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(54) **BIOMASS CHAR COMPOSITIONS FOR CATALYTIC GASIFICATION**

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(57) **ABSTRACT**

Particulate compositions are described comprising an intimate mixture of a biomass char produced from the combustion of a biomass, such as switchgrass or hybrid poplar, with at least a second carbonaceous material, such as petroleum coke or coal, and, optionally a gasification catalyst, for gasification in the presence of steam to yield a plurality of gases including methane and at least one or more of hydrogen, carbon monoxide, and other higher hydrocarbons are formed. Processes are also provided for the preparation of the particulate compositions and converting the particulate composition into a plurality of gaseous products.

BIOMASS CHAR COMPOSITIONS FOR CATALYTIC GASIFICATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Ser. No. 61/032,734 (filed Feb. 29, 2008), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

FIELD OF THE INVENTION

[0002] The present disclosure relates to particulate compositions comprising biomass gasification or combustion char and at least a second carbonaceous component as well as at least one gasification catalyst, where the char provides at least a portion of a gasification catalyst in the composition. Further, the disclosure relates to processes for preparation of the particulate compositions and for gasification of the same in the presence of steam to form gaseous products, and in particular, methane.

BACKGROUND OF THE INVENTION

[0003] In view of numerous factors such as higher energy prices and environmental concerns, the production of value-added gaseous products from lower-fuel-value carbonaceous feedstocks, such as biomass, coal and petroleum coke, is receiving renewed attention. The catalytic gasification of such materials to produce methane and other value-added gases is disclosed, for example, in U.S. Pat. No. 3,828,474, U.S. Pat. No. 3,998,607, U.S. Pat. No. 4,057,512, U.S. Pat. No. 4,092,125, U.S. Pat. No. 4,094,650, U.S. Pat. No. 4,204,843, U.S. Pat. No. 4,468,231, U.S. Pat. No. 4,500,323, U.S. Pat. No. 4,541,841, U.S. Pat. No. 4,551,155, U.S. Pat. No. 4,558,027, U.S. Pat. No. 4,606,105, U.S. Pat. No. 4,617,027, U.S. Pat. No. 4,609,456, U.S. 5,017,282, U.S. Pat. No. 5,055,181, U.S. Pat. No. 6,187,465, U.S. Pat. No. 6,790,430, U.S. Pat. No. 6,894,183, U.S. Pat. No. 6,955,695, US2003/0167961A1, US2006/0265953A1, US2007/000177A1, US2007/083072A1, US2007/0277437A1 and GB1599932.

[0004] An efficient process for the catalytic gasification of a carbonaceous material to synthetic natural gas generally requires the presence of a catalyst to encourage the formation of methane with respect to other products, such as syngas. It has generally been contemplated to provide such a catalyst from a source external to the gasification process, for example, by providing solutions or solid compositions of a catalyst which are acquired separately from the feedstocks, adding additional costs to the process. However, as certain types of feedstock can contain intrinsic catalytic compounds, there exists a need in the art to develop processes for the catalytic gasification of carbonaceous materials which take advantage of such intrinsic catalysts to enable lower cost per unit energy stored by increasing the utilization and conversion of the feedstocks in the process.

SUMMARY OF THE INVENTION

[0005] The present disclosure relates to particulate compositions comprising a biomass char, a biomass and/or a non-biomass, and a gasification catalyst. Further, the disclosure relates to processes for preparation of the particulate compositions and for gasification of the same in the presence of steam to form gaseous products, and in particular, methane. Through blending appropriate levels of biomass and/or non-

biomass materials with the biomass char in the feedstock, more efficient utilization of the carbon in the biomass can be realized as well as taking advantage of intrinsic levels of alkali metal compounds present in particular types of biomass char.

[0006] In a first aspect, the present invention provides a particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone, the particulate composition comprising an intimate mixture of: (a) a first carbonaceous feedstock that is a biomass char; (b) a second carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and (c) a gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed, wherein (i) the first carbonaceous feedstock and second carbonaceous feedstock are present in the particulate composition at a weight ratio of from about 5:95 to about 95:5; (ii) the gasification catalyst comprises a source of at least one alkali metal and is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms of the gasification catalyst to carbon atoms ranging from about 0.01 to about 0.10, wherein the biomass char comprises at least a portion of the source of at least one alkali metal.

[0007] In a second aspect, the present invention provides a process for converting a particulate composition into a plurality of gaseous products, the process comprising the steps of: (a) supplying a particulate composition according to the first aspect to a gasifying reactor; (b) reacting the particulate composition in the gasifying reactor in the presence of steam and under suitable temperature and pressure to form a plurality of gaseous products including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons; and (c) at least partially separating the plurality of gaseous products to produce a stream comprising a predominant amount of one of the gaseous products.

[0008] In a third aspect, the present invention provides a process for preparing a particulate composition according to the first aspect, the process comprising the steps of: (a) providing a first particulate carbonaceous feedstock that is a biomass char, a second particulate carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and, optionally, an alkali metal gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed from the particulate composition; (b) mixing the first particulate carbonaceous feedstock, the second particulate carbonaceous feedstock and, optionally, the alkali metal gasification catalyst to form a mixture; and (c) optionally thermally treating the mixture under a flow of inert dry gas to form the particulate composition, wherein the gasification catalyst comprises a source of at least one alkali metal and is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms of the gasification catalyst to carbon atoms ranging from about 0.01 to about 0.10, wherein the biomass char comprises at least a portion of the source of at least one alkali metal.

DETAILED DESCRIPTION

[0009] The present disclosure relates to a particulate composition, methods for the preparation of the particulate com-

position, and methods for the catalytic gasification of the particulate composition. Generally, the particulate composition includes a biomass char in various blends with one or more biomass and/or non-biomass carbonaceous materials, for example, coals and/or petroleum coke.

[0010] The present invention can be practiced, for example, using any of the developments to catalytic gasification technology disclosed in commonly owned US2007/0000177A1, US2007/0083072A1 and US2007/0277437A1; and U.S. patent application Ser. No. 12/178,380 (filed 23 Jul. 2008), Ser. No. 12/234,012 (filed 19 Sep. 2008) and Ser. No. 12/234,018 (filed 19 Sep. 2008). All of the above are incorporated by reference herein for all purposes as if fully set forth.

[0011] Moreover, the present invention can be practiced in conjunction with the subject matter of the following U.S. patent applications, each of which was filed on Dec. 28, 2008: Ser. No. 12/342,554, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Ser. No. 12/342,565, entitled "PETROLEUM COKE COMPOSITIONS FOR CATALYTIC GASIFICATION"; Ser. No. 12/342,578, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION"; Ser. No. 12/342,596, entitled "PROCESSES FOR MAKING SYNTHESIS GAS AND SYNGAS-DERIVED PRODUCTS"; Ser. No. 12/342,608, entitled "PETROLEUM COKE COMPOSITIONS FOR CATALYTIC GASIFICATION"; Ser. No. 12/342,628, entitled "PROCESSES FOR MAKING SYNGAS-DERIVED PRODUCTS"; Ser. No. 12/342,663, entitled "CARBONACEOUS FUELS AND PROCESSES FOR MAKING AND USING THEM"; Ser. No. 12/342,715, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Ser. No. 12/342,736, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Ser. No. 12/343,143, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Ser. No. 12/343,149, entitled "STEAM GENERATING SLURRY GASIFIER FOR THE CATALYTIC GASIFICATION OF A CARBONACEOUS FEEDSTOCK"; and Ser. No. 12/343,159, entitled "CONTINUOUS PROCESSES FOR CONVERTING CARBONACEOUS FEEDSTOCK INTO GASEOUS PRODUCTS". All of the above are incorporated by reference herein for all purposes as if fully set forth.

[0012] Further, the present invention can be practiced in conjunction with the subject matter of the following U.S. patent applications, each of which was filed concurrently herewith: Ser. No. _____, entitled "PROCESSES FOR MAKING ABSORBENTS AND PROCESSES FOR REMOVING CONTAMINANTS FROM FLUIDS USING THEM" (attorney docket no. FN-0019 US NP1); Ser. No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1); Ser. No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1); Ser. No. _____, entitled "PROCESS AND APPARATUS FOR THE SEPARATION OF METHANE FROM A GAS STREAM" (attorney docket no. FN-0022 US NP1); Ser. No. _____, entitled "SELECTIVE REMOVAL AND RECOVERY OF ACID GASES FROM GASIFICATION PRODUCTS" (attorney docket no. FN-0023 US NP1); Ser. No. _____, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0024 US

NP1); Ser. No. _____, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0025 US NP1); Ser. No. _____, entitled "CO-FEED OF BIOMASS AS SOURCE OF MAKEUP CATALYSTS FOR CATALYTIC COAL GASIFICATION" (attorney docket no. FN-0026 US NP1); Ser. No. _____, entitled "COMPACTOR-FEEDER" (attorney docket no. FN-0027 US NP1); Ser. No. _____, entitled "CARBONACEOUS FINES RECYCLE" (attorney docket no. FN-0028 US NP1); Ser. No. _____, entitled "CATALYTIC GASIFICATION PARTICULATE COMPOSITIONS" (attorney docket no. FN-0030 US NP1); and Ser. No. _____, entitled "BIOMASS COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0031 US NP1). All of the above are incorporated herein by reference for all purposes as if fully set forth.

[0013] All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

[0014] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In case of conflict, the present specification, including definitions, will control.

[0015] Except where expressly noted, trademarks are shown in upper case.

[0016] Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described herein.

[0017] Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

[0018] When an amount, concentration, or other value or parameter is given as a range, or a list of upper and lower values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper and lower range limits, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the end-points thereof, and all integers and fractions within the range. It is not intended that the scope of the present disclosure be limited to the specific values recited when defining a range.

[0019] When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

[0020] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but can include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0021] The use of "a" or "an" to describe the various elements and components herein is merely for convenience and to give a general sense of the disclosure. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0022] The term “predominant” as used herein, means that the referenced item comprises the highest population of a referenced component with respect to any additional components within the referenced item.

[0023] The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting.

Biomass

[0024] The term “biomass” as used herein refers to carbonaceous materials derived from recently (for example, within the past 100 years) living organisms, including plant-based biomass, animal-based biomass, and catalytic biomass. For clarification, biomass does not include fossil-based carbonaceous materials, such as coal.

[0025] The term “plant-based biomass” as used herein means materials derived from green plants, crops, algae, and trees, such as, but not limited to, sweet sorghum, bagasse, sugarcane, bamboo, hybrid poplar, hybrid willow, albizia trees, eucalyptus, alfalfa, clover, oil palm, switch-grass, sudangrass, millet, jatropha, and miscanthus (e.g., *Miscanthus×giganteus*). Biomass further include wastes from agricultural cultivation, processing, and/or degradation such as corn cobs and husks, corn stover, straw, nut shells, vegetable oils, canola oil, rapeseed oil, biodiesels, tree bark, wood chips, sawdust, and yard wastes.

[0026] The term “animal-based biomass” as used herein means wastes generated from animal cultivation and/or utilization. For example, biomass includes, but is not limited to, wastes from livestock cultivation and processing such as animal manure, guano, poultry litter, animal fats, and municipal solid wastes (e.g., sewage).

[0027] The term “catalytic biomass” as used herein refers to biomass, as defined herein, whose combustion produces an ash comprising of one or a combination of alkali metal compounds (e.g., K_2O and/or Na_2O) that can function as a gasification catalyst in the context of the present invention. The amount of such alkali metal compounds may, for example, be at least 5 wt % based on the weight of the ash. For example, catalytic biomass includes, but is not limited to, switchgrass, hybrid poplar, hybrid willow, sugarcane, bamboo, miscanthus, cotton stalks, flax, verge grass, alfalfa, sunflower, poultry litter, kenaf (*hibiscus cannabimus*), thistle, and almond shells and husks.

Non-Biomass

[0028] The term “non-biomass”, as used herein, means those carbonaceous materials which are not encompassed by the term “biomass” as defined herein. For example, non-biomass include, but is not limited to, anthracite, bituminous coal, sub-bituminous coal, lignite, petroleum coke, or mixtures thereof.

[0029] (a) Petroleum Coke

[0030] The terms “petroleum coke” and “petcoke” as used herein includes both (i) the solid thermal decomposition product of high-boiling hydrocarbon fractions obtained in petroleum processing (heavy residues—“resid petcoke”); and (ii) the solid thermal decomposition product of processing tar sands (bituminous sands or oil sands—“tar sands petcoke”). Such carbonization products include, for example, green, calcined, needle and fluidized bed petcoke.

[0031] Resid petcoke can also be derived from a crude oil, for example, by coking processes used for upgrading heavy-

gravity residual crude oil, which petcoke contains ash as a minor component, typically about 1.0 wt % or less, and more typically about 0.5 wt % or less, based on the weight of the coke. Typically, the ash in such lower-ash cokes comprises metals such as nickel and vanadium.

[0032] Tar sands petcoke can be derived from an oil sand, for example, by coking processes used for upgrading oil sand. Tar sands petcoke contains ash as a minor component, typically in the range of about 2 wt % to about 12 wt %, and more typically in the range of about 4 wt % to about 12 wt %, based on the overall weight of the tar sands petcoke. Typically, the ash in such higher-ash cokes comprises materials such as silica and/or alumina.

[0033] Petroleum coke has an inherently low moisture content, typically, in the range of from about 0.2 to about 2 wt %. (based on total petroleum coke weight); it also typically has a very low water soaking capacity to allow for conventional catalyst impregnation methods. The resulting particulate compositions contain, for example, a lower average moisture content which increases the efficiency of downstream drying operation versus conventional drying operations.

[0034] The petroleum coke can comprise at least about 70 wt % carbon, at least about 80 wt % carbon, or at least about 90 wt % carbon, based on the total weight of the petroleum coke. Typically, the petroleum coke comprises less than about 20 wt % percent inorganic compounds, based on the weight of the petroleum coke.

[0035] (b) Coal

[0036] The term “coal” as used herein means peat, lignite, sub-bituminous coal, bituminous coal, anthracite, or mixtures thereof. In certain embodiments, the coal has a carbon content of less than about 85%, or less than about 80%, or less than about 75%, or less than about 70%, or less than about 65%, or less than about 60%, or less than about 55%, or less than about 50% by weight, based on the total coal weight. In other embodiments, the coal has a carbon content ranging up to about 85%, or up to about 80%, or up to about 75% by weight, based on the total coal weight. Examples of useful coal include, but are not limited to, Illinois #6, Pittsburgh #8, Beulah (N. Dak.), Utah Blind Canyon, and Powder River Basin (PRB) coals. Anthracite, bituminous coal, sub-bituminous coal, and lignite coal may contain about 10 wt %, from about 5 to about 7 wt %, from about 4 to about 8 wt %, and from about 9 to about 11 wt %, ash by total weight of the coal on a dry basis, respectively. However, the ash content of any particular coal source will depend on the rank and source of the coal, as is familiar to those skilled in the art [see, for example, *Coal Data: A Reference*, Energy Information Administration, Office of Coal, Nuclear, Electric and Alternate Fuels, U.S. Department of Energy, DOE/EIA-0064(93), February 1995].

[0037] The ash produced from a coal typically comprises both a fly ash and a bottom ash, as are familiar to those skilled in the art. The fly ash from a bituminous coal can comprise from about 20 to about 60 wt % silica and from about 5 to about 35 wt % alumina, based on the total weight of the fly ash. The fly ash from a sub-bituminous coal can comprise from about 40 to about 60 wt % silica and from about 20 to about 30 wt % alumina, based on the total weight of the fly ash. The fly ash from a lignite coal can comprise from about 15 to about 45 wt % silica and from about 20 to about 25 wt % alumina, based on the total weight of the fly ash [Meyers,

et al. *Fly Ash. A Highway Construction Material*. Federal Highway Administration, Report No. FHWA-IP-76-16, Washington, D.C., 1976].

[0038] The bottom ash from a bituminous coal can comprise from about 40 to about 60 wt % silica and from about 20 to about 30 wt % alumina, based on the total weight of the bottom ash. The bottom ash from a sub-bituminous coal can comprise from about 40 to about 50 wt % silica and from about 15 to about 25 wt % alumina, based on the total weight of the bottom ash. The bottom ash from a lignite coal can comprise from about 30 to about 80 wt % silica and from about 10 to about 20 wt % alumina, based on the total weight of the bottom ash. [Moulton, Lyle K. "Bottom Ash and Boiler Slag," *Proceedings of the Third International Ash Utilization Symposium*. U.S. Bureau of Mines, Information Circular No. 8640, Washington, D.C., 1973.]

Biomass Char

[0039] The term "biomass char" as used herein, means a char which is produced from the partial or complete gasification or combustion of a biomass. Such chars comprise an ash and can comprise residual carbon. The ash can contain alkali metal compounds such as, but not limited to, sodium oxide and potassium oxide, and alkaline earth metal compounds such as, but not limited to, calcium oxide, and mixtures thereof. One skilled in the art will readily recognize that the residual carbon content of a biomass char is dependent on the extent of combustion and/or gasification of a biomass as well as the composition of the biomass prior to gasification and/or combustion. Further, one skilled in the art will readily recognize that the composition of the ash within a biomass char is dependent on the composition of a biomass, prior to gasification and/or combustion and can be readily adjusted by, for example, blending appropriate biomass feedstocks, as well as by the percent conversion of carbon in the biomass to gaseous products prior to withdrawal of the biomass char from the relevant reactor.

[0040] A biomass char can be generated by providing a biomass particulate to any type of combustion and/or gasification reactor. Such reactors may be integrated into a catalytic gasification process. For example, in an integrated process, a biomass particulate can be provided to a combustion reactor in contact with a water source for the production of steam; such steam can be provided, in whole or in part, to a catalytic gasification reactor and the biomass char produced therein may be extracted and utilized for the preparation of a particulate composition for the catalytic gasification reactor. In various embodiments, a portion of the generated steam may be provided to a steam turbine for the production of electricity. In other examples, a biomass char may be produced from a biomass particulate to a gasification reactor for the production of a syngas. The syngas may be provided to a combustion turbine for the production of electricity.

[0041] In the preceding examples, the exhaust from the combustion reactor, gasification reactor, steam turbine, and/or combustion turbine producing the biomass char may be exhausted to the atmosphere. Alternatively, in the latter two embodiments, the exhaust from the steam turbine and/or combustion turbine may be directed through a catalytic gasification reactor wherein carbon dioxide in the exhausts may be recovered. For example, see previously incorporated U.S. patent applications Ser. No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1), and Ser.

No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1).

[0042] Preferably, the biomass char comprises an alkali metal source such that the biomass char provides at least a portion of the gasification catalyst in the particulate compositions described herein. In one embodiment, the biomass char comprises substantially all, or all, of the gasification catalyst in the particulate compositions described herein.

[0043] While a biomass char can be produced from any of the biomass sources discussed above, as used throughout, the biomass char used in preparing the particulate compositions herein is not required to be prepared from the same biomass as is utilized in preparing the particulate compositions.

Particulate Compositions

[0044] The particulate compositions according to the present disclosure are based on the above-described biomass char in combination with a biomass and/or a non-biomass, such as coal and/or petroleum coke, and a gasification catalyst. Generally, the biomass char comprises an alkali metal source such that the biomass char provides at least a portion of the gasification catalyst in the particulate composition. A further portion of the gasification catalyst can be optionally added to supplement the biomass char. The further portion of gasification catalyst generally comprises an alkali metal source, typically, as an alkali metal and/or an alkali metal compound.

[0045] Certain types of biomass, referred to herein as catalytic biomass, intrinsically contain significant levels of alkali metal compounds which can be found concentrated within a char produced from their gasification and/or combustion. For example, catalytic biomass can be reacted in any type of combustion or gasifying reactor to produce a biomass char having increased levels of alkali metal compounds (e.g., K_2O and/or Na_2O), with respect to other biomass sources. Such biomass chars rich in such alkali metal compounds can be extracted from a gasifier or combustion reactor and utilized for the preparation of the particulate compositions of the present invention. Examples of catalytic biomass include, but are not limited to, switchgrass, hybrid poplar, hybrid willow, sugarcane, bamboo, miscanthus, cotton stalks, flax, verge grass, alfalfa, sunflower, poultry litter, kenaf (*hibiscus cannabinus*), thistle, and almond shells and husks.

[0046] When an additional alkali metal source is present in the particulate compositions, the alkali metal source may be loaded onto any of the biomass char, the biomass, non-biomass particulates, as well as mixtures thereof. However, the alkali metal component may be blended into the particulate composition as a separate particulate source.

[0047] The alkali metal source may be provided within the particulate compositions to achieve an alkali metal content of from about 3 to about 10 times more than the combined ash content of the particulate composition, on a mass basis. Typically, one or more alkali metal sources are present in an amount sufficient to provide, a ratio of alkali metal atoms to carbon atoms in the particulate composition ranging from about 0.01, or from about 0.02, or from about 0.03, or from about 0.04, to about 0.10, or to about 0.08, or to about 0.07, or to about 0.06.

[0048] Suitable alkali metals are lithium, sodium, potassium, rubidium, cesium, and mixtures thereof. Particularly useful are potassium sources. Suitable alkali metal compounds include alkali metal carbonates, bicarbonates, for-

mates, oxalates, amides, hydroxides, acetates, or similar compounds. For example, the catalyst can comprise one or more of sodium carbonate, potassium carbonate, rubidium carbonate, lithium carbonate, cesium carbonate, sodium hydroxide, potassium hydroxide, rubidium hydroxide or cesium hydroxide, and particularly, potassium carbonate and/or potassium hydroxide.

[0049] Co-catalysts or other catalyst additives may also be utilized, such as disclosed in the previously incorporated references.

[0050] Each of biomass, biomass char, and non-biomass sources for the particulate composition are typically supplied as a fine particulate having an average particle size of from about 25 microns, or from about 45 microns, up to about 2500 microns, or up to about 500 microns. One skilled in the art can readily determine the appropriate particle size for the individual particulates and the particulate composition. For example, when a fluid bed gasification reactor is used, the particulate composition can have an average particle size which enables incipient fluidization of the particulate composition at the gas velocity used in the fluid bed gasification reactor.

[0051] The ratio of the various particulates in each of the particulate compositions can be selected based on technical considerations, processing economics, availability, and proximity of the non-biomass and biomass sources. The availability and proximity of the sources for the particulate compositions affect the price of the feeds, and thus, the overall production costs of the catalytic gasification process. For example, the biomass char and non-biomass and/or biomass, can be blended in at about 5:95, about 10:90, about 15:85, about 20:80, about 25:75, about 30:70, about 35:65, about 40:60, about 45:55, about 50:50, about 55:45, about 60:40, about 65:35, about 70:20, about 75:25, about 80:20, about 85:15, about 90:10, or about 95:5 by weight on a wet or dry basis, depending on the processing conditions.

[0052] In one embodiment, at least the non-biomass particulate of the particulate composition comprises the gasification catalyst. In another embodiment, the biomass particulate comprises the gasification catalyst. In another embodiment, both the biomass and non-biomass particulates comprise a gasification catalyst. In yet another embodiment, the biomass char comprises the gasification catalyst. In each of the preceding embodiments, an optional a co-catalyst/catalyst additive, as discussed previously, may be added to any one or more of the particulates.

[0053] The biomass and non-biomass sources, as well as the ratio of the biomass particulate to the non-biomass particulate, can be used to control other material characteristics of the feedstock blend.

[0054] Non-biomass materials, such as coals, typically include significant quantities of inorganic matter including calcium, alumina and silica which form inorganic oxides (i.e., ash) in the gasification reactor. At temperatures above about 500° C. to about 600° C., potassium and other alkali metals can react with the alumina and silica in ash to form insoluble alkali aluminosilicates. In this form, the alkali metal is substantially water-insoluble and inactive as a catalyst. To prevent buildup of the residue in the gasification reactor, a solid purge of char comprising ash, unreacted carbonaceous material, and various alkali metal compounds (both water soluble and water insoluble) are routinely withdrawn. Preferably, the alkali metal is recovered from the char, and any unrecovered catalyst is generally compensated by a catalyst make-up

stream. The more alumina and silica that is in the feedstock, the more costly it is to obtain a higher alkali metal recovery.

[0055] In preparing the particulate compositions of the present invention, the ash content of the biomass, biomass char, and non-biomass particulates can be selected to be, for example, to be about 20 wt % or less, or about 15 wt % or less, or about 10 wt % or less, or about 5 wt % or less, depending on ratio of the particulates and/or the starting ash in the non-biomass source. In other embodiments, the resulting particulate composition can comprise an ash content ranging from about 5 wt %, or from about 10 wt %, to about 20 wt %, or to about 15 wt %, based on the weight of the particulate composition. In other embodiments, the ash content of the particulate composition can comprise less than about 20 wt %, or less than about 15 wt %, or less than about 10 wt %, or less than about 8 wt %, or less than about 6 wt % alumina, based on the weight of the ash. In certain embodiments, the resulting particulate composition can comprise an ash content of less than about 20 wt %, based on the weight of the particulate composition where the ash content of the particulate composition comprises less than about 20 wt % alumina, or less than about 15 wt % alumina, based on the weight of the ash.

[0056] Such lower alumina values in the particulate composition allow for decreased losses of alkali catalysts in the gasification process. Typically, alumina can react with alkali source to yield an insoluble char comprising, for example, an alkali aluminate or aluminosilicate. Such insoluble char can lead to decreased catalyst recovery (i.e., increased catalyst loss), and thus, require additional costs of make-up catalyst in the overall gasification process, as will be discussed later.

[0057] Additionally, the resulting particulate compositions can have a significantly higher carbon content, and thus btu/lb value and methane product per unit weight of the particulate composition. In certain embodiments, the resulting particulate composition has a carbon content ranging from about 75 wt %, or from about 80 wt %, or from about 85 wt %, or from about 90 wt %, up to about 95 wt %, based on the combined weight of the non-biomass and biomass.

[0058] Through the recycling or reuse of a biomass char, whether from a catalytic biomass or any other type of biomass, increased carbon conversion efficiencies may be realized for the catalytic biomass.

Methods for Making the Particulate Composition

[0059] The biomass char, and biomass, and non-biomass sources typically require initial processing to prepare the particulate composition for gasification. Each component of the particulate composition may be separately processed, for example, to crush the sources to prepare appropriately sized particulates and/or to add one or more gasification catalysts, and subsequently mixed.

[0060] The particulates can be prepared via crushing and/or grinding, either separately or together, according to any methods known in the art, such as impact crushing and wet or dry grinding to yield particulates. Depending on the method utilized for crushing and/or grinding, the resulting particulates may be sized (i.e., separated according to size) to provide an appropriate feedstock.

[0061] Any method known to those skilled in the art can be used to size the particulates. For example, sizing can be preformed by screening or passing the particulates through a screen or number of screens. Screening equipment can include grizzlies, bar screens, and wire mesh screens. Screens

can be static or incorporate mechanisms to shake or vibrate the screen. Alternatively, classification can be used to separate the biomass char, biomass, and non-biomass particulates. Classification equipment can include ore sorters, gas cyclones, hydrocyclones, rake classifiers, rotating trommels, or fluidized classifiers. The biomass char, biomass, and non-biomass can be also sized or classified prior to grinding and/or crushing.

[0062] Additional feedstock processing steps may be necessary. Biomass may contain high moisture contents, such as green plants and grasses, can require drying prior to crushing; like-wise, non-biomass such as high-moisture coals, can require drying prior to crushing. Some caking coals can require partial oxidation to simplify gasification reactor operation. Non-biomass feedstocks deficient in ion-exchange sites, such as anthracites or low-sulfur petroleum cokes, can be pre-treated to create additional ion-exchange sites to facilitate catalysts loading and/or association. Such pre-treatments can be accomplished by any method known to the art that creates ion-exchange capable sites and/or enhances the porosity of the feedstock (see, for example, previously incorporated U.S. Pat. No. 4,468,231 and GB1599932). Often, pre-treatment is accomplished in an oxidative manner using any oxidant known to the art.

[0063] In one example, the non-biomass and/or biomass and/or biomass char is wet ground and sized (e.g., to a particle size distribution of 25 to 2500 microns) and then drained of its free water (i.e., dewatered) to a wet cake consistency. Examples of suitable methods for the wet grinding, sizing, and dewatering are known to those skilled in the art; for example, see previously incorporated U.S. patent application Ser. No. 12/178,380 (filed 23 Jul. 2008).

[0064] The particulate filter cakes formed by the wet grinding in accordance with one embodiment of the present disclosure can have a moisture content ranging from about 40% to about 60%, about 40% to about 55%, or below 50%, based on the total weight of the cakes. It will be appreciated by one of ordinary skill in the art that the moisture content of dewatered wet ground biomass char and/or non-biomass and/or biomass particulates depends on the particular type of non-biomass or biomass, the particle size distribution, and the particular dewatering equipment used.

[0065] In certain embodiments, the biomass char comprises all of the gasification catalyst for preparing the particulate compositions of the present invention. In such cases, each of the particulates can be mixed as a wet cake or as a dry particulate, depending on the techniques used for preparation

of each the particulates, to form a mixture (supra). For example, a dry particulate can be prepared by thermally treating the particulate wet cakes generated from wet grinding of a biomass char, biomass, and/or non-biomass. When the particulates are mixed as dry particulates, then the mixture can be the particulate composition of the invention. However, the mixture may be optionally thermally treated to provide the particulate composition having, for example, a residual moisture content of less than about 4 wt %. Optionally, a second catalytic component (e.g., a second gasification catalyst or a co-catalyst or other additive) can be provided to one or more of the particulates; in such instances, the particulates can be treated in separate processing steps to provide the second component, as discussed below.

[0066] Alternatively, when a portion of the gasification catalyst is supplied by the biomass char, the biomass char and/or non-biomass and/or biomass particulates can subsequently be treated to associate the remaining portion of the gasification catalyst therewith. Optionally, a second catalytic component (e.g., a second gasification catalyst or a co-catalyst or other additive) can be provided to one or more of the particulates; in such instances, the particulates can be treated in separate processing steps to provide the first catalyst and second component. For example, at least a portion of the primary gasification catalyst can be supplied to a biomass char, non-biomass, and/or biomass particulate (e.g., a potassium and/or sodium source), followed by a separate treatment to provide a calcium gasification co-catalyst source to the non-biomass and/or biomass particulate. Alternatively, at least a portion of the first catalyst and second component can be provided as a mixture in a single treatment to a particulate; or a particulate (e.g., the non-biomass) may be treated with a first catalyst and a second particulate (e.g., biomass) may be treated with a second component and the two treated particulates blended. Any of the particulate wet cakes may be mixed (e.g. by kneading) and the resulting mixture may be treated with a first and optionally, second catalyst (see, previously incorporated US2007/0000177A1).

[0067] In particular, the particulates may be treated with catalysts and blended according to any of the following permutations shown in Table 1, where A is a biomass char particulate comprising a portion of the gasification catalyst, B is a biomass particulate, and C is a non-biomass particulate; "*" indicates that the particulate or particulate mixture has been treated with part or all of the remaining portion of the catalyst ('cat.');

TABLE 1

Mixing particulates before catalyst treatment:			
A + B → AB	A + C → AC	B + C → BC	A + B + C → ABC
AB + C → ABC	BC + A → ABC		
Catalyst treatment:			
A + cat. → A*	B + cat. → B*	C + cat. → C*	
AB + cat. → (AB)*	AC + cat. → (AC)*	BC + cat. → (BC)*	
ABC + cat. → (ABC)*			
Mixing particulates after catalyst treatment:			
(a) One component treated with catalyst			
A* + B → A*B	A* + C → A*C	A* + BC → A*BC	
A + B* → AB*	AC + B* → (AC)B*		
A + C* → AC*	AB + C* → (AB)C*		
(AB)* + C → (AB)*C	(AC)* + B → (AC)*B	(BC)* + A → A(BC)*	

TABLE 1-continued

(b) Two components treated with catalyst		
$A^* + B^* \rightarrow A^*B^*$	$A^* + C^* \rightarrow A^*C^*$	$A^* + (BC)^* \rightarrow A^*(BC)^*$
$A^* + B^* + C \rightarrow A^*B^*C$	$A^* + B + C^* \rightarrow A^*BC^*$	
$B^* + (AC)^* \rightarrow B^*(AC)^*$	$C^* + (AB)^* \rightarrow (AB)^*C^*$	
(c) Three components treated with catalyst		
$A^* + B^* + C^* \rightarrow A^*B^*C^*$		

[0068] Any methods known to those skilled in the art can be used to associate one or more gasification catalysts with the biomass char, non-biomass, biomass particulates, and/or mixtures thereof to provide a catalyzed particulate thereof. Such methods include but are not limited to, ad-mixing with a solid catalyst source and impregnating the catalyst on to particulates. Several impregnation methods known to those skilled in the art can be employed to incorporate the gasification catalysts. These methods include but are not limited to, incipient wetness impregnation, evaporative impregnation, vacuum impregnation, dip impregnation, ion exchanging, and combinations of these methods.

[0069] In one embodiment, an alkali metal gasification catalyst can be impregnated into one or more of the particulates by slurring with a solution (e.g., aqueous) of the catalyst. When a particulate is slurried with a solution of the catalyst and/or co-catalyst, the resulting slurry can be dewatered to provide a catalyzed particulate, again typically, as a wet cake. The catalyst solution for slurring the particulate can be prepared from any catalyst source in the present methods, including fresh or make-up catalyst and recycled catalyst or catalyst solution (infra). Methods for dewatering the slurry to provide a wet cake of the catalyzed particulate include filtration (gravity or vacuum), centrifugation, and a fluid press.

[0070] One particular method suitable for combining coal with a gasification catalyst to provide a catalyzed particulate is via ion exchange as described in in previously incorporated U.S. patent application Ser. No. 12/178,380 (filed 23 Jul. 2008). Catalyst loading by ion exchange mechanism may be maximized based on adsorption isotherms specifically developed for the coal, as discussed in the incorporated reference. Such loading provides a catalyzed particulate as a wet cake. Additional catalyst retained on the ion-exchanged particulate wet cake, including inside the pores, can be controlled so that the total catalyst target value can be obtained in a controlled manner. The catalyst loaded and dewatered wet cake may contain, for example, about 50 % moisture. The total amount of catalyst loaded can be controlled by controlling the concentration of catalyst components in the solution, as well as the contact time, temperature and method, as can be readily determined by those of ordinary skill in the relevant art based on the characteristics of the starting coal.

[0071] Alternatively, the slurried particulates may be dried with a fluid bed slurry drier (i.e., treatment with superheated steam to vaporize the liquid), or the solution evaporated, to provide a dry catalyzed particulate.

[0072] The catalyzed particulates may comprise greater than about 10%, greater than about 20%, greater than about 30%, greater than about 40%, greater than about 50%, greater than about 70%, greater than about 85%, or greater than about 90% of the total amount of the gasification catalyst of the particulate composition. The percentage of total gasification

catalyst that is associated with the particulates can be determined according to methods known to those skilled in the art.

[0073] Separate particulates, with or without catalyst, can be blended appropriately to control, for example, the total catalyst loading or other qualities of the particulate composition, as discussed previously. The appropriate ratios of the separate particulates will depend on the qualities of the feedstocks as well as the desired properties of the particulate composition. For example, a biomass char particulate and a catalyzed non-biomass particulate can be combined in such a ratio to yield a particulate composition having a predetermined ash content, as discussed previously.

[0074] Separate particulates, as one or more dry particulates and/or one or more wet cakes, can be combined by any methods known to those skilled in the art including, but not limited to, kneading, and vertical or horizontal mixers, for example, single or twin screw, ribbon, or drum mixers. The resulting particulate composition can be stored for future use or transferred to a feed operation for introduction into a gasification reactor. The particulate composition can be conveyed to storage or feed operations according to any methods known to those skilled in the art, for example, a screw conveyor or pneumatic transport.

[0075] Ultimately, the particulate composition may be dried, under a flow of an inert gas, with a fluid bed slurry drier (i.e., treatment with superheated steam to vaporize the liquid), or the solution evaporated, to provide a catalyzed particulate typically having a residual moisture content of, for example, less than about 8 wt %, or less than about 6 wt %, or less than about 4 wt %.

[0076] In an embodiment of the third aspect, the present invention provides a process for preparing a particulate composition according to the first aspect, the process comprising the steps of: (a) providing a first particulate carbonaceous feedstock that is a biomass char, a second particulate carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and a gasification catalyst; (b) contacting the first carbonaceous feedstock and the second carbonaceous feedstock with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; (c) dewatering the slurry to form a catalyst-loaded wet cake; and (d) thermally treating the wet coal cake under a flow of inert dry gas to form the particulate composition.

[0077] In another embodiment of the third aspect, the present invention provides a process for preparing a particulate composition according to the first aspect, the process comprising the steps of: (a) providing a first particulate carbonaceous feedstock that is a biomass char, a second particulate carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and a gasification catalyst; (b) contacting the first carbonaceous feedstock with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; (c) dewatering the slurry to form a catalyst-

loaded wet cake; (d) mixing the catalyst-loaded wet cake with and the second carbonaceous feedstock to form a mixture; and (e) thermally treating the mixture under a flow of inert dry gas to form the particulate composition.

[0078] In another embodiment of the third aspect, the present invention provides a process for preparing a particulate composition according to the first aspect, the process comprising the steps of: (a) providing a first particulate carbonaceous feedstock that is a biomass char, a second particulate carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and a gasification catalyst; (b) contacting the second carbonaceous feedstock with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; (c) dewatering the slurry to form a catalyst-loaded wet cake; (d) mixing the catalyst-loaded wet cake with and the first carbonaceous feedstock to form a mixture; and (e) thermally treating the mixture under a flow of inert dry gas to form the particulate composition.

Catalytic Gasification Methods

[0079] The particulate compositions of the present disclosure are particularly useful in integrated gasification processes for converting biomass and non-biomass to combustible gases, such as methane. The gasification reactors for such processes are typically operated at moderately high pressures and temperature, requiring introduction of the particulate composition to the reaction zone of the gasification reactor while maintaining the required temperature, pressure, and flow rate of the feedstock. Those skilled in the art are familiar with feed systems for providing feedstocks to high pressure and/or temperature environments, including, star feeders, screw feeders, rotary pistons, and lock-hoppers. It should be understood that the feed system can include two or more pressure-balanced elements, such as lock hoppers, which would be used alternately.

[0080] In some instances, the particulate composition can be prepared at pressures conditions above the operating pressure of gasification reactor. Hence, the particulate composition can be directly passed into the gasification reactor without further pressurization.

[0081] Any of several catalytic gasifiers can be utilized. Suitable gasification reactors include counter-current fixed bed, co-current fixed bed, fluidized bed, entrained flow, and moving bed reactors.

[0082] The particulate compositions are particularly useful for gasification at moderate temperatures of at least about 450° C., or of at least about 600° C. or above, to about 900° C., or to about 750° C., or to about 700° C.; and at pressures of at least about 50 psig, or at least about 200 psig, or at least about 400 psig, to about 1000 psig, or to about 700 psig, or to about 600 psig.

[0083] The gas utilized in the gasification reactor for pressurization and reactions of the particulate composition typically comprises steam, and optionally, oxygen or air, and are supplied to the reactor according to methods known to those skilled in the art. For example, any of the steam boilers known to those skilled in the art can supply steam to the reactor. Such boilers can be powered, for example, through the use of any carbonaceous material such as powdered coal, biomass etc., and including but not limited to rejected carbonaceous materials from the particulate composition preparation operation (e.g., fines, supra). Steam can also be supplied from a second gasification reactor coupled to a combustion turbine where the exhaust from the reactor is thermally exchanged to a water

source and produce steam. Alternatively, the steam may be provided to the gasification reactor as described previously incorporated U.S. patent applications Ser. No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1), and Ser. No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1).

[0084] Recycled steam from other process operations can also be used for supplying steam to the reactor. For example, when the slurried particulate composition is dried with a fluid bed slurry drier, as discussed previously, the steam generated through vaporization can be fed to the gasification reactor.

[0085] The small amount of required heat input for the catalytic gasification reaction can be provided by superheating a gas mixture of steam and recycle gas feeding the gasification reactor by any method known to one skilled in the art. In one method, compressed recycle gas of CO and H₂ can be mixed with steam and the resulting steam/recycle gas mixture can be further superheated by heat exchange with the gasification reactor effluent followed by superheating in a recycle gas furnace.

[0086] A methane reformer can be included in the process to supplement the recycle carbon monoxide and hydrogen fed to the reactor to ensure that enough recycle gas is supplied to the reactor so that the net heat of reaction is as close to neutral as possible (only slightly exothermic or endothermic), in other words, that the reaction is run under thermally neutral conditions. In such instances, methane can be supplied for the reformer from the methane product, as described below.

[0087] Reaction of the particulate composition under the described conditions typically provides a crude product gas and a char. The char produced in the gasification reactor during the present processes typically is removed from the gasification reactor for sampling, purging, and/or catalyst recovery. Methods for removing char are well known to those skilled in the art. One such method taught by EP-A-0102828, for example, can be employed. The char can be periodically withdrawn from the gasification reactor through a lock hopper system, although other methods are known to those skilled in the art. Processes have been developed to recover alkali metal from the solid purge in order to reduce raw material costs and to minimize environmental impact of a catalytic gasification process.

[0088] The char can be quenched with recycle gas and water and directed to a catalyst recycling operation for extraction and reuse of the alkali metal catalyst. Particularly useful recovery and recycling processes are described in U.S. Pat. No. 4,459,138, as well as previously incorporated U.S. Pat. No. 4,057,512 and US2007/0277437A1, and previously incorporated U.S. patent application Ser. Nos. 12/342,554, 12/342,715, 12/342,736 and 12/343,143. Reference can be had to those documents for further process details.

[0089] Crude product gas effluent leaving the gasification reactor can pass through a portion of the gasification reactor which serves as a disengagement zone where particles too heavy to be entrained by the gas leaving the gasification reactor (i.e., fines) are returned to the fluidized bed. The disengagement zone can include one or more internal cyclone separators or similar devices for removing fines and particulates from the gas. The gas effluent passing through the disengagement zone and leaving the gasification reactor gener-

ally contains CH₄, CO₂, H₂ and CO, H₂S, NH₃, unreacted steam, entrained fines, and other contaminants such as COS.

[0090] The gas stream from which the fines have been removed can then be passed through a heat exchanger to cool the gas and the recovered heat can be used to preheat recycle gas and generate high pressure steam. Residual entrained fines can also be removed by any suitable means such as external cyclone separators, optionally followed by Venturi scrubbers. The recovered fines can be processed to recover alkali metal catalyst, or directly recycled back to feedstock preparation as described in previously incorporated U.S. patent application Ser. No. _____, entitled "CARBON-ACEOUS FINES RECYCLE" (attorney docket no. FN-0028 US NP1).

[0091] The gas stream from which the fines have been removed can be fed to COS hydrolysis reactors for COS removal (sour process) and further cooled in a heat exchanger to recover residual heat prior to entering water scrubbers for ammonia recovery, yielding a scrubbed gas comprising at least H₂S, CO₂, CO, H₂, and CH₄. Methods for COS hydrolysis are known to those skilled in the art, for example, see U.S. Pat. No. 4,100,256.

[0092] The residual heat from the scrubbed gas can be used to generate low pressure steam. Scrubber water and sour process condensate can be processed to strip and recover H₂S, CO₂ and NH₃; such processes are well known to those skilled in the art. NH₃ can typically be recovered as an aqueous solution (e.g., 20 wt %).

[0093] A subsequent acid gas removal process can be used to remove H₂S and CO₂ from the scrubbed gas stream by a physical absorption method involving solvent treatment of the gas to give a cleaned gas stream. Such processes involve contacting the scrubbed gas with a solvent such as monoethanolamine, diethanolamine, methyldiethanolamine, diisopropylamine, diglycolamine, a solution of sodium salts of amino acids, methanol, hot potassium carbonate or the like. One method can involve the use of Selexol® (UOP LLC, Des Plaines, Ill. USA) or Rectisol® (Lurgi A G, Frankfurt am Main, Germany) solvent having two trains; each train consisting of an H₂S absorber and a CO₂ absorber. The spent solvent containing H₂S, CO₂ and other contaminants can be regenerated by any method known to those skilled in the art, including contacting the spent solvent with steam or other stripping gas to remove the contaminants or by passing the spent solvent through stripper columns. Recovered acid gases can be sent for sulfur recovery processing. The resulting cleaned gas stream contains mostly CH₄, H₂, and CO and, typically, small amounts of CO₂ and H₂O. Any recovered H₂S from the acid gas removal and sour water stripping can be converted to elemental sulfur by any method known to those skilled in the art, including the Claus process. Sulfur can be recovered as a molten liquid. One method for removing acid gases from the scrubbed gas stream is described in previously incorporated U.S. patent application Ser. No. _____, entitled "SELECTIVE REMOVAL AND RECOVERY OF ACID GASES FROM GASIFICATION PRODUCTS" (attorney docket no. FN-0023 US NP1).

[0094] The cleaned gas stream can be further processed to separate and recover CH₄ by any suitable gas separation method known to those skilled in the art including, but not limited to, cryogenic distillation and the use of molecular sieves or ceramic membranes. One method for separating and recovering methane from the cleaned gas stream is described in previously incorporated U.S. patent application Ser. No.

_____, entitled "PROCESS AND APPARATUS FOR THE SEPARATION OF METHANE FROM A GAS STREAM" (attorney docket no. FN-0022 US NP1).

[0095] Typically, two gas streams can be produced by the gas separation process, a methane product stream and a syngas stream (H₂ and CO). The syngas stream can be compressed and recycled to the gasification reactor. If necessary, a portion of the methane product can be directed to a reformer, as discussed previously and/or a portion of the methane product can be used as plant fuel.

EXAMPLES

Example 1

[0096] Feedstock Preparation

[0097] Switchgrass can be dried and crushed to produce a particulate having an average size of about 250 microns. The biomass feedstock can be provided to a combustion reactor fed by an enriched oxygen source. The resulting exhaust gas from the combustion reactor would contain hot CO₂. The exhaust gas can be passed through a heat exchanger in contact with a water source to produce steam, a portion of which can be provided to a steam turbine to generate electricity. The biomass char produced from the biomass combustion reactor can be withdrawn and directed to a feedstock preparation operation where the biomass char can be crushed to a particle size ranging from about 0.85 to about 1.4 mm. Fines (<0.85 mm) can be separated from the crushed biomass char by vibratory screening.

[0098] Separately, as-received coal (Powder River Basin) can be stage-crushed to maximize the amount of material having particle sizes ranging from about 0.85 to about 1.4 mm. Fines (<0.85 mm) can be separated from the crushed materials by vibratory screening and the crushed coal can be slurried with an aqueous solution of potassium carbonate and dewatered to provide a wet cake of a catalyzed coal feedstock.

[0099] The wet cake of the catalyzed coal feedstock can be kneaded together, in a 9:1 w/w ratio on a dry basis, with the crushed biomass char to provide a blended feedstock which can be dried via a fluid bed slurry drier to a final state having about 5 wt % residual moisture.

Example 2

[0100] Catalytic Gasification

[0101] A portion of the generated steam from the heat exchanger of Example 1 can be superheated and then introduced to a fluidized bed gasification reactor (catalytic gasifier) supplied with the blended feedstock of Example 1. The blended feedstock can be introduced under a positive pressure of nitrogen. Typical conditions for the catalytic gasifier could be: total pressure, 500 psi and temperature, 1200° F. The effluent of the catalytic gasifier could contain methane, CO₂, H₂, CO, water, H₂S, ammonia, and nitrogen, which can be passed to a scrubber to remove ammonia and an acid gas removal unit to remove H₂S and CO₂. The CO₂ can be recovered.

We claim:

1. A particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone, the particulate composition comprising an intimate mixture of:
 - (a) a first carbonaceous feedstock that is a biomass char;
 - (b) a second carbonaceous feedstock that is a biomass, non-biomass, or a mixture thereof, and

(c) a gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed, wherein:

- (i) the first carbonaceous feedstock and second carbonaceous feedstock are present in the particulate composition at a weight ratio of from about 5:95 to about 95:5; and
- (ii) the gasification catalyst comprises a source of at least one alkali metal and is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms of the gasification catalyst to carbon atoms ranging from about 0.01 to about 0.10, wherein the biomass char comprises at least a portion of the source of at least one alkali metal.

2. The particulate composition according to claim 1, wherein a portion of the gasification catalyst is loaded on at least one of the first carbonaceous feedstock and the second carbonaceous feedstock.

3. The particulate composition according to claim 1, wherein the alkali metal comprises potassium, sodium or both.

4. The particulate composition according to claim 1, wherein the alkali metal is potassium.

5. The particulate composition according to claim 1, wherein the biomass char comprises all of the gasification catalyst.

6. The particulate composition according to claim 5, wherein the alkali metal is potassium.

7. The particulate composition according to claim 1, having a particle size ranging from about 25 microns to about 2500 microns.

8. The particulate composition according to claim 1, having a residual moisture content of less than about 4 wt. %.

9. The particulate compositions according to the claim 1, wherein the second carbonaceous feedstock is a non-biomass.

10. A process for converting a particulate composition into a plurality of gaseous products, the process comprising the steps of:

- (a) supplying a particulate composition according to claim 1 to a gasifying reactor;
- (b) reacting the particulate composition in the gasifying reactor in the presence of steam and under suitable temperature and pressure to form a plurality of gaseous including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons; and
- (c) at least partially separating the plurality of gaseous products to produce a stream comprising a predominant amount of one of the gaseous products.

11. The process according to claim 10, wherein the stream comprises a predominant amount of methane.

12. The process according to claim 10, wherein a char is formed in step (b), and the char is removed from the gasifying reactor and sent to a catalyst recovery and recycle process.

13. The process according to claim 12, wherein the gasification catalyst comprises gasification catalyst recycled from the catalyst recovery and recycle process.

14. A process for preparing a particulate composition, the process comprising the steps of:

- (a) providing a first particulate carbonaceous feedstock that is a biomass char, a second particulate carbonaceous feedstock that is a biomass, non-biomass, or mixture thereof, and, optionally, an alkali metal gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases including methane and at least one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed from the particulate composition;
- (b) mixing the first particulate carbonaceous feedstock, the second particulate carbonaceous feedstock and, optionally, the alkali metal gasification catalyst to form a mixture; and
- (c) optionally thermally treating the mixture under a flow of inert dry gas to form the particulate composition, wherein

the gasification catalyst comprises a source of at least one alkali metal and is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms of the gasification catalyst to carbon atoms ranging from about 0.01 to about 0.10, wherein the biomass char comprises at least a portion of the source of at least one alkali metal.

15. The process according to claim 14, wherein the first carbonaceous feedstock and second carbonaceous feedstock are contacted separately with an aqueous solution comprising at least a portion of the gasification catalyst to form first and second slurries; the first and second slurries are dewatered separately to form first and second catalyst-loaded wet cakes; and the first and second catalyst-loaded wet cakes are mixed to form the mixture.

16. The process according to claim 14, wherein the first carbonaceous feedstock and second carbonaceous feedstock are contacted separately with an aqueous solution comprising at least a portion of the gasification catalyst to form first and second slurries; the first and second slurries are dewatered separately to form first and second catalyst-loaded wet cakes; the first and second catalyst-loaded wet cakes are separately thermally treated to form first and second dry particulates; and the first and second dry particulates are mixed to form the mixture.

17. The process according to claim 14, wherein the first carbonaceous feedstock and second carbonaceous feedstock are mixed to form a blend; the blend is contacted with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; and the slurry is dewatered to form a catalyst-loaded wet cake which is the mixture.

18. The process according to claim 14, wherein the first carbonaceous feedstock is contacted with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; the slurry is dewatered to form a catalyst-loaded wet cake; and the catalyst-loaded wet-cake is mixed with the second carbonaceous feedstock to form the mixture.

19. The process according to claim 14, wherein the second carbonaceous feedstock is contacted with an aqueous solution comprising at least a portion of the gasification catalyst to form a slurry; the slurry is dewatered to form a catalyst-loaded wet cake; and the catalyst-loaded wet-cake is mixed with the first carbonaceous feedstock to form the mixture.

20. The process according to claim 14, wherein the first carbonaceous feedstock and the second carbonaceous feedstocks are mixed to form the mixture.