temperature of the char-laden process vapors from the first reaction stage to the temperature desired for the second reaction stage hydroconversion process while removing fine particulates of char and catalyst. Another advantage of employing liquid filtration is that the use of hot gas filtration with its attendant, well-documented problems of filter cleaning is completely avoided.

**[0027]** In accordance with one embodiment of this invention, large-size NiMo or CoMo catalysts, deployed in an ebullated bed, are used for char removal to provide further deoxygenation simultaneous with the removal of fine particulates. Particles of this catalyst should be large, preferably about  $1/8$ - $1/16$  inch in size, thereby rendering them easily separable from the fine char carried over from the first reaction stage, which is typically less than 200 mesh (~70 micrometers).

**[0028]** After removal of the char, the pyrolysis liquid, together with  $H_2$ , CO,  $CO_2$ ,  $H_2O$ , and  $C_1$ - $C_4$  gases from the first reaction stage hydrolysis step is introduced into a hydroconversion reactor vessel 11 in which it is subjected to a second reaction stage hydroconversion step, which preferably is carried out at a lower temperature (600-800° F.) than the first reaction stage hydrolysis step to increase catalyst life and at substantially the same pressure (300 -800 psig) as the first reaction stage hydrolysis step. The liquid hourly space velocity (LHSV) of this step is in the range of about 0.3 to about 0.7. The catalyst used in this step should be protected from Na, K, Ca, P, and other metals present in the biomass which can poison the catalyst, which will tend to increase catalyst life. This catalyst also should be protected from olefins and free radicals by the catalytic upgrading carried out in the first reaction stage process. Catalysts typically selected for this step are high activity hydroconversion catalysts, e.g. sulfided NiMo and sulfided CoMo catalysts. In this reaction stage, the catalyst is used to catalyze a water-gas-shift reaction of  $CO+H_2O$  to make  $CO_2+H_2$ , thereby enabling in-situ production of hydrogen in the second reaction stage reactor 11, which, in turn, reduces the hydrogen required for hydroconversion. NiMo and CoMo catalysts both catalyze the water-gas-shift reaction. The objective in this second reaction stage is once again to balance the deoxygenation reactions. This balancing is done by using relatively low pressures (300-800 psig) along with the right choice of catalyst. In conventional hydrodeoxygenation processes, pressures in the range of about 2000 psig to about 3000 psig are typically employed. This is because the processes are intended to convert pyrolysis oils, which are extremely unstable and difficult to process at lower pressures of  $H_2$ .

**[0029]** Following the hydroconversion step, the oil product will be substantially totally deoxygenated so that it can be



directly utilized as a transportation fuel, after it is separated by means of high pressure separators **12**, **13** and low pressure separator **14**, by distillation into gasoline and diesel portions. A key aspect of this process is to adjust temperature and pressure and space velocity to balance the level of decarbonylation, decarboxylation and hydrodeoxygenation so that all the  $H_2$  required for the process can be made by reforming the light gases that are produced within the process. If too much hydrodeoxygenation occurs, then too much  $H_2$  will be required for the process and the system will be driven out of balance. Likewise, if too much decarboxylation or decarbonylation occurs, too much carbon will be lost to  $CO_2$  and  $CO$  instead of being converted into liquid product, as a result of which liquid yields will be reduced.

**[0030]** After the hydroconversion step, the effluent therefrom is cooled substantially so that gasoline and diesel boiling materials condense and only the light gases remain in the vapor phase. These gases (containing  $CO$ ,  $CO_2$ ,  $CH_4$ , ethane, propane, butanes, heptanes, etc.) are sent to the steam reformer **15** together with water from the process for conversion into  $H_2$  and  $CO_2$ . A portion of these gases are burned in a furnace or other combustor to heat up the remaining portion of gases to the operating temperature of the steam reformer, about  $1700^\circ F$ . Steam reformers have a 3/1 steam-to-hydrocarbon ratio in their feed to push the reaction equilibrium, but this is far more than the amount required for reaction. The steam is recovered and recycled around inside the steam reformer. The  $CO_2$  is removed from the process by pressure swing absorption (PSA) and the  $H_2$  is recirculated back to the first reaction stage (hydropyrolysis) of the process. The product liquid is separated into diesel and gasoline fraction which are suitable for use as transportation fuels.

**[0031]** In addition, this process is also balanced with respect to water so that enough water is made in the process to provide all the water needed in the steam reforming step. In accordance with one embodiment of this invention, the amount of water employed is such that the overall process output contains substantially only  $CO_2$  and liquid products, thereby avoiding an additional process step for excess water disposal. It will be appreciated by those skilled in the art that the use of steam reforming in combination with hydropyrolysis and hydroconversion steps as set forth herein only makes sense where the objective is to provide a self-sustaining process in which the ratio of  $O_2$  in  $H_2O$  to  $O_2$  in  $CO$  and  $CO_2$  produced by the process is about 1.0. In the absence of such an objective, steam reforming is not necessary because  $H_2$  required for the hydropyrolysis process would still be provided by external sources. If one were to employ steam reforming in the absence of the objectives stated herein, one would not end up with the self-sustaining process of this invention in which the process output consists essentially of liquid product and  $CO_2$ .

**[0032]** In accordance with one embodiment of this invention, the heat generated in the second reaction stage may be used to supply all or part of the heat needed to drive the hydropyrolysis process in the first reaction stage. In accordance with one embodiment of this invention, the process also employs recirculation of the heavy finished products as a wash liquid in the second step as stated herein above to capture process fines exiting the first stage pyrolysis reactor

and control the heat of reaction. In accordance with one embodiment of this invention, this liquid is also recirculated to the hydroconversion and possibly to the first stage hydropyrolysis step to regulate the generation of heat in each step. The rate of recirculation is preferably in the range of about 3-5 times the biomass feed rate. This is necessary because hydrodeoxygenation is a strongly exothermic reaction.

**[0033]** In accordance with one embodiment of this invention, the biomass feed is a high lipid containing biomass such as algae, enabling production of the same deoxygenated diesel oil which would be made from lipids extracted from the algae plus additional gasoline and diesel which can be made from the remainder of the algae biomass. This is particularly attractive because lipid extraction is expensive. By contrast, conventional fast pyrolysis of algae biomass would be very unattractive because the uncontrolled thermal reactions characteristic of fast pyrolysis would degrade these lipids. Thus, the integrated process of this invention is ideal for algae conversion because it can be carried out on algae which are usually only partially dewatered and still produce high quality diesel and gasoline product.

**[0034]** The process of this invention provides several distinct advantages over conventional fast pyrolysis-based processes in that it produces a negligible to low-char, partially deoxygenated, stabilized product from which residual char can be easily separated by hot gas filtration or contacting with a recirculated liquid; clean, hot hydropyrolysis oil vapors can be directly upgraded to a final product in a close-coupled second catalytically-enhanced process unit operated at almost the same pressure as was employed upstream; and upgrading is carried out quickly before degradation can occur in the vapor produced from the hydropyrolysis step.

**[0035]** The liquid product produced by this process should contain less than 5% oxygen and preferably less than 2% oxygen with a low total acid number (TAN) and exhibit good chemical stability to polymerization or a reduced tendency to reactivity. In the preferred embodiment of this invention wherein the total oxygen content of the product is reduced below 2%, the water and hydrocarbon phases will easily separate out in any normal separation vessel because the hydrocarbon phase has become hydrophobic. This is a significant advantage when compared to conventional pyrolysis in which the water is miscible with and mixed in with the highly oxygenated pyrolysis oil. Table 1 presents an estimated material balance for a balanced hydropyrolysis+hydroconversion process in accordance with this invention utilizing a mixed hardwood feed. Because the fungible fuels produced in the proposed process have low oxygen content, any excess water produced from this process is relatively free of dissolved hydrocarbons and will likely contain less than 2000 ppm dissolved total organic carbon (TOC), rendering it suitable for irrigation in arid areas. Additionally, the finished hydrocarbon product is now easily transportable, has low total acid number (TAN), and excellent chemical stability. In conventional fast pyrolysis, the pyrolysis oils typically contain 50-60% oxygen in the form of oxygenated hydrocarbons and 25% dissolved water. Therefore, final products transportation costs for the integrated hydropyrolysis+hydroconversion process of this invention are less than half of the costs for conventional fast pyrolysis. Furthermore, water produced in the proposed process becomes a valuable byproduct especially for arid regions.



TABLE 1

Estimated Material Balance for a Balanced Hydropyrolysis + Hydroconversion Process Utilizing a Mixed Hardwood Feed*		
	Hydropyrolysis + hydroconversion balance, Wt %	Overall system process balance, Wt %
Biomass feed	100	100
H <sub>2</sub> feed	3.7	—
Gasoline + diesel product	29	29
Char product	8	8
Water	22.5	.7
CO <sub>2</sub>	27.5	59.4
Hydrocarbon gas	16.7	2.9

\*All H<sub>2</sub> is made by reforming light gases and no external natural gas is required

[0036] While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

1. A process for producing liquid products from biomass comprising the steps of:

- introducing biomass and reformed molecular hydrogen into a hydropyrolysis reactor vessel containing a deoxygenating catalyst and hydropyrolyzing said biomass, producing CO<sub>2</sub>, CO and C<sub>1</sub>-C<sub>4</sub> gas, a partially deoxygenated pyrolysis liquid, char, and first stage heat;
- removing said char from said partially deoxygenated pyrolysis liquid;
- hydroconverting said partially deoxygenated pyrolysis liquid in a hydroconversion reactor vessel using a hydroconversion catalyst in the presence of the CO<sub>2</sub>, CO and C<sub>1</sub>-C<sub>4</sub> gas generated in step a), producing a substantially fully deoxygenated pyrolysis liquid, a gaseous mixture comprising CO, CO<sub>2</sub>, and light hydrocarbon gases (C<sub>1</sub>-C<sub>4</sub>), and second stage heat;
- steam reforming a portion of said gaseous mixture using water produced in step a) and step c), producing said reformed molecular hydrogen, wherein steps a) and c) are operated at conditions under which about 40-60% of oxygen in said biomass is converted to H<sub>2</sub>O and about 40-60% of said oxygen is converted to CO and CO<sub>2</sub>; and
- recycling a portion of said liquid product created in step c) to said hydropyrolysis reactor vessel or said hydroconversion reactor vessel to control temperature therein.

2. The process of claim 1, wherein said hydroconversion catalyst catalyzes both a water-gas-shift reaction and hydroconversion.

3. The process of claim 1, wherein all of said steps a), c), and d) are carried out at a substantially same pressure.

4. The process of claim 3, wherein said pressure is in a range of about 300 to about 800 psig.

5. The process of claim 4, wherein said hydropyrolysis is carried out at a temperature in a range of about 800° F. to about 950° F. and said hydroconversion is carried out at a temperature in a range of about 600° F. to about 800° F.

6. The process of claim 1, wherein said hydroconversion is carried out with a liquid hourly space velocity in a range of about 0.3 to about 0.7.

7. The process of claim 1, wherein said substantially fully deoxygenated pyrolysis liquid is separated into diesel and gasoline fractions suitable for use as transportation fuel.

8. The process of claim 1, wherein said hydropyrolysis reactor vessel is a fluidized bed reactor containing a fluidized bed and a gas residence time in said hydropyrolysis reactor vessel is less than about one minute.

9. The process of claim 8, wherein said char is removed from said fluidized bed reactor substantially only from above said fluidized bed.

10. The process of claim 1, wherein char is removed from said partially deoxygenated pyrolysis liquid by bubbling gases output by said hydropyrolysis through a recirculating liquid using a high boiling point portion of said substantially fully deoxygenated pyrolysis liquid.

11. The process of claim 1, wherein output from said process consists essentially of liquid product and CO<sub>2</sub>.

12. The process of claim 8, wherein said deoxygenation catalyst is granulated and sufficiently resistant to attrition such that it attrits said char, thereby enabling removal of said char from said fluidized bed reactor substantially only from above said fluidized bed.

13. A process for producing liquid products from biomass comprising the steps of:

- introducing said biomass and reformed H<sub>2</sub> into a reactor vessel containing a deoxygenating catalyst and pyrolyzing said biomass, producing a pyrolysis process output comprising partially deoxygenated pyrolysis liquid, char, and a first portion of heat;
- separating said char from said pyrolysis process output;
- hydroconverting said partially deoxygenated pyrolysis liquid in the presence of a hydroconversion catalyst, producing substantially fully deoxygenated pyrolysis liquid, a gaseous mixture comprising CO and C<sub>1</sub>-C<sub>5</sub> light hydrocarbon gases and a second portion of heat; and
- steam reforming a portion of said gaseous mixture, producing said reformed H<sub>2</sub>; used in said reactor vessel,

14. The process of claim 13, wherein in a range of about 40-60% of oxygen in said biomass is converted to H<sub>2</sub>O and about 40-60% of said oxygen is converted to CO and CO<sub>2</sub>.

15. The process of claim 13, wherein said hydroconversion catalyst catalyzes both a water-gas-shift reaction and hydroconversion.

16. The process of claim 13, wherein said hydropyrolyzing and said hydroconverting are carried out at substantially a same pressure.

17. The process of claim 16, wherein said pressure is in a range of about 300 psig to about 800 psig.

18. The process of claim 13, wherein said hydropyrolyzing is carried out at a hydropyrolysis temperature in a range of about 800° F. to about 950° F. and said hydroconverting is carried out at a hydroconversion temperature in a range of about 600° F. to about 800° F.

19. The process of claim 13, wherein said substantially fully deoxygenated pyrolysis liquid is separated into diesel and gasoline fractions suitable for use as transportation fuel.

20. The process of claim 13, wherein said reactor vessel is a fluidized bed reactor containing a fluidized bed.

21. The process of claim 13, wherein output from said process consists essentially of liquid product and CO<sub>2</sub>.

\* \* \* \* \*