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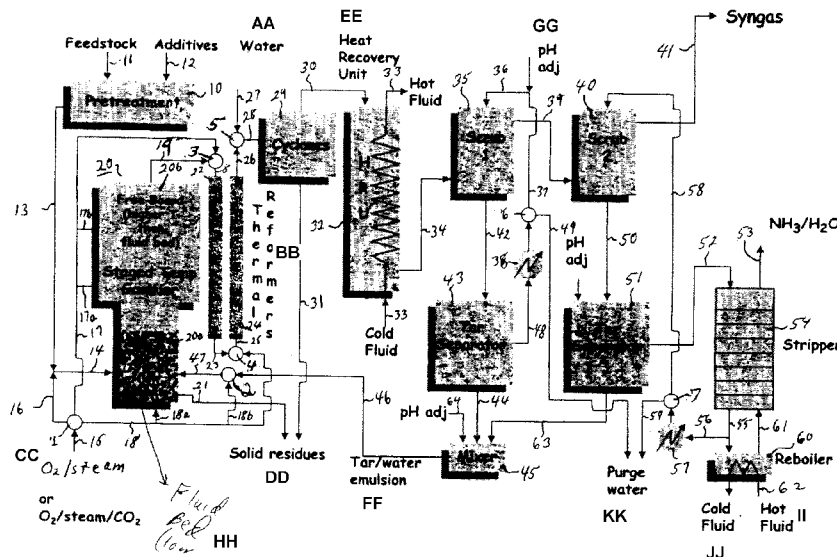


Fig. 1

(57) Abstract: A process for producing synthesis gas from biomass in which biomass is contacted with oxygen and steam, where-  
in the oxygen is present in an amount effective to oxidize the biomass partially and to heat the biomass to a temperature of at least  
500°C and no greater than 750°C At least a portion of the partially oxidized biomass then is treated with oxygen and steam to heat  
the biomass to a temperature of at least 800°C, thereby producing a synthesis gas, which then is recovered

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## **PRODUCTION OF SYNTHESIS GAS THROUGH CONTROLLED OXIDATION OF BIOMASS**

This application claims priority based on provisional application Serial No. 61/203,181, filed December 19, 2008, the contents of which are incorporated herein by reference in their entirety.

This invention relates to the production of synthesis gas, or of syngas, from biomass. More particularly, this invention relates to the production of synthesis gas from biomass by contacting biomass, in a first step, with oxygen and steam, wherein the oxygen is present in an amount effective to oxidize the biomass, thereby producing heat sufficient to heat the biomass to a temperature of at least 500°C and no greater than 750°C. In a second step, at least a portion of the oxidized biomass produced in the first step is treated with oxygen and steam to heat the biomass to a temperature of at least 800°C, thereby producing synthesis gas.

Synthesis gas, or syngas, includes carbon monoxide (CO) and hydrogen (H<sub>2</sub>), with small amounts of carbon dioxide and residual hydrocarbons, and has a variety of uses. Synthesis gas may be used as a fuel gas in internal combustion engines, in gas turbines, as well as in gas fired steam boiler plants, or may be used to produce other desired materials, such as methanol and ethanol.

Synthesis gas may be produced by gasifying residual biomass materials, such as forest residues, agricultural residues, spent structural wood materials, and urban biomass, such as municipal solid waste. The gasification of biomass provides a crude synthesis gas which may include impurities such as ammonia (NH<sub>3</sub>), sulfur compounds (such as hydrogen sulfide (H<sub>2</sub>S) and carbonyl sulfide (COS)), chlorine compounds (such as HCl), volatile metals, tars, fines (in the form of submicron particles containing metals

and metal salts), and char (solid particulates typically above 0.001 mm and containing metals and metal salts). Such impurities, however, limit the ability of the synthesis gas to be used as a fuel or to be employed in the synthesis of other useful materials.

For example, when synthesis gas is used to produce methanol, the synthesis gas is reacted under pressure in the presence of a catalyst. The impurities in a crude synthesis gas produced as a result of gasifying biomass may poison or deactivate the catalyst.

Various methods have been devised for producing crude synthesis gas from biomass, and then cleaning or conditioning the crude synthesis gas. German Patent No. 4317319 discloses the gasification of biomass in the form of granular, shredded raw materials in two high-pressure, fixed-bed gasification units at temperatures up to 1200°C. Oxygen, water vapor, and raw carbon dioxide (CO<sub>2</sub>) gas also were introduced into the fixed-bed gasification units. The raw synthesis gas produced in the fixed-bed gasification units is scrubbed and cooled with water and then cooled further with the use of indirect heat exchangers. From these steps, various organic components are removed from the gas stream, such as phenol and tars. These can be recycled back to the fixed bed gasifier or fed to the entrained-flow gasifier described below. The gas stream, free of phenol and tars, then is sent to a combined two-stage gas cooling and scrubbing process step, where mixtures of water and methanol are used to reduce the gas temperature to - 25°C and to remove ammonia, hydrogen cyanide, and residual phenolic compounds. Hydrocarbons, some of which may be halogenated, also are removed by the chilled mixture of water and methanol. The hydrocarbon-rich compounds recovered from the chilled water and methanol mixture subsequently can

be sent to the entrained-flow gasification unit while the gas stream exiting the low temperature scrubbing unit is dried before it proceeds to a carbonyl sulfide (COS) hydrolysis unit. In that part of the process, the COS in the synthesis gas is reacted with steam to form hydrogen sulfide (H<sub>2</sub>S) and CO<sub>2</sub>. The H<sub>2</sub>S then is removed from the gas stream in a selective H<sub>2</sub>S scrubbing process step. The conditioned synthesis gas is used as fuel in a gas and steam power plant. The H<sub>2</sub>S-rich stream exiting the selective H<sub>2</sub>S scrubbing process is sent to a sulfur recovery process which will produce pure sulfur and a stream of raw CO<sub>2</sub>. The raw CO<sub>2</sub> then is subjected to further purification steps before it is compressed and/or liquefied to manufacture high purity CO<sub>2</sub> gas.

Biomass fractions, such as tars and phenols, are used with the fines present in the raw material as feedstock for a high pressure, entrained-flow gasification unit at temperatures reaching 1400°C. Raw synthesis gas from the fixed-bed gasification units also can be introduced and converted in the entrained flow gasifier. The crude synthesis gas stream leaving the entrained flow gasifier is subjected to soot scrubbing. The gas stream then is split into two parallel streams, one of which is fed to a COS hydrolysis unit and the other is fed to a carbon monoxide (CO) conversion unit. The distribution of the synthesis gas stream between those two process units is effected to achieve a desired hydrogen to carbon monoxide (H<sub>2</sub>/CO) ratio of the gas, which is to be used for a methanol synthesis plant. Both gas streams then are mixed and sent to a cooling stage before the gas is fed to a very-low temperature gas scrubbing process, which uses chilled methanol to reduce to trace levels the H<sub>2</sub>S and CO<sub>2</sub> concentrations in the synthesis gas. Through solvent regeneration steps, the H<sub>2</sub>S and CO<sub>2</sub> are removed from the methanol and sent to the same sulfur recovery and/or purification steps as

described for the fixed-bed gasification's synthesis gas conditioning process. The scrubbed synthesis gas is fed to a methanol synthesis plant.

German Patent No. 1003150 discloses the gasification of biomass in three gasification units, two of which are of the fixed-bed type and the third is the entrained-flow type. The synthesis gas, which exits the fixed-bed gasification units, is rich in CO<sub>2</sub>. The CO<sub>2</sub>-rich synthesis gas is quenched and cooled. The entrained-flow gasification unit's synthesis gas is scrubbed to remove soot before some of the CO<sub>2</sub>-rich synthesis gas is added to provide the desired H<sub>2</sub>/CO ratio for the methanol synthesis plant. The recombined synthesis gas is sent to a CO conversion stage and a cooling stage before it is cooled. All the synthesis gas streams then are sent to a very low temperature scrubbing to purify the synthesis gas further, which then is fed to the methanol synthesis plant. The remainder of the gas is sent either to a gas and steam power plant, or burnt in a boiler after it is mixed with raw, synthesis, and/or natural gas.

The processes described in the above-mentioned German patents are conducted under high severity conditions, and incur high capital and operating costs.

United States published patent Application No. 2007/0270511 discloses the gasification of biomass to produce syngas in which a first portion of biomass is gasified in the presence of air to produce syngas. This syngas is combusted to produce a hot flue gas. A second portion of the biomass is gasified in a steam gasifier, at a temperature of from 750°C to 900°C, to produce syngas. The steam gasifier includes a heat exchanger tubing system, through which is passed the hot flue gas, thereby providing heat to the steam gasifier.

Biomass materials in general are rich in inorganic materials, and such inorganic materials may contain salts that have low melting points, such as, for example, NaCl (801°C), KCl (776°C), CaCl<sub>2</sub> (772°C), MgCl<sub>2</sub> (714°C), and FeCl<sub>2</sub> (677°C). Such biomass materials also may include aluminum, which melts at 660°C.

Thus, when biomass is gasified at temperatures such as those described in the above-mentioned German patents and published U.S. patent application, the inorganic materials mentioned hereinabove will melt and induce agglomerations and the formation of deposits in the gasifier. In addition, if the gasification is conducted in the presence of a fluidized bed of particulate material, such melting of inorganic material also will cause agglomeration of the particulate material in the fluidized bed, which leads to eventual loss of fluidization.

The present invention provides an efficient method of producing synthesis gas from biomass.

In accordance with an aspect of the present invention, there is provided a process for producing synthesis gas from biomass. The process comprises, in a first step, contacting the biomass with an oxidizing gas comprising oxygen and steam. The oxygen is present in an amount effective to oxidize the biomass and to heat the biomass to a temperature of at least 500°C and no greater than 750°C. In a second step, at least a portion of the oxidized biomass produced in the first step is treated with an oxidizing gas comprising oxygen and steam to heat the biomass to a temperature of at least 800°C, to produce synthesis gas. The synthesis gas produced then is recovered.

Biomass-rich materials which may be gasified in accordance with the present

invention include, but are not limited to, homogeneous biomass-rich materials, non-homogeneous biomass-rich materials, heterogeneous biomass-rich materials, and urban biomass.

In general, homogeneous biomass-rich materials are biomass-rich materials which come from a single source. Such materials include, but are not limited to, materials from coniferous trees or deciduous trees of a single species, agricultural materials from a plant of a single species, such as hay, corn, or wheat, for example, primary sludge from wood pulp, and wood chips.

Non-homogeneous biomass-rich materials in general are materials which are obtained from plants of more than one species. Such materials include, but are not limited to, forest residues from mixed species, and tree residues from mixed species obtained from debarking operations or sawmill operations.

Heterogeneous biomass-rich materials in general are materials that include biomass and non-biomass materials such as plastics, metals, and/or contaminants such as sulfur, halogens, or non-biomass nitrogen contained in compounds such as inorganic salts or organic compounds. Examples of such heterogeneous biomass-rich materials include, but are not limited to, urban biomass such as municipal solid waste, such as refuse derived fuel, solid recovered fuel, sewage sludge, used electrical transmission poles and railroad ties, which may be treated with creosote, pentachlorophenol, or copper chromium arsenate, and wood from construction and demolition operations which may contain one or more of the above chemicals as well as paints and resins.

In a non-limiting embodiment, prior to the contacting of the biomass with oxidizing gas in the first step, the biomass is admixed with at least one additive material,

which neutralizes impurities such as chlorine, fluorine, and sulfur, which may be present in the biomass. In a non-limiting embodiment, the at least one additive is at least one adsorbent material. Such adsorbent materials include, but are not limited to, calcium oxide, or mixtures of calcium oxide, calcined limestone, ash materials, olivine (a silicate of iron and magnesium), and mixtures of calcium and magnesium oxides.

In another non-limiting embodiment, the at least one additive material is added to the biomass in an amount of from about 1.25 to about 3.0 times the stoichiometric quantity required for full neutralization of chlorine and other halogens, as well as sulfur present in the biomass. The term "neutralization," as used herein, includes the formation of stable salts such as  $\text{CaCl}_2$ ,  $\text{CaF}_2$ ,  $\text{CaS}$ , and the corresponding salts of magnesium and iron.

In the first step, the biomass is contacted with the oxidizing gas under conditions which effect a partial oxidation of the biomass. As a result of such partial oxidation, the biomass decomposes thermally, and there are produced a solid carbonaceous residue, gases such as  $\text{CO}_2$ , steam, and some carbon monoxide and hydrogen, and vapors of intermediate species such as low molecular weight alkyl and aromatic hydrocarbons, and phenolics such as phenol, catechols, and methoxylated, alkylated, and alkoxyated phenols.

As noted hereinabove, the biomass, in the first step, is heated to a temperature of at least  $500^\circ\text{C}$  and no greater than  $750^\circ\text{C}$ . In another non-limiting embodiment, the biomass, in the first step, is heated to a temperature of at least  $600^\circ\text{C}$  and no greater than  $750^\circ\text{C}$ . In another non-limiting embodiment, the biomass, in the first step, is heated to a temperature of at least  $600^\circ\text{C}$  and no greater than  $725^\circ\text{C}$ . In a further non-

limiting embodiment, the biomass, in the first step, is heated to a temperature of at least 600°C and no greater than 700°C. In yet another non-limiting embodiment, the biomass, in the first step, is heated to a temperature of at least 600°C and no greater than 660°C.

In a non-limiting embodiment, the oxidizing gas, in the first step, further comprises nitrogen in an amount which does not exceed 60 vol.% of the oxidizing gas. In one non-limiting embodiment, the oxidizing gas includes oxygen-enriched air and steam, in which oxygen is present in an amount of up to about 40 vol.% of the oxidizing gas, and nitrogen is present in an amount that does not exceed 60 vol.% of the oxidizing gas.

In another non-limiting embodiment, the biomass, in the first step, is contacted with oxygen and steam in the absence of nitrogen. In a non-limiting embodiment, oxygen is present in such nitrogen-free gas in an amount which does not exceed 40 vol.%. In yet another non-limiting embodiment, oxygen is present in such nitrogen-free gas in an amount of from about 30 vol.% to about 40 vol.%.

In another non-limiting embodiment, the oxidizing gas, in the first step, further comprises carbon dioxide. In a further non-limiting embodiment, carbon dioxide is present in the oxidizing gas in an amount that does not exceed 20 vol.%. In yet another non-limiting embodiment, carbon dioxide is present in the oxidizing gas in an amount of from about 10 vol.% to about 20 vol.%.

In a further non-limiting embodiment, oxygen is present in the oxidizing gas in an amount of from about 30 vol.% to about 40 vol.%, carbon dioxide is present in the oxidizing gas in an amount of from about 10 vol.% to about 20 vol.%, and the remainder

of the oxidizing gas essentially is steam. Trace amounts of argon may be present.

In another non-limiting embodiment, the biomass, in the first step, is contacted with oxygen at a weight ratio of oxygen to biomass that does not exceed 0.35 times the stoichiometric weight ratio needed for complete combustion, i.e., total oxidation of the biomass.

In a further non-limiting embodiment, the biomass, in the first step, is contacted with oxygen at a weight ratio of oxygen to biomass of from about 0.2 to about 0.35 weight of the stoichiometric weight ratio needed for complete combustion of the biomass. In yet another non-limiting embodiment, the biomass is contacted with oxygen at a weight ratio of oxygen to biomass of from about 0.25 to about 0.30 of the stoichiometric weight ratio needed for complete combustion of the biomass.

In another non-limiting embodiment, in the first step, the biomass is contacted with oxygen and steam in a bed of particulate material, whereby the passage of oxygen and steam through such bed provides a fluidized bed of the particulate material. Such particulate materials include, but are not limited to, alumina, olivine, silica, anthracite, desulfurized petroleum coke, and in general, any stable refractory material. In a non-limiting embodiment, the particulate material is selected from the group consisting alumina, olivine and silica. In another non-limiting embodiment, the particles have a diameter of from about 200 microns to about 600 microns.

In another non-limiting embodiment, the biomass is contacted, in the first step, with oxygen and steam for a period of time that does not exceed 10 seconds. In a further non-limiting embodiment, the biomass is contacted, in the first step, with oxygen and steam for a period of time that does not exceed 3 seconds. In yet another non-

limiting embodiment, the biomass is contacted, in the first step, with oxygen and steam for a period of time that does not exceed one second.

Although the scope of the present invention is not intended to be limited to any theoretical reasoning, as the biomass is contacted with oxygen and steam in the first step, the biomass is oxidized partially, and is decomposed thermally, thereby producing a solid carbonaceous residue, gases such as CO<sub>2</sub>, steam, and some carbon monoxide (CO) and hydrogen (H<sub>2</sub>), and vapors of intermediate species such as low molecular weight alkyl and aromatic hydrocarbons, and phenolics as hereinabove described.

When the biomass is contacted with oxygen and steam, in the first step, in the presence of a fluidized bed, the solid carbonaceous residue produced in the first step remains in the fluidized bed and provides the bulk of the exothermal heat of oxidation, thereby maintaining the fluidized bed at the temperatures hereinabove described. The oxygen used in the first step essentially is consumed in such step, while a portion of the carbonaceous residue formed during the first step is consumed as well, and another portion of the carbonaceous residue is entrained as char. The char particles also may contain inorganic materials initially present in the biomass feedstock.

Some cracking of intermediates, i.e., low molecular weight hydrocarbons, phenolics, and aromatics, may occur during the first step; however, higher temperatures are required to convert the residual carbon in the entrained char particles, and additionally to crack and reform the intermediate vapors containing the low molecular weight alkyl and aromatic hydrocarbons, and phenolics. Thus, in the second step, at least a portion of the partially oxidized biomass produced in the first step is treated with an oxidizing gas comprising oxygen and steam to heat the biomass to a temperature of

at least 800°C to produce synthesis gas.

In a non-limiting embodiment, the partially oxidized and thermally decomposed biomass, in the second step, is heated to a temperature of from about 800°C to about 1,000°C. In yet another non-limiting embodiment, the oxidized biomass, in the second step, is heated to a temperature of from about 925°C to about 1,000°C.

In a non-limiting embodiment, the oxidizing gas, in the second step, further comprises nitrogen in an amount which does not exceed 60 vol.% of the oxidizing gas. In one non-limiting embodiment, the oxidizing gas includes oxygen-enriched air and steam, in which oxygen is present in an amount of up to about 40 vol.% of the oxidizing gas, and nitrogen is present in an amount that does not exceed 60 vol.% of the oxidizing gas.

In another non-limiting embodiment, the partially oxidized biomass, in the second step, is contacted with oxygen and steam in the absence of nitrogen. In a non-limiting embodiment, oxygen is present in such nitrogen-free gas in an amount which does not exceed 40 vol. %. In yet another non-limiting embodiment, oxygen is present in such nitrogen-free gas in an amount of from about 30 vol. % to about 40 vol. %.

In another non-limiting embodiment, the oxidizing gas, in the second step, further comprises carbon dioxide. In a further non-limiting embodiment, carbon dioxide is present in the oxidizing gas in an amount that does not exceed 20 vol.%. In yet another non-limiting embodiment, carbon dioxide is present in the oxidizing gas in an amount of from about 10 vol. % to about 20 vol. %.

In a further non-limiting embodiment, oxygen is present in such oxidizing gas in an amount of from about 30 vol. % to about 40 vol. %, carbon dioxide is present in the

oxidizing gas in an amount of from about 10 vol. % to about 20 vol. %, and the remainder of the oxidizing gas essentially is steam. Trace amounts of argon may be present.

In a non-limiting embodiment, the oxidized biomass, in the second step, is treated with the oxygen and steam for a period of time of from about 0.5 seconds to about 10 seconds. In another non-limiting embodiment, the oxidized biomass, in the second step, is treated with the oxygen and steam for a period of time of from about 4 seconds to about 8 seconds.

Alternatively, in a further non-limiting embodiment, the oxidized biomass, in the second step, is treated with oxygen and steam in a first stage to a temperature of at least 800°C, followed by further treatment with oxygen and steam in a second stage. The oxidized biomass is heated to a temperature in the second stage which is higher than that of the first stage. In a non-limiting embodiment, the oxidized biomass is heated in the first stage to a temperature of at least 800°C and does not exceed 850°C.

In another non-limiting embodiment, the oxidized biomass is heated in the second stage to a temperature of at least 900°C. In a further non-limiting embodiment, the oxidized biomass is heated in the second stage to a temperature of from about 900°C to about 1,000°C. In yet another non-limiting embodiment, the oxidized biomass is heated in the second stage to a temperature of from about 925°C to about 975°C.

In yet another non-limiting embodiment, the oxidized biomass is heated in the first stage to a temperature of from 800°C to 850°C, and is heated in the second stage to a temperature of from 925°C to 975°C.

When the oxidized biomass is contacted with oxygen and steam in the second

step, whereby the oxidized biomass is heated to a temperature of at least 800°C, carbon in the char is converted fully by the steam to generate hydrogen and carbon monoxide, and steam reforming of the intermediates yields more hydrogen and carbon monoxide. In general, the inorganic materials which are present in the char in general are exposed to temperatures higher than their melting points. Such inorganic materials will melt and stay melted in the char particles. Deposition of char particles and/or inorganic materials on the walls of the gasification vessel is minimal because the particles are entrained under plug flow conditions.

In a non-limiting embodiment, the biomass is gasified to produce syngas in a gasification vessel or gasifier which has a fluidized bed section and a freeboard section. The biomass is fed to the fluidized bed section of the gasifier by means known to those skilled in the art, such as, for example, through pressure tight star valves (as used in the pulp and paper sector to feed digesters) and a lock hopper system equipped with interlocking valves, and coupled to a belt conveyor which feeds a transfer screw, which ejects the biomass into the fluidized bed section of the gasifier. Alternatively, the biomass may be fed into the fluidized bed section of the gasifier by means of a compression screw working against a plug to create a pressure seal against the gasifier.

In general, the gasifier is operated at a pressure that does not exceed 10 atm. The fluidized bed section includes particles of a fluidizable material, such as alumina or olivine, having a particle size of from about 200 microns to about 600 microns. Oxygen and steam are introduced into the fluidized bed section of the gasifier to provide a gas velocity of from about 0.7 m/sec. to about 1.5 m/sec., thereby providing a bubbling

fluidized bed of the particulate material. The oxygen is introduced into the fluidized bed section at a weight ratio of oxygen to biomass of from about 0.20 to about 0.35 of the stoichiometric weight ratio required for complete combustion of the biomass, and thereby maintaining the fluidized bed section of the gasifier at a temperature of from about 600°C to about 700°C.

As the biomass is introduced into the fluidized bed section, the biomass is oxidized partially as it decomposes thermally to produce a solid carbonaceous residue that stays in the fluidized bed, gases, such as CO<sub>2</sub> and some CO and H<sub>2</sub>, steam from moisture in the biomass as well as from dehydration reactions, and vapors of intermediate species such as low molecular weight alkyl and aromatic hydrocarbons, and phenolics as hereinabove described. The gases and vapors leave the fluidized bed rapidly. In general, the biomass is treated with the oxygen and steam in the first step, for a period of time not exceeding 3 seconds.

The solid carbonaceous material that remains in the fluidized bed reacts with the oxygen that is fed to the fluidized bed section, thereby providing the exothermal heat of oxidation as well as providing CO and CO<sub>2</sub> because the oxidation of the biomass in the fluidized bed section is substoichiometric. The oxygen essentially is consumed in the fluidized bed section, whose carbon loading is constant over time, i.e., carbon is produced by thermal decomposition of the biomass, then is consumed by the oxidation, and then the small particles become entrained as char when the size of the particles shrinks to a size which results in their entrainment (typically less than 200 microns). The char particles contain inorganic materials such as salts, for example, which initially are present in the biomass.

The gas and vapors produced as a result of the partial oxidation of the biomass move from the fluidized bed section of the gasifier through a disengaging zone (i.e., a zone separating the fluidized bed section from the freeboard section) prior to entering the freeboard section.

Although some cracking of the intermediate species hereinabove described takes place in the fluidized bed section of the gasifier, in general higher temperatures are required to effect conversion of the residual carbon in the entrained char particles and additionally to crack and steam reform the vapors of the intermediate species. Such intermediate species include low molecular weight hydrocarbons, such as methane, ethylene, ethane, monomeric and dimeric aromatic hydrocarbons, phenol, functionalized phenols, i.e., catechols, methoxylated phenol, alkylated phenol and alkoxyated phenol, and higher molecular weight hydrocarbons known as "tar," i.e., a complex mixture of functionalized polyaromatics and polyphenolic compounds.

The gas and vapors produced in the fluidized bed section pass through the disengaging zone into the freeboard section, in which the gas and vapors are contacted with oxygen and steam to reach a temperature of from about 925°C to about 1,000°C. The oxygen and steam are introduced into the freeboard section of the gasifier in such an amount that the velocity of the gaseous phase is maintained from about 0.3 m/sec. to about 0.7 m/sec. In general, gas residence times in the freeboard section of the gasifier are from about 4 seconds to about 8 seconds.

In the freeboard section, the phenolics are converted into simple aromatics, and tar cracking and tar reforming are effected. Carbon in the char essentially is converted fully by the steam and CO<sub>2</sub> to generate H<sub>2</sub> and CO, and steam reforming of the vapors

of the intermediate hydrocarbons also generates H<sub>2</sub> and CO. Inorganic materials present in the char will melt. Deposition of inorganic materials on the walls of the gasifier, however, is minimal due to particle entrainment in the existing plug flow regime.

As noted hereinabove, in one alternative embodiment, the heating of the partially oxidized biomass to produce synthesis gas may be effected in a combination of a first stage, and a second stage, wherein the partially oxidized biomass is heated to a temperature in the second stage which is greater than that of the first stage.

In one non-limiting embodiment, the first stage is conducted in the freeboard section of the gasifier, and the second stage is conducted in one or more tubular flow reactors. In a non-limiting embodiment, the one or more tubular flow reactor(s) is (are) in the form of refractorized and insulated carbon steel pipes. In another non-limiting embodiment, the heating in the second stage is conducted in two tubular flow reactors which are connected to each other so as to form a U-shaped configuration.

In a non-limiting embodiment, the oxidized biomass is contacted with oxygen and steam in the freeboard section of the gasifier at a temperature of from about 800°C to about 850°C. The oxygen and steam are introduced into the freeboard section of the gasifier in such amounts that maintain a gaseous velocity of from about 0.3 m/sec. to about 0.7 m/sec., and the reaction time is from about 4 seconds to about 8 seconds, as hereinabove described, to begin the conversion of the oxidized biomass to a crude synthesis gas. The gas produced in the freeboard section also has char particles entrained therein.

The gas and entrained particles then are passed from the freeboard section of the gasifier to one or more tubular flow reactors. In a non-limiting embodiment,

additional oxygen and steam are added to the tubular flow reactor(s). In the tubular flow reactor(s), the gas is heated to a temperature of from about 925°C to about 975°C, and in general, the reaction time in the tubular flow reactor(s) is from about 1 second to about 2 seconds, which is sufficient to complete the conversion of the oxidized biomass to a crude synthesis gas.

A crude synthesis gas product thus is produced by gasifying biomass in the fluidized bed and freeboard sections of the gasifier, and optionally in one or more tubular flow reactors, under the conditions hereinabove described. Such crude synthesis gas then may be conditioned to provide a clean synthesis gas product which may be used as a fuel or may be used to synthesize other compounds such as alcohols (eg., methanol or ethanol) or hydrocarbons.

For example, the crude synthesis gas may be cooled, using water, to a temperature lower than 750°C. The crude synthesis gas then is passed to one or more cyclones to remove any remaining particles having a size over 10 microns. The gas which leaves the cyclone(s) is passed to a heat recovery unit in which the gas travels in a tube contained in the unit. Thermal oil or water surrounding the tube recovers heat from the gas.

The crude synthesis gas then is scrubbed in a scrubbing system having two scrubbers. The first scrubber is a Venturi scrubber that captures at least 95% of the fines and solubilizes traces of HCl and H<sub>2</sub>S via alkaline water scrubbing. In the second scrubber, any ammonia which may be left in the gas is scrubbed at neutral pH, and after a stripping operation is returned to the gasifier for additional conversion to N<sub>2</sub> and H<sub>2</sub>.

The process of the present invention enables one to obtain a purified synthesis gas, which can be processed and/or reacted efficiently to provide useful products, such as methanol and ethanol, for example. More particularly, in accordance with another aspect of the present invention, there is provided a purified synthesis gas in which contaminants are present in amounts which do not exceed the following levels as given below:

Particulates greater than submicron in size

- no greater than 1 mg/Nm<sup>3</sup>

Metals in particulates

Hg and Cd

- no greater than 0.1 mg/Nm<sup>3</sup>

Pb

- no greater than 0.1 mg/Nm<sup>3</sup>

As

- no greater than 0.05 mg/Nm<sup>3</sup>

Alkali metals

- no greater than 0.5 mg/Nm<sup>3</sup>

Al

- no greater than 0.5 mg/Nm<sup>3</sup>

Si

- no greater than 0.5 mg/Nm<sup>3</sup>

heavy metals

- no greater than 0.01 mg/Nm<sup>3</sup>

Metal vapors in gas

Hg

- no greater than 0.001 mg/Nm<sup>3</sup>

As (as oxides)

- no greater than 0.010 mg/Nm<sup>3</sup>

Cl (as HCl)

- not measurable

S (as H<sub>2</sub>S or COS)

- not measurable

Tar

- no greater than 0.1 mg/Nm<sup>3</sup>

The term "mg/Nm<sup>3</sup>", as used herein, means the amount of contaminant in milligrams per cubic meter, under normal conditions, i.e., 0°C and 1 bar as absolute pressure.

The invention now will be described with respect to the drawing, wherein:

The drawing is a schematic of the process for producing a synthesis gas in accordance with the present invention.

Referring now to the drawing, a biomass is fed to pretreatment zone 10 through line 11. Additives are fed to pretreatment zone 10 through line 12. The additives which are fed to pretreatment zone 10 include calcium oxide, mixtures of calcium oxide and magnesium oxide, calcined limestone, olivine, and/or mixtures of calcium and magnesium oxides, to neutralize impurities such as chlorine, fluorine, and sulfur, which may be present in the biomass. The additives also may include ash materials, which contain metals that, once reduced in gasifier 20, may have a beneficial catalytic effect during reforming in the freeboard section 20b. In general, such additives are present in an amount of from about 0.5 wt.% to about 3.0 wt.%, based on the weight of the biomass.

The biomass and additives are withdrawn from pretreatment zone 10 through line 13 and fed into the fluid bed section 20a of gasifier 20 through a feeding system (not shown) including either a series of star valves or a lock hopper system with interlocking valves coupled to a weighted belt conveyor, which feeds a transfer screw to inject the biomass and additives. The feeding system is illustrated schematically as line 14.

A fluidizing gas, such as oxygen and steam, or a mixture of oxygen, steam, and carbon dioxide, is passed from line 15, through compressor 1, to lines 16 and 18, and fed, via a distributed nozzle system (not shown), into the fluid bed section 20a of the gasifier 20 through lines 14 and 18a.

The fluid bed section 20a of gasifier 20 includes a fluidized bed of an appropriate particulate material, such as alumina, olivine, anthracite, desulfurized petroleum coke, or other refractory materials. In general, the fluidized bed material has a particle size of from about 200 microns to about 600 microns.

The fluid bed section 20a of the gasifier 20 is operated under conditions which effect partial oxidation and thermal decomposition of the biomass. In general, the temperature of the fluidized bed section 20a of the gasifier 20 is maintained at from about 600°C to about 700°C, and the fluidization gas is fed to the fluidized bed section 20a to provide a fluidization velocity of from about 0.7 m/sec. to about 1.5 m/sec. Such fluidization velocity is maintained by the fluidization gas which is fed to the fluid bed section 20a of the gasifier 20, as well as by gases formed by the conversion of biomass material in the fluid bed section 20a. In general, the fluid bed section 20a is operated at a pressure that does not exceed 10 atm.

Oxygen is present in the fluidizing gas in an amount effective to oxidize the biomass and to heat the biomass to a temperature of at least 600°C and no greater than 700°C. In general, the fluidization gas is fed to the fluid bed section 20a such that the weight ratio of oxygen to biomass is from about 0.20 to about 0.35 of the stoichiometric weight ratio required for complete combustion of the biomass.

When the biomass enters the fluid bed section 20a, the biomass is oxidized partially as it decomposes thermally, thereby producing a solid carbonaceous residue that remains in the fluid bed section 20a, true gases (such as CO<sub>2</sub>, steam, including that introduced into fluid bed section 20a and from dehydration reactions, and some carbon monoxide and hydrogen), and vapors of intermediate species, such as low molecular weight alkyl and aromatic hydrocarbons, phenolics, and condensed and functionalized aromatics, which pass from the fluid bed section 20a with the true gases and the fluidizing gas, to the freeboard section 20b.

The biomass is contacted with the fluidizing gas in fluid bed section 20a for a

period of time which is effective for effecting partial oxidation and thermal decomposition of the biomass. In general, such period of time does not exceed 3 seconds.

The carbonaceous residue that remains in the fluid bed section 20a reacts with the incoming oxygen to provide the exothermal heat of oxidation. Carbon monoxide and carbon dioxide are formed because the partial oxidation of the biomass is sub-stoichiometric, and the temperature of the fluid bed section 20a is maintained at from about 600°C to about 700°C. The oxygen which was introduced into the fluid bed section 20a essentially is consumed in the fluid bed section 20a. Carbon also is produced as a result of the thermal decomposition of the biomass. As the biomass continues to be decomposed and oxidized partially in the fluid bed section 20a, the carbon particles which were formed as a result of the thermal decomposition also begin to be consumed as a result of partial oxidation of such particles, whereby the carbon particles shrink and become entrained in the fluidizing gas as char particles. In general, such entrained char particles are less than 200 microns in size. The char particles contain inorganic materials, such as salts (eg., alkali chlorides), initially present in the biomass feedstock, except for larger pieces of inorganic material that accumulates in fluid bed section 20a. Excess solid inorganic material, which does not become entrained in the fluidizing gas, and which may be coated with carbon, is withdrawn from fluid bed section 20a through line 21. A differential pressure sensor (not shown) activates a valving system (not shown) that permits adjustment of the level of fluidized bed material in the fluid bed section 20a to maintain a uniform fluidization of the fluidized bed material.

The gases, such as CO<sub>2</sub>, CO, and hydrogen, and steam, and the vapors of the

intermediate species hereinabove described, which are produced by the partial oxidation and thermal decomposition of the biomass, as well as the remainder of the fluidizing gas, constitute a primary synthesis gas which passes from the fluid bed section 20a into the freeboard section 20b of gasifier 20. Char particles also become entrained in the gases and vapors as they pass from the fluid bed section 20a to the freeboard section 20b.

Some cracking of the intermediate species takes place in the fluid bed section 20a; however, higher temperatures are required to crack and steam reform effectively the vapors of the intermediate species, and to convert the residual carbon in the entrained char particles.

The partially oxidized biomass material, now in the form of the primary synthesis gas material hereinabove described, is contacted with additional oxidizing gas in the freeboard section 20b. The oxidizing gas, which is a mixture of oxygen and steam, or a mixture of oxygen, steam, and carbon dioxide as hereinabove described, is introduced into freeboard section 20b through lines 17a and 17b.

The partially oxidized biomass material is contacted with the oxidizing gas in freeboard section 20b at a temperature and for a period of time which are effective to convert the partially oxidized biomass material to a synthesis gas. In general, the partially oxidized biomass is contacted with the oxidizing gas in freeboard section 20b at a temperature of from about 800°C to about 850°C, and for a period of time of from about 4 seconds to about 8 seconds. The oxidizing gas is introduced into the enlarged freeboard section 20b from lines 17a and 17b so that a velocity of from about 0.3 m/sec. to about 0.7 m/sec. is maintained.

In the freeboard section 20b, carbon in the char is converted fully by the steam in the oxidizing gas, thereby generating hydrogen and carbon monoxide, while steam reforming of intermediates provide further hydrogen and carbon monoxide. The inorganic materials in the char (such as alkali chlorides, for example) are heated to temperatures which are higher than their melting points. Such materials melt and stay melted in the char particles. Deposition of inorganic or other materials on the walls of the freeboard section 20b is minimal given the existing plug flow regime and the encapsulation of the melted material within the char. Also, the char particles do not return to the fluid bed section 20a of gasifier 20 because the fluid dynamic plug flow makes it impossible.

A crude synthesis gas, formed by reacting the partially oxidized biomass material with the oxidizing gas in freeboard section 20b as hereinabove described, is withdrawn from the freeboard section 20b through line 19, and passed into mixer 3, where the crude synthesis gas is mixed with oxidizing gas, as hereinabove described, from line 17. The crude synthesis gas and oxidizing gas then are passed from mixer 3 through line 8 and into thermal reformer 22. Thermal reformer 22 has a simple tubular flow reactor configuration, and may be in the form of a refractory and insulated carbon steel pipe. In thermal reformer 22, further conversion of any carbon in the char particles, and of intermediate hydrocarbon materials remaining in the crude syngas occurs. In general, this further conversion is conducted by contacting the crude synthesis gas with the oxidizing gas at a temperature of from about 925°C to about 1,000°C, and for a period of time of from about 1 second to about 3 seconds.

The crude synthesis gas then is withdrawn from thermal reformer 22 through line

23, and passed into mixer 4. Oxidizing gas also is introduced into mixer 4 from line 18. The mixture of crude synthesis gas and oxidizing gas then is passed through line 25 and into thermal reformer 24. In thermal reformer 24, additional conversion of carbon and intermediates occurs. In general, thermal reformer 24 has the same configuration as thermal reformer 22, and is operated under the same conditions as thermal reformer 22.

In thermal reformers 22 and 24, further conversion of carbon and intermediate hydrocarbons remaining in the crude synthesis gas occurs, to provide a synthesis gas which also includes residual methane and only trace amounts of hydrocarbons having two or more carbon atoms.

The synthesis gas then is withdrawn from thermal reformer 24 through line 26, and passed into mixer 5, and cooled in mixer 5 with water from line 27 to a temperature of less than 750°C. The cooled synthesis gas then is passed through line 28 into one or more cyclones, depicted schematically as 29.

In the cyclones 29, any remaining particles having a size greater than 10 microns are separated from the synthesis gas and withdrawn from the cyclones 29 through line 31. Such particles are comprised essentially of inorganic materials coated with carbon.

The synthesis gas is withdrawn from the cyclones 29 through line 30, and passed into heat recovery unit 32, wherein the synthesis gas is subjected to further cooling. Such cooling is effected by passing a cold fluid, such as water or a thermal oil, in line 33 through heat recovery unit 32. The fluid in line 33 exits heat recovery unit 32 as a hot fluid, and the cooled synthesis gas is withdrawn from heat recovery unit 32 through line 34, and passed into Venturi scrubber 35. Venturi scrubber 35 includes a throat portion

and a demister (not shown). In Venturi scrubber 35, any tars and at least 95% of particulate fines remaining in the synthesis gas are removed. In addition, the synthesis gas is scrubbed with alkaline water from line 36, which dissolves any traces of HCl or H<sub>2</sub>S remaining in the synthesis gas and forming corresponding sodium salts.

The water containing the sodium salts, tar, and particulate fines is withdrawn from the Venturi scrubber 35 through line 42 and passed to tar separator 43. Tar and fines are withdrawn from tar separator 43 through line 44 and passed to mixer 45. Water is withdrawn from tar separator 43 through line 48, and passed through cooler 38 and into line 37 and pump 6. A portion of the water is withdrawn from line 37 and pump 6, and passed into line 49 as purge water. Such purge water may be subjected to further treatment and then sent to line 27 as the water used to cool the crude synthesis gas from line 26 prior to the cyclone treatment. The remaining water in line 37 is subjected to an alkaline pH adjustment, and passed to line 36 for recycle to Venturi scrubber 35.

The synthesis gas is withdrawn from Venturi scrubber 35 through line 39 and passed into scrubber 40. In scrubber 40, the synthesis gas is contacted with water, at a neutral pH, from line 58. In scrubber 40, any remaining ammonia, as well as any tars and fines, in the synthesis gas is removed from the synthesis gas.

The treated synthesis gas is withdrawn from scrubber 40 through line 41. Such treated synthesis gas may be, if desired, be subjected to further conditioning, reforming, and/or carbon dioxide removal, prior to being used as a fuel. Alternatively, the synthesis gas may be used as a feed for the synthesis of other desired materials, such as methanol or ethanol, for example.

The water, ammonia, tars, and fines are withdrawn from scrubber 40 through line 50 and passed into tar separator 51, in which the tars and fines are separated from the water and ammonia. The tars and fines are withdrawn from tar separator 51 through line 63 and passed into mixer 45. A tar and water emulsion is formed in mixer 45 as a result of mixing the tar and fines with water from line 64. The water has a pH which is adjusted to approximate that of the biomass which is fed to the fluid bed section 20a of gasifier 20. The tar and water emulsion is withdrawn from mixer 45 through line 46, and is contacted with a fluidization gas from line 18b. The emulsion and the fluidization gas then are passed through pump 2 and fed into the fluid bed section 20a of gasifier 20 through line 47, whereby the tar and fresh or raw biomass are subjected to partial oxidation under the conditions hereinabove described.

Water and ammonia are withdrawn from tar separator 51 through line 52, and passed into stripper 54, in which the ammonia is stripped from the water. Ammonia is withdrawn from stripper 54 through line 53. The ammonia then may be processed further to remove any remaining water, or may be sent, along with pretreated biomass, to the fluid bed section 20a of gasifier 20.

Water is withdrawn from stripper 54 through line 55. If desired, the water may be passed to reboiler 60 to facilitate the removal of any ammonia which may be remaining in the water. The water and ammonia are heated in reboiler 60 by passing a hot fluid, such as a hot thermal oil, through reboiler 60 in line 62. The fluid heats the water and ammonia, and exits reboiler 60 through line 62 as a cold fluid. The heated water and ammonia are withdrawn from reboiler 60 through line 61 and recycled to stripper 54, wherein the ammonia is stripped from the heated water.

When the stripping of the ammonia from the water is completed, the water is withdrawn from stripper 54 through line 55, passed through line 56, cooled in cooler 57, and passed through pump 7 and into line 58. A portion of the water in line 58 is withdrawn as purge water through line 59. Such purge water may be subjected to further treatment, and then be sent to line 27 to cool the crude synthesis gas in line 26. The remaining water in line 58 is passed to scrubber 40 for scrubbing of ammonia, tars, and fines, from the synthesis gas.

The disclosures of all patents and publications, including published patent applications, are incorporated herein by reference to the same extent as if each patent and publication individually were incorporated by reference.

It is to be understood, however, that the scope of the present invention is not to be limited to the specific embodiments described above. The invention may be practiced other than as particularly described and still be within the scope of the accompanying claims.

**WHAT IS CLAIMED IS:**

1. A process for producing synthesis gas from biomass, comprising:
  - (a) contacting said biomass with oxygen and steam, wherein said oxygen is present in an amount effective to oxidize said biomass and to heat said biomass to a temperature of at least 500°C and no greater than 750°C;
  - (b) treating at least a portion of the oxidized biomass produced in step (a) with oxygen and steam to heat said biomass to a temperature of at least 800°C, thereby producing synthesis gas; and
  - (c) recovering said synthesis gas produced in step (b).
2. The process of Claim 1 wherein, in step (a), said biomass is heated to a temperature of from about 600°C to about 750°C.
3. The process of Claim 2 wherein, in step (a), said biomass is heated to a temperature of from about 600°C to about 725°C.
4. The process of Claim 1 wherein, in step (a), said biomass is contacted with said oxygen at a weight ratio of oxygen to biomass of from about 0.20 to about 0.35 of the stoichiometric weight ratio needed for complete combustion of said biomass.
5. The process of Claim 4 wherein, in step (a), said biomass is contacted with said oxygen at a weight ratio of oxygen to biomass of from about 0.20 to about 0.30 of the stoichiometric weight ratio needed for complete combustion of said biomass.
6. The process of Claim 5 wherein, in step (a), said biomass is contacted with said oxygen at a weight ratio of oxygen to biomass of from about 0.25 to about 0.30 of the stoichiometric weight ratio needed for complete combustion of said biomass.

7. The process of Claim 1 wherein, in step (b), said oxidized biomass is heated to a temperature of from about 800°C to about 1,000°C.
8. The process of Claim 7 wherein, in step (b), said oxidized biomass is heated to a temperature of from about 925°C to about 1,000°C.
9. The process of Claim 1 wherein, in step (a), said biomass is contacted with said oxygen and said steam in a fluidized bed of particulate material.
10. The process of Claim 1 wherein in step (a), said biomass is contacted with oxygen and steam in the absence of nitrogen.
11. The process of Claim 1 wherein, in step (b), said oxidized biomass is contacted with oxygen and steam in the absence of nitrogen.
12. The process of Claim 1, wherein step (b) comprises:
  - (i) treating at least a portion of said oxidized biomass produced in step (a) with oxygen and steam in a first stage to heat said oxidized biomass to a temperature of at least 800°C; and
  - (ii) treating said oxidized biomass with oxygen and steam in a second stage to heat said oxidized biomass to a temperature higher than that of said first stage, thereby producing synthesis gas.
13. The process of Claim 12, wherein, in said first stage, said oxidized biomass is heated to a temperature of at least 800°C and does not exceed 850°C.
14. The process of Claim 12, wherein, in said second stage, said oxidized biomass is heated to a temperature of at least 900°C.
15. The process of Claim 14, wherein, in said second stage, said oxidized biomass is heated to a temperature of at least 900°C and does not exceed 1,000°C.

16. A purified synthesis gas which includes particulates greater than submicron in size in an amount no greater than  $1 \text{ mg/Nm}^3$ ; mercury and cadmium in an amount no greater than  $0.1 \text{ mg/ Nm}^3$ ; lead in an amount no greater than  $0.1 \text{ mg/ Nm}^3$ ; arsenic in an amount no greater than  $0.05 \text{ mg/ Nm}^3$ ; alkali metals in an amount no greater than  $0.5 \text{ mg/ Nm}^3$ ; aluminum in an amount no greater than  $0.5 \text{ mg/ Nm}^3$ ; silicon in an amount no greater than  $0.5 \text{ mg/ Nm}^3$ ; heavy metals in an amount no greater than  $0.01 \text{ mg/ Nm}^3$ ; tar in an amount no greater than  $0.1 \text{ mg/ Nm}^3$ ; mercury vapor in an amount no greater than  $0.001 \text{ mg/ Nm}^3$ ; arsenic oxide vapors in an amount no greater than  $0.010 \text{ mg/ Nm}^3$ ; and is essentially free of chlorine and sulfur vapors.



**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/CA2009/001851

A. CLASSIFICATION OF SUBJECT MATTER  
IPC: **C10J 3/54** (2006.01)  
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
Minimum documentation searched (classification system followed by classification symbols)  
IPC (2006.01) & ECLA: C10J 3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)  
EPODOC, WPI, Canadian Patent Database with keywords: biomass, oxygen, steam, stage(s), zone(s), step(s), temperature(s), clean(ed), wash(ed), purify(ing, ied), mercury, arsenic, particulate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO2009/132449 A1 (CHORNET, E. et al.) 05 November 2009 (05-11-2009) *Figure 1; pages 6-9, 16, 17; Example 4*	1-3, 7-15
X,P	WO2009/050494 A2 (WYATT, K.L.) 23 April 2009 (23-04-2009) *Figure 1; page 2, line 23- page 3, line 7; page 4, lines 6-8; page 4, lines 27 - page 5, line 10; page 6, line 1; page 7, line 30 - page 8, line 4; page 8, line 20 - page 9, line 11*	1-8, 10, 11
X Y	EP 0 979 857 A2 (LIPP, J. et al.) 16 February 2000 (16-02-2000) *Figures: §5, 9-13; claims 1-8 and 24*	1, 7, 8, 9 2-6
Y A	EP 0 908 672 A1 (FUJINAMI, S. et al.) 14 April 1999 ( 14-04-1999) *Abstract; col. 6, lines 37-41*	2-6 1, 10, 11
Y A	US 2005/0109603 A1 (GRAHAM, R.G.) 26 May 2005 (26-05-2005) *Figure 1; §12, 61, 43, 145*	4-6 1, 7, 8
Y A	WO 01/68789 A1 (BENTZEN, J. D. et al.) 20 September 2001 (20-09-2001) *Abstract; Figure 1; page 2, lines 11-19; page 11, lines 26-32*	2, 3 1, 9

Further documents are listed in the continuation of Box C.       See patent family annex.

* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 10 March 2010 (10-03-2010)	Date of mailing of the international search report 14 April 2010 (14-04-2010)
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Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer  <b>Sebastien Chouinard (819) 994-1607</b>
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**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1.  Claim Nos. :  
because they relate to subject matter not required to be searched by this Authority, namely :
  
2.  Claim Nos. :  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :
  
3.  Claim Nos. :  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows :

See extra sheet.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

- Remark on Protest**  The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/CA2009/001851

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA 2424805 C (CARABIN, P. et al.) 04 October 2004 (04-10-2004) *Figure 1; Abstract; page 11, lines 1-5; page 14, line 6 - page 15, line 10*	16
Y	CA 2210981 A1 (KISS, G.) 22 January 1998 (22-01-1998) *Figure 1; Abstract; page 3, lines 1-8; page 9, lines 16-26; claims 1&5*	16

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/CA2009/001851**

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
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CA2210981A1	22-01-1998	BR9704019 (A) CN1176297 (A) CZ9701935 (A3) DE19629500 (C1) EP0820802 (A2) HU9701231 (A1) JP10113533 (A) MX9705506 (A) PL321237 (A1) SG65000 (A1) US5879434 (A)	09-02-1999 18-03-1998 18-02-1998 16-04-1998 28-01-1998 28-07-1998 06-05-1998 31-07-1998 02-02-1998 25-05-1999 09-03-1999

Continuation of Box III (Unity):

The following groups of inventions were identified:

Group A: Claims 1-15

A process for producing synthesis gas from biomass, comprising: oxidizing the biomass with oxygen and steam at a temperature between 500°C and 750°C; treating the oxidized biomass with oxygen and steam at a temperature of at least 800°C to produce the synthetic gas; and recovering the synthetic gas.

Group B: Claim 16

A purified synthesis gas with a specific content of impurities: particulate, mercury, cadmium, arsenic, alkali metals, aluminum, silicon, heavy metals, tar, mercury vapors, arsenic oxide vapors, chlorine and sulfur.

There is no common inventive link between Group A and Group B. Claims of Group A are directed to a process to produce synthesis gas using a specific raw material, oxidizer, steam and temperature ranges. The claim of Group B is directed to a purified synthesis gas with a specific impurities content.

Therefore, the Authority considers that there are two invention claimed in the international application.