US 20070000177A1

(19) **United States**

(12) **Patent Application Publication**

Hippo et al.

(10) **Pub. No.: US 2007/0000177 A1**

(43) **Pub. Date: Jan. 4, 2007**

(54) **MILD CATALYTIC STEAM GASIFICATION PROCESS**

(76) Inventors: **Edwin J. Hippo**, Makanda, IL (US);
Atul C. Sheth, Fairfield, CA (US)

Correspondence Address:
MORGAN & FINNEGAN, L.L.P.
3 WORLD FINANCIAL CENTER
NEW YORK, NY 10281-2101 (US)

(21) Appl. No.: **11/421,507**

(22) Filed: **Jun. 1, 2006**

Related U.S. Application Data

(60) Provisional application No. 60/695,994, filed on Jul. 1, 2005.

Publication Classification

(51) **Int. Cl.**
C10J 3/00 (2006.01)

(52) **U.S. Cl.** **48/210**

(57) **ABSTRACT**

The present invention provides an improved alkali metal catalyzed steam gasification process that utilizes a CO_2 trap material and/or a mineral binder material within the gasifier. The process optimally achieves over 90% carbon conversion with over 80% yield of methane. The raw gas product can be used directly as fuel. The catalyst can be recovered from the solid purge and recycled to the gasifier and/or the CO_2 trap can be regenerated and recycled to the gasifier.

PROCESS FLOW DIAGRAM OF ENVISIONED MCCG PROCESS

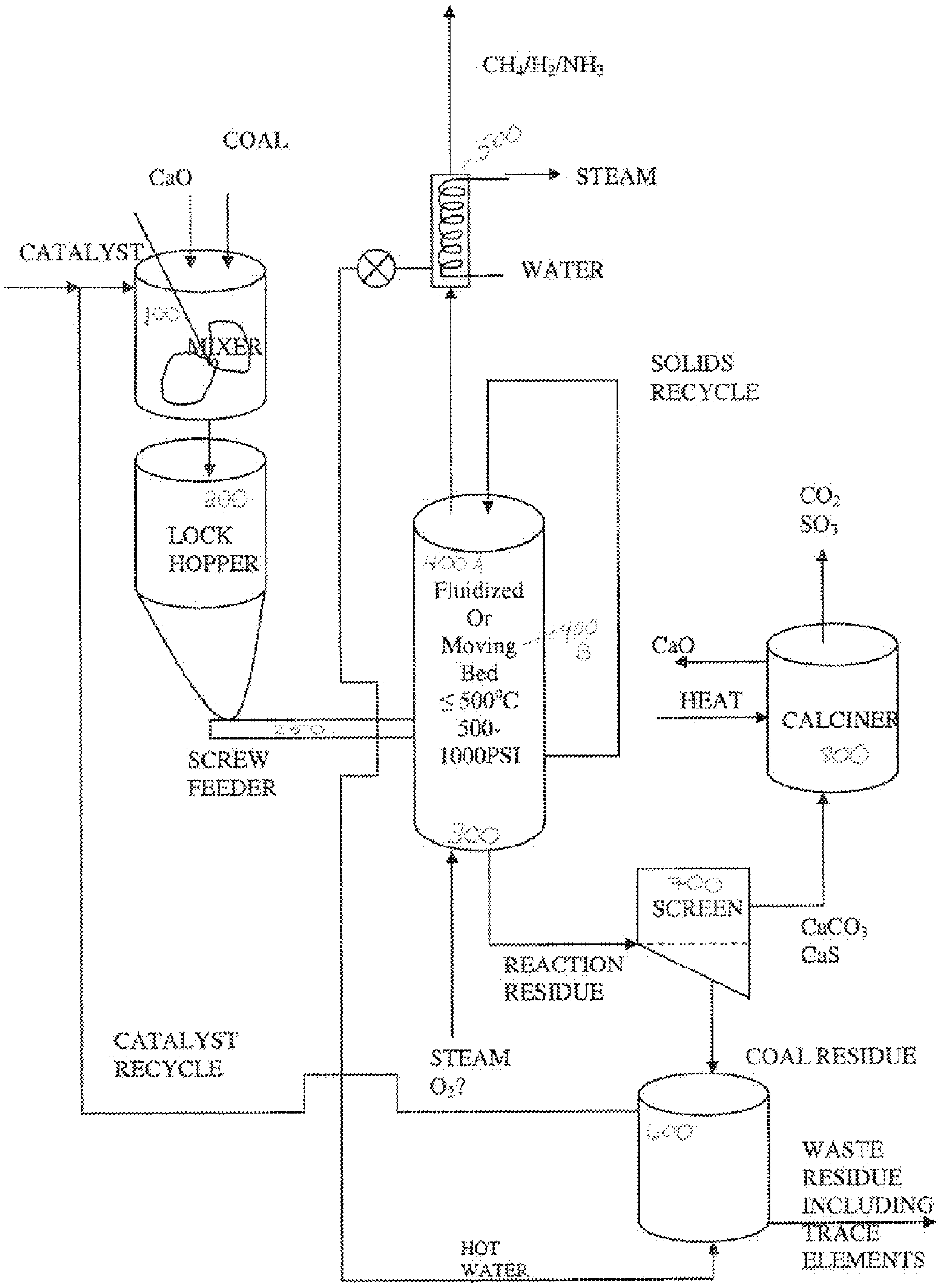
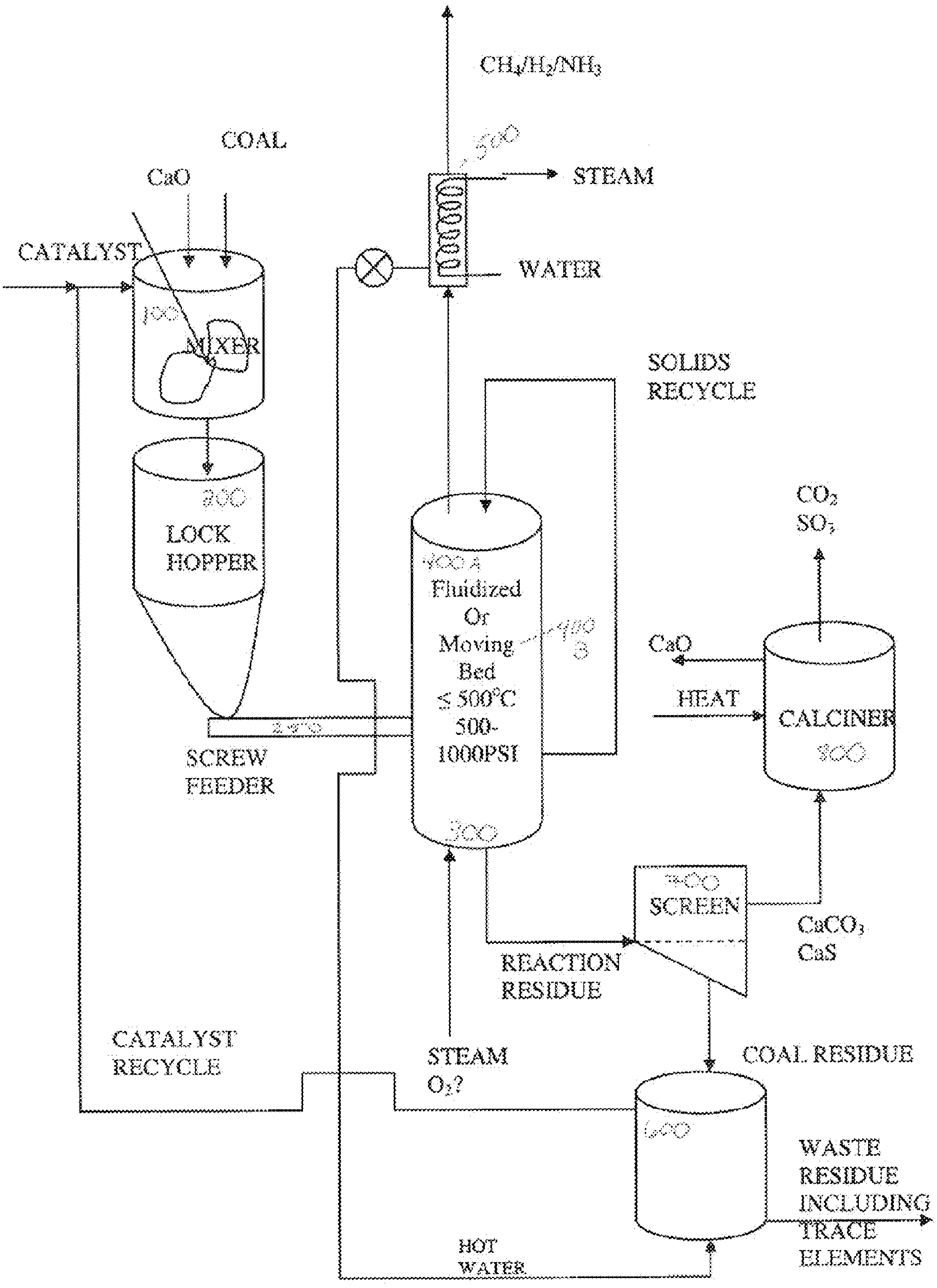


Figure 1: PROCESS FLOW DIAGRAM OF ENVISIONED MCCG PROCESS



MILD CATALYTIC STEAM GASIFICATION PROCESS

[0001] This application claims priority under 35 U.S.C. 119(e) to provisional application 60/695,994 which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to low temperature catalytic gasification of carbonaceous material. More particularly, the present invention relates to an improved process for gasifying carbonaceous material that achieves high carbon conversion to methane at mild temperatures.

BACKGROUND—DESCRIPTION OF RELATED ART

[0003] The world-wide availability of petroleum is predicted to peak and then decline rapidly. Rapid economic, technological and industrial growth of populous countries such as China and India serves to increase this demand, making the need for alternative sources of energy even more severe. To meet this growing demand it has been suggested to convert coal into more useful and transportable forms. One such technique is to gasify coal into combustible gases. A coal gasification process for producing pipeline grade fuel, such as methane, would be especially desirable because of the existing infrastructure adapted to transport methane as natural gas.

[0004] In typical coal gasification systems, coal or other carbonaceous materials and steam are reacted with oxygen (or air) to produce a syngas, comprised primarily of hydrogen and carbon monoxide. Commercial, non-catalyzed, coal gasification systems and designs face a number of economic and technical challenges. These processes are expensive to operate since, in order to drive the endothermic non-catalytic gasification of carbonaceous materials, they utilize severe temperatures (2400 to 2600° F.) and can consume high levels of oxygen. Slagging and corrosion also can present operating and maintenance issues which reduce economic viability and increase product cost.

[0005] A current concept of an Integrated Gasification Combined Cycle (IGCC) system incorporates a non-catalyzed coal gasification system to produce syngas as an intermediate and burns the syngas to produce electricity. The capital cost of an IGCC system is estimated to range from about $1,250 to $1,400 per KW, depending upon the design and process integration. One way to reduce the cost significantly would be to develop a process that enables one to gasify coal at lower temperature and without added oxygen. Toward this end, it is useful to consider the thermodynamics of gasifying coal.

[0006] The gasification of coal and similar materials generally involves the following reactions:

$$C+H_2O \rightarrow CO+H_2 \text{ (Endothermic)} \tag{1}$$

$$C+2H_2 \rightarrow CH_4 \text{ (Exothermic)} \tag{2}$$

$$C+CO_2 \rightarrow 2CO \text{ (Endothermic)} \tag{3}$$

$$CO+H_2O \rightleftharpoons CO_2+H_2 \text{ (Exothermic)} \tag{4}$$

The reaction kinetics during conventional (i.e. thermal) gasification generally produce only small amounts of methane. Direct hydrogenation/gasification of carbon such as depicted by equation (2) above is very slow compared to the endothermic reactions of steam and carbon dioxide with carbon, as depicted in equations (1) and (3). The gasification of coal and similar materials thus normally produces a synthesis gas composed primarily of hydrogen and carbon monoxide.

[0007] Addition of alkali metal catalysts enables steam gasification to proceed at lower temperatures and can enhance the production of methane through the following exothermic reactions:

$$2CO+2H_2 \rightarrow CO_2+CH_4 \text{ (Exothermic)} \tag{5}$$

$$CO+3H_2 \rightarrow H_2O+CH_4 \text{ (Exothermic)} \tag{6}$$

$$CO_2+4H_2 \rightarrow 2H_2O+CH_4 \text{ (Exothermic)} \tag{7}$$

[0008] One such catalytic steam gasification process is disclosed in U.S. Pat. No. 4,094,650 to Koh et al. ("the '650 process"). The preferred temperature and pressure ranges disclosed therein are around 1300° F. (700° C.) and 500 psia (34 atm). Potassium carbonate is disclosed as a preferred catalyst. Though the temperature is lower than in non-catalyzed gasification, the main raw products are still H_2 and CO. In order to suppress the formation of H_2 and CO, and drive the carbon conversion to methane, the '650 process teaches recycling the H_2 and CO from the raw product. A catalyst makeup stream is also required in the '650 process because, at the temperatures therein, the alkali metal catalyst can volatilize and/or react with ash constituents of the coal causing a substantial decrease in catalyst activity.

[0009] Various combinations of compounds have been investigated to find less expensive coal gasification catalysts. For example, U.S. Pat. No. 4,336,034 to Lang et al. discloses that at catalyst loadings up to 12% by weight, the relatively inexpensive combination of K_2SO_4 and calcium compounds such as CaO, $Ca(OH)_2$, or $CaCO_3$ can provide gasification rates comparable to relatively expensive K_2CO_3. The '034 patent reports better performance for mixtures having a K/Ca ratio of 2.0 (i.e., 1/3 calcium) than for mixtures with more calcium. Lang reports the use of small amounts of calcium to enhance the activity of a relatively poor catalyst such as K_2SO_4. There is no suggestion in Lang that higher quantities of calcium can influence the catalytic activity of potassium hydroxide or potassium carbonate, or that calcium salts can be used to enhance product yield, change the reaction kinetics, or enable gasification to proceed at lower operating temperatures. There is also no suggestion that the presence of calcium can improve catalyst recovery.

[0010] Other modifications have been proposed to attain more complete carbon conversion in a catalytic coal gasification process, examples being U.S. Pat. No. 4,558,027 to McKee et al. which discloses using eutectic alkali catalyst mixtures, and U.S. Pat. Nos. 4,077,778 and 6,955,695 to Nahas which disclose, respectively, using two reactors, or a two-stage reactor. These processes, like that of the '650 patent, report recycling substantial quantities of H_2 and CO from the raw product gases to the gasifier to maximize the production of methane.

[0011] Thermodynamically, methane generation is favored at mild temperatures below about 540° C. and high pressures, but catalytic coal gasification processes typically operate hotter, i.e., at temperatures between about 700° C. to about 820° C., because the gasification rate, and yield, are low in conventional catalytic coal gasification processes at lower temperatures.

[0012] Mild temperature coal gasification can achieve higher direct conversion of carbon to methane and can reduce or avoid catalyst losses which can occur at higher temperatures due to binding with mineral matter in the carbonaceous feed or volatilization. Mild temperature coal gasification can also minimize the conversion of coal to significantly less reactive char. However, catalysts have not heretofore been identified that can catalyze mild temperature gasification at acceptably high reaction rates.

[0013] Several metals (other than alkali metals) have been identified that can catalyze steam/coal gasification, but have not shown promise for mild temperature gasification. Transition metals such as iron or nickel can catalyze coal gasification, but are subject to being deactivated rapidly, after only about 10 or 15% carbon conversion. (D. Tandon, Low Temperature and Elevated Pressure Steam Gasification of Illinois Coal (1996) (Ph.D. dissertation, Southern Illinois University at Carbondale)). Research has found that unsupported Raney Ni can be severely deactivated by H_2S, possibly due to the formation of $NiAl_2S_4$ on the surface of the catalyst, but can be less affected when supported by ZrO_2 and Al_2O_3.

[0014] Catalytic metals, in combination, can be less vulnerable to deactivation than single-metal catalysts. For example, eutectic catalyst mixtures can maintain catalytic activity longer than one constituent of the mixture. Similarly, Tandon reported that potassium combined with nickel or iron as a steam/graphite gasification catalyst can remain active longer than iron or nickel alone. It is possible that highly dispersed alkali metal salts can provide a reducing atmosphere for transition metal salts and thus sustain their catalytic activity.

[0015] A catalytic effect from highly dispersed calcium has also been observed. For example, the article by Yasuo Ohtsuka and Kenji Asami, "Highly active catalysts from inexpensive raw materials for coal gasification", *Catalysis Today* 39:111 (1997) reports that calcium salts, such as $CaCO_3$ or $Ca(OH)_2$, that have been "kneaded" with coal particles, can promote steam gasification of lignite at about 550° C., but are reportedly not effective with low-oxygen containing higher rank coals.

[0016] CaO or lime can also be used with coal conversion processes to absorb CO_2. For example, U.S. Pat. No. 4,747,938 to Khan, which is directed to coal pyrolysis at about 550° C., discloses that using particulate CaO at up to 25 wt % loading can yield a product stream with less H_2S and CO_2. Neither the Khan nor the Ohtsuka and Asami processes utilize alkali catalysts.

[0017] Though coal gasification catalysis has been extensively researched, it is still not completely understood. Without intending to limit this invention to any particular theory, it is believed that transition metals that can catalyze coal gasification are those which can oscillate between two oxidation states and participate in oxidation-reduction cycles on the carbon surface, and that gasification with alkali metal catalysts involves the alkali metals donating electrons to the carbon lattice, or forming alkali/carbon complexes, thereby increasing the number of active CO complexes on the carbon surface. It is also believed that combinations of such catalysts exhibit sustained activity because different types of active sites on the carbon surface can be activated by different catalytic moieties, making more reaction sites available and reducing the impact of the deactivation of any particular type of reaction site or reaction mechanism.

[0018] It is further believed that transition metals and alkali metals are catalytically inactive when they are oxidized, and that they can be oxidized by components of the gasification environment such as H_2O, CO_2, CO and H_2S. The alkali metal catalysts can also become inactive or ineffective by volatilizing and/or binding with mineral constituents of coal.

[0019] It would be highly desirable to develop a catalytic coal gasification process that could sustain high reactivity with high carbon conversion, and even more desirable to develop a catalytic process capable of high carbon conversion to methane without recycling from the raw product (or feeding) a substantial H_2 and CO stream. It would be further desirable if such a process could operate at mild temperatures where catalyst losses by vaporization or deactivation by interaction with mineral constituents of the carbonaceous feed could be minimized. These and other objects are the subject of the process disclosed herein.

SUMMARY OF THE INVENTION

[0020] It has been found that using calcium salts to remove or "trap" carbon dioxide and other oxidizing agents from a catalytic coal gasification environment can shift the kinetics towards greater carbon conversion to methane, and can also drive the conversion of CO to CO_2 such that the process can yield a dry raw gaseous product comprised mainly of H_2 and CH_4 and substantially free of carbon oxides. The overall coal/carbon conversion can be at least 50% but conversions greater than 95% are also obtainable. The process disclosed herein can directly produce a dry raw gaseous product comprised of about 40% methane or more, by volume, without the need for substantial recycling or feeding H_2 and CO to the environment. Advantageously, the dry raw gaseous product can be used as a fuel without further enrichment, and can provide pipeline quality methane with little additional treatment.

[0021] Calcium salts and other compounds can react with CO_2 and H_2S and form solids which can be withdrawn in a solid purge, thereby eliminating or greatly reducing the need to treat the raw gaseous product for acid gas removal. According to the present invention, calcium salts can also bind with, and render inert or relatively inert, mineral constituents of the carbonaceous feed so the alkali metal salt catalysts can remain active longer. By preventing such minerals from reacting with and deactivating the alkali metal catalysts, greater catalyst recovery from the solid purge can be achieved and catalyst losses can be reduced. The process can allow for up to ~90% catalyst recovery.

[0022] While the invention is not limited to any theory, it is believed that CO_2 in the gasifier causes the catalyst to deactivate, so that by eliminating the CO_2, high catalytic activity can be sustained and more complete conversion can be achieved. In addition, removal of CO_2 from the gas phase can substantially alter the ratio of hydroxide to carbonate forms of the catalyst. Eliminating CO_2 effectively increases the activity of the catalyst and enables a high rate of gasification to occur at mild operating temperatures. At mild temperatures, the kinetics favor greater direct conversion of coal (or other carbonaceous materials) to methane, and the coal, which can convert to less reactive char at conventional catalytic coal gasification temperatures, can remain more reactive. Mild temperature operation can also reduce catalyst losses and corrosion of system components caused by volatilization of the catalyst and hazardous trace elements in the carbonaceous feed.

[0023] The catalytic gasification processes of the present invention can also be simpler and less costly to build and operate than known prior processes, and can be less prone to overheating, corrosion, char build-up and other problems long associated with other gasification processes and systems. The estimated Btu in, versus Btu out, efficiency can be on the order of 80 to 85% overall.

[0024] In one embodiment of the invention there is provided a method for direct catalytic gasification of carbonaceous material to methane comprising causing a reaction of the carbonaceous material in an environment including steam and an alkali metal salt catalyst at mild temperatures in the range from about 300 to about 700° C. and a pressure from about 15 to about 100 atmospheres, and removing CO_2 (and H_2O) from the products of the reaction in the environment so as to produce a dry raw gaseous product consisting of from about 30% to about 90% methane. Thus, the dry raw gaseous product can include at least about 40% methane, or at least about 50%, or at least about 60%, or even at least about 70% methane by volume. This embodiment can be carried out in the absence of or without extensive added or recycled H_2 or CO.

[0025] Another embodiment provides an improved method for direct catalytic gasification of carbonaceous material to combustible gases, which can be carried out in the absence of added or recycled H_2 or CO, wherein the gasification reaction occurs at a temperature range from about 300 to about 700° C. and a pressure from about 15 to about 100 atmospheres in an environment including steam, an alkali catalyst, and a mineral binder material, and wherein said carbonaceous material includes silica and/or alumina, and other mineral constituents. The mineral binder material can combine with at least a portion of these mineral constituents to inhibit the silica and/or alumina, and other mineral constituents from combining with the alkali catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] The foregoing features of the invention will be more readily understood by reference to the following detailed description. FIG. **1** is a general Flow Diagram of a Mild Catalytic Coal Gasification (MCCG) Process in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

[0027] As used in this description and the accompanying claims, the following terms shall have the meanings indicated, unless the context otherwise requires:

[0028] The term "catalyst" refers to compositions that are introduced to the process to facilitate the gasification reactions. The term is not meant to be limited to the specific chemical moiety or moieties that activate the carbon surface or otherwise actually participate in the gasification reactions.

[0029] "Mild temperature gasification" as used herein, means steam gasification of carbonaceous material at about 550° C. or lower.

[0030] "Syngas " as used herein, means synthetically produced fuel gas, typically produced from standard coal gasification processes, comprising mostly CO and H_2 by volume.

[0031] "Dry raw gaseous product" as used herein means non-steam or substantially non-steam products of direct catalytic steam gasification. Although steam can be a component of the raw gaseous reaction products from direct catalytic steam gasification of carbonaceous materials, reference to 'dry raw gaseous product' herein means the gaseous products, other than steam, that flow from the gasification reactor and have not been further purified.

[0032] "CO_2 trap material" as used herein can be CaO, $Ca(OH)_2$, dolomite, limestone, Trona, or other compounds effective for regeneratively combining with CO_2 to form solid carbonates or bicarbonates, and combinations thereof.

[0033] "Mineral binder material" as used herein can be a calcium salt, such as CaO, $Ca(OH)_2$, $CaCO_3$, or any other alkaline earth metal salts which can react with and tie up silica, alumina, and other mineral constituents of the carbonaceous feed so as to inhibit such constituents from reacting with and deactivating the catalyst.

[0034] The present invention provides a catalytic steam gasification process for converting carbonaceous materials to gases substantially comprising methane or other combustible gases. The process can operate at mild temperatures and produce a dry raw gaseous product that can be used either directly as fuel or purified to pipeline quality methane without the need to remove therefrom substantial quantities of carbon monoxide or acid gases. The process can include a feed preparation zone, a gasification reactor, a catalyst recovery system, and a CO_2 trap regeneration zone.

[0035] In the gasification reactor operating at between about 300° C. to about 700° C. and with pressure in the range from about 10 atm to about 100 atm, carbonaceous material can be reacted with oxidizing agents such as steam and/or oxygen in the presence of CO_2 trap material, and one or more alkali metal salt catalysts, to produce predominantly methane as the raw product gas. In preferred embodiments, the operating temperature in the reactor is below about 550° C., and the pressure is in the range from about 12 to about 40 atm. The gasification reactor can have a moving bed or a fluidized bed. Mineral binder material can also be present in the reactor, and can bind with silica, alumina, and other mineral constituents of the carbonaceous feed and thereby prevent or inhibit such constituents from reacting with and deactivating the catalyst.

[0036] The feed preparation zone can include one or more mixers for combining the carbonaceous material, the alkali metal catalyst, the mineral binder material, and the CO_2 trap material, and a feed system for introducing the catalyst/carbon/CO_2 trap mixture to the gasification reactor as dry solids or as a liquid slurry. The feed system can be a star feeder, screw feeder, or other mechanism effective in maintaining required temperature, pressure and flow rate of the materials to be introduced to the gasification reactor.

[0037] The carbonaceous material can be coal, heavy oils, petroleum coke, other petroleum products, residua, or byproducts, biomass, garbage, animal, agricultural, or biological wastes and other carbonaceous waste materials, etc., or mixtures thereof. The coal or other carbonaceous material can be ground or pulverized to an average particle size of about 30 to 100 mesh before its delivery for use in the gasification process. Such particles can be impregnated with alkali catalyst in aqueous solution and dried by known methods. The impregnated and dried particles can be mixed with the CO_2 trap material and/or mineral binder material and introduced to the gasifier as a single stream, or such streams can be fed separately, or in combination, as convenient.

[0038] In a preferred embodiment, however, the carbonaceous materials for use in the process can be more coarse, with an average particle size of about 1-2 mm. Such coarse particles can be combined and ground with an aqueous slurry of finely divided mineral binder material. The resulting paste can be ground with alkali catalyst, dried at about 100° C. with superheated steam to recover a fine powder of carbonaceous material with highly dispersed mineral binder and alkali catalyst having an average particle size of less than roughly 0.02 mm, pelletized to a particle size of about 30-100 mesh, and fed to the gasification reactor. The CO_2 trap material can be combined and fed with the prepared carbonaceous material, or can be fed separately.

[0039] The CO_2 trap material can be CaO or $Ca(OH)_2$, or any other compound that can react with CO_2 to form solid carbonates or bicarbonates, so as to shift the kinetics in the direction of increased methane concentration in the raw gas product. In particular embodiments the CO_2 trap material is CaO. Sufficient CO_2 trap material can be used so as to remove substantially all the CO_2 from the products of the reaction to yield a dry raw gaseous product containing less than about 2% CO_2 by volume. The molar ratio of CO_2 trap material to carbon in the reactor can be in the range of about 0.1:1 to about 1:1, or more particularly in the range of about 0.3:1 to about 0.7:1, and more particularly about 0.5:1. On a weight basis, if CaO is used as the CO_2 trap material, the CaO to carbon ratio fed to the reactor can be in the range of about 0.5:1 to about 4:1, or more particularly in the range of about 1:1 to about 3:1, and more particularly about 2:1. The CO_2 trap material can be effective without being highly dispersed on the carbon surface. Thus operating convenience can dictate whether the CO_2 trap material and the carbonaceous feed are mixed and then fed or introduced separately to the gasifier.

[0040] The alkali catalyst can comprise any of Na_2CO_3, K_2CO_3, Rb_2CO_3, Li_2CO_3, Cs_2CO_3, KNO_3, K_2SO_4, LiOH, NaOH, KOH, or any suitable alkali metal salts, or naturally occuring minerals containing alkali metal salts such as Trona, or mixtures thereof. The catalyst can be a single compound or a combination of alkali metal salts, which can be binary or ternary salt mixtures. The alkali catalyst loading can be from 1 to 50 weight percent based on the carbonaceous feed on a dry, ash-free basis. Preferably, the alkali loading is in the range of about 1 to 30 wt %. The alkali catalyst can be effective without the presence of any fluorinated compounds.

[0041] The alkali metal salt catalyst can comprise a eutectic salt mixture of Li_2CO_3, Na_2CO_3, K_2CO_3, Rb_2CO_3, and Cs_2CO_3 or mixtures thereof. In one embodiment, the eutectic salt mixture can be a binary salt mixture of about 29% Na_2CO_3 and about 71% K_2CO_3, mole percent. In other embodiments the eutectic salt mixture can be a ternary composition of about 43.5% Li_2CO_3, 31.5% Na_2CO_3 and 25% K_2CO_3, mole percent, or a ternary salt mixture of about 39% Li_2CO_3, 38.5% Na_2CO_3 and 22.5% Rb_2CO_3, mole percent.

[0042] The mineral binder material can be a compound or a mixture of compounds selected from the group consisting of CaO, $Ca(OH)_2$, $CaCO_3$, and other alkaline earth metal salts. The mineral binder can be kneaded or otherwise dispersed on the carbonaceous feed particles in a feed pretreatment step before the alkali catalyst is contacted with the carbonaceous feed. In the present invention, kneading calcium salts with the carbonaceous feed particles can be used to help prevent mineral interactions with the alkali metal catalyst. In other embodiments, the carbonaceous feed, the mineral binder, and alkali catalyst can be mixed together simultaneously by conventional methods. In still further embodiments, the mineral binder material can be fed separately to the gasifier and/or mineral binder material can form in the gasifier, wherein such mineral binder material (e.g., $CaCO_3$) can react with silica, alumina, and other mineral constituents present in the carbonaceous feed and prevent or inhibit some alkali catalyst loss and deactivation.

[0043] The mineral binder can combine with at least a portion of any reactive mineral constituents in the carbonaceous feed such as aluminum and silicon constituents, and thereby prevent or inhibit such reactive mineral constituents from reacting with the alkali catalysts. The mineral binder material can thus be effective at stoichiometric quantities about equal to that of the reactive mineral constituents in the carbonaceous feed. Thus, for example, if the carbonaceous feed material is Illinois #6 coal which contains on a dry basis about 10 to 11 wt % ash of which silica comprises about 51 wt % and alumina comprises about 18 wt %, then 7.1 tons of $CaCO_3$ or the equivalent amount of another mineral (e.g., about 4.0 tons of CaO) would be enough to react with all the silica and alumina in 100 tons of Illinois #6 coal. It may be preferable to use a higher or lower than stoichiometric amount, e.g. in the range of about 0.5 to about 1.5. Higher amounts of mineral binder can promote more complete material binding, particularly at higher operating temperatures. Lower amounts can be sufficient at milder operating temperatures.

[0044] It may be desired to process carbonaceous feeds according to this invention promoting mineral binding or CO_2 trapping or both. Thus, for the example of using CaO for either purpose with Illinois #6 coal, to promote only mineral binding, the amount of CaO utilized can be in the range of about 2 to 6 wt % and is preferably highly dispersed with the feed; whereas to promote CO_2 trapping, higher amounts in the range of 50 to 200 wt %, which need not be highly dispersed with the feed can be utilized. It is expected that substantial amounts in the range of at least 60% to about 90% of the CO_2 trap material can be recovered in the CO_2 trap regenerator and recycled within the process, such that the amount of fresh CO_2 trap material can be about 5 to 80 wt % CaO. To promote both mineral binding and CO_2 trapping, the feed can include about 5% CaO highly dispersed within the feed and the balance as a separate stream.

[0045] The reactor is designed so that a solid purge can be periodically or continuously withdrawn. The CO_2 trap material reacts with CO_2 in the reactor and is withdrawn in the "carbonated" form with the solid purge. If the CO_2 trap material is CaO or $Ca(OH)_2$, the solid purge can include particles of $CaCO_3$, as well as particles of unreacted carbon, the ash or mineral constituents of the carbonaceous feed, and some alkali catalyst in various forms.

[0046] The process of the invention can include a regeneration process of conventional design to recover and recycle active CO_2 trap material, if desired or necessary. If the CO_2 trap material is CaO, for example, the CO_2 trap material regenerator can be a calciner. In such case, $CaCO_3$ particles can be separated from said withdrawn solids by passing through a coarse sieve, or by elutriation of fine particles or other techniques, and can be directed to the calciner to recover the CaO. If necessary, the recovered CaO can be activated or its surface area increased by steam treatment or similar treatment, during or after calcination and prior to recycling. The regenerated CaO recycled to the gasifier can constitute as much as about 90% of the calcium value withdrawn in the solid purge. The calcined off-gas, mostly CO_2 and possibly some $CaCO_3$, CaS and $CaSO_4$, as well as H_2S and possibly SO_2 and O_2, can be sequestered or otherwise properly disposed.

[0047] The solid purge fraction that passes through the sieve can include soluble alkali metal salts, and can also include insoluble alkali and/or calcium aluminosilicates. These can be treated in a catalyst recovery system for recovery and recycle of the catalyst. The catalyst recovery system can comprise a water wash system and optionally can comprise a lime digestion system. In one embodiment, the hot carbon/ash particles can be contacted with water and soluble catalyst constituents of the particles can dissolve into solution. If the particles contain small amounts of alkali aluminosilicates, then the water contacting step can be sufficient to accomplish essentially complete catalyst recovery. If the washed solids contain appreciable amounts of insoluble alkali components, the washed solids can be digested in an alkaline solution or slurry to recover insoluble alkali moieties. The washed solids can contain sufficient calcium or other alkaline compounds such that little or no additional lime or other alkaline solution is necessary for digestion.

[0048] The partial pressure and/or concentration of steam can be monitored and controlled to maximize conversion rates and maximize overall conversion to methane or other desired gaseous product such as syngas. In some embodiments, causing the reaction includes maintaining a molar ratio of steam to carbon in the range of about 1.5 to 3 and/or controlling partial pressure of the steam by addition of a non-reactive gas to the gasification environment.

[0049] The catalytic steam gasification process can produce a dry raw gaseous product that includes at least about 40% methane and can include at least about 50%, or at least about 60%, or even at least about 70% or higher, methane by volume, without the need for H_2 and CO recycling, or extensive recycling, and without the need for separate stage water-gas shift reactions. Other embodiments produce a dry raw gaseous product that can include about 80% methane or higher.

[0050] The overall direct carbon conversion of carbonaceous material to methane can be at least about 50%, more particularly at least about 65%, still more particularly at least about 80%, and still more particularly at least about 90%. In still more particular embodiments, the carbon conversion of the carbonaceous material can be at least about 50% or at least about 65% at less than about 550° C.

[0051] The invention and specific embodiments are described more fully in the following examples:

EXAMPLE 1

Low Temperature Steam Gasification Results

[0052] Steam gasification of Illinois #6 coal was studied at elevated pressures and low temperatures. In the absence of a catalyst at 500° C. and elevated pressure (500-1000 psig—i.e. ~34 to 68 atm), no coal conversion was observed. When the temperature was increased to 700° C., a significant amount of conversion was observed. Apparently the lower temperature is insufficient to overcome the activation energy barrier. Gas analyses at 700° C. showed no or substantially no methane formation for de-mineralized coal samples. A small amount of methane was detected for the raw coal gasification. These observations are in agreement with the findings that significant amounts of methane cannot be generated in the absence of catalysts, and that minerals in coal can contribute to catalysis.

[0053] The catalytic effects of iron, nickel and potassium in steam gasification were also studied. In the presence of these catalysts a substantial amount of Illinois #6 coal was gasified at 500° C. With single catalysts at about 10 wt % loading, almost 30-35 wt % coal was gasified and most was gasified in the first 5 minutes. Methane and carbon dioxide were the main product gases, with little to no carbon monoxide produced. Thus, at low temperatures and elevated pressures the equilibrium is shifted to methane formation and syngas formation is minimized. Higher coal conversion and methane formation were observed at 1000 psig (~68 atm) as expected. Iron- and nickel-catalyzed reactions were reactive for about 15 minutes, after which a sharp drop in reactivity was observed. Overall, higher conversions were obtained for de-mineralized coal samples but the methane concentrations were slightly higher for the raw coal gasification.

[0054] When a potassium salt was used with either iron or nickel salts as a catalyst for raw coal gasification, synergistic effects were observed. At 500° C. and 500 psig (~34 atm) a potassium/iron salt catalyst system (5 wt % each) resulted in 42 wt % carbon conversion. The conversion went up to 53 wt % when the catalyst loading was increased to 10 wt % each. The gas analyses showed that with this catalyst, a combination of methane and hydrogen production was favored. A nickel/potassium mixture 5 wt % each did not show significant synergistic effects (39% conversion), which may be attributed to mineral interactions with these salts. At 10 wt % each, however, a conversion of 55 wt % was achieved. When the pressure was increased from 500 (~34 atm) to 1000 psig (~68 atm) the conversion increased to 58 wt %. The gas analyses for the potassium/nickel catalyst were comparable to the potassium/iron system under similar conditions.

[0055] These conversions indicate that alkali metal salts compliment transition metal salts in that they keep them active for longer reaction times. The active catalyst state may actually contain three metals (two outside catalysts and one from the mineral in coal). Studies also indicated that at 500° C. and in the pressure range of 500 to 1000 psig, sodium salts were more effective than potassium salts or any transition metal—potassium salt mixture. Conversions as high as 70% were obtained with Illinois coal. Transition metal—sodium salt mixtures were not investigated.

[0056] The results indicate that coal can be gasified at low temperatures and elevated pressures to produce methane, and that lower temperatures help to minimize syngas formation.

EXAMPLE 2

MCCG in Accordance with an Embodiment of the Invention

[0057] A process flow diagram for the envisioned low temperature steam gasification process, mild catalytic coal gasification (MCCG), is shown in FIG. **1**. Among the advantages for this process is, as discussed above, that it is a simple process. Particulate coal or other carbonaceous material, particles of CO_2 trap material and/or mineral binder material, and an alkali metal catalyst solution, can be combined and mixed in mixer **100** to form a feed stream and fed to one or more lock hoppers shown generally as lock hopper **200**. Said particulate streams can be fed separately to mixer **100** or combined (not shown) before being fed to mixer **100**. From lock hopper **200**, the feed stream can be fed to gasifier **300** by a screw feeder **250**, which alternatively can be a star feeder, or a mechanism that feeds the carbonaceous material as a liquid slurry, or any other feed mechanism known in the art which allows carbonaceous material to be fed to a gasifier at a rate, temperature and pressure necessary to achieve the desired gasification result.

[0058] Gasifier **300** can be operated in a fluid bed **400**A or a moving bed **400**B mode. Advantages of fluid bed mode **400**A include ease of design and easy tar control. One disadvantage of the fluid bed is that fresh feed particles of coal and the CO_2 trap material may be removed with converted residue (solid purge). Also the steam concentration in the outlet gas will be higher than in the moving bed. In contrast, the moving bed mode is more complex because solid recycle is needed to move partially gasified coal to the top of the bed to prevent tar from leaving the reactor with the product gas. Still, an advantage of the moving bed is that the steam concentration in the outlet gas will be substantially reduced and attrition of the CO_2 trap material is minimized. This mode also maximizes coal conversion.

[0059] When CaO, $Ca(OH)_2$, $CaCO_3$, or another alkaline earth metal salt is present in gasifier **300**, such compounds can react with and tie up minerals in the coal or other carbonaceous material, preventing or inhibiting the minerals from reacting with the alkali metal salt catalysts so the alkali metal salt catalysts will remain active longer, increasing the carbon conversion efficiency and carbon conversion rate and improving catalytic recovery. For example, such compounds can react with alumina, silica, or other mineral constituents of the coal. The coal or other carbonaceous feed can also be pretreated with CaO, $Ca(OH)_2$, $CaCO_3$, or other alkaline earth metal salts to tie up the minerals/ash in the coal.

[0060] Gasifier **300** is operated at about 550° C. or less and at an operating pressure of less than about 1000 psig (68 atm). CaO, $Ca(OH)_2$, or other compounds effective for regeneratively combining with CO_2 can be used as a trap for CO_2 and sulfur gases. This will enhance catalytic activity by driving the reaction forward and will also enhance production of methane by shifting the reaction kinetics toward increased production of methane.

[0061] Steam is fed to the bottom of gasifier **300**. It can be beneficial to add a small quantity of O_2/air to the steam to activate the catalyst. In such embodiments, between about 0.1% to 3% oxygen or air is added to the steam to provide oxidized sites on the coal surface and provide complexes where catalyst can interact with the coal to produce higher gasification rates and carbon conversion. Product gases will leave the top of gasifier **300** and pass through a condenser **500** to remove steam. The condensed water can be used within the catalyst recovery system **600**. The product gases, mostly CH_4, with lesser amounts of H_2 and NH_3 can be diverted for separation (not shown) using traditional methods, as needed. Gas separation will be dependent on target product end use. If desired, syngas is produced by lowering pressure and reducing CaO feed (or other CO_2 trap) to control the H_2/CO ratio.

[0062] Spent residue leaves the bottom of reactor/gasifier **300** and is separated (**700**) by a screen or other device to separate the larger sized $CaCO_3$ particles, which form when CaO or $Ca(OH)_2$ is used as the CO_2 trap material. The smaller sized residue is fed to extractor/catalyst recovery system, shown generally as **600**, where the catalyst is dissolved, concentrated (if necessary) and recycled. Residue from extractor **600** then goes to waste, perhaps landfill, or for by-product utilization after determination of hazard waste potential. The calcium carbonate is calcined in calciner **800** and recycled to mixer **100**. The calcined off gas, (mostly CO_2 and possibly some particulate $CaCO_3$, CaS and $CaSO_4$ as well as H_2S and possibly SO_2 and O_2) is ready for sequestration if the system is operated under pressure.

EXAMPLE 3

MCCG in Accordance with Another Embodiment

[0063] In other particular embodiments, coal or other carbonaceous material; a CO_2 trap material such as CaO or $Ca(OH)_2$ particles; and an alkali metal catalyst solution, are mixed in mixer **100**, fed to lock hopper **200**, and fed to gasifier **300** as described above. Mixer **100** can comprise an impeller and means to heat the contents such that the carbonaceous particles can become impregnated with alkali catalyst therein.

[0064] Gasifier **300** can be operated in a fluid bed **400**A or a moving bed **400**B mode, as described, and is operated at a temperature between about 300° C. about 700° C. and a pressure from about 12 to about 40 atm. As described in Example 2, CaO or $Ca(OH)_2$ can be used as a trap for CO_2 and sulfur gases, and CaO, $Ca(OH)_2$, $CaCO_3$, or other alkaline earth metal salts can react with alumina, silica, or other mineral constituents of the coal.

[0065] The remainder of the process follows that described for Example 2.

EXAMPLE 4

Test Results of Steam Gasification using KOH and CaO

[0066] Carbon conversion rate for steam gasification of Powder River Basin coal (PRB) was studied in the temperature range of 500° C. and 700° C. Carbon conversion without catalyst was about 60% after 15 minutes at 700° C. and increased to about 75% after 30 minutes. With KOH catalyst, the conversion increased to about 65% and 85% respectively. Interestingly, with KOH catalyst and CaO/C loading of 1:2 molar (about 2:1 weight ratio), conversion increased to about 95% irrespective of the reaction time. Thus, with the CaO trap material, the coal conversion is essentially complete in just about 15 minutes, showing that a gasification reactor for these conditions can be designed for a short residence time and achieve good conversion.

[0067] The effect of temperature can be shown by comparing the conversion after 30 minutes at 650° C., 600° C., and 550° C. The uncatalyzed conversion was about 70% at 650° C., and decreased to about 50% at lower temperatures. With KOH catalyst, the conversion was about 80% at 650° C. and decreased to about 65% and about 60% at 600° C. and 550° C. respectively. With KOH and CaO (loaded at CaO/C of 1:2 molar as above), the conversion at 650° C. was nearly 100% and decreased only slightly at the lower temperatures to about 90%. (The conversion at 650° C. was better than that observed at 700° C., which was about 95%.)

[0068] The conversion at 500° C. after just 20 minutes, using the same KOH and CaO loading, was at least 90%, and increased slightly after 50 or 60 minutes. This demonstrates that the CO_2 trap enables the use of lower gasification temperatures (where methane formation is favored) and small residence times without unduly sacrificing conversion.

[0069] Carbon conversion rate for steam gasification of petroleum coke was studied at 700° C. and 650° C. Carbon conversion without catalyst at 700° C. was about 35% after 15 minutes and only increased to about 45% after 60 minutes and about 55% after 90 minutes. With KOH catalyst, the conversion increased to about 45% after 15 minutes, and to about 55%, 60%, and 80% after 30, 60, and 90 minutes respectively. With KOH catalyst and CaO (again loaded at 1:2 molar CaO/C), conversion increased to about 85% after 15 or 30 minutes and to about 95% after 60 or 90 minutes. The corresponding conversions at 650° C. and 60 minutes, were 15% for uncatalyzed petroleum coke, about 50% with KOH, and about 80% with the CO_2 trap. The increase in conversion with the CO_2 trap at 650° C. indicates that steam gasification of petroleum coke at 650° C. can be economically feasible.

EXAMPLE 5

Test Results of Steam Gasification using KOH, LiOH, NaOH, and $Ca(OH)_2$

[0070] Carbon conversion for catalytic steam gasification in the temperature range of 500° C. and 700° C. of Powder River Basin coal (PRB) in the presence of KOH, LiOH, NaOH, and $Ca(OH)_2$ was measured. The conversion with KOH was about 90% and 85% respectively at 700° C. and 650° C., and decreased to about 70% at 600° C. and to about 60% at 550° C. and 500° C. Surprisingly, NaOH showed significantly better performance of about 80% conversion at 600° C. and 70% at 550° C., and performed about the same as KOH at 700° C., 650° C. and 500° C. This suggests NaOH as a preferred low cost catalyst for low temperature steam gasification.

[0071] The conversion with LiOH was 5 to 10% lower than with NaOH, except at 500° C. where LiOH gave about 65% conversion compared to about 60% conversion with NaOH, KOH, or $Ca(OH)_2$. The conversion with $Ca(OH)_2$ was about 70% at temperatures from 700° C. to 550° C., and dropped below 60% at 500° C.

EXAMPLE 6

Steam Gasification of Coal and Residua in Accordance with the Invention

[0072] In other particular embodiments, coal is mixed with an alkali metal catalyst, and calcium salts selected from CaO, $Ca(OH)_2$, $CaCO_3$ and other alkaline earth metal salts as described above, and then mixed with petroleum residua. The coal/residua mixture is heated to about 400 to 500° C. for about 3 to 30 minutes to disperse the catalyst, and then is gasified and further processed as described above.

[0073] Dispersing the catalyst allows for better catalyst contact, allowing temperatures to be dropped to about 300° C. to about 550° C. Such dispersal also provides better contact and reaction between reactive mineral components of the carbonaceous feed and such alkaline earth salts, thereby avoiding mineral/catalyst interactions and enhancing catalyst recovery. Dispersal also allows for more efficient sulfur removal, reduced catalyst quantities, and enables extensive gasification to result in only unreactive solids and minerals remaining after gasification is complete. In particular embodiments, the coal to residua weight ratio is in the range of about 1:1 to about 1:10.

[0074] The four feed components can be combined first into two streams, one comprising coal and calcium salts, and the other comprising alkali catalyst and residua; and such combined streams can then be mixed together and heated, as above, to about 400 to 500° C. for about 3 to 30 minutes to disperse the alkali catalyst onto the coal. This advantageously allows catalyst to be removed from potential poisons more quickly and leaves the coal mixture exposed to the catalyst only in a dilute phase. Again, such dispersal allows more complete gasification of the carbon/residue mixture to gaseous product.

[0075] Alternatively, a small amount of residua can be combined with the coal, blended with the catalyst, and then blended with the balance of the residua. The coal/residua/catalyst mixture is then introduced into a reactor at the dispersing temperature described above (400 to 500° C.) for about 3 to 30 minutes as described, and the dispersed mixture is introduced into another reactor where steam is added. Gasification is then done with steam to produce gases (methane, ethane, propane and butane) and light distillate C5 to C10 fraction (gasoline fraction). In this embodiment, catalyst remains dispersed in the liquid phase and only a small amount is removed with unreacted material, allowing for better catalyst recovery and recycling, enhancing economics.

[0076] While the invention has been described in conjunction with a particular flow diagram, operating conditions and examples, various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention. No limitation should be imposed other than those indicated by the following claims.

The invention claimed is:

1. A method for catalytic gasification of carbonaceous material to combustible gases, the method comprising:

reacting carbonaceous material and steam in the presence of an alkali catalyst at a temperature in the range of from about 300° C. to about 700° C. to form a gas comprising CO_2, CH_4, H_2O and H_2;

combining said CO_2 in said gas with a CO_2 trap material;

removing H_2O from said gas to form a dry raw gaseous product;

wherein said CO_2 trap material is present in an amount sufficient to combine with sufficient quantities of CO_2 to form a dry raw gaseous product comprising at least about 40% methane by volume.

2. A method for catalytic gasification of carbonaceous material to combustible gases, the method comprising:

reacting carbonaceous material and steam in the presence of an alkali catalyst at a temperature in the range of from about 300° C. to about 700° C. to form a gas comprising CO_2, CH_4 and H_2, wherein said carbonaceous material includes silica, alumina, and other mineral constituents; and

providing a mineral binder material to combine with at least a portion of said mineral constituents to inhibit said mineral constituents from combining with said alkali catalyst.

3. A method for catalytic gasification of carbonaceous material to combustible gases, the method comprising:

reacting carbonaceous material and steam in the presence of an alkali catalyst at a temperature in the range of from about 300° C. to about 700° C. to form a gas comprising CO_2, CH_4, H_2O and H_2, wherein said carbonaceous material includes silica, alumina, and other mineral constituents;

providing a mineral binder material to combine with at least a portion of said mineral constituents to inhibit said mineral constituents from combining with said alkali catalyst.

combining said CO_2 in said gas with a CO_2 trap material;

removing H_2O from said gas to form a dry raw gaseous product;

wherein said CO_2 trap material is present in an amount sufficient to combine with sufficient quantities of CO_2 to form a dry raw gaseous product comprising at least about 40% methane by volume.

4. A method according to claim 1, 2, or **3**, wherein the temperature is in the range from about 300° C. to about 550° C.

5. A method according to claim 1, 2, or **3**, wherein substantial quantities of H_2 and/or CO are not recycled or added to the reactor.

6. A method according to claim 1, 2, or **3**, wherein the alkali catalyst comprises one or more compounds selected from the group consisting of Na_2CO_3, K_2CO_3, Rb_2CO_3, Li_2CO_3, Cs_2CO_3, KNO_3, K_2SO_4, LiOH, NaOH, KOH and naturally occuring minerals containing alkali metal salts.

7. A method according to claim 1 or 3, wherein said CO_2 trap material comprises one or more compounds selected from the group consisting of CaO, $Ca(OH)_2$, dolomite, limestone, Trona, and other compounds effective for regeneratively combining with CO_2 to form solid carbonates and bicarbonates.

8. A method according to claim 7 wherein said CO_2 trap material comprises CaO.

9. A method according to claim 8 wherein the weight ratio of CaO to carbon in the reactor is in the range of about 0.5:1 to about 4:1.

10. A method according to claim 9 wherein the weight ratio of CaO to carbon in the reactor is about 2:1.

11. A method for catalytic gasification of carbonaceous material to combustible gases, the method comprising:

reacting carbonaceous material and steam in an environment in the presence of an alkali catalyst and a quantity of CO_2 trap material at a temperature in the range from about 300° C. to about 700° C. to form a gas comprising CH_4 and H_2O and solid particles comprising carbonated CO_2 trap material;

removing H_2O from said gas to form a dry raw gaseous product comprising at least about 30% methane;

removing said solid particles from the environment, regenerating CO_2 trap material therefrom, and returning said regenerated CO_2 trap material to said environment.

12. A method according to claim 11 wherein said regenerated CO_2 trap material comprises at least 50% of said quantity of CO_2 trap material.

13. A method according to claim 12 wherein said regenerated CO_2 trap material comprises at least 90% of said quantity of CO_2 trap material.

14. A method according to claim 2 or 3, wherein said mineral binder material comprises one or more compounds selected from the group consisting of CaO, $Ca(OH)_2$, $CaCO_3$, and other alkaline earth metal salts.

15. A method according to claim 2 or 3 further comprising dispersing said mineral binder material into said carbonaceous material prior to said reacting.

16. A method according to claim 14 wherein the stoichiometric ratio of said mineral binder material relative to said mineral constituents of said carbonaceous material is in the range of about 0.5 to about 1.5.

17. A method according to claim 14 wherein the stoichiometric ratio of said mineral binder material relative to said mineral constituents of said carbonaceous material is about 1:1.

18. A method according to claim 1, 2 or **3** wherein the carbon conversion of the carbonaceous material is at least about 50%.

19. A method according to claim 18 wherein the carbon conversion of the carbonaceous material is at least about 65%.

20. A method according to claim 19, wherein the carbon conversion of the carbonaceous material is at least 80%.

21. A method according to claim 1 or 3 wherein the dry raw gaseous product includes at least about 50% methane by volume.

22. A method according to claim 21 wherein the dry raw gaseous product includes at least about 60% methane by volume.

23. A method according to claim 21 wherein the dry raw gaseous product includes at least about 70% methane by volume.

24. A method according to claim 21 wherein the dry raw gaseous product includes at least about 80% methane by volume.

25. A method according to claim 1, 2, or **3**, further comprising maintaining the molar ratio of steam to carbon in the reactor within the range of about 1.5:1 to 3:1.

26. A method according to claim 1, 2, or **3**, further comprising controlling the partial pressure of the steam by addition of a non-reactive gas to the reactor.

27. The method according to claim 1, 2, or **3** wherein the reactor comprises a fluid bed or a moving bed.

28. A method according to claim 6 wherein the alkali catalyst comprises a eutectic salt mixture.

29. A method according to claim 28, wherein the eutectic salt mixture is a binary salt mixture.

30. A method according to claim 29 wherein the binary salt mixture is 29% Na_2CO_3 and 71% K_2CO_3 by mole percent.

31. A method according to claim 28, wherein the eutectic salt mixture is a ternary salt mixture.

32. A method according to claim 31 wherein the ternary salt mixture is 43.5% Li_2CO_3, 31.5% Na_2CO_3 and 25% K_2CO_3 by mole percent.

33. A method according to claim 31 wherein the ternary salt mixture is 39% Li_2CO_3, 38.5% Na_2CO_3 and 22.5% Rb_2CO_3 by mole percent.

34. A method according to claim 4 wherein the alkali catalyst comprises NaOH, Na_2CO_3, or Trona.

35. A method for catalytic gasification of carbonaceous material to combustible gases, the method comprising:

reacting carbonaceous material and steam in the presence of an alkali catalyst at a temperature in the range of from about 300° C. to about 700° C. to form a gas comprising CO_2, CH_4, H_2O and H_2;

combining said CO_2 in said gas with a CO_2 trap material;

removing H_2O from said gas to form a dry raw gaseous product;

wherein said CO_2 trap material is present in an amount sufficient to combine with sufficient quantities of CO_2 so said dry raw gaseous product comprises less than about 2% CO_2 by volume.

* * * * *