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(54) **METHODS AND APPARATUS FOR  
PRODUCING SYNGAS AND ALCOHOLS**

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(57) **ABSTRACT**

The present invention features methods and apparatus for the  
pyrolysis or torrefaction of a carbon-containing feedstock  
before it is converted to syngas. In some embodiments, bio-  
mass is first pretreated by torrefaction and/or pyrolysis, fol-  
lowed by devolatilization and/or steam reforming to produce  
syngas. Various mixtures of such pretreated biomass, com-  
bined with fresh biomass, can be employed to produce syn-  
gas. The syngas can be converted to alcohols, such as ethanol,  
or to other products.

## METHODS AND APPARATUS FOR PRODUCING SYNGAS AND ALCOHOLS

### PRIORITY DATA

**[0001]** This patent application claims priority under 35 U.S.C. §120 from U.S. Provisional Patent Application Nos. 61/014,408, 61/014,410, 61/014,412, and 61/014,415, each filed Dec. 17, 2007, and each of which is hereby incorporated herein by reference for all purposes.

### FIELD OF THE INVENTION

**[0002]** This invention relates to flexible, efficient, and scalable methods and systems to convert carbonaceous materials (such as biomass) into synthesis gas and other downstream products (such as alcohols).

### BACKGROUND OF THE INVENTION

**[0003]** Synthesis gas (hereinafter referred to as “syngas”) is a mixture of gas comprising predominantly hydrogen ( $H_2$ ) and carbon monoxide (CO). Syngas is essentially a gaseous mixture of stable molecules that contain the elements carbon (C), hydrogen (H), and oxygen (O). Syngas is a platform intermediate in the chemical and biorefining industries and has a vast number of uses, as is well-known in the art. Syngas can be converted into alkanes, olefins, oxygenates, and alcohols. Some of these chemicals can be blended into, or used directly as, diesel fuel, gasoline, and other liquid fuels. Syngas can also be directly combusted to produce heat and power.

**[0004]** Syngas can be produced, in principle, from virtually any material containing C, H, and O. Such materials commonly include fossil resources such as natural gas, petroleum, coal, and lignite; and renewable resources such as lignocellulosic biomass and various carbon-rich waste materials. It is preferable to utilize a renewable resource to produce syngas because of the rising economic, environmental, and social costs associated with fossil resources.

**[0005]** When biomass feedstocks are used, a significant portion of feedstock costs can be attributed to the handling associated with moving the feedstocks from their point of production to their point of further conversion or use. Handling solid forms of biomass is expensive for a number of reasons, including the number of operations required and the low bulk density of the feedstocks, which causes high transportation costs.

**[0006]** Furthermore, it has been estimated that over 1 billion tons of dry biomass are available in the United States for conversion to renewable fuels. Much of this biomass, however, is located in remote locations. Economical transportation of biomass is usually limited to a distance of up to about 75 miles because of transportation costs. Thus, there is a significant amount of feedstock in locations that extend beyond the range of economical transportation using standard methods.

**[0007]** In view of the aforementioned limitations of the art, improved methods and apparatus are needed to convert carbon-containing feedstocks such as biomass into syngas, which can then be converted to alcohols or other products. Preferably, improved methods would alleviate some of the economic burden associated with transportation.

### SUMMARY OF THE INVENTION

**[0008]** In a first aspect relating to methods, the present invention provides a method of forming syngas, the method

comprising the steps of: (a) pyrolyzing or torrefying a carbon-containing first feed material to form a pyrolyzed or torrefied first feed material; and (b) converting the pyrolyzed or torrefied first feed material into syngas. Step (a) can be conducted in the presence of a catalyst.

**[0009]** The method can further include converting into syngas a second feed material that has not been pyrolyzed or torrefied. The method can further include combining the pyrolyzed or torrefied first feed material with a second feed material that has not been pyrolyzed or torrefied such that both the pyrolyzed or torrefied first feed material and the second feed material are converted into syngas.

**[0010]** In some embodiments, the method includes pyrolyzing a carbon-containing first feed material to form a pyrolyzed first feed material, torrefying a carbon-containing feed second material to form a torrefied second feed material, and converting the pyrolyzed first feed material and the torrefied second feed material into syngas. In some embodiments, the method includes introducing the torrefied first feed material into a pyrolysis reactor to form a pyrolyzed first feed material. The method can be conducted, at least in part, in the presence of a catalyst.

**[0011]** The pyrolyzed or torrefied first feed material can be converted into syngas by passing the pyrolyzed or torrefied first feed material through a heated reaction vessel, such as a steam reformer or partial-oxidation reactor, to form syngas. In some embodiments, conversion to syngas comprises the substeps of: (i) devolatilizing the pyrolyzed or torrefied first feed material to form a gas phase and/or solid phase in a devolatilization unit; and (ii) passing the gas phase and/or solid phase through a heated reaction vessel to form syngas.

**[0012]** Certain embodiments provide for converting into syngas a pyrolyzed or torrefied first feed material and a second carbon-containing feed material that has not been pyrolyzed or torrefied. Certain embodiments include pyrolyzing a carbon-containing first feed material to form the pyrolyzed first feed material, torrefying a carbon-containing third feed material to form a torrefied third feed material, and converting the pyrolyzed first feed material, the second feed material, and the torrefied third feed material into syngas. Other embodiments combine, prior to converting the material into syngas, the pyrolyzed or torrefied first feed material and the second feed material.

**[0013]** In some embodiments, methods include converting the pyrolyzed or torrefied first feed material and the second feed material into syngas. This particular method comprises the steps of: (i) devolatilizing the pyrolyzed or torrefied first feed material and the second feed material to form a gas phase and/or solid phase in a devolatilization unit; and (ii) passing the gas phase and/or solid phase through a heated reaction vessel to form syngas. The torrefied first feed material can be introduced into a pyrolysis reactor to form a pyrolyzed first feed material.

**[0014]** Some embodiments provide a method of forming syngas, the method comprising the steps of: (a) devolatilizing a pyrolyzed or torrefied first feed material to form a gas phase and solid phase in a devolatilization unit; and (b) passing the gas phase and solid phase through a heated reaction vessel to form syngas.

**[0015]** Pyrolysis of a carbon-containing feed material, optionally in the presence of a catalyst, can form the first feed material. Or, torrefaction of a carbon-containing feed material, optionally in the presence of a catalyst, can form the first feed material. A second feed material that has not been pyro-



lyzed or torrefied can be mixed with the first feed material and converted into syngas. In some embodiments, both the pyrolyzed or torrefied first feed material and the second feed material are converted into syngas.

**[0016]** Certain embodiments include pyrolyzing a carbon-containing first feed material to form the pyrolyzed first feed material, torrefying a carbon-containing third feed material to form a torrefied third feed material, and converting the pyrolyzed first feed material, the second feed material, and the torrefied third feed material into syngas. The pyrolyzed or torrefied first feed material and the second feed material can be combined prior to converting the pyrolyzed or torrefied first feed material and the second feed material into syngas. The torrefied first feed material can be used to form a pyrolyzed first feed material.

**[0017]** Some embodiments employ modular units for at least some steps of the methods previously described.

**[0018]** Some embodiments further include the step of converting the syngas to a product, such as a product selected from the group consisting of an alcohol, an olefin, an aldehyde, a hydrocarbon, an ether, hydrogen, ammonia, and/or acetic acid. The hydrocarbon can be a linear or branched  $C_5$ - $C_{15}$  hydrocarbon. The alcohol can be methanol and/or ethanol.

**[0019]** A second aspect relates to apparatus for practicing some embodiments of the invention. In some of these embodiments, an apparatus is provided for producing syngas comprising a pyrolysis and/or torrefaction reactor in communication with a devolatilization unit that is in communication with a heated reaction vessel. In some embodiments, the pyrolysis reactor, torrefaction reactor, or both of these reactors, is suitable for containing one or more catalysts for pyrolysis or torrefaction.

**[0020]** In some embodiments, the apparatus further includes a device for combining pyrolyzed feed material with feed material that has not been pyrolyzed. In some embodiments, the apparatus further includes a device for combining torrefied feed material with feed material that has not been torrefied.

**[0021]** Some embodiments of this aspect provide an apparatus for producing syngas comprising a pyrolysis and/or torrefaction reactor (which can be catalytic) in communication with a device for combining a pyrolyzed or torrefied first feed material with a second feed material that has not been pyrolyzed or torrefied, wherein the device is in communication with a syngas reactor for converting the first feed material and the second feed material into syngas.

**[0022]** Certain apparatus include a device for combining pyrolyzed feed material with torrefied feed material, wherein the device is in communication with: (i) the pyrolysis reactor and/or the torrefaction reactor, and (ii) the syngas reactor. The syngas reactor can comprise a devolatilization unit that is in communication with a heated reaction vessel.

**[0023]** Some apparatus of the invention further include a product reactor for converting syngas into a product, such as  $C_1$ - $C_4$  alcohols (e.g., methanol and/or ethanol), wherein the product reactor is in communication with the syngas reactor.

#### DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

**[0024]** This detailed description illustrates by way of example, not by way of limitation, the principles of the invention. This description will enable one skilled in the art to make and use the invention, and describes several embodiments,

adaptations, variations, alternatives, and uses of the invention, including what is presently believed to be the best mode of carrying out the invention. It should also be noted that, as used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly indicates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of ordinary skill in the art to which this invention belongs. If a definition set forth in this section is contrary to or otherwise inconsistent with a definition set forth in patents, published patent applications, and other publications that are herein incorporated by reference, the definition set forth in this section prevails over the definition that is incorporated herein by reference.

**[0025]** Unless otherwise indicated, all numbers expressing reaction conditions, stoichiometries, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending at least upon the specific measurement technique.

**[0026]** The present invention features methods and apparatus for the pyrolysis or torrefaction of a feedstock before it is converted to syngas. Pyrolysis and torrefaction produce a relatively energy-dense feedstock (e.g., by the removal of water and/or the densification of the feedstock), thereby reducing the transportation costs of the resulting feedstocks.

**[0027]** In some embodiments, a pyrolyzed feedstock and a torrefied feedstock are converted to syngas. In other embodiments, a pyrolyzed feedstock and a feedstock that has not undergone pyrolysis or torrefaction are converted to syngas. Some embodiments convert a torrefied feedstock and a feedstock that has not undergone pyrolysis or torrefaction to syngas. In some embodiments, a torrefied feedstock, a pyrolyzed feedstock, and a feedstock that has not undergone pyrolysis or torrefaction are converted to syngas. In some embodiments, a fossil fuel (e.g., crude oil, coal, and/or petroleum) and one or more of the following are converted to syngas: a pyrolyzed feedstock, a torrefied feedstock, and a feedstock that has not undergone pyrolysis or torrefaction.

**[0028]** In one aspect, the invention features methods and systems that use modular units for the pyrolysis or torrefaction of a feedstock. For example, a feedstock can be reacted in a modular pyrolysis or torrefaction reactor and then transported to a plant for further processing, such as the conversion of the reacted feedstock to syngas or other downstream products. In some embodiments, modular units are also used to devolatilize and/or stream reform the pyrolyzed or torrefied feedstock. For example, a pyrolyzed or torrefied feedstock can be introduced into a modular unit for devolatilizing the feedstock. In some embodiments, the modular devolatilization unit is in communication with (such as operably linked to) a modular unit for steam reforming the product of the devolatilization unit, thereby forming syngas. In some embodiments, the product from the modular devolatilization unit is transported to a plant for further processing, such as the conversion to syngas or other downstream products.

**[0029]** “Biomass,” for the purposes of the present invention, is any material not derived from fossil resources and comprising at least carbon, hydrogen, and oxygen. Biomass includes, for example, plant and plant-derived material, vegetation, agricultural waste, forestry waste, wood waste, paper waste, animal-derived waste, poultry-derived waste, and



municipal solid waste. Other exemplary feedstocks include cellulose, hydrocarbons, carbohydrates or derivatives thereof, charcoal, and renewable feedstocks. The present invention can also be used for carbon-containing feedstocks other than biomass, such as a fossil fuel (e.g., coal or petroleum). Thus, any method, apparatus, or system described herein in reference to biomass can alternatively be used with any other feedstock.

**[0030]** The methods and systems of the invention can accommodate a wide range of feedstocks of various types, sizes, and moisture contents. In some embodiments of the invention, the biomass feedstock can include one or more materials selected from: timber harvesting residues, softwood chips, hardwood chips, tree branches, tree stumps, leaves, bark, sawdust, off-spec paper pulp, corn, corn stover, wheat straw, rice straw, sugarcane bagasse, switchgrass, miscanthus, animal manure, municipal garbage, municipal sewage, commercial waste, grape pumice, almond shells, pecan shells, coconut shells, coffee grounds, grass pellets, hay pellets, wood pellets, cardboard, paper, plastic, and cloth. A person of ordinary skill in the art will readily appreciate that the feedstock options are virtually unlimited.

**[0031]** According to the present invention, selection of a particular feedstock or feedstocks is not regarded as technically critical, but is carried out in a manner that tends to favor an economical process. Typically, regardless of the feedstocks chosen, there can be (in some embodiments) screening to remove undesirable materials. The feedstock can optionally be dried prior to processing. There can also, but need not, be reduction of particle size prior to conversion of the feedstock to syngas. Particle size is not, however, regarded as critical to the invention.

**[0032]** For the purposes of the present invention, “reforming” or “steam reforming” refers to the production of syngas when steam is the reactant. “Partial oxidation” refers to the production of syngas when oxygen is the reactant. “Gasification” generally refers to the production of a mixture of at least CO, CO<sub>2</sub>, and H<sub>2</sub>, and can include one or more of devolatilization, reforming, or partial oxidation, as well as some amount of pyrolysis, combustion, water-gas shift, and other chemical reactions.

**[0033]** Some exemplary variations provide a process for synthesizing syngas from biomass or other carbon-containing material. Part or all of the feedstock is introduced into a feedstock reactor, such as a pyrolysis reactor or torrefaction reactor. The product from the feedstock reactor is then introduced into a syngas reactor. In some embodiments, a portion of the feedstock is not introduced into the feedstock reactor. Instead, this portion is added directly to a syngas reactor.

**[0034]** In some embodiments, the syngas reactor includes a devolatilization unit and/or reformer reactor. The syngas produced in the syngas reactor can be cooled and compressed. In some variations, the syngas is filtered, purified, or otherwise conditioned prior to being converted to another product. For example, syngas may be introduced to a syngas conditioning section, where benzene, toluene, ethyl benzene, xylene, sulfur compounds, nitrogen, metals, and/or other impurities or potential catalyst poisons are optionally removed from the syngas. In some embodiments, the syngas is introduced into one or more product reactors for the conversion of syngas into another product, such as methanol and/or ethanol.

**[0035]** Exemplary feedstock reactors include one or more standard pyrolysis reactors and/or torrefaction reactors. In some embodiments, a pyrolysis reactor is used to pyrolyze a

portion of or the entire feedstock using standard methods (see, for example, Czernik and Bridgwater, *Energy & Fuels*, 18:590-598, 2004, and Mohan et al., *Energy & Fuels*, 20:848-889, 2006, which are each hereby incorporated by reference in their entireties, particularly with respect to pyrolysis reactors and methods).

**[0036]** Pyrolysis is the thermal decomposition of a feedstock. Preferably, less oxygen is present than required for complete combustion of the feedstock (such as about or less than 40, 30, 20, 10, 5, 1, 0.5, or 0.01% of the oxygen that is required for complete combustion of the feedstock). In some embodiments, pyrolysis is performed in the absence of oxygen.

**[0037]** Exemplary changes that may occur during pyrolysis include any of the following: (i) heat transfer from a heat source increases the temperature inside the feedstock; (ii) the initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms a char; (iii) the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed feedstock; (iv) condensation of some of the volatiles in the cooler parts of the feedstock, followed by secondary reactions, can produce tar; (v) autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and (vi) further thermal decomposition, reforming, water-gas shift reactions, free-radical recombination, and/or dehydrations can also occur, which are a function of the residence time, temperature, and pressure profile.

**[0038]** Pyrolysis partially dehydrates the feedstock. In various embodiments, pyrolysis removes greater than or about 5, 10, 20, 30, 40, 50, 60, 70, 80, 90% or more of the water from the feedstock. It can be beneficial, but not necessary, to remove at least 90% of the water initially present. The products from the pyrolysis reactor are typically a gas, an oil (also referred to as “pyrolysis oil” or “bio-oil”), and a char.

**[0039]** Any standard pyrolysis reactor can be used to pyrolyze the feedstock. Exemplary reactor configurations include, but are not limited to, augers, ablative reactors, rotating cones, fluidized-bed reactors (e.g., circulating fluidized-bed reactors), entrained-flow reactors, vacuum moving-bed reactors, transported-bed reactors, fixed-bed reactors, and microwave-assisted pyrolysis reactors.

**[0040]** In some embodiments in which an auger is used, the feedstock and sand are fed at one end of a screw. The screw mixes the sand and feedstock and conveys them through the reactor. The screw can provide good control of the feedstock residence time and does not dilute the pyrolyzed products with a carrier or fluidizing gas. The sand is reheated in a separate vessel.

**[0041]** In some embodiments in which an ablative process is used, the feedstock is moved at a high speed against a hot metal surface. Ablation of any char forming at the particle surface maintains a high rate of heat transfer. Preferably, the apparatus utilizes a metal surface spinning at a high speed within a bed of feedstock, which prevents any dilution of the products. As an alternative, the feedstock particles may be suspended in a carrier gas and introduced at a high speed through a cyclone whose wall is heated. The products are diluted with the carrier gas.

**[0042]** In some embodiments, preheated hot sand and feedstock are introduced into a rotating cone. Due to the rotation of the cone, the mixture of sand and feedstock is transported



across the cone surface by centrifugal force. Like other shallow transported-bed reactors, relatively fine particles are used to obtain a good liquid yield.

**[0043]** In some embodiments in which a fluidized-bed reactor is used, the feedstock is introduced into a bed of hot sand fluidized by a gas, which is usually a recirculated product gas. High heat transfer rates from fluidized sand result in rapid heating of the feedstock. There can be some ablation by attrition with the sand particles. Heat is usually provided by heat-exchanger tubes through which hot combustion gas flows. There is some dilution of the products, which makes it more difficult to condense and then remove the bio-oil mist from the gas exiting the condensers.

**[0044]** In some embodiments in which a circulating fluidized-bed reactor is used, the feedstock is introduced into a circulating fluidized-bed of hot sand. Gas, sand, and feedstock move together. Exemplary transport gases include recirculated product gases and combustion gases. High heat-transfer rates from the sand ensure rapid heating of the feedstock, and ablation is stronger than with regular fluidized beds. A fast separator separates the product gases and vapors from the sand and char particles. The sand particles are reheated in a fluidized burner vessel and recycled to the reactor.

**[0045]** Any standard reaction conditions can be used to pyrolyze the feedstock in the pyrolysis reactor (see, for example, Czernik and Bridgwater, *Energy & Fuels*, 18:590-598, 2004; and Mohan et al, *Energy & Fuels*, 20:848-889, 2006). One skilled in the art can select a combination of temperature, pressure, and residence time that produces a liquid as a product of the pyrolysis process (rather than only forming a solid and/or gas). For example, if the reaction temperature, pressure, and/or residence time is too low or too high, the product may be primarily a solid. A skilled artisan, by routine experimentation, can adjust the parameters to obtain primarily a liquid as the pyrolyzed product.

**[0046]** In some embodiments, fast pyrolysis is used. Fast pyrolysis is a high-temperature process in which feedstock is rapidly heated. In some embodiments, the feedstock is heated in the absence of oxygen. The feedstock decomposes to generate vapors, aerosols, and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. Rapid heating and rapid quenching can produce the intermediate pyrolysis liquid products, which condense before further reactions break down higher-molecular-weight species into gaseous products. Fast pyrolysis processes typically produce 60-75 wt % of liquid bio-oil, 15-25 wt % of solid char, and 10-20 wt % of noncondensable gases, for example, depending on the feedstock used.

**[0047]** Pyrolysis can be performed in the presence of a catalyst. Exemplary catalysts include heterogeneous catalysts (such as  $\text{SiO}_2\text{—Al}_2\text{O}_3$ ,  $\text{Pt/SiO}_2\text{—Al}_2\text{O}_3$ ,  $\text{WO}_x/\text{ZrO}_2$ ,  $\text{SO}_x/\text{ZrO}_2$ ), zeolites (such as HY-zeolite,  $\alpha$ -zeolite, HZSM-5, ZSM-5, or clinoptilolite), acid catalysts, clay catalysts (e.g., acidified or activated clay catalysts), Al-MCM-41 type mesoporous catalysts, activated alumina, Co—Mo catalysts (such as Criterion-534), and Ni/Al co-precipitated catalysts. In some embodiments, a cation such as  $\text{K}^+$ ,  $\text{Li}^+$ , or  $\text{Ca}^{2+}$  can be used to increase the selectivity and yield of char and/or to lower the selectivity and yield of tar during pyrolysis.

**[0048]** In some embodiments, the feedstock is finely ground before it is added to the pyrolysis reactor to facilitate high heating rates and fast heat transfer. In some embodi-

ments, the reaction temperature is between about 300-600° C., such as about 450° C., when a pyrolysis catalyst is used. In particular embodiments, the temperature is between about 300-400° C., about 400-500° C., or about 500-600° C. In some embodiments, use of a pyrolysis catalyst allows a lower temperature to be used, such as about 250-450° C. High reaction rates minimize char formation. Under some conditions, no char is formed.

**[0049]** In some embodiments, the pressure is between about 0 to about 2,000 psi, such as between about 0 to about 50 psi. In some embodiments, the residence time is between about 0.1 seconds to about 10 seconds, such as about 1-5 seconds. In some embodiments, the pyrolysis vapors and aerosols are rapidly cooled to generate pyrolysis oil.

**[0050]** Slow pyrolysis can also be used. In slow pyrolysis, the feedstock is heated to about 500° C. The vapor residence time varies from about 5 minutes to about 30 minutes. Vapors do not escape as rapidly in slow pyrolysis as they do in fast pyrolysis. Thus, components in the vapor phase continue to react with each other as the solid char and any liquid are being formed. The heating rate in slow pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock can be held at constant temperature or slowly heated. Vapors can be continuously removed as they are formed.

**[0051]** In some embodiments, vacuum pyrolysis is used. In this method, the feedstock is heated in a vacuum to decrease the boiling point and/or avoid adverse chemical reactions. Slow or fast heating rates can be used. Some embodiments employ a temperature of about 450° C. and a pressure of between about 1-5 psi.

**[0052]** The pyrolysis oil may contain water, such as about 10 to about 25% water (weight %). If desired, part or the entire water layer of the pyrolysis oil can be removed before it is added to a devolatilization unit and/or reformer reactor using standard methods, such as phase separation or separation based on differences in volatility. Exemplary methods include phase separation by decanting, distillation, and separation using membranes. In some embodiments, none of the water is removed from the pyrolysis oil before it is added to the devolatilization unit and/or reformer reactor. The water in the pyrolysis oil can provide a source of steam, which can be used to increase the hydrogen content of the syngas through the water-gas shift reaction, if desired.

**[0053]** In some embodiments, the gas and/or solid products from the pyrolysis reactor are recycled through the pyrolysis reactor or are burned to generate energy.

**[0054]** Some variations of the present invention utilize the principles of torrefaction. Torrefaction can improve the properties of a carbon-containing feedstock (e.g., biomass). Torrefaction consists of a slow heating of feedstock in an inert atmosphere to a maximum temperature of about 300° C. The treatment yields a solid uniform product with a lower moisture content and a higher energy content compared to the initial feedstock. The process may be called mild pyrolysis, with removal of smoke-producing compounds and formation of a solid product, retaining (in some embodiments) about 70% of the initial weight and about 90% of the original energy content.

**[0055]** Torrefied material typically has the following properties: (i) hydrophobic nature (e.g., the material does not regain humidity in storage and therefore, unlike wood and charcoal, is stable with a well-defined composition); (ii) lower moisture content and higher calorific values compared to the initial feedstock; (iii) formation of less smoke when



burned; and (iv) higher density and similar mechanical strength compared to the initial feedstock.

**[0056]** In some embodiments, a torrefaction reactor is used to torrefy a portion of or the entire feedstock using standard methods, such as those described in WO 2007/078199 or in Bergman and Kiel, "Torrefaction for biomass upgrading," 14<sup>th</sup> European Biomass Conference & Exhibition, ENC-RX-05-180, Paris, France, 2005, which publications are each hereby incorporated by reference in their entireties, particularly with respect to torrefaction reactors and methods.

**[0057]** Any standard torrefaction reactor can be used to torrefy the feedstock. Exemplary reactor configurations include, but are not limited to, augers, ablative reactors, rotating cones, fluidized-bed reactors (e.g., circulating fluidized-bed reactors), entrained-flow reactors, vacuum moving-bed reactors, transported-bed reactors, and fixed-bed reactors. In some embodiments, a feedstock is torrefied before it is added to a devolatilization unit or reformer reactor. In other embodiments, a feedstock is torrefied while it is contained in a devolatilization unit.

**[0058]** Any standard reaction conditions can be used to torrefy the feedstock in the torrefaction reactor. One skilled in the art can readily select a combination of temperature, pressure, and residence time that produces a dried solid as a product of the torrefaction process. In some embodiments, the reaction temperature is between about 150-300° C., such as about 200-300° C. A variety of pressures can be used for torrefaction, such as atmospheric pressure or greater. In some embodiments, the residence time is between about 10 minutes to about 8 hours. The residence time is preferably adjusted based on the type of feedstock used. In some embodiments, torrefaction is performed in the absence of oxygen. In some embodiments, the torrefied feedstock is crushed or densified (e.g., compressed to form pellets using a pelletizer) using standard methods to form smaller particles that are easier to transport and/or easier to mix with other feedstocks.

**[0059]** In some embodiments, torrefaction is performed in the presence of a catalyst. Exemplary catalysts for torrefaction include heterogeneous catalysts (such as SiO<sub>2</sub>—Al<sub>2</sub>O<sub>3</sub>, Pt/SiO<sub>2</sub>—Al<sub>2</sub>O<sub>3</sub>, WO<sub>x</sub>/ZrO<sub>2</sub>, SO<sub>x</sub>/ZrO<sub>2</sub>), zeolites (such as HY-zeolite,  $\alpha$ -zeolite, HZSM-5, ZSM-5, or clinoptilolite), acid catalysts, clay catalysts (e.g., acidified or activated clay catalysts), Al-MCM-41 type mesoporous catalysts, activated alumina, Co-Mo catalysts (such as Criterion-534), and Ni/Al co-precipitated catalysts.

**[0060]** A torrefied feedstock (such as a solid product from a torrefaction reactor) can be added to a pyrolysis reactor (such as a pyrolysis reactor described herein) to further process the torrefied feedstock before adding it to a syngas reactor, devolatilization unit, and/or reformer reactor.

**[0061]** In some embodiments, a pyrolyzed product (such as the pyrolysis oil and/or solid product from a pyrolysis reactor) is combined with a torrefied product (such as a solid product from a torrefaction reactor) before they are added to a devolatilization unit and/or reformer reactor. Any standard method can be used for this mixing. In some embodiments, a screw is used to mix the pyrolyzed products and torrefied products. In some embodiments, a feed mixer is used, such as a vertical or horizontal mixer. A vertical mixer consists, for example, of a vertical screw which takes material to the top where it falls back down again, and repeats that process to mix materials. A horizontal mixer includes, for example, paddles or blades attached to a horizontal rotor.

**[0062]** In some embodiments, a mixer with two counter-rotating rotors in a large housing is used to mix the pyrolyzed products and torrefied products. In some embodiments, a Banbury mixer is used. A Banbury mixer includes, for example, two contra-rotating spiral-shaped blades encased in segments of cylindrical housings, intersecting so as to leave a ridge between the blades. The blades may be cored for circulation of heating or cooling media.

**[0063]** In some embodiments, pyrolysis oil is sprayed onto the torrefied product, using, for example, a standard spray pump and nozzle to distribute the pyrolysis oil as a mist over the torrefied product. If desired, the pyrolyzed products and torrefied products can be further mixed after the pyrolysis oil is sprayed onto the torrefied product.

**[0064]** In some embodiments, a pyrolyzed product (such as the pyrolysis oil and/or solid product from a pyrolysis reactor) and/or a torrefied product (such as a solid product from a torrefaction reactor) is combined with another feedstock (such as a feedstock that has not undergone pyrolysis or torrefaction) before they are added to a devolatilization unit. Any standard method can be used for this mixing, such as any of the methods described above for mixing pyrolyzed products and torrefied products.

**[0065]** When different feedstocks are used, they can be used in any ratio and they can be introduced in the same or different locations of a devolatilization unit or reformer reactor. Any ratio of pyrolyzed products to torrefied products can be used, such as a ratio of about 1:0.01 to about 1:100 by weight, such as about 1:0.1, 1:1, or 1:10. Any ratio of pyrolyzed products to another feedstock (such as a feedstock that has not undergone pyrolysis or torrefaction) can be used, such as a ratio of about 1:0.01 to about 1:00 by weight, such as about 1:0.1, 1:1, or 1:10. Any ratio of torrefied products to another feedstock (such as a feedstock that has not undergone pyrolysis or torrefaction, e.g., biomass or a fossil fuel) can be used, such as a ratio of about 1:0.01 to about 1:100 by weight. It will be understood that the specific selection of feedstock ratios can be influenced by many factors, including economics (feedstock prices and availability), process optimization (depending on feedstock composition profiles), utility optimization, equipment optimization, and so on.

**[0066]** Any standard syngas reactor can be used convert a feedstock or a mixture of feedstocks (such as a mixture of two or more of the following: a pyrolyzed feedstock, a torrefied feedstock, and a feedstock that has not been pyrolyzed or torrefied) into syngas. Exemplary reactor configurations include, but are not limited to, fixed-bed reactors (such as countercurrent or co-current fixed-bed reactors), stationary fluidized-bed reactors, circulating fluid-bed reactors (such as those developed by Varnamo, Sweden), oxygen-driven fluid-bed reactors (such as those developed by Biosyn, Canada), bubbling fluid-bed reactors, pressurized fluid-bed reactors (such as pressurized bubbling or circulating fluid-bed reactors), moving-bed gasifiers (such as those developed by BMG, Finland), countercurrent moving-bed reactors, co-current moving-bed reactors, cross-current moving-bed reactors, entrained flow reactors (such as slagging or slag bath entrained-flow reactors), oxygen-blown gasifiers, steam gasifiers, and multistage gasifiers (such as those with a unit for combustion and a unit for gasification or those with a devolatilization unit and a reformer reactor). In some embodiments, the syngas reactor includes a devolatilization unit and a reformer reactor (see, for example, U.S. Pat. No. 6,863,878



and U.S. Patent. App. Pub. No. 2007/0205092, which are each incorporated herein by reference in their entireties).

**[0067]** In some embodiments in which a counter-current fixed-bed reactor is used, the reactor consists of a fixed bed of a feedstock through which a “gasification agent” (such as steam, oxygen, and/or air) flows in counter-current configuration. The ash is either removed dry or as a slag.

**[0068]** In some embodiments in which a co-current fixed-bed reactor is used, the reactor is similar to the counter-current type, but the gasification agent gas flows in co-current configuration with the feedstock. Heat is added to the upper part of the bed, either by combusting small amounts of the feedstock or from external heat sources. The produced gas leaves the reactor at a high temperature, and much of this heat is transferred to the gasification agent added in the top of the bed, resulting in good energy efficiency. Since tars pass through a hot bed of char in this configuration, tar levels are much lower than the counter-current type.

**[0069]** In some embodiments in which a fluidized-bed reactor is used, the feedstock is fluidized in oxygen and steam or air. The ash is removed dry or as heavy agglomerates that defluidize. The temperatures are relatively low in dry-ash reactors, so the feedstock is desirably highly reactive. The agglomerating reactors have slightly higher temperatures. Feedstock throughput is higher than for the fixed bed, but not as high as for the entrained flow reactor. Recycle or subsequent combustion of solids can be used to increase conversion. Fluidized-bed reactors are most useful for feedstocks that form highly corrosive ash that would damage the walls of slagging reactors.

**[0070]** In some embodiments in which an entrained-flow reactor is used, a dry pulverized solid, an atomized liquid feedstock, or a feedstock slurry is gasified with oxygen or air in co-current flow. The gasification reactions take place in a dense cloud of very fine particles. The high temperatures and pressures also mean that a higher throughput can be achieved; thermal efficiency is somewhat lower, however, as the gas is cooled before it can be cleaned with existing technology. The high temperatures also mean that tar and methane are not present in the product gas; the oxygen requirement can be higher than for the other types of reactors.

**[0071]** Entrained-flow reactors remove the major part of the ash as a slag, as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced either as a very fine dry fly ash or as a black-colored fly-ash slurry. Some feedstocks, in particular certain types of biomass, can form slag that is corrosive for ceramic inner walls that serve to protect the reactor outer wall. However, some entrained-bed reactors do not possess a ceramic inner wall but have an inner water- or steam-cooled wall covered with partially solidified slag. These types of reactors do not suffer from corrosive slags. Some feedstocks have ashes with very high ash-fusion temperatures. In this case, limestone can be mixed with the feedstock prior to gasification. Addition of limestone usually can lower the fusion temperatures. In some embodiments, the feedstock is pulverized, which requires somewhat more energy than for the other types of reactors.

**[0072]** Torrefied or pyrolyzed biomass (or other C-containing feedstock) can be transported by any known means, such as by truck, train, ship, barge, tractor trailer, or any other vehicle or means of conveyance (e.g., a pipeline). In some embodiments, a heated truck is used to transport pyrolysis oil or torrefied material to a unit for conversion to products.

**[0073]** The present invention, in certain variations, can utilize modular units for the pyrolysis, torrefaction, devolatilization, reforming, and/or gasification of biomass and other feedstocks to form useful products. A “modular unit” means an apparatus that is capable of either operably standing alone or of being operably connected with at least one other modular unit.

**[0074]** In some embodiments, a modular unit for the pyrolysis or torrefaction is in communication with (such as operably linked to) a modular unit for converting the pyrolyzed or torrefied feedstock into syngas. In some embodiments, a modular unit for the pyrolysis or torrefaction is in communication with (such as operably linked to) a modular unit for devolatilizing the feedstock. In some embodiments, these modular units are also in communication with a modular unit for reforming the product of the devolatilization unit and/or one or more modular units for the conversion of syngas to another product, such as an alcohol.

**[0075]** Placement of modular units near feedstock sources can minimize transportation energy and thereby increase the yield of syngas (and/or derivatives of syngas) per amount of energy expended.

**[0076]** In some embodiments, the modular unit is a portable unit, such as a unit mounted on skids, a platform, or a conveyor to facilitate the movement of the modular unit between different locations. In some embodiments, the modular unit can be assembled and/or disassembled in fewer steps or in less time than for a unit that is not capable of being transported.

**[0077]** In some embodiments, a modular unit can be easily dismantled into one or more pieces that can be transported on the back of a tractor trailer. In some embodiments, the modular unit weighs less than or about 80,000, 60,000, or 40,000 lbs. In some embodiments, the modular unit can be transported in a vehicle that satisfies the specifications for vehicle size and weight established by the U.S. Department of Transportation, which governs the use of the interstate highway system.

**[0078]** Certain embodiments use modular units and/or methods of distribution of these units in accordance with the description in co-pending U.S. patent application Ser. No. 12/166,117, entitled “MODULAR AND DISTRIBUTED METHODS AND SYSTEMS TO CONVERT BIOMASS TO SYNGAS,” with an effective priority date of Jul. 9, 2007, whose assignee is the same as the assignee of this patent application, and which is hereby incorporated herein by reference.

**[0079]** The syngas produced as described according to the present invention can be utilized in a number of ways. Syngas can generally be chemically converted and/or purified into hydrogen, carbon monoxide, methane, graphite, olefins (such as ethylene), oxygenates (such as dimethyl ether), alcohols (such as methanol and ethanol), paraffins, and other hydrocarbons.

**[0080]** The syngas produced according to the methods and systems of the invention can further produce: a linear or branched C<sub>5</sub>-C<sub>15</sub> hydrocarbon, diesel fuel, gasoline, waxes, or olefins by Fischer-Tropsch chemistry; methanol, ethanol, and mixed alcohols by a variety of catalysts; isobutane by isosynthesis; ammonia by hydrogen production followed by the Haber process; aldehydes and alcohols by oxosynthesis; and many derivatives of methanol including dimethyl ether, acetic acid, ethylene, propylene, and formaldehyde by various processes.



**[0081]** In certain embodiments, the syngas is converted to high yields of alcohols, particularly ethanol. Syngas can be selectively converted to ethanol by means of a chemical catalyst, such as described in U.S. patent application Ser. No. 12/166,203, entitled "METHODS AND APPARATUS FOR PRODUCING ALCOHOLS FROM SYNGAS," filed Jul. 1, 2008, whose assignee is the same as the assignee of this patent application, and which is hereby incorporated herein by reference. As is known in the art, syngas can also be fermented to a mixture comprising ethanol using microorganisms.

**[0082]** The syngas produced according to the methods and systems of the invention can also be converted to energy. Syngas-based energy-conversion devices include a solid-oxide fuel cell, Stirling engine, micro-turbine, internal combustion engine, thermoelectric generator, scroll expander, gas burner, thermo-photovoltaic device, or gas-to-liquid device. In some cases, the output syngas of two, or more, reactors can be combined to supply syngas to downstream subsystems comprised of syngas coolers, syngas cleaners, and syngas-based energy-conversion devices.

**[0083]** This invention has been described and specific examples of the invention have been portrayed. While the invention has been described in terms of particular variations, those of ordinary skill in the art will recognize that the invention is not limited to the variations described. In addition, where methods and steps described above indicate certain events occurring in certain order, those of ordinary skill in the art will recognize that the ordering of certain steps may be modified and that such modifications are in accordance with the variations of the invention. Additionally, certain of the steps may be performed concurrently in a parallel process when possible, as well as performed sequentially as described above.

**[0084]** All publications, patents, and patent applications cited in this specification are herein incorporated by reference in their entirety as if each publication, patent, or patent application were specifically and individually put forth herein.

**[0085]** In this detailed description, reference has been made to multiple embodiments. Other embodiments that do not provide all of the features and advantages set forth herein may be utilized, without departing from the spirit and scope of the present invention. To the extent there are variations of the invention, which are within the spirit of the disclosure or equivalent to the inventions found in the claims, it is the intent that this patent will cover those variations as well.

What is claimed is:

1. A method of forming syngas, the method comprising the steps of:

- (a) pyrolyzing or torrefying a carbon-containing first feed material to form a pyrolyzed or torrefied first feed material; and
- (b) converting the pyrolyzed or torrefied first feed material into syngas.

2. The method of claim 1, further comprising converting a second feed material that has not been pyrolyzed or torrefied into syngas.

3. The method of claim 1, further comprising combining the pyrolyzed or torrefied first feed material with a second feed material that has not been pyrolyzed or torrefied such that both the pyrolyzed or torrefied first feed material and the second feed material are converted into syngas.

4. The method of claim 1, comprising pyrolyzing a carbon-containing first feed material to form a pyrolyzed first feed material, torrefying a carbon-containing feed second material

to form a torrefied second feed material, and converting the pyrolyzed first feed material and the torrefied second feed material into syngas.

5. The method of claim 1, further comprising introducing the torrefied first feed material into a pyrolysis reactor to form a pyrolyzed first feed material.

6. The method of claim 1, wherein converting the pyrolyzed or torrefied first feed material into syngas comprises passing the pyrolyzed or torrefied first feed material through a heated reaction vessel to form syngas.

7. The method of claim 1, wherein converting the pyrolyzed or torrefied first feed material into syngas comprises the substeps of:

- (i) devolatilizing the pyrolyzed or torrefied first feed material to form a gas phase and/or solid phase in a devolatilization unit; and
- (ii) passing the gas phase and/or solid phase through a heated reaction vessel to form syngas.

8. The method of claim 1, wherein step (a) is conducted in the presence of a catalyst.

9. A method of forming syngas, the method comprising converting a pyrolyzed or torrefied first feed material and a second carbon-containing feed material that has not been pyrolyzed or torrefied into syngas.

10. The method of claim 9, comprising pyrolyzing a carbon-containing first feed material to form the pyrolyzed first feed material, torrefying a carbon-containing third feed material to form a torrefied third feed material, and converting the pyrolyzed first feed material, the second feed material, and the torrefied third feed material into syngas.

11. The method of claim 9, further comprising combining the pyrolyzed or torrefied first feed material and the second feed material prior to converting the pyrolyzed or torrefied first feed material and the second feed material into syngas.

12. The method of claim 9, wherein the method is conducted, at least in part, in the presence of a catalyst.

13. The method of claim 9, wherein converting the pyrolyzed or torrefied first feed material and the second feed material into syngas comprises the steps of:

- (a) devolatilizing the pyrolyzed or torrefied first feed material and the second feed material to form a gas phase and/or solid phase in a devolatilization unit; and
- (b) passing the gas phase and/or solid phase through a heated reaction vessel to form syngas.

14. The method of claim 9, further comprising introducing the torrefied first feed material into a pyrolysis reactor to form a pyrolyzed first feed material.

15. A method of forming syngas, the method comprising the steps of:

- (a) devolatilizing a pyrolyzed or torrefied first feed material to form a gas phase and solid phase in a devolatilization unit; and
- (b) passing the gas phase and solid phase through a heated reaction vessel to form syngas.

16. The method of claim 15, comprising pyrolyzing a carbon-containing feed material, optionally in the presence of a catalyst, to form the first feed material.

17. The method of claim 15, comprising torrefying a carbon-containing feed material, optionally in the presence of a catalyst, to form the first feed material.

18. The method of claim 15, further comprising converting a second feed material that has not been pyrolyzed or torrefied into syngas.



**19.** The method of claim **18**, further comprising combining the pyrolyzed or torrefied first feed material with a second feed material that has not been pyrolyzed or torrefied such that both the pyrolyzed or torrefied first feed material and the second feed material are converted into syngas.

**20.** The method of claim **18**, comprising pyrolyzing a carbon-containing first feed material to form the pyrolyzed first feed material, torrefying a carbon-containing third feed material to form a torrefied third feed material, and converting the pyrolyzed first feed material, the second feed material, and the torrefied third feed material into syngas.

**21.** The method of claim **15**, further comprising combining the pyrolyzed or torrefied first feed material and the second feed material prior to converting the pyrolyzed or torrefied first feed material and the second feed material into syngas.

**22.** The method of claim **15**, further comprising introducing the torrefied first feed material into a pyrolysis reactor to form a pyrolyzed first feed material.

**23.** The method of any of claims **1**, **9**, or **15**, wherein the method is conducted, at least in part, in one or more modular units.

**24.** The method of any of claims **1**, **9**, or **15**, further comprising the step of converting the syngas to a product.

**25.** The method of claim **24**, wherein the product is selected from the group consisting of an alcohol, an olefin, an aldehyde, a hydrocarbon, an ether, hydrogen, ammonia, and acetic acid.

**26.** The method of claim **25**, wherein the hydrocarbon is a linear or branched C<sub>5</sub>-C<sub>15</sub> hydrocarbon.

**27.** The method of claim **25**, wherein the alcohol is methanol.

**28.** The method of claim **25**, wherein the alcohol is ethanol.

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