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(54) Title: CATALYTIC GASIFICATION PARTICULATE COMPOSITIONS

(57) Abstract: Particulate compositions are described comprising a carbonaceous material, such as petroleum coke and/or coal, treated or otherwise associated with a gasification catalyst, where the catalyst is at least in part derived from a leachate from a biomass char, 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.



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CATALYTIC GASIFICATION PARTICULATE COMPOSITIONS

Field of the Invention

[0001] The present disclosure relates to particulate compositions comprising a leachate derived from biomass gasification or combustion char, carbonaceous materials, and at least one 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.

Background of the Invention

[0002] 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 US3828474, US3998607, US4057512, US4092125, US4094650, US4204843, US4468231, US4500323, US4541841, US4551155, US4558027, US4606105, US4617027, US4609456, US5017282, US5055181, US6187465, US6790430, US6894183, US6955695, US2003/0167961A1, US2006/0265953A1, US2007/000177A1, US2007/083072A1, US2007/0277437A1 and GB1599932.

[0003] 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 compounds having catalytic activity 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 overall utilization and conversion of the feedstocks in the process.

Summary of the Invention

[0004] The present disclosure relates to particulate compositions comprising a leachate of a biomass char, a carbonaceous material, and at least one 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 particulate carbonaceous materials with the biomass char leachate in the feedstock, more efficient utilization of the elemental content of the biomass can be realized, particularly taking advantage of intrinsic alkali metal compounds present in certain types of biomass char.

[0005] 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 a carbonaceous feedstock and a gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases comprising methane and one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed, 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 to carbon atoms ranging from about 0.01 to about 0.10, and wherein the particulate composition comprises an intimate mixture of (a) a biomass char leachate comprising one or more soluble alkali metal compounds, and (b) a carbonaceous feedstock, wherein the biomass char leachate comprises an aqueous extract of a biomass char, and the gasification catalyst comprises the one or more soluble alkali metal compounds from the biomass char leachate.

[0006] In a second aspect, the present invention provides a process for preparing a particulate composition having a particle size distribution suitable for gasification in a fluidized bed zone, the process comprising the steps of: (a) providing particulates of a biomass char and a particulate carbonaceous feedstock other than the biomass char, the biomass char comprising a source of one or more soluble alkali metal compounds as a gasification catalyst; (b) contacting the biomass char with water under suitable temperature and pressure so as to substantially extract the water-soluble alkali metal compounds from the biomass char and form a leachate, the leachate comprising one or more soluble alkali metal compounds; (c) contacting the carbonaceous feedstock with the leachate to form a slurry; (d) dewatering the slurry to form a wet cake; and (e) thermally treating the wet cake with an inert dry gas to provide a particulate composition, wherein: (i) the gasification catalyst, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases comprising methane and one or more of hydrogen, carbon monoxide,

carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed; and (ii) the gasification catalyst is present in an amount sufficient to provide, in the gasification catalyst-loaded carbonaceous feedstock, a ratio of alkali metal atoms to carbon atoms ranging from about 0.01 to about 0.10.

[0007] In a third 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, and/or prepared according to the second 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 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.

Detailed Description

[0008] The present disclosure relates to a particulate composition, methods for the preparation of the particulate composition, and methods for the catalytic gasification of the particulate composition. Generally, the particulate composition comprises a biomass char leachate in combination with one or more carbonaceous materials, for example, coals and/or petroleum coke.

[0009] 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 Serial Nos. 12/178,380 (filed 23 July 2008), 12/234,012 (filed 19 September 2008) and 12/234,018 (filed 19 September 2008). All of the above are incorporated by reference herein for all purposes as if fully set forth.

[0010] 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 December 28, 2008: Serial No. 12/342,554, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Serial No. 12/342,565, entitled "PETROLEUM COKE COMPOSITIONS FOR CATALYTIC GASIFICATION"; Serial No. 12/342,578, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION";

Serial No. 12/342,596, entitled "PROCESSES FOR MAKING SYNTHESIS GAS AND SYNGAS-DERIVED PRODUCTS"; Serial No. 12/342,608, entitled "PETROLEUM COKE COMPOSITIONS FOR CATALYTIC GASIFICATION"; Serial No. 12/342,628, entitled "PROCESSES FOR MAKING SYNGAS-DERIVED PRODUCTS"; Serial No. 12/342,663, entitled "CARBONACEOUS FUELS AND PROCESSES FOR MAKING AND USING THEM"; Serial No. 12/342,715, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Serial No. 12/342,736, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Serial No. 12/343,143, entitled "CATALYTIC GASIFICATION PROCESS WITH RECOVERY OF ALKALI METAL FROM CHAR"; Serial No. 12/343,149, entitled "STEAM GENERATING SLURRY GASIFIER FOR THE CATALYTIC GASIFICATION OF A CARBONACEOUS FEEDSTOCK"; and Serial 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.

[0011] 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: Serial No. _____, entitled "PROCESSES FOR MAKING ABSORBENTS AND PROCESSES FOR REMOVING CONTAMINANTS FROM FLUIDS USING THEM" (attorney docket no. FN-0019 US NP1); Serial No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1); Serial No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1); Serial No. _____, entitled "PROCESS AND APPARATUS FOR THE SEPARATION OF METHANE FROM A GAS STREAM" (attorney docket no. FN-0022 US NP1); Serial No. _____, entitled "SELECTIVE REMOVAL AND RECOVERY OF ACID GASES FROM GASIFICATION PRODUCTS" (attorney docket no. FN-0023 US NP1); Serial No. _____, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0024 US NP1); Serial No. _____, entitled "COAL COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0025 US NP1); Serial No. _____, entitled "CO-FEED OF BIOMASS AS SOURCE OF MAKEUP CATALYSTS FOR CATALYTIC COAL GASIFICATION" (attorney docket no. FN-0026 US NP1); Serial No. _____, entitled "COMPACTOR-FEEDER" (attorney

docket no. FN-0027 US NP1); Serial No. _____, entitled "CARBONACEOUS FINES RECYCLE" (attorney docket no. FN-0028 US NP1); Serial No. _____, entitled "BIOMASS CHAR COMPOSITIONS FOR CATALYTIC GASIFICATION" (attorney docket no. FN-0029 US NP1); and Serial 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.

[0012] All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein their entirety for all purposes as if fully set forth.

[0013] 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.

[0014] Except where expressly noted, trademarks are shown in upper case.

[0015] 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.

[0016] Unless stated otherwise, all percentages, parts, ratios, *etc.*, are by weight.

[0017] When an amount, concentration, or other value or parameter is given as a range, or a list of upper and lower values, this 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 endpoints 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.

[0018] 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.

[0019] 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).

[0020] 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.

[0021] 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.

[0022] The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting.

Biomass

[0023] 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.

[0024] 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, switchgrass, sudangrass, millet, jatropha, and miscanthus (*e.g.*, *Miscanthus x 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.

[0025] 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).

[0026] 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 cannabinus*), thistle, and almond shells and husks.

Biomass Char

[0027] 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.

[0028] 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.

[0029] 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 US Patent Applications Serial No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1), and Serial No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1).

[0030] Preferably, the biomass char comprises an alkali metal source such that the biomass char provides at least a portion of the gasification catalyst for preparation of the particulate compositions described herein. In one embodiment, the biomass char comprises substantially all, or all, of the gasification catalyst for preparation of the particulate compositions described herein.

[0031] 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 biomass char leachate herein is not required to be prepared from the same biomass as may be utilized in preparing the particulate compositions.

Biomass Char Leachate

[0032] A leachate can be prepared from any of the biomass chars described above. Preferably, the biomass char is a char from the gasification or combustion of a catalytic biomass, as defined herein. Such chars can be extracted from a gasification or combustion reactor and forwarded to a leachate preparation operation, where soluble alkali metal compounds can be extracted from the char. Due to agglomeration of the char within the gasification or combustion reactor, the biomass char may need to be crushed or ground to a particulate size appropriate for a solid extraction. The particulate can be prepared via crushing and/or grinding according to any methods known in the art, such as impact crushing and wet or dry grinding to yield the particulate. Examples of suitable methods for the wet

grinding, sizing, and dewatering are known to those skilled in the art; for example, see previously incorporated US Patent Application Serial No. 12/178,380 (filed 23 July 2008).

[0033] Alternatively, the biomass char may be reduced in particle size by quenching a hot biomass char with water, such that the stress induced in the char by the rapid temperature change causes the char to shatter into smaller particles and provide a slurry (*infra*). See, for example, previously incorporated US2007/0277437A1.

[0034] In one example, the biomass char is reduced to a particle size distribution of about 25 to 2500 microns.

[0035] For quenching, the invention places no particular limits on the ratio of aqueous medium to char, or on the temperature of the aqueous medium. In some embodiments, however, the wt/wt ratio of water in the aqueous medium to the water-insoluble component of the char ranges from about 3:1, or from about 5:1, up to about 7:1, or up to about 15:1. Additionally, in some embodiments, the aqueous medium has a temperature that ranges from about 95°C up to about 110°C, or up to about 140°C, up to about 200°C, or up to about 300°C. The pressure need not be elevated above atmospheric pressure. In some embodiments, however, the quenching occurs at pressures higher than atmospheric pressure. For example, the quenching may occur at pressures up to about 25 psig, or up to about 40 psig, or up to about 60 psig, or up to about 80 psig, or up to about 400 psig. The quenching process preferably occurs under a stream of gas that is substantially free of oxygen or other oxidants, and may optionally comprise carbon dioxide.

[0036] The biomass char leachate may also be preparing by washing the char, either before or after quenching, via methods well known to those of ordinary skill in the art. In some embodiments of the invention, the biomass char is washed with an aqueous medium to produce a wash stream comprising at least a portion of the soluble alkali metal compounds in the char.

[0037] As used herein, the term “washing” is not limited to a single flush of the insoluble matter with an aqueous medium, such as water. Rather, each washing step may include multiple staged counter-washings of the insoluble matter. In some embodiments of the invention, the washing of the biomass char comprises at least two staged counter-washings. In some embodiments, the washing of the biomass char comprises at least five staged counter-washings. The washing may be performed according to any suitable method known

to those of skill in the art. For example, the washing step may be performed using a continuous multi-stage counter-current system whereby solids and liquids travel in opposite directions. As known to those of skill in the art, the multi-stage counter current wash system may include mixers/settlers (CCD or decantation), mixers/filters, mixers/hydrocyclones, mixers/centrifuges, belt filters, and the like.

[0038] The wash stream (leachate) is recovered by typical means of separating a solid particulate from a liquid. Illustrative methods include, but are not limited to, filtration (gravity or vacuum), centrifugation, and use of a fluid press.

[0039] Under the described suitable temperature and pressure conditions, alkali metal compounds can be substantially extracted from the biomass char and form a leachate and a depleted biomass char, the leachate comprising one or more soluble alkali metal compounds from the biomass char.

[0040] After separation, the leachate can be forwarded to a unit operation for preparing a particulate composition for catalytic gasification, as discussed below.

[0041] Optionally, the leachate may be dried, such as by exposure to a stream of an inert gas and/or heating, to provide a solid leachate which can be utilized in the preparation of the feedstocks of the invention.

Carbonaceous Materials

[0042] The term “carbonaceous material” as used herein means any carbon containing material including, but not limited to “biomass” as defined herein, coal, and petroleum coke, as defined herein. For example, carbonaceous materials include, but are not limited to, anthracite, bituminous coal, sub-bituminous coal, lignite, petroleum coke, asphaltenes, liquid petroleum residues, or mixtures thereof.

(a) Petroleum Coke

[0043] The terms “petroleum coke” and “petcoke” as used here 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.

[0044] 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.

[0045] 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.

[0046] 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.

[0047] 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.

[0048] The term “asphaltene” as used herein is an aromatic carbonaceous solid at room temperature, and can be derived, from example, from the processing of crude oil and crude oil tar sands.

[0049] The term “liquid petroleum residue” as used herein includes both (i) the liquid thermal decomposition product of high-boiling hydrocarbon fractions obtained in petroleum processing (heavy residues – “resid liquid petroleum residue”) and (ii) the liquid thermal decomposition product of processing tar sands (bituminous sands or oil sands – “tar sands liquid petroleum residue”). The liquid petroleum residue is substantially non-solid; for example, it can take the form of a thick fluid or a sludge.

[0050] Resid liquid petroleum residue can also be derived from a crude oil, for example, by processes used for upgrading heavy-gravity crude oil distillation residue. Such liquid

petroleum residue 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 residue. Typically, the ash in such lower-ash residues predominantly comprises metals such as nickel and vanadium.

[0051] Tar sands liquid petroleum residue can be derived from an oil sand, for example, by processes used for upgrading oil sand. Tar sands liquid petroleum residue 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 residue. Typically, the ash in such higher-ash residues predominantly comprises materials such as compounds of silicon and/or aluminum.

(b) Coal

[0052] 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 (ND), 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].

[0053] 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, DC, 1976].

[0054] 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, DC, 1973.]

Particulate Compositions

[0055] The particulate compositions according to the present disclosure are based on the above-described biomass char leachate in combination with a one or more carbonaceous materials, such as coal and/or petroleum coke, and a gasification catalyst. The gasification catalyst comprises an alkali metal source, typically, as an alkali metal and/or an alkali metal compound. In general, the alkali metal source is the biomass char leachate produced from gasification and/or combustion of a catalytic biomass. In such embodiments, an additional alkali metal source may or may not be added to the leachate as a make-up stream as a solid or a solution. 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.

[0056] Catalytic biomass, as defined herein, intrinsically contains significant levels of alkali metal compounds which can be found concentrated within the char produced from their gasification and/or combustion. For example, catalytic biomass can be reacted in any type of combustion or gasification reactor to produce a biomass char having increased levels of alkali metal compounds (*e.g.*, K_2O and/or Na_2O), with respect to chars produced from other biomass sources. Such biomass chars, rich in such alkali metal compounds, can be extracted from a gasification or combustion reactor and extracted, as described above, to produce a leachate which can be utilized for the preparation of the particulate compositions of the present invention

[0057] The alkali metal source is 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 carbonaceous materials in the particulate composition, on a mass basis. Such catalysts typically comprise a source of at least one alkali metal, and is 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.

[0058] 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, formates, 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.

[0059] Co-catalysts or other catalyst additives may also be utilized, such as disclosed in the previously incorporated references.

[0060] Each of carbonaceous materials (*e.g.*, coal, petcoke, biomass) 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.

[0061] Various particulates may be blended in preparing the particulate compositions of the invention. The ratio of the various particulates in the particulate compositions can be selected based on technical considerations, processing economics, availability, and proximity of the carbonaceous material 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, coal and petroleum coke particulates 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.

[0062] The ratio of the various carbonaceous material particulates can be used to control other material characteristics of the feedstock blend. Carbonaceous 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.

[0063] In preparing the particulate compositions of the present invention, the ash content of the various carbonaceous material 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 carbonaceous material 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.

[0064] 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.

[0065] 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 carbonaceous material.

[0066] Through the recycling of a biomass char, particularly from a catalytic biomass, higher utilization of the biomass constituents may be realized, reducing materials input.

Methods for Making the Particulate Composition

[0067] The carbonaceous material sources typically require initial processing to prepare the particulate composition of the present invention. 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.

[0068] 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.

[0069] Any method known to those skilled in the art can be used to size the particulates. For example, sizing can be performed 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 particulates. Classification equipment can include ore sorters, gas cyclones, hydrocyclones, rake classifiers, rotating trommels, or fluidized classifiers. The carbonaceous materials can be also sized or classified prior to grinding and/or crushing.

[0070] Additional feedstock processing steps may be necessary. Biomass may contain high moisture contents, such as green plants and grasses, and may require drying prior to crushing. Likewise, carbonaceous materials such as high-moisture coals, can require drying prior to crushing. Some caking coals can require partial oxidation to simplify gasification reactor operation. 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 US4468231 and GB1599932). Often, pre-treatment is accomplished in an oxidative manner using any oxidant known to the art.

[0071] In one example, carbonaceous materials are 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 Serial No. 12/178,380 (filed 23 July 2008).

[0072] 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 carbonaceous material particulates depends on the particular type of carbonaceous materials (*e.g.*, coal, petcoke, and/or biomass), the particle size distribution, and the particular dewatering equipment used.

[0073] The various carbonaceous material particulates, alone or in combination and typically as wet cakes, can subsequently be treated with a leachate or solid leachate of a biomass char to associate at least a first catalyst (*e.g.*, gasification catalyst) therewith, and provide a catalyzed particulate. Any methods known to those skilled in the art can be used to associate one or more gasification catalysts with the particulates to provide a catalyzed particulate. Such methods include but are not limited to, admixing with a solid catalyst source (*i.e.*, comprising the solid leachate) 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. In the present invention, the gasification catalyst is provided, at least in part, according to any one or combination of the preceding methods utilizing the leachate or solid leachate from a biomass char, as described previously. One particular method suitable for combining a coal particulate with a gasification catalyst, utilizing the leachate or solid leachate from a biomass char, to provide a catalyzed particulate is via ion exchange as described in previously incorporated U.S. Patent Application Serial No. 12/178,380 (filed 23 July 2008). In each of the preceding methods, the catalyzed particulate is often obtained as a wet cake.

[0074] The catalyzed particulates typically comprise greater than about 50%, greater than about 70%, greater than about 85%, or greater than about 90% of the total amount of the loaded catalyst associated with the particulate, for instance, as ion-exchanged catalyst on acidic functional groups of the particulates. The percentage of total loaded catalyst that is associated with the particulates can be determined according to methods known to those skilled in the art.

[0075] Optionally, a second catalytic component (*e.g.*, a second gasification catalyst or a co-catalyst) 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 catalysts.

[0076] In one embodiment, an alkali metal gasification catalyst can be impregnated into one or more of the particulates by slurrying the same with the leachate from a biomass char. When a particulate is slurried with the leachate from a biomass char and/or co-catalyst, the resulting slurry can be dewatered to provide a catalyzed particulate, typically, as a wet cake. Methods for dewatering the slurry to provide a wet cake of the catalyzed particulate include filtration (gravity or vacuum), centrifugation, and a fluid press.

[0077] Separate carbonaceous particulates, at least one treated with a leachate or solid leachate from a biomass char, 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 particulate and a catalyzed coal particulate can be combined in such a ratio to yield a particulate composition having a predetermined ash content, as discussed previously. One or more particulates, 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.

[0078] 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 having a residual moisture content, for example, of less than about 8 wt%, or less than about 6 wt%, or less than about 4 wt%. 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 conveyer or pneumatic transport.

[0079] In a specific example, a particulate composition may be prepared according to the preceding methods by providing a first particulate carbonaceous feedstock that is a coal, a second particulate carbonaceous feedstock that is a petroleum coke, and a leachate from a gasification or combustion of a catalytic biomass. The first particulate carbonaceous feedstock and second particulate carbonaceous feedstock can be contacted as a blend with the leachate to form a slurry. The resulting slurry can be dewatered to form a catalyst-loaded wet cake, and the wet cake can be thermally treated under a flow of inert dry gas to form the particulate composition.

[0080] In another example, a particulate composition may be prepared according to the preceding methods by providing a first particulate carbonaceous feedstock that is a coal, a second particulate carbonaceous feedstock that is a petroleum coke, and a leachate from a gasification or combustion of a catalytic biomass. The first particulate carbonaceous feedstock can be contacted with the leachate to form a slurry, and the slurry dewatered to form a catalyst-loaded wet cake. The catalyst-loaded wet cake can be mixed with the second particulate carbonaceous feedstock to form a mixture. Finally, the mixture can be thermally treated, under a flow of inert dry gas, to form the particulate composition.

[0081] In another yet example, a particulate composition may be prepared according to the preceding methods by providing a first particulate carbonaceous feedstock that is a coal, a second particulate carbonaceous feedstock that is a petroleum coke, and a leachate from a gasification or combustion of a catalytic biomass. The second particulate carbonaceous feedstock can be contacted with the leachate to form a slurry and the slurry dewatered to form a catalyst-loaded wet cake. The catalyst-loaded wet cake can be mixed with the first

particulate carbonaceous feedstock to form a mixture, and the mixture thermally treated under a flow of inert dry gas to form the particulate composition.

Catalytic Gasification Methods

[0082] The particulate compositions of the present disclosure are particularly useful integrated gasification processes for converting carbonaceous materials 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.

[0083] 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.

[0084] Any of several catalytic gasifiers can be used. Suitable gasification reactors include counter-current fixed bed, co-current fixed bed, fluidized bed, entrained flow, and moving bed reactors. A catalytic gasifier for gasifying liquid feeds, such as liquid petroleum residues, is disclosed in previously incorporated US6955695.

[0085] 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.

[0086] 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 Serial No. _____, entitled "STEAM GENERATION PROCESSES UTILIZING BIOMASS FEEDSTOCKS" (attorney docket no. FN-0020 US NP1), and Serial No. _____, entitled "REDUCED CARBON FOOTPRINT STEAM GENERATION PROCESSES" (attorney docket no. FN-0021 US NP1).

[0087] 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.

[0088] 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.

[0089] A methane reformer can be included in the process to supplement the recycle CO and H₂ 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.

[0090] 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.

[0091] 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 US4459138, as well as previously incorporated US4057512 and US2007/0277437A1, and previously incorporated U.S. Patent Application Serial 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.

[0092] 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 generally contains CH₄, CO₂, H₂ and CO, H₂S, NH₃, unreacted steam, entrained fines, and other contaminants such as COS.

[0093] 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 U.S. Patent Application Serial No. _____, entitled "CARBONACEOUS FINES RECYCLE" (attorney docket no. FN-0028 US NP1).

[0094] 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 US4100256.

[0095] 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%).

[0096] 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, IL USA) or Rectisol[®] (Lurgi AG, 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 Serial No. _____, entitled "SELECTIVE REMOVAL AND RECOVERY OF ACID GASES FROM GASIFICATION PRODUCTS" (attorney docket no. FN-0023 US NP1).

[0097] 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 are described in as disclosed in previously incorporated U.S. Patent Application Serial No. _____, entitled "PROCESS AND APPARATUS FOR THE SEPARATION OF METHANE FROM A GAS STREAM" (attorney docket no. FN-0022 US NP1).

[0098] 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

[0099] Example 1

[00100] Feedstock Preparation

[00101] 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 could 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 and extracted with water to form a leachate comprising alkali metal compounds.

[00102] 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 the leachate from the switchgrass char and dewatered to provided a wet cake of a catalyzed coal feedstock which can be dried via a fluid bed slurry drier to a final state having about 5 wt% residual moisture.

[00103] Example 2

[00104] *Catalytic Gasification*

[00105] 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 feedstock of Example 1. The 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 a carbonaceous feedstock and a gasification catalyst which, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases comprising methane and one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed, 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 to carbon atoms ranging from about 0.01 to about 0.10, characterized in that the particulate composition comprises an intimate mixture of (a) a biomass char leachate comprising one or more soluble alkali metal compounds, and (b) a carbonaceous feedstock, wherein the biomass char leachate comprises an aqueous extract of a biomass char, and the gasification catalyst comprises the one or more soluble alkali metal compounds from the biomass char leachate.
2. The particulate composition according to claim 1, characterized in that the gasification catalyst further comprises a source of soluble alkali metal compounds that is not from biomass char leachate.
3. The particulate composition according to claim 1 or claim 2, characterized in that the alkali metal comprises potassium, sodium or both.
4. The particulate composition according to claim 3, characterized in that the alkali metal is potassium.
5. The particulate composition according to any of claims 1-4, characterized in that the carbonaceous feedstock comprise a coal, a petroleum coke or a mixture thereof.
6. The particulate composition according to any of claims 1-5, characterized in that the composition has a residual moisture content of less than about 8 wt%.

7. A process for preparing a particulate composition having a particle size distribution suitable for gasification in a fluidized bed zone, characterized in that the process comprising the steps of:

(a) providing particulates of a biomass char and a particulate carbonaceous feedstock other than the biomass char, the biomass char comprising a source of one or more soluble alkali metal compounds as a gasification catalyst;

(b) contacting the biomass char with water under suitable temperature and pressure so as to substantially extract the alkali metal compounds from the biomass char and form a leachate, the leachate comprising one or more soluble alkali metal compounds;

(c) contacting the carbonaceous feedstock with the leachate to form a slurry;

(d) dewatering the slurry to form a wet cake; and

(e) thermally treating the wet cake with an inert dry gas to provide a particulate composition, wherein:

(i) the gasification catalyst, in the presence of steam and under suitable temperature and pressure, exhibits gasification activity whereby a plurality of gases comprising methane and one or more of hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia and other higher hydrocarbons are formed; and

(ii) the gasification catalyst is present in an amount sufficient to provide, in the gasification catalyst-loaded carbonaceous feedstock, a ratio of alkali metal atoms to carbon atoms ranging from 0.01 to about 0.10.

8. The process according to claim 7, characterized in that the contacting step (c) further comprises wet-grinding the carbonaceous feedstock with the leachate.

9. The process according to claim 7 or claim 8, characterized in that the carbonaceous feedstock is contacted with the leachate and additional gasification catalyst.

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 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 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

characterized in that the particulate composition is as set forth in any of claims 1-6, or the particulate composition is prepared by the process of any of claims 7-9.

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

12. The process according to claim 10 or claim 11, characterized in that 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, and the gasification catalyst comprises gasification catalyst recycled from the catalyst recovery and recycle process.