A process for producing hydrogen, comprising the steps of: (a) gasifying a fuel into a raw synthesis gas comprising CO, hydrogen, steam and sulfur and halide contaminants in the form of H₂S, COS and HX, where X is a halide; (b) passing the raw synthesis gas
(57) **Abstract (continued):** through a water gas shift reactor (WGSR) into which CaO and steam are injected, the CaO reacting with the shifted gas to remove CO2, sulfur and halides in a solid-phase calcium-containing product comprising CaCO3, CaS and CaX; (c) separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and (d) regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO2, in the presence of synthesis gas, in the presence of H2 and O2, under partial vacuum, and combinations thereof. The CaO may have a surface area of at least 12.0 m2/g and a pore volume of at least 0.015 cm3/g, the CaO having a sorption capacity of at least about 70 grams of CO2 per kilogram of CaO.
(54) Title: CALCIUM LOOPING PROCESS FOR HIGH PURITY HYDROGEN PRODUCTION

(55) Abstract: A process for producing hydrogen, comprising the steps of: (a) gasifying a fuel into a raw synthesis gas comprising CO, hydrogen, steam and sulfur and halide contaminants in the form of H₂S, COS and HX, where X is a halide; (b) passing the raw synthesis gas through a water gas shift reactor (WGSR) into which CaO and steam are injected, the CaO reacting with the shifted gas to remove CO₂, sulfur and halides in a solid phase calcium-containing product comprising CaO₂Ca and CaX₂; (c) separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and (d) regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof. The CaO may have a surface area of at least 12.0 m²/g and a pore volume of at least 0.015 cm³/g, the CaO having a sorption capacity of at least about 70 grams of CO₂ per kilogram of CaO.
HIGH PURITY, HIGH PRESSURE HYDROGEN PRODUCTION WITH IN-SITU CO₂ AND SULFUR CAPTURE IN A SINGLE STAGE REACTOR

TECHNICAL FIELD OF THE INVENTION

The present invention is in the field of hydrogen production.

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention includes a process for producing hydrogen, comprising the steps of: (a) gasifying a fuel into a raw synthesis gas comprising CO, hydrogen, steam and sulfur and halide contaminants in the form of H₂S, COS and HX, where X is a halide; (b) passing the raw synthesis gas through a water gas shift reactor (WGSR) into which CaO and steam are injected, the CaO reacting with the shifted gas to remove CO₂, sulfur and halides in a solid-phase calcium-containing product comprising CaCO₃, CaS and CaX₂; (c) separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and (d) regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

In one embodiment, there is provided a process for producing hydrogen, comprising the steps of: gasifying a fuel into a raw synthesis gas comprising CO, hydrogen, steam, sulfur contaminants in the form of H₂S and COS, and halide contaminants in the form of HX, where X is a halide; injecting the raw synthesis gas, CaO and steam into a water gas shift reactor (WGSR), wherein the raw synthesis gas transforms into a shifted gas without a catalyst; allowing the shifted gas to react with the CaO in the WGSR so as to remove CO₂, sulfur and halides in a solid-phase calcium-containing product comprising CaCO₃, CaS and CaX₂; separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

The fuel could be coal, biomass, oil sands, coke, tar, wax oil shales, or combinations of these materials.
Although the steam may be injected into the WGSR in any functional quantity, it is preferred that the steam injected is in the range of from about the stoichiometric requirement to about 3 times the stoichiometric requirement.

In some embodiments, the raw synthesis gas, CaO and steam may be injected simultaneously into the WGSR.

In one embodiment, the enriched hydrogen product has a purity of at least 60%. In one embodiment, the H2:CO ratio of the enriched hydrogen product is in the range of from about 0.5:1 to about 1000:1. In some embodiments the enriched hydrogen product has a purity in the range of from about 70% to about 99.99%, at temperature in the range of from about 400 – 1000 °C, and a pressure in the range of from about 1 to about 100 atmospheres.

The WGSR may be of a type selected from the group consisting of: fixed bed reactors, fluidized bed reactors, entrained flow reactors, moving bed reactors rotary kilns, or combinations thereof. Additionally, the calcinations step may be performed in a calcinations reactor of a type selected from the group consisting of: fixed bed reactors, fluidized bed reactors, entrained flow reactors, moving bed reactors rotary kilns, or combinations thereof.

In some embodiments, the WGSR does not have a catalyst disposed therein. As such the WGSR operates at a temperature in the range of from about 550 – 750 °C, in the pressure range of from about 1 to about 60 atm, it is preferred that the WGSR reactor operate in a temperature range of from about 600 – 700°C and at a pressure in the range of from about 20 to about 30 atm. In some embodiments, the enriched hydrogen product is 99% pure when 3 times the stoichiometric steam requirement is used. At the stoichiometric steam requirement the process produces an enriched hydrogen product that is 90% pure. In another catalytic embodiment, the enriched hydrogen product has a H2/Co ratio of at least 2.5 and a maximum sulfur (H2S/COS) concentration of less than 10 ppm using only the stoichiometric requirement of steam.

In some embodiments, a catalyst may be used in the WGSR. A suitable high temperature shift catalyst which may include: Fe, Cu, Co, Mo, W, Cs, Pt, Ph, Pd, and other precious metal catalysts or their oxides or sulfides or combinations thereof. Suitable supports for use with the foregoing high temperature shift catalysts include: Cr2O3, ZnO, MgO, ceria, alumina, silica, zirconia and combinations thereof.
A WGSR reactor with a catalyst operates in the temperature range of from about 550 – 750 °C and at a pressure in the range of from about 1 to about 100 atm. It is preferred that the WGSR reactor operate in the temperature range of from about 600 – 700 °C and at a pressure of from about 20 to about 30 atm. When a catalyst is used the enriched hydrogen product may achieve 99.99% purity when 3x the stoichiometric requirement of steam is used in the WGSR. The enriched hydrogen product may achieve 98% purity when the stoichiometric requirement of steam is used. Some embodiments may attain a purity of at least 80% with a maximum sulfur (H2S/COS) concentration of less than 10 ppm when 3X the stoichiometric requirement of steam is used and at least 70% purity with a maximum sulfur concentration of less than 1 ppm when the stoichiometric requirement of steam is used.

The process may also comprise the step of (e) recycling at least a portion of a product stream from a Fischer-Tropsch reactor, fed by the WGSR, so as to introduce a chemical species selected from the group consisting of: methane, C1 – C4 hydrocarbons, CO, hydrogen and combinations thereof back into the WGSR.

In all embodiments, the CaO may have a surface area of at least 12.0 m2/g and a pore volume of at least 0.015 cm3/g, said CaO having a sorption capacity of at least about 70 grams of CO2 per kilogram of CaO.

The CaO may be provided in any usable form including, but not limited to, pellets, granules, fines, monoliths and combinations thereof. The CaO may be obtained by processing chicken eggshells.

Although the regeneration of CaO step may be performed any functional process, it is preferred that it is conducted by a process selected from the group consisting of: (a) calcining in the presence of steam and/or CO2 and/or H2 with O2, and/or synthesis gas with O2 and/or under partial vacuum or combinations thereof; (b) a process in which the heat is added to the calciner using steam and a combination of calciner fuel and oxidant; (c) a process in which the calciner fuel is H2 or natural gas or synthesis gas or coal or combinations thereof; (d) a process in which the oxidant is air or oxygen or combinations thereof; (e) a process in which heat is provided to the calciner directly or indirectly; (f) calciner reactor temperatures ranging from about 700 – 1100 °C; and (a process for adjusting the calciner temperature by modifying the CaO to CaCO3 ratio in the calciner. The gas phase product from the calciner may comprise pure CO2 and could also contain trace amounts of H2S.
The present invention also includes a process for producing hydrogen, comprising the steps of: (a) reforming a gaseous hydrocarbon fuel in the presence of CaO and steam to remove CO2, sulfur and halide contaminants in the form of H2S, COS and HX, where X is a halide, in a solid-phase calcium-containing product comprising CaCO3, CaS and CaX2, thereby producing a mixture of CO and hydrogen; (b) separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and (c) regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO2, in the presence of synthesis gas, in the presence of H2 and O2, under partial vacuum, and combinations thereof.

In one embodiment, there is provided a process for producing hydrogen, comprising the steps of: reforming a gaseous hydrocarbon fuel in the presence of CaO and steam to remove CO2, sulfur contaminants in the form of H2S and COS, and halide contaminants in the form of HX, where X is a halide, in a solid-phase calcium-containing product comprising CaCO3, CaS and CaX2, thereby producing a mixture of CO and hydrogen; separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO2, in the presence of synthesis gas, in the presence of H2 and O2, under partial vacuum, and combinations thereof.

The gaseous fuel may be natural gas, C1 – C4 hydrocarbons, or mixtures thereof. The reforming step may involve the introduction of CO2, so called dry reforming.

The reforming step may involve a reforming catalyst. Suitable reforming catalysts include those comprising: Ni, Pt, Rh, Pd, Ru, W, Mo, their oxide or carbides or sulfides. The reforming catalyst may use a support. Suitable supports for use with the foregoing reforming or pre-reforming catalysts include: alumina, silica, titania, zirconia, and combinations thereof. It is preferred that the reforming catalyst is sulfur intolerant.

The reforming operation may occur in a temperature range of from about 550 to about 750 °C and at a pressure in the range of from about 1 to about 60 atm. Preferably, it operates in the temperature range of from about 600 to about 700 °C and at a pressure in the range of from about 20 to about 30 atm.
The enriched hydrogen product produced may be as pure as 99.9% when 3X the stoichiometric requirement of steam is used and 95% pure when the stoichiometric requirement of steam is used.

This process may additionally comprise the step of: (d) recycling at least a portion of a product stream from a Fischer-Tropsch reactor, fed by the reformer, so as to introduce a chemical species selected from the group consisting of: methane, C1 – C4 hydrocarbons, CO, hydrogen and combinations thereof back into the reformer.

In all embodiments, the CaO may have a surface area of at least 12.0 m2/g and a pore volume of at least 0.015 cm3/g, said CaO having a sorption capacity of at least about 70 grams of CO2 per kilogram of CaO.

The CaO may be provided in any usable form including, but not limited to, pellets, granules, fines, monoliths and combinations thereof. The CaO may be obtained by processing chicken eggshells.

When a catalyst is used the enriched hydrogen product may achieve 99.99% purity when 3x the stoichiometric requirement of steam is used. The enriched hydrogen product may achieve 98% purity when the stoichiometric requirement of steam is used. Some embodiments may attain a purity of at least 80% with a maximum sulfur (H2S/COS) concentration of less than 10 ppm when 3X the stoichiometric requirement of steam is used and at least 70% purity with a maximum sulfur concentration of less than 1 ppm when the stoichiometric requirement of steam is used. The process allows for a hydrogen purity of at least 80% with a maximum sulfur (H2S/COS) concentration of less than 10 ppm when 3X the stoichiometric requirement of steam is used and at least 70% purity with a maximum sulfur concentration of less than 1 ppm when the stoichiometric requirement of steam is used.

Another process of the present invention for producing hydrogen, comprising the steps of: (a) at least partially oxidizing a fuel into a raw gas comprising CO, hydrogen, steam and sulfur and halide contaminants in the form of H2S, COS and HX, where X is a halide; (b) passing the raw gas through a water gas shift reactor (WGSR) into which CaO and steam are injected, the CaO reacting with the shifted gas to remove CO2, sulfur and halides in a solid-phase calcium-containing product comprising CaCO3, CaS and CaX2; (c) separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and (d) regenerating the CaO by calcining the solid-phase calcium-containing product at a condition
selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

In one embodiment, there is provided a process for producing hydrogen, comprising the steps of: at least partially oxidizing a fuel into a raw gas comprising CO, hydrogen, steam, sulfur contaminants in the form of H₂S and COS, and halide contaminants in the form of HX, where X is a halide; injecting the raw gas, CaO and steam into a water gas shift reactor (WGSR), wherein the raw gas transforms into a shifted gas without a catalyst; allowing the shifted gas to react with the CaO in the WGSR so as to remove CO₂, sulfur and halides in a solid-phase calcium-containing product comprising CaCO₃, CaS and CaX₂; separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

In all embodiments, the CaO may have a surface area of at least 12.0 m²/g and a pore volume of at least 0.015 cm³/g, said CaO having a sorption capacity of at least about 70 grams of CO₂ per kilogram of CaO.

The CaO may be provided in any usable form including, but not limited to, pellets, granules, fine, monoliths and combinations thereof. The CaO may be obtained by processing chicken egshells.

Although the steam may be injected into the WGSR in any functional quantity, it is preferred that the steam injected is in the range of from about the stoichiometric requirement to about 3 times the stoichiometric requirement.

In some embodiments, the raw gas, CaO and steam may be injected simultaneously into the WGSR.

The WGSR may be of a type selected from the group consisting of: fixed bed reactors, fluidized bed reactors, entrained flow reactors, moving bed reactors rotary kilns, or combinations thereof. Additionally, the calcinations step may be performed in a calcinations reactor of a type selected from the group consisting of: fixed bed reactors, fluidized bed reactors, entrained flow reactors, moving bed reactors rotary kilns, or combinations thereof.
In some embodiments, the WGSR does not have a catalyst disposed therein. As such the WGSR operates at a temperature in the range of from about 550 – 750 °C, in the pressure range of from about 1 to about 60 atm, it is preferred that the WGSR reactor operate in a temperature range of from about 600 – 700°C and at a pressure in the range of from about 20 to about 30 atm. In some embodiments, the enriched hydrogen product is 99% pure when 3 times the stoichiometric steam requirement is used. At the stoichiometric steam requirement the process produces an enriched hydrogen product that is 90% pure. In another catalytic embodiment, the enriched hydrogen product has a H2/Co ration of at least 2.5 and a maximum sulfur (H2S/COS) concentration of less than 10 ppm using only the stoichiometric requirement of steam.

In some embodiments, a catalyst may be used in the WGSR. A suitable high temperature shift catalyst which may include: Fe, Cu, Co, Mo, W, Cs, Pt, Ph, Pd, and other precious metal catalysts or their oxides or sulfides or combinations thereof. Suitable supports for use with the foregoing high temperature shift catalysts include: Cr2O3, ZnO, MgO, ceria, alumina, silica, zirconia and combinations thereof.

A WGSR reactor with a catalyst operates in the temperature range of from about 550 – 750 °C and at a pressure in the range of from about 1 to about 100 atm. It is preferred that the WGSR reactor operate in the temperature range of from about 600 – 700 °C and at a pressure of from about 20 to about 30 atm. When a catalyst is used the enriched hydrogen product may achieve 99.99% purity when 3x the stoichiometric requirement of steam is used in the WGSR. The enriched hydrogen product may achieve 98% purity when the stoichiometric requirement of steam is used. Some embodiments may attain a purity of at least 80% with a maximum sulfur (H2S/COS) concentration of less than 10 ppm when 3X the stoichiometric requirement of steam is used and at least 70% purity with a maximum sulfur concentration of less than 1 ppm when the stoichiometric requirement of steam is used.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows the effect of concentrations of different surface modifiers on the zeta potential and specific surface area of the sorbent (a) Ligno-sulfonate (b) Dispex N40V (c) Dispex A40 (adapted from Agnihotri et al., 1999).

Figure 2 provides pore size distributions for various calcium sorbents (Gupta and Fan, 2002).
Figure 3 shows the carbonation reactions of CaO obtained from different precursors at 650 °C (adapted from Gupta and Fan, 2002).

Figure 4 presents the carbonation reactions of PCC-CaO at different temperatures (Gupta and Fan, 2002).

Figure 5 provides the extended Calcination-Carbonation cycles with Linwood Carbonate (LC) fines at 700 °C in a TGA in a 10% CO₂ stream (Iyer et al., 2004).

Figure 6 provides the extended Calcination- Carbonation cycles with Precipitated Calcium (PCC) fines at 700 °C in a TGA in a 10% CO₂ stream (Iyer et al., 2004).

Figure 7 shows the CO₂ capture capacity of various high temperature sorbents over multiple carbonation-regeneration cycles (Iyer et al., 2004; White et al., 2003; Kato et al., 2002; Kato et al., 1999; Barker 1973; Ortiz 2001; Barker 1974) (Iyer et al., 2004).

Figure 8 illustrates the direct and indirect fired calcination options for designing a calciner.

Figure 9 provides thermodynamic data for predicting the temperature zones for hydration and carbonation of CaO in a fuel gas mixture.

Figure 10(a) provides thermodynamic data for predicting the equilibrium H₂S concentration for CaO sulfidation with varying steam concentration (P_Total = 30 atm).

Figure 10(b) provides thermodynamic data for predicting the equilibrium COS carbonyl sulfide concentration for CaO sulfidation with varying CO₂ concentration (P_Total = 30 atm).

Figure 10(c) provides thermodynamic data for predicting the equilibrium HCl concentration for CaO reaction with HCl with varying steam concentration (P_Total = 30 atm).

Figure 11 shows the reactivity of different CaO sorbents towards H₂S removal.

Figure 12 (a) is a comparison of breakthrough curves depicting CO conversion for PCC-HTS and LC-HTS systems.

Figure 12(b) shows the gas composition during the combined WGS carbonation reactions using PCC-HTS systems (T = 600 °C, 10.3% CO, 31% H₂O, Total flow = 0.725 slpm).
Figure 13 is a comparison of H₂ gas composition at 1 and 20 bar for a 3:1 steam : CO ratio.

Figure 14(a) is a comparison of CO conversion for different steam : CO ratios at 1 bar.

Figure 14(b) is a comparison of CO conversion for different steam : CO ratios at 20 bar.

Figure 15(a) shows the outlet gas composition from the reactor at 650°C and 20 bar.

Figure 15(b) provides the conversion achieved at 650°C and 20 bar.

Figure 16 presents a conceptual flowsheet depicting integration of various units in the Calcium Looping Processes for H₂ generation in typical coal-gasifier facility.

Figure 17 presents a conceptual schematic of Carbonation-Calcination Reaction (CCR) process integration in a 300 MWe coal fired power plant depicting heat integration strategies (Fan and Iyer, 2006).

Figure 18 illustrates a calcium looping system integrated in a coal to liquid plant.

Figure 19 provides a conventional hydrogen production from Steam Methane reforming and pressure swing adsorption.

Figure 20 is a schematic representation of calcium looping integrated with SMR to produce high purity hydrogen.

Figure 21 is a comparison of the CO₂ capture capacity for various sorbents.

Figure 22(a) shows the H₂S concentration in the outlet gas stream with change in pressure.

Figure 22(b) shows the H₂ gas composition(T = 600 °C, 10.3% CO,S/C : 1:1, H₂S=5000ppm, Total flow = 0.725 slpm).

Figure 23 illustrates the effect of steam:CO ratio on CO conversion during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P= 0psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 24 illustrates the effect of steam:CO ratio on CO conversion during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P= 150psig, 10.3%CO, Total flow = 0.725 slpm).
Figure 25 shows the effect of steam:CO ratio on CO conversion during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P= 300psig, 10.3%CO, Total flow = 0.725 slpm).

Figure 26 shows the effect of steam:CO ratio on the purity of hydrogen produced during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P=0psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 27 illustrates the effect of steam:CO ratio on the purity of hydrogen produced during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P= 150psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 28 shows the effect of steam:CO ratio on the purity of hydrogen produced during the combined WGS carbonation reaction using PCC-HTS system (T = 650 °C, P= 300psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 29 shows the effect of steam:CO ratio on CO conversion during the combined WGS carbonation reaction using PCC sorbent without catalyst (T = 650 °C, P= 300psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 30 shows the effect of steam:CO ratio on purity of hydrogen produced during the combined WGS carbonation reaction using PCC sorbent without catalyst (T = 650 °C, P= 300psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 31 illustrates the real time nitrogen and steam free gas composition at the outlet of the reactor system during the combined WGS-carbonation reaction using PCC sorbent without catalyst(T = 650 °C, P=0psig, 10.3% CO, 10.3% H₂O, Total flow = 0.725 slpm).

Figure 32 presents the CO conversion in the reactor system during the combined WGS-carbonation reaction using PCC sorbent without catalyst (T = 650 °C, P=0psig, 10.3% CO, 10.3% H₂O, Total flow = 0.725 slpm).

Figure 33 shows the effect of steam:CO ratio on the concentration of H₂S in the outlet of the reactor during the combined WGS carbonation reaction with insitu H₂S removal using PCC sorbent without catalyst (T = 600 °C, P= 0psig, 10.3% CO, Total flow = 0.725 slpm).

Figure 34 shows the real time nitrogen and steam free gas composition at the outlet of the reactor system during the combined WGS-carbonation reaction with insitu H₂S removal
using PCC sorbent without catalyst \( (T = 600 \, ^\circ C, P= 0 \, \text{psig}, 10.3\% \text{ CO}, 31\% \text{ H}_2\text{O}, \text{Total flow} = 0.725 \, \text{slpm}) \).

Figure 35 shows the real time nitrogen and steam free gas composition at the outlet of the reactor system during the combined WGS-carbonation reaction with in situ \( \text{H}_2\text{S} \) removal using PCC sorbent without catalyst \( (T = 600 \, ^\circ C, P= 0 \, \text{psig}, 10.3\% \text{ CO}, 10.3\% \text{ H}_2\text{O}, \text{Total flow} = 0.725 \, \text{slpm}) \).

Figure 36 provides the real time nitrogen and steam free gas composition at the outlet of the reactor system during the combined WGS-carbonation reaction with in situ \( \text{H}_2\text{S} \) removal using PCC sorbent without catalyst \( (T = 600 \, ^\circ C, P= 0 \, \text{psig}, 10.3\% \text{ CO}, 7.73\% \text{ H}_2\text{O}, \text{Total flow} = 0.725 \, \text{slpm}) \).

Figure 37 shows the effect of steam:CO ratio on CO conversion during the combined WGS carbonation reaction with in situ \( \text{H}_2\text{S} \) removal using PCC sorbent without catalyst \( (T = 600 \, ^\circ C, P= 0 \, \text{psig}, 10.3\% \text{ CO}, \text{Total flow} = 0.725 \, \text{slpm}) \).

Figure 38 is a schematic illustrating a conventional process for Hydrogen production.

Figure 39 is a schematic illustrating a conventional process for Hydrogen production.

Figure 40 is a schematic illustrating traditional liquid fuel production.

Figure 41 is a graphical comparison of the international energy demands and the international energy supply.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)**

In accordance with the foregoing summary, the following presents a detailed description of the preferred embodiments of the invention that is currently considered to be the best mode.

Enhancement in the production of high purity hydrogen (H2) from synthesis gas, obtained by coal gasification, is limited by the thermodynamics of the water-gas shift reaction (WGSR). However, this constraint can be overcome by concurrent WGSR and carbonation (of calcium oxide) reaction to enhance H2 production. The carbonation of any typical metal oxide (eg. calcium oxide) forming metal carbonate (eg. calcium carbonate) incessantly drives the equilibrium-limited WGSR forward by removing the carbon dioxide \( (\text{CO}_2) \) product from
the reaction mixture. The metal carbonate (calcium carbonate) can be separately calcined to yield a pure CO₂ stream for its subsequent sequestration and the calcium oxide recycled back. This **calcium looping scheme** not only improves the hydrogen yield and purity but also integrates a CO₂ management scheme and gas cleanup in the hydrogen production process.

The proposed scheme simplifies high purity H₂ production by integrating the water gas shift reaction (WGSR) with in-situ CO₂, sulfur (H₂S + COS) and hydrogen halide removal from the synthesis gas at high temperatures in a single stage reactor process while eliminating the need for WGS catalyst requirement. We have identified our high reactivity OSU patented, mesoporous calcium oxide sorbent for the in-situ CO₂ capture as well as H₂S/COS and halides (HCl/HBr etc) removal. The morphological properties of our patented calcium sorbent (PCC) can be tailored using surface modifiers to demonstrate a high CO₂ capture capacity of about 70% by weight (≈700g of CO2/kg sorbent), yield a high calcium conversion of above 80% while removing H₂S at high temperatures (700-900 °C) and producing H₂ with purity greater than 95% without the WGS catalyst. The process highlights include:

1. **reduction in excess steam requirement and for operating at near-stoichiometric steam consumption**

2. simultaneous removal of CO₂ as well as sulfur (H₂S + COS) and halides (HCl/HBr etc) impurities

3. production of either a 90-95% H₂ stream (without WGS catalyst) or a 99+% high purity H₂ stream (with WGS catalyst) at high temperatures (400-1000 °C) and pressures (1-40 atmospheres). The H₂ concentrations can vary all the way from 60 to 99+ % purity.

4. **Flexibility in carbon monoxide conversion to produce H₂:CO ratios of varying composition which can range from 0.5 to 20, while capturing sulfur and halide impurities resulting in minimal impurity levels in the product gas stream (ppm to ppb levels), suitable for fuels/chemical synthesis from Fischer Tropsch reactions**

5. production of a sequestrable CO₂ stream by spent sorbent regeneration at high temperatures (700-1100°C). Sorbent regeneration includes calcining the carbonated sorbent (CaCO₃) using H₂ and oxygen and/or steam to generated calcium oxide. The calcium sulfide sorbent can be regenerated to calcium oxide by treatment with steam and carbon dioxide. The
calcium halide (for example calcium chloride) can be regenerated to calcium oxide using hydrogen and oxygen mixtures.

The various reaction schemes being integrated in the process are:

**Reaction phase**

- **Coal Gasification:** \( C_2H_4O + H_2O \rightarrow xCO + \left(\frac{3}{2} + 1\right)H_2 \)
- **WGSR:** \( CO + H_2O \leftrightarrow H_2 + CO_2 \)
- **Carbonation:** \( CaO + CO_2 \rightarrow CaCO_3 \)
- **Sulfur capture (H_2S):** \( CaO + H_2S \rightarrow CaS + H_2O \)
- **Sulfur capture (COS):** \( CaO + COS \rightarrow CaS + CO_2 \)
- **Halide capture (HCl):** \( CaO + 2HCl \rightarrow CaCl_2 + H_2O \)

**Regeneration phase**

- **CaCO_3 regeneration:** \( CaCO_3 \rightarrow CaO + CO_2 \)
- **CaS regeneration:** \( CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S \)
- **Halide (CaCl_2) regeneration:** \( CaCl_2 + H_2 + \frac{1}{2}O_2 \rightarrow CaO + 2HCl \)

The proposed technology aims on enhancing \( H_2 \) production, from a typical coal gasification stream, by integrating the water gas shift reaction (WGSR) through in-situ \( CO_2 \), sulfur and hydrogen halide removal from the synthesis gas at high temperatures in a single stage reactor process while eliminating the need for a WGS catalyst. Thus, this integrated process indeed consolidates several unit operations *viz.* WGS reactor, \( CO_2 \) capture, sulfur removal, halide removal and hydrogen production in one process module, downstream of a coal gasification system to produce a pure hydrogen stream. The goals of this calcium looping process are (1) to reduce the excess steam requirement and operate at near-stoichiometric steam consumption (2) to simultaneously remove \( CO_2 \) as well as sulfur and halides (3) to produce a sequestrable \( CO_2 \) stream by sorbent regeneration, (4) to produce either a 90-95% \( H_2 \) stream (without WGS catalyst) or a 99+% high purity \( H_2 \) stream (with WGS catalyst) at high temperatures and pressures. This integrated “one box” process depicts the potential to achieve higher system efficiencies with lower overall footprint by combining different process units in one stage. The envisioned system has the flexibility and the potential to produce hydrogen of different purity levels by reducing the amount of WGS catalyst and reducing the excess steam.
requirement. This novel process removes the need for hydrogen separation membranes and the high temperature operation increases the overall conversion and process efficiency.

**Background**

**Catalytic Hydrogen Production Processes**

Hydrogen is a useful fuel and a feedstock for various other fuels, processes and commodities. The future role of hydrogen in the world energy cycle might gain critical significance. Economical hydrogen production from fossil fuels in a sequestration ready manner remains a challenge. It is envisaged that hydrogen would be used to carry the energy contained in fossil fuels for numerous mobile applications while the CO₂ generated from the fossil fuels would be safely sequestered from these large local facilities. The major processes for hydrogen production from fossil fuels involve steam reforming of methane (SMR), coal gasification, catalytic cracking of natural gas, and partial oxidation of heavy oils (Rosen and Scott, 1998; Rosen, 1996).

**Coal Gasification:** \[ CxHy + H₂O \rightarrow xCO + (\frac{1}{2} + 1) H₂ \]  

**Steam Methane Reforming (SMR):** \[ CH₄ + H₂O \rightarrow CO + 3H₂ \]  

**Partial oxidation of hydrocarbons:** \[ CxHy + O₂ \rightarrow xCO + (\frac{1}{2} + 1) H₂ \]

The gases coming from these reactions are then sent to the downstream water gas shift (WGS) reactors to enhance the hydrogen production by the WGS reaction given as:

\[ (\text{WGSR}) \; CO + H₂O \leftrightarrow CO₂ + H₂ \quad (\Delta H = -40.6 \text{ kJ/mol}) \]  

To obtain high purity H₂, the WGS reaction is generally carried out in two stages for: (1) high temperature shift (250-500 °C) using iron catalysts and (2) low temperature shift (210-270 °C) using copper-based catalysts (Gerhartz, 1993; Bohlbro, 1969). The shortcomings of the current reaction scheme are:

1. Copper based catalysts are extremely intolerant to small quantities of sulfur (< 0.1 ppm) and hence the fuel gases need to be desulfurized upstream of the WGS reactor.

2. A high steam:CO ratio is required to enhance CO conversion and the consequent hydrogen production. The steam to CO ratio at 550 °C can be as high as 50 in a single-stage operation or 7.5 for a more expensive dual-stage process to obtain 99.5 % pure H₂ (David,
1980). For example, to lower the CO content of the typical fuel gas from 45 % (inlet) to 3% (outlet) a total steam addition of 1.18 kg/m$^3$ of the gas is required, at a total pressure of 60 bars and 410 ºC (Gerhardt, 1993).

3. While higher temperature enhances the kinetics of the WGSR, thermodynamics adversely affects the hydrogen production due to the equilibrium limitation of the WGSR with the H$_2$ yield falling with rising temperature.

**Enhancing the Water gas Shift Reaction and Hydrogen Purification**

An effective technique to shift the WGSR to the right for enhanced hydrogen generation has been to remove hydrogen from the reaction mixture. This premise has lead to the development of hydrogen separation membranes. However, membranes cannot completely remove hydrogen from the mixture and there is also the effect of a considerable pressure drop across them (Roark, et al 2002). In addition, any remaining hydrogen in the main stream would dilute CO$_2$ and would lead to poor process economics.

The other option is to remove the CO$_2$ from the reaction gas mixture. Various solvents such as amines, Selexol, Rectisol etc have been used to scrub the CO$_2$ from the WGS reaction gas mixture (Steigel and Ramezan, 2006) between two stages. However, these solvents operate at ambient temperatures and consequently this method involves severe energy penalties due to cooling and reheating of the reaction gas mixture. Hence, high temperature CO$_2$ membranes were developed which operate in the same temperature range as that of the WGSR. Thus the development of these membranes has led to the concept of membrane reactors. However, the use of these membranes leads to the development of a pressure drop and the costs associates with these membranes make the overall process expensive.

**Calcium Assisted Hydrogen production**

There are several processes that enhance hydrogen production using limestone sorbents such as the ZECA process and the HyPr-RING Process (Lin et al., 2002; Ziock et al., 2001). However, these processes operate at very high pressures (12-100 MPa) to produce H$_2$, which is not economically viable. On the other hand processes such as HyPr-RING result in the gasification of coal with in-situ CO$_2$ capture using CaO/Ca(OH)$_2$ systems (Lin et al., 2005). However, these systems operate at very high pressures (70 bar) and require excess
steam and produce only 91% pure hydrogen. In addition, there have been several reports on sorption enhanced hydrogen production by coupling SMR and in-situ CO₂ capture using a sorbent (Hufton et al., 1999; Balasubramanian et al., 1999; Lopez Ortiz; Harrison, 2001 and, Akita et al (2004) Eng. Chem. Res. 41:587). Calcium oxide assisted steam methane reforming (SMR) was attempted in earlier studies (Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001). They detailed the performance of a single-step sorption-enhanced process using a Ni-based catalyst to produce hydrogen. However they also mixed dolomite-CaO powder with the Ni-based catalyst to separate CO₂ and enhance H₂ concentration to 97%.

Our proposed process under consideration involves removing CO₂ from the gas mixture by reacting it with CaO (carbonation). The exothermic carbonation reaction can be given as:

$$\text{CaO (s) + CO}_2 (g) \rightarrow \text{CaCO}_3 (s) \quad (\Delta H = -183 \text{ kJ/mol}) \quad \text{(5)}$$

The continuous removal of the CO₂ product from the WGS reactor will incessantly drive the equilibrium-limited water-gas shift reaction in the forward direction. This will ensure a high yield and purity of H₂ with near stoichiometric amounts of steam needed for the reaction. Besides, the reaction can now be carried out at higher temperatures leading to superior kinetics in the forward direction. Thus the major equilibrium related drawback in this process could be overcome. The spent calcium sorbent (CaCO₃) can then be regenerated separately by calcining it at high temperatures (660-900 °C) to obtain back the calcium oxide and a pure sequestration ready CO₂ stream (eqn. 3), separated from the fuel gas mixture (Gupta and Fan, 2002) completing the calcium looping process.

$$\text{CaCO}_3 (s) \rightarrow \text{CaO (s) + CO}_2 (g) \quad (\Delta H = +183 \text{ kJ/mol}) \quad \text{(6)}$$

This calcium oxide assisted WGS process offers the following advantages over the catalytic and other membrane processes:

1. High temperatures/pressures characterizing the syngas/fuel gas are beneficial to the carbonation reaction kinetics. Hence we can remove CO₂ from the gas mixture at high temperatures (500-800 °C), enabling a more efficient hot gas cleanup. Catalyst based processes or CO₂ removal membranes do not operate >700 °C and thereby necessitate lowering the gas temperature, leading to slower kinetics as well.
2. The removal of CO₂ would not require drastically high steam:CO ratio necessary for the catalyst based processes described above. This would lead to lower costs due to the management of a smaller quantity of steam.

3. Calcium based processes are not adversely affected by sulfur gases such as H₂S and COS. In fact, calcium has been actively used for the removal of H₂S and COS.

4. The use of calcium-based processes has lead to the generation of gas streams with purities as high as 97% hydrogen purity at high temperature, a feat not achievable by catalytic processes.

5. CaO also separates CO₂ from the gas mixture and generates a pure stream of CO₂ upon calcination of the resulting CaCO₃. CO₂ separation cannot be achieved by catalytic system. Thus, this process can be integrated in a carbon management scheme.

Shortcomings of previous studies on Calcium assisted processes

The calcium conversion in the dolomite was only about 50%. On a weight basis, the CO₂ capture capacity achieved by their sorbent would be lower than 35%. Lower conversions would translate to higher sorbent requirement and higher reactor volumes.

1. They regenerated the sorbent in streams of N₂, 4%O₂ in N₂ and pure CO₂. Providing heat to the CaCO₃ sorbent in the form of hot CO₂ maintains the high purity of the CO₂ stream. However, thermodynamics necessitates higher calcination temperature that leads to the sintering of CaO and a subsequent loss in its reactivity. They had to use high regeneration temperatures of 800-950 °C. They observed a decrease in “calcium” conversion from 83 % in the 1st cycle to about 69 % in the 10th cycle and to 27% conversion after 148 cycles.

2. Exposure of the reforming catalyst to an oxidizing atmosphere (viz. O₂/N₂ or CO₂) during the regeneration phase oxidizes Ni in the catalyst to NiO. Since the metallic form is the active form for WGS catalysis, the catalyst requires an additional processing step, besides the calcination step required for CaCO₃ regeneration, where NiO could be reduced to Ni.

3. Calcination in nitrogen would lower the operating temperature. However, it would not solve the problem of CO₂ separation due to the formation of a CO₂/N₂ gas mixture.
4. In addition, the effect of fuel gas impurities (sulfur, halides) in the feed stream on the sorbent performance as well as the hydrogen production capability has not been reported.

Hydrogen production using the Calcium Looping Process

This process overcomes these operational hurdles by the implementation of the following practices:

1. Use of High Reactivity PCC-CaO Sorbent synthesized at OSU

The OSU patented PCC-CaO sorbent can achieve almost complete conversions (> 95%) unlike those observed by Harrison and co-workers for dolomite (~50% calcium conversion). Besides, it has a very high CO₂ capture capacity of about 700 g/kg of the sorbent. This is in contrast to dolomite, which has a substantial amount of unreacted magnesium component (nearly 50%). We will be using the pure calcium oxide sorbent obtained from a patented mesoporous CaCO₃ structure. This CaO has captured 70% by weight of CO₂ over multiple cycles. This would ensure minimal sorbent usage and possibly smaller reactors. In retrospect, we have successfully identified our patented calcium carbonate precursor (Fan et al., 1998) for CaO, which is to be used for hydrogen production with in-situ CO₂ capture. Highly reactive Precipitated Calcium Carbonate (PCC) can be obtained by bubbling in CO₂ gas in a Ca(OH)₂ slurry. The surface properties of this novel calcium sorbent can be tailored by using specific surface modifying agents in the slurry (Agnihotri et al., 1999; Ghosh-Dastidar et al., 1996; Wei et al., 1997; Gupta and Fan, 2002). The surface area, pore size and the pore size distribution of PCC have been controlled to give an optimum internal structure for high gas solid reaction kinetics. The sorbent possesses a surface area of 60 m²/g and a pore volume of 0.18 cc/g. The scientific principle of electric double layer (zeta potential) can help understand this sorbent structure optimization process. Without any surfactant in the slurry, the precipitated CaCO₃ particles have a high positive charge with a positive zeta potential. Different surface modifiers can then be added to the slurry in appropriate concentrations to neutralize the surface charges of the particles or the zeta potential. The system reaches an optimum only when the zeta potential equals zero depicting the maxima in the surface area as shown in Figure 1 below.
Besides, the structurally altered "PCC" has a unique mesoporous structure (5-30 nm) with a maximum pore size distribution occurring at 15 nm. In contrast, the pores of the naturally occurring or commercial calcium minerals were predominantly microporous (<5 nm) as seen in Figure 2. The other CaO precursors are Linwood calcium carbonate (LC) and dolomite (DL). The mesoporous pores would make the sorbent less susceptible to pore pluggage and filling, a phenomenon observed due to the presence of microspores (as seen by Harrison and co-workers). This now leads to almost 100% sorbent conversions. PCC and, CaO obtained from PCC were found to have extraordinarily high reactivity towards SO₂, H₂S and CO₂ (Ghosh-Dastidar et al., 1996; Chauk et al., 2000; Gupta and Fan, 2002) giving very high conversions.

Commercial demonstration plants have been established for SO₂ control based on this sorbent, contributing to the Clean Coal Technology (Fan and Jadhav, 2002). The performance of CaO obtained from different precursors (PCC, LH, LC, dolomite) for carbonation reactions in a pure CO₂ stream is shown in Figure 3. These experiments clearly show that the activity of PCC-CaO was remarkable in reaching high conversions (> 90%) as compared to the other sorbents (Gupta and Fan, 2002). It can be observed that the reaction has an initial rapid kinetically controlled regime followed by a slow diffusion controlled regime. However, unlike other sorbents the PCC-CaO does not seems to taper off after 60 min of reaction. This can be further confirmed at different temperatures as shown in Figure 4.

*Extended Life Cycle Testing of the PCC Sorbent*

Preliminary cyclical calcination-carbonation studies with PCC at 700°C showed sustained reactivity (~90%) while those with commercial Aldrich CaCO₃ showed loss in reactivity over 2 cycles (Gupta and Fan, 2002). The calcination is carried out in a pure N₂ stream while the carbonation was carried out in pure CO₂. However, the cycles were carried out in isothermal conditions at 700 °C. Extended life cycle studies with PCC were then carried out for 11 cycles in a TGA. The sorbent shows almost sustained reactivity in N₂ regeneration.

Earlier studies from our group have shown that PCC-CaO achieves high conversions (>90%) towards carbonation compared to ~45-60% attained by CaO derived from naturally occurring calcium sources (Gupta et al.,2002). Life cycle testing on PCC-CaO, carried out in
100% CO₂ for an hour, did not show a significant drop in reactivity for 2-3 CCR cycles. However, there is sufficient literature that mentions a loss in reactivity over a higher number of cycles. We carried out extended isothermal life cycle testing of naturally occurring limestone powder (LC) and PCC sorbent at 700 °C. Figure 5 gives the data collected for 50 cycles with LC sorbent while Figure 6 shows that for 100 CCR cycles with the PCC sorbent. The carbonation was carried out in a 10% CO₂ stream while pure N₂ was used for calcination. Each of the carbonation-calcination steps was performed for 30 minutes.

Figures 5 and 6 depict the sorption capacity of the sorbent, quantified in kg CO₂ captured/kg sorbent. Theoretically, 56 grams of unsupported CaO sorbent should react with 44 grams of CO₂ corresponding to a maximum CO₂ sorption capacity of 78.6 wt% at 100% conversion. From Figure 5 it is evident that the wt% capacity of the LC based sorbent towards CO₂ capture reduces from 58% in the first cycle to 20% at the end of the 50th cycle, due to the dominant microporosity in the LC precursor, which makes the structure susceptible to pore pluggage and pore mouth closure (Gupta et al., 2002; Wu et al., 2002). This is due to the formation of CaCO₃, whose molar volume (36.9 cc/mol) is higher than that of the reactant CaO (16.9 cc/mol). In contrast, we see from Figure 6 that the conversion of PCC-CaO over 100 cycles is distinctly higher. The capacity, which is ~68 wt% in the first cycle, drops to 40 wt% in the 50th and slightly to 36 wt% by the 100th cycle (~6000 minutes on stream). The high reactivity over multiple cycles can be attributed to the predominant mesoporous structure of PCC, which allows the reactant gases to access the entire surface of particle through the larger pores. The extent of carbonation continues to rise significantly beyond the kinetic controlled regime. This fact was ascertained by extending the carbonation reaction time to 120 minutes over 40 cycles. These results provide evidence that the reactivity of the PCC-CaO is governed solely by the reaction time provided and there is no structural limitation in attaining high conversion.

Figure 7 depicts graphically the wt% CO₂ capture attained by LC, PCC and a host of other high temperature metal oxide sorbents reported in the literature for multiple CCR cycles (White et al., 2003). While numerous studies have been conducted on a variety of metal oxide based CCR process, a metal oxide that shows consistently high reactivity and sorption capacity over multiple cycles remains to be identified. The experimental conditions used in
the studies referred to in Figure 7 are detailed in a table elsewhere (Iyer et al., 2004). The table highlights important process conditions such as carbonation/calcination temperatures and residence times, number of cycles, sorption capacities, and the CO2 concentration in the gas mixture during the reaction and regeneration steps. PCC-CaO attains a 66.8 wt% increase in 30 minutes and 71.5 wt% after 120 min at the end of the first cycle. In contrast, earlier studies (Gupta et al., 2002) have shown a sorption capacity of about 71 wt% (90% conversion) in a pure CO2 stream after 60 mins at 650 °C. Hence, factors like CO2 concentration, temperature and cycle time play a significant role in determining the sorption capacity for the same sorbent.

The experiments conducted by Barker on 10 micron CaO powder demonstrate a drop in the sorption capacity from ~59 wt% in the first carbonation cycle to 8 wt% at the end of the 25th cycle (Barker, 1973). This work suggests that due to the formation of a 22nm thick product layer, particles smaller than 22 nm in diameter should be able to achieve stoichiometric conversion. The author later proved this hypothesis by obtaining repeated 93% conversion (73% weight capture) of 10nm CaO particles over 30 cycles with a carbonation time of 24 hours under 100% CO2 at 577 °C (Barker.1974). In a PbO-CaO based chemical heat pump process, PbO attained 3.6 wt% CO2 capture in the first cycle, decreasing to 1.6 wt% by the 6th cycle and CaO showed a drop in CO2 capture from 53 wt% in the 1st cycle to 27.5 wt% by the 5th cycle (Kato et al., 1998). A lithium zirconate (Li2ZrO3) based sorbent provided a 20 wt% capacity over two cycles (Ida et al., 2003). In another study, researchers at Toshiba Corp. observed that the reactivity of lithium orthosilicate was better than that of lithium zirconate (White et al., 2003; Kato et al., 2002). Extended cyclical studies performed on lithium orthosilicate samples revealed a consistent 26.5 wt% capacity over 25 cycles (Nakagawa et al., 2003). Harrison and coworkers, reported earlier, have been developing an enhanced hydrogen production process from the water gas shift reaction by removing CO2 from the gas mixture through the carbonation of CaO from dolomite (Ortiz et al., 2001). Dolomitic limestone based CCR process yielded a 35 wt% capacity in the first cycle that fell to 11.4 wt% by the 148th cycle when the carbonation experiments were performed in pure CO2 at 800 °C and calcination was conducted at 950 °C. They observed a decrease in calcium
conversion from 83 % in the 1st cycle to about 69 % in the 10th cycle itself, followed by 27% conversion after 148 cycles (Ortiz et al., 2001).

Sorbent regeneration by Vacuum/Steam/CO₂ calcinations

We will be employing steam/CO₂ calcination, both of which lead to the regeneration of CaCO₃ at low enough temperatures that sintering is not in effect. Our prior investigation has focused on vacuum calcination, which results in a pure stream of CO₂. Steam Calcination can be quite suitable as the steam can be condensed out from the CO₂-steam mixture to yield pure CO₂ stream for sequestration. It has been suggested in literature that CaO procured from the calcination of limestone under vacuum has a higher reactivity (Beruto and Searcy, 1976; Dash et al., 2000; Beruto et al., 1980). Repeated calcination in N₂ leads to a loss in the surface area. Vacuum calcination of PCC followed by the carbonation of PCC-CaO was repeated over two cycles. PCC was first vacuum calcined to CaO-1 at 750 °C. CaO-1 was then carbonated to CC-2 at 700 °C in pure CO₂ followed by its vacuum decomposition to CaO-2 which was then carbonated to CC-3. The values of surface area (SA) and pore volume (PV) of the sorbent at various stages are provided in Table 1. The extent of carbonation was beyond 90% for every vacuum calcination-carbonation cycle. Besides, these results prove that there is no systematic decline in SA and PV of sorbents with increasing cycles. This combination is also capable of providing a sustained conversion over many cycles due to effective retention of the sorbent morphology.

Table 1: Structural properties of Calcium based sorbents undergoing vacuum calcination at 750 °C and carbonation at 700 °C.

<table>
<thead>
<tr>
<th></th>
<th>SA (m²/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC</td>
<td>38.3</td>
<td>0.1416</td>
</tr>
<tr>
<td>CaO-1</td>
<td>12.63</td>
<td>0.02409</td>
</tr>
<tr>
<td>CC-2</td>
<td>6.5</td>
<td>0.0103</td>
</tr>
<tr>
<td>CaO-2</td>
<td>15.93</td>
<td>0.04008</td>
</tr>
<tr>
<td>CC-3</td>
<td>2.361</td>
<td>0.004483</td>
</tr>
</tbody>
</table>

Figure 8 below gives the options for direct and indirect fired calciners to regenerate the CaCO₃ sorbent. The fuel in the direct calcination option could also be the hydrogen
produced in the plant. Thus the heat for calcination could be obtained by H₂ combustion and the steam formed could be easily condensed out.

_Thermodynamic analyses of CaO-CaCO₃, CaO-CaS, CaO-COS, CaO-HCl and CaO-Ca(OH)₂ systems_

Primarily three important gas-solid reactions can occur when calcium oxide (CaO) is exposed to a fuel gas mixture obtained from coal gasification. CaO can undergo hydration, carbonation and sulfidation reactions with H₂O, CO₂ and H₂S, respectively. These can be stoichiometrically represented as:

- **Hydration:** \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \) (a)
- **Carbonation:** \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \) (b)
- **Sulfur capture (H₂S):** \( \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \) (c)
- **Sulfur capture (COS):** \( \text{CaO} + \text{COS} \rightarrow \text{CaS} + \text{CO}_2 \) (d)
- **Halide capture (HCl):** \( \text{CaO} + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \) (e)

All these reactions are reversible and the extent of each of these reactions depends on the concentrations of the respective gas species and the reaction temperature. Detailed thermodynamic calculations were performed to obtain equilibrium curves for the partial pressures of H₂O (P_{H₂O}), CO₂ (P_{CO₂}) and H₂S (P_{H₂S}) as a function of temperature, for the hydration, carbonation, and sulfidation reactions using HSC Chemistry v 5.0 (Outokumpu Research Oy, Finland). The equilibrium calculations were based on the fuel gas compositions that are typical of the different types of coal gasifiers. The details of the fuel gas mixtures are illustrated in Table 2.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Moving Bed, dry air</th>
<th>Moving Bed, slagging</th>
<th>Fluidized Bed</th>
<th>Entrained Flow, slurry</th>
<th>Entrained Flow, dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>Sub-bituminous</td>
<td>Bituminous</td>
<td>Lignite</td>
<td>Bituminous</td>
<td>Bituminous</td>
</tr>
<tr>
<td>Pressure (psia)</td>
<td>295</td>
<td>465</td>
<td>145</td>
<td>615</td>
<td>365</td>
</tr>
<tr>
<td>CO</td>
<td>17.4</td>
<td>48.2</td>
<td>41</td>
<td>41</td>
<td>60.3</td>
</tr>
<tr>
<td>H₂</td>
<td>23.3</td>
<td>30.6</td>
<td>28.8</td>
<td>28.8</td>
<td>30</td>
</tr>
<tr>
<td>CO₂</td>
<td>14.8</td>
<td>8.2</td>
<td>10.2</td>
<td>10.2</td>
<td>1.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>...</td>
<td>9.1</td>
<td>17.1</td>
<td>17.1</td>
<td>2</td>
</tr>
<tr>
<td>N₂</td>
<td>28.5</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
<td>4.7</td>
</tr>
<tr>
<td>CH₄+H₂O</td>
<td>5.8</td>
<td>2.8</td>
<td>0.3</td>
<td>0.3</td>
<td>...</td>
</tr>
<tr>
<td>H₂S+COS</td>
<td>0.2</td>
<td>0.4</td>
<td>1.1</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 2: Typical fuel gas compositions obtained from different gasifiers. (Stultz and Kitto,
The relationship between the reaction temperature and the equilibrium partial pressures of H\textsubscript{2}O and CO\textsubscript{2} for the hydration and carbonation reactions are shown in Figure 9 (a). For a typical gasifier moisture composition ranging from 12-20 atm (P\textsubscript{H\textsubscript{2}O}) the hydration of CaO occurs for all temperatures below 550--575 °C, respectively. By operating above these temperatures, the CaO-hydration can be prevented. Figure 9 shows the typical equilibrium CO\textsubscript{2} partial pressures (P\textsubscript{CO2}) as a function of temperature. From the data in Table 2, it can be inferred that the typical P\textsubscript{CO2} in the gasifiers ranges from 0.4-4.3 atm for entrained flow (slurry) and entrained flow (dry) gasifier systems respectively. The equilibrium temperatures corresponding to those P\textsubscript{CO2} lie in the 830--1000 °C range as shown in Figure 9. Thus, by operating below these temperatures, we can effect the carbonation of CaO.

For the reversible sulfidation of CaO (eqn c) the thermodynamic calculations depend on the concentration of moisture in the system as well as the CO\textsubscript{2} in the system. The thermodynamics of the sulfidation of CaCO\textsubscript{3} given below is not favorable for H\textsubscript{2}S removal as compared to CaO.

**Sulfidation of CaCO\textsubscript{3}**: \[ CaCO_3 + H_2S \rightarrow CaS + H_2O + CO_2 \]

Hence, based on CaO-CaCO\textsubscript{3} thermodynamics, it is imperative to operate under those P\textsubscript{CO2} such that carbonation of CaO does not occur and CaO is available for H\textsubscript{2}S capture. Hence, Figure 10 (a) depicts the equilibrium H\textsubscript{2}S concentrations in ppm for varying moisture concentrations (P\textsubscript{H\textsubscript{2}O}) and 30 atm total pressure. The proposed integrated WGS-carbonator reactor system will be operating at near-stoichiometric steam requirement resulting in low concentrations of steam in the reactor system. In addition, the CO\textsubscript{2} concentration will also be minimal due to the continuous removal of the CO\textsubscript{2} product via carbonation. Thus, the reactor system will now favor H\textsubscript{2}S removal using CaO at around 600-700 °C. Figure 10 shows the thermodynamic equilibrium H\textsubscript{2}S concentration for varying steam concentrations (0.02-20 atm). Thus, for a steam concentration of about 0.2 atm at 600 °C, the equilibrium H\textsubscript{2}S concentration corresponds to about 1 ppm. Thus, the reactor system can achieve CO\textsubscript{2} as well as H\textsubscript{2}S removal while producing a pure H\textsubscript{2} stream. On the other hand, the typical gasifier conditions enable H\textsubscript{2}S removal to only 100-300 ppm. Similarly the concepts of COS capture and HCl capture by calcium oxide in a gas mixture with minimal CO\textsubscript{2} and steam can be
explained via Figures 10 (b) and 10 (c).

**Removal of Sulfur and halides**

The main drawback, which all the hydrogen production processes do not address, is the effect of sulfur (H$_2$S + COS) and halides (HCl) in the feed. Sulfur is present in syngas in the form of H$_2$S and COS and halides such as HCl. These sulfur impurities are known to deactivate the reforming catalysts as well as react with CaO to form CaS as given by eqn (5) below. None of these technologies address sulfur removal schemes. Hence they might have to resort to conventional scrubbing techniques, upstream or downstream. This leads to additional steps as well as energy penalties in the hydrogen production process. This process aims at removing the sulfur (H$_2$S and COS) in the system using the high reactivity calcium oxide sorbent, which is also used to capture CO$_2$ in the WGS reactor to produce hydrogen.

Synthesis gas obtained from the gasification of coal contains chloride impurities in the form of hydrogen chloride which causes severe corrosion in the equipment downstream of the gasifier. Although the concentration of hydrogen chloride in the gas stream from the gasifier depends on the type of coal, gasifier, temperature of operation used it typically varies within the range of 50 to 400 ppmv. Traditional methods of HCl removal include using a chloride guard which is expensive and can only be operated at temperatures below 450 °C resulting in severe energy penalties.

**Reduction of steam requirements for Hydrogen Production**

One of the major drawbacks to produce hydrogen using the conventional water gas shift catalyst reaction route is the excess steam requirement. The excess steam varies from 7 to 50 times the stoichiometric values. Hence, the main objective in developing this process is to reduce the excess steam requirement for hydrogen production. The excess steam is generally used to drive the equilibrium limited WGS reaction forward. However, due to in situ removal of CO$_2$ product, the WGS reaction proceeds in the forward direction to yield high conversions of CO to hydrogen. The high hydrogen yields make it possible to operate with a lower steam ratio in this process. Lowering the steam requirement will reduce the operating cost as well as favor H$_2$S and COS removal as excess steam impedes sulfur (H$_2$S/COS) capture by CaO means of the sulfidation reaction mentioned earlier. Similarly, the
presence of CO₂ impedes HCl capture as shown by thermodynamic analyses. Hence, by removing CO₂ in the system we can remove halides (HCl) to very low levels (ppbs).

The effect of sulfidation reaction with three different CaO sorbents was studied (Chauk et al., 2000). CaO was obtained from Aldrich chemicals, PCC and Linwood calcium carbonate. The reaction was conducted at 800 °C with a total pressure of 1MPa and P₁₂S of 3kPa (0.3%). Figure 11 clearly points out the high reactivity of the PCC-CaO as compared to the other CaO sorbents. This can again be attributed to the superior sorbent morphology of PCC. Similar results have also been seen with this sorbent for SO₂ removal.

CaS Regeneration: Steam as well as CO₂ can also react with CaS to form CaO given by the reactions (Turgoden et al., 1973, Ruth et al., 1978) (Adanez, et al, 2001). These reactions can occur in the range of 400-900 °C and will be evaluated in this project.

\[
\begin{align*}
\text{CaS} + \text{H}_2\text{O} & \rightarrow \text{CaO} + \text{H}_2\text{S} \\
\text{CaS} + 3\text{CO}_2 & \rightarrow \text{CaO} + 3\text{CO} + \text{SO}_2 \\
\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{H}_2\text{S}
\end{align*}
\]

Combined WGS and carbonation reaction (without H₂S)

The combined carbonation and WGS reaction for enhanced H₂ production was conducted in an integral fixed bed reactor assembly described elsewhere (Gupta et al., 2004). Different calcium oxide precursors such as naturally occurring limestone: Linwood Carbonate (LC) and Linwood Hydroxide (LH) in addition to the structurally modified PCC were tested. The high temperature shift (HTS) iron oxide catalyst on chromium oxide support was procured from Süd-Chemie, Inc.

Figure 12(a) illustrates the CO conversion breakthrough curve for both the PCC and LC sorbent-catalyst systems. It is evident from the figure that the presence of CaO enhances the CO conversion and hence the hydrogen production. In both the systems we observe 100% initial conversion and the system finally reaches steady state. In addition, we observe that PCC-CaO system dominates over the LC-CaO system at any given time demonstrating the superior performance of the PCC sorbent towards hydrogen production. Figure 12 (b) describes the nitrogen and steam free product gas compositions for a PCC-HTS system at 600°C. It is clear from this figure that during the initial breakthrough period the system
demonstrates the production of a **100% pure hydrogen stream** while the CO and CO₂ concentrations are negligible. As the system reaches steady state the CO₂ and H₂ concentrations tend to converge.

**Effect of Pressure on H₂ yield**

The combined water gas shift reaction and the carbonation reaction were carried out in a fixed bed reactor containing the calcined PCC sorbent and the HTS catalyst. The experiments were carried out at two pressures of 1 and 20 bar and this was done to study the performance of the combined reactions in a commercial setup where the fuel gas is typically around 20-30 bar. As shown in Figure 13 the combined reactions demonstrated a superior performance at 20 bar as compared to ambient pressures, leading to the formation of 100% pure hydrogen during the initial stages of the reaction.

**Effect of reducing excess steam requirement**

The combined reactions were also conducted at different steam: CO ratios of 3:1, 2:1 and 1:1. Figure 14(a) below illustrates the CO conversion at 0 bar for different steam : CO ratios. Figure 14(b) describes the CO conversion at 20 bar for different steam : CO ratios and it is evident that 100% conversion is achieved for all the three ratios for almost the same time in the initial stages of the reaction. This clearly demonstrates the ability to use a lower amount of steam at high pressures without altering the performance of the system.

**Non-Catalytical Production of H₂**

Due to the poisoning of the HTS (iron) catalysts in the presence of H₂S impurities and the issues related to economics in using sulfur tolerant catalysts we conducted preliminary tests to determine the efficiency of the system to produce pure hydrogen in the absence of the catalyst. It was found from preliminary experiments that at a pressure of 20 bar in the presence of the sorbent the water gas shift reaction achieved 100% conversion and a 100% pure hydrogen stream was produced for 600 mins. Hence it is clear that the sorbent is effective in shifting the equilibrium of the WGSR to such an extent that pure hydrogen can be produced in the absence of a catalyst. Operating in this manner will eliminate the complexities and costs involved in the separation of the sorbent and catalyst mixture and in the regeneration of the catalyst.
Likelihood of developing a commercially viable technology

Figure 16 below describes the integration of the proposed hydrogen production process in a typical coal gasifier. The syngas from the gasifier flows into the combined “one box” WGS-carbonator reactor where stoichiometric amount of steam is injected along with CaO leading to enhanced WGSR coupled with CO₂ and H₂S capture in the system. The proposed integrated WGS-carbonator reactor system will be operating at near-stoichiometric steam requirement resulting in low concentrations of steam in the reactor system. In addition, the CO₂ concentration will also be minimal due to the continuous removal of the CO₂ product via carbonation. Thus, the reactor system will now favor sulfur (H₂S and COS) removal using CaO at around 500-700 °C. to about 10 ppb—20 ppm. Thus, the reactor system can achieve CO₂ as well as H₂S removal while producing a pure H₂ stream. Thus the proposed technology has an immense likelihood of success and this evident from the support letters from companies such as Shell Oil, American Electric Power, Sasol etc.

As described in earlier sections, the proposed technology has several benefits over current technology as it offers a novel integrated one stage process for producing high purity high temperature high-pressure hydrogen with carbon management incorporated in it. Besides, it also includes sulfur removal and halide removal from the system making the process economical and energy efficient.

The process can be optimized for various configurations such as:

1. Air blown gasification with sorbent (CaO) injection producing electrical power from an advanced turbine.

2. Oxygen blown gasification with sorbent (CaO) to produce greater than 90 percent purity hydrogen steam without any water gas shift catalyst.

3. Oxygen blown gasification with additional WGS catalysts (sulfur tolerant) and CaO produce hydrogen of purity compatible with solid oxide fuel cells and PEM fuel cells.

4. Oxygen blown gasification with sorbent (CaO) injection without catalyst to shift the fuel gas to a mixture of H₂ : CO ranging from 0.5 – 20 for various fuels and chemical synthesis using Fischer Tropsch reactions.
Applications of Calcium Looping Process

A. High temperature CO₂ capture from flue gas mixtures

Implementing CO₂ capture technologies induces severe energy losses. For example, the parasitic energy consumption, which decreases the total power plant capacity, is 30% for the conventional amine scrubbing process while it improves to 28% for the oxy-combustion system (Châtel et al., 2005). In this regard, a successful alternative will require the incorporation of effective process integration schemes to minimize the parasitic energy requirement for CO₂ separation. One scheme for heat integration is based on the calcium based carbonation-calcination reaction (CCR) process which uses the re-engineered limestone sorbent mentioned earlier at 600-700 °C for efficient and economical CO₂ separation. Figure 17 delineates the heat integration strategies for retrofitting the CCR process to an existing boiler without any significant modifications to the coal-based power plant. The flue gas that leaves the economizer of the boiler is routed to the CCR process system for CO₂ capture. This flue gas from the economizer (stream 1), is used to combust additional fuel with air to provide heat to the indirect calciner. Heat is extracted from the total flue gas mixture (stream 2), which contains all the CO₂ emitted by the entire plant, before it can be sent into the carbonator/sulfator system, to produce high quality steam. CO₂ and SO₂ are removed in the carbonator/sulfator system and the CO₂ free flue gas (stream 3), which is at ~650 °C, is cooled before it is sent into the air pre-heater followed by ESP (electrostatic precipitator). The carbonated sorbent, CaCO₃, is sent to the calciner to regenerate the calcium oxide (CaO) sorbent for subsequent cycles while yielding a pure CO₂ stream. The sulfated sorbent and fly ash are removed from the system by means of a purge stream. This process is designed to capture both CO₂ and SO₂ simultaneously, rendering it a multi-pollutant control technology. The heat of carbonation can be as high as one-third of the total thermal capacity of a power plant. In the CCR process, steam is generated using high quality heat available from three different sources: (a) carbonator/sulfator (b) hot flue gas after supplying energy to calciner (between 600-850°C) (c) a pure CO₂ stream from calciner at 800-850 °C. This steam can be used in a secondary steam turbine system for additional electricity generation or in the existing plant steam cycle by offsetting the boiler load and in driving various feed water pumps in the plant. Thus, the total parasitic energy consumption of the plant is immensely
reduced to 15%, including CO₂ compression (10%), which is half of that of the conventional amine scrubbing process.

B. Integrated H₂ production, CO₂ capture and sulfur removal in a coal gasification process

Figure 18 below describes the integration of the proposed hydrogen production process in a typical coal gasifier. The syngas from the gasifier flows into the combined “one box” WGS-carbonator reactor where stoichiometric amount of steam is injected along with CaO leading to enhanced WGSR coupled with CO₂ and H₂S capture in the system. The proposed integrated WGS-carbonator reactor system will be operating at near-stoichiometric steam requirement resulting in low concentrations of steam in the reactor system. In addition, the CO₂ concentration will also be minimal due to the continuous removal of the CO₂ product via carbonation. Thus, the reactor system will now favor sulfur (H₂S and COS) removal using CaO at around 500-700 °C to about 10 ppb--20 ppm. Thus, the reactor system can achieve CO₂ as well as H₂S removal while producing a pure H₂ stream.

As described in earlier sections, the proposed technology has several benefits over current technology as it offers a novel integrated one stage process for producing high purity high temperature high-pressure hydrogen with carbon management incorporated in it. Besides, it also includes sulfur removal and halide removal from the system making the process economical and energy efficient.

The process can be optimized for various configurations such as:

1. Air blown gasification with sorbent (CaO) injection producing electrical power from an advanced turbine.

2. Oxygen blown gasification with sorbent (CaO) to produce greater than 90 percent purity hydrogen steam without any water gas shift catalyst.

3. Oxygen blown gasification with additional WGS catalysts (sulfur tolerant) and CaO produce hydrogen of purity compatible with solid oxide fuel cells and PEM fuel cells.

4. Oxygen blown gasification with sorbent (CaO) injection without catalyst to shift the fuel gas to a mixture of H₂ : CO ranging from 0.5 – 20 for various fuels and chemical
synthesis using Fischer Tropsch reactions.

C. Enhanced Coal to Liquids (CTL) Process with sulfur and CO₂ capture

The rising energy demand coupled with the depleting global oil reserves and the dependence on foreign oil, has brought coal to liquid technologies, to the forefront. Currently, synthetic fuels are mainly produced via coal gasification and Fischer-Tropsch (F-T) synthesis process. A conventional coal to liquid plant consists of a gasifier which produces the syngas. The H₂/CO ratio of the syngas is around 0.63, which is much lower than the ratio of ~2, required for liquid fuel production. Hence, in order to modify the amount of hydrogen in the syngas, part of the syngas is introduced to a WGS reactor to be shifted into H₂. Since the gas stream contains sulfur impurities a sulfur tolerant WGS catalyst is used, which is expensive. The rest of the syngas stream passes through a hydrolysis unit where the COS is converted into H₂S.

The gas stream from the WGS reactor and the hydrolysis reactor are mixed together and passed through several gas cleanup units that consist of a mercury removal bed, bulk sulfur removal units, sulfur polishing unit, and CO₂ removal units. After the pollutants are removed, a clean syngas stream with a H₂ to CO ratio of around 2 is obtained which is sent to the F-T reactor for the production of liquid fuel. The F-T reactor is capable of converting more than 70% syngas into a wide range of hydrocarbons ranging from methane to wax. The products from the F-T reactor are sent to a product upgrader where the high molecular weight hydrocarbons are refined into liquid fuel or naphtha while the low molecular weight fuel gas stream is sent to a power generation block to generate electricity for the air separation unit and other parasitic energy consumption (Robert A. Mayer (2005) “Handbook of Petroleum Refining” McGraw Hill). In this process, expensive gas cleanup units for sulfur and CO₂ removal are needed and the parasitic energy consumption for cooling and reheating the gas stream is very large. This parasitic energy consumption requires the off gases to be burnt in a turbine which reduces the total liquid fuel yield from the coal.

In contrast when the calcium looping process is used in the production of liquid fuels, a H₂:CO ratio of the desired level can be obtained by converting the C1-C4 hydrocarbons and unconverted syngas produced from the FT reactor and the syngas from the gasifier in an
efficient manner, while achieving CO₂ and H₂S removal in the same reactor system. Since contaminant removal is achieved at high temperatures the parasitic energy requirement is greatly reduced and also the issues related to procurement and deactivation of the sulfur tolerant catalyst for the WGSR are eliminated. As shown in Figure 19 the unreacted syngas and light hydrocarbons from the FT reactor are mixed with the syngas from the gasifier and sent into the single reactor system which adjusts the ratio of the H₂:CO in the syngas stream by reforming the hydrocarbons (eqn. (13)) and shifting the syngas (eqn. (14)) in the presence of CaO. The concomitant carbonation of the metal oxide (CaO) leading to the formation of the metal carbonate (CaCO₃) incessantly drives the equilibrium-limited WGSR and the reforming reaction forward by removing the CO₂ product from the gas mixture(eqn. (15)). The metal carbonate can then be regenerated by heating, to give back the metal oxide and a pure CO₂ stream (eqn. (17)). By improving the equilibrium conversion of the reforming and WGS reaction, steam addition can be greatly reduced. The reduction in steam consumption not only reduces energy consumption but also aids in the removal of H₂S to ppb levels by the CaO (eqn. (16)) as steam poses an equilibrium constrain to the removal of H₂S. Various reactions occurring in this system are as follows:

Reforming:  \( \text{C}_x\text{H}_y + x\text{H}_2\text{O} \rightarrow x\text{CO} + \left(\frac{y}{2}+x\right)\text{H}_2 \)  \hspace{1cm} (13)

WGSR:  \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \)  \hspace{1cm} (14)

Carbonation:  \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \)  \hspace{1cm} (15)

Sulfidation:  \( \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \)  \hspace{1cm} (16)

Calcination:  \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)  \hspace{1cm} (17)

The calcium looping process aids in:

a) Converting all the C1-C4 hydrocarbons and unconverted syngas from the FT process, and syngas from the gasifier, into a 2:1 H₂:CO stream by shifting the equilibrium of the WGS and reforming reaction in the forward direction by removing the CO₂ product insitu,

b) Achieving simultaneous CO₂ and H₂S capture at high temperatures to ppb levels,

c) Producing a sequestration ready CO₂ stream,

d) Reducing the excess steam requirement which reduces the parasitic energy consumption
and aids in higher levels of H₂S removal,
e) Reforming and reusing all the C1-C4 hydrocarbons produced from the FT reaction to produce more liquid fuel than the conventional process, for the same amount of coal consumed.

Hence by using the calcium looping process it is possible to combine various unit operations (reforming, WGS, CO₂ capture and H₂S removal) into a single reactor system and to improve the overall efficiency of the coal to liquid technology.

D. Integrated H₂ production using SMR with CO₂ capture and sulfur removal

Conventional Steam Methane Reforming without CO₂ capture

Steam Methane Reforming (rxn 1) forms the industrial workhorse and is most widespread technology for hydrogen manufacture from natural gas (McHugh 2005; and Bareli et al. (2007) Energy 32:834). However, the reaction is highly endothermic (206 kJ/mol) and is equilibrium limited at lower temperatures. Hence, the SMR is usually conducted at high temperatures of 800-950 °C and pressures of about 20-30 atm. In addition, a minimum steam to carbon ratio of three or more is used to achieve reasonable methane conversions (65-90%). A simplified schematic of a conventional SMR to produce pure hydrogen is shown in Figure 19 below.

The natural gas (NG) is initially split into two parts (a) for feed to the reformer to make hydrogen and (b) fuel for the reformer and steam generator. The natural gas feed is then compressed, cleaned of sulfur impurities and is then fed to a performer which operates at lower temperatures and catalytically converts all the C2-C5 streams in the NG to CO₂ or methane. The feed now enters the SMR unit at high temperatures which converts the NG to syngas. The commercial nickel alumina catalyst is the industry workhorse for SMR. Process. The process stream is now rich in CO and H₂ with a H₂/CO ratio of about 3. The stream then undergoes high and low temperature water gas shift reaction (WGSR) where all the CO gets converted to H₂. The stream is then fed to a pressure swing adsorption (PSA) unit where all the gases except H₂ get adsorbed in the beds leading to a pure H₂ product stream which can be
more than 99.999\% pure. The unconverted CO, CO\textsubscript{2} and CH\textsubscript{4} stream are subsequently desorbed from the PSA unit that forms the fuel stream to reformer burner.

The drawback of the SMR is the capital cost of the reformer due to the high temperature operation and heat integration requirements due the severe endothermicity of the reaction. Other approaches include partial oxidation (POX) where oxygen is used to partially oxidize natural gas to produce synthesis gas. This scheme results in in-situ combustion of the natural gas to provide heat for the reaction. Novel system includes autothermal reforming (ATR) which is a combination of partial oxidation and SMR to produce synthesis gas. These approaches result in almost complete methane conversions (95-99\%) and better heat integration schemes due to in-situ combustion. While the SMR has better system efficiency of about 80\% as compared to 72\% for ATR, the capital costs for ATR units are about 75\% of that of SMR. Further, the SMR process also produces the maximum H\textsubscript{2} per mole of natural gas used. Hence, we need a better system that has the efficiency of an SMR but has better heat integration and lower capital costs like that of an ATR. Finally, incorporation of CO\textsubscript{2} control technology would reduce the process efficiency and increase the capital cost of SMR process making hydrogen production via SMR uneconomical as the price of natural gas escalates.

**Integrated H\textsubscript{2} production using SMR with CO\textsubscript{2} capture and sulfur removal via calcium looping process**

A simplified schematic of enhanced hydrogen production using steam methane reforming (SMR) coupled integrated with the calcium looping scheme is shown in Figure 20. The reaction scheme which includes SMR, WGSR, carbonation, calcinations and sulfur capture is shown below.

\[
\begin{align*}
\text{SMR:} & \quad \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H = + 206 \text{ kJ/mol}) \quad (13) \\
\text{WGSR:} & \quad \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad (\Delta H = - 41 \text{ kJ/mol}) \quad (14) \\
\text{Carbonation:} & \quad \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (\Delta H = + 178 \text{ kJ/mol}) \quad (15) \\
\text{Overall:} & \quad \text{CH}_4 + 2\text{H}_2\text{O} + \text{CaO} \rightarrow \text{CaCO}_3 + 4\text{H}_2 \quad (\Delta H = - 13 \text{ kJ/mol}) \quad (13) \\
\text{Calcination:} & \quad \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (\Delta H = + 178 \text{ kJ/mol}) \quad (17) \\
\text{Sulfidation:} & \quad \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \quad (16)
\end{align*}
\]

As discussed earlier, the drawback of a conventional SMR process is the huge heat
requirement due to the endothermic reaction (13) requiring higher temperature operation leading to operating temperatures of about 800-950 °C. The integrated indirect heat transfer system coupled with high temperature operation leads to large capital costs for the reformer. On the other hand, the carbonation reaction is exothermic which also drives the equilibrium limited WGSR forward at high temperatures. Thus the SMR, WGSR and carbonation reactions can be conducted in one single step at a reaction temperature of about 550-700 °C at high operating pressures of 20 atm. Thus the overall heat balance for the reactions is almost neutral (-13 kJ/mol) and the process can be achieved at lower temperatures resulting in lower capital costs. In addition, the process results in complete carbon conversions, lower steam requirement, simultaneous in-situ sulfur removal and integrated CO₂ capture while producing high pressure hydrogen (20 bar). Compression of hydrogen is very expensive and this process obviates the need for first stage H₂ compression. Thus the incorporation of the calcium looping scheme results in integration of steam reforming, WGSR, CO₂ capture, sulfur removal and hydrogen separation in “one single step” while reducing excess steam requirement and producing high purity high pressure hydrogen resulting in improved process efficiency and reduced capital costs.

**Conclusions on Calcium Looping Process**

The calcium looping process simplifies the production of H₂ by integrating the water gas shift reaction (WGSR) with in-situ carbon dioxide, sulfur and hydrogen halide removal from the synthesis gas at high temperatures in a single stage reactor process while eliminating the need for WGSR catalyst requirement. This technology provides a “one box” mode of operation for production of high purity hydrogen with integrated CO₂, sulfur and chloride capture that integrates WGSR, hydrogen separation (PSA/membranes), CO₂ capture, and sulfur removal in one consolidated unit. Another advantage is that in addition to generating a pure hydrogen stream, it is also capable of adjusting the H₂ to CO ratio in the outlet to the required level while removing sulfur very low levels thus making it an attractive scheme for the production of liquid fuels by the Fisher Tropsch’s reaction. This integrated “one box” process depicts the potential to achieve higher system efficiencies with lower overall footprint by combining different process units in one stage. The envisioned system has the flexibility and the potential to produce hydrogen of different purity levels by reducing the amount of
WGS catalyst and reducing the excess steam requirement. This novel process which enables high temperature operation can also be deployed for reactive CO₂ capture from flue gases. Thus, the technology increases the overall conversion and process efficiency for various process applications.

A high reactivity mesoporous calcium oxide sorbent is described in US Patents 5,779,464 and 7,067,456 B2.

Objectives

The rising energy demand coupled with the depleting global oil reserves and the dependence on foreign oil, has brought coal to liquid technologies, to the forefront. Currently, synthetic fuels are mainly produced via coal gasification and Fischer-Tropsch (F-T) synthesis process. Syngas produced from gasifiers has a low H₂/CO ratio ranging from 0.5 to 0.7 while a ratio of ~2 is required for liquid fuel synthesis through the FT process. The equilibrium limited water gas shift (WGS) process is utilized to meet this hydrogen deficit in the syngas. In addition the FT process usually has a conversion of only 78% and a selectivity of 87%¹. Hence a process which can efficiently produce the required H₂:CO ratio from the syngas produced in the gasifier and the unreacted as well as the undesirable products of the FT process would enhance the efficiency of the coal to liquid technology.

The disclosed embodiments combine various unit operations (reforming, WGS, CO₂ capture and H₂S removal) into a single reactor system and improve the overall efficiency of the coal to liquid technology by using the calcium looping process. The specific objectives are as follows a) To convert all the C₁-C₄ hydrocarbons and unconverted syngas from the FT process, and syngas from the gasifier, into a 2:1 H₂:CO stream by shifting the equilibrium of the WGS and reforming reaction in the forward direction by removing the CO₂ product in situ, b) To achieve simultaneous CO₂ and H₂S capture at high temperatures to ppb levels, c) To produce a sequestration ready CO₂ stream, d) To reduce the excess steam requirement which aids in higher levels of H₂S removal, e) To reform and reuse all the C₁-C₄ hydrocarbons produced from the FT reaction to produce more liquid fuel than the conventional process, for the same amount of coal consumed.

Background and Literature Review

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A conventional coal to liquid plant consists of a gasifier which produces the syngas. The H₂/CO ratio of the syngas is around 0.63, which is much lower than the ratio of ~2, required for liquid fuel production. Hence, in order to modify the amount of hydrogen in the syngas, part of the syngas is introduced to a WGS reactor to be shifted into H₂. Since the gas stream contains sulfur impurities a sulfur tolerant WGS catalyst is used, which is expensive. The rest of the syngas stream passes through a hydrolysis unit where the COS is converted into H₂S.

The gas stream from the WGS reactor and the hydrolysis reactor are mixed together and passed through several gas cleanup units that consist of a mercury removal bed, bulk sulfur removal units, sulfur polishing unit, and CO₂ removal units. After the pollutants are removed, a clean syngas stream with a H₂ to CO ratio of around 2 is obtained which is sent to the F-T reactor for the production of liquid fuel. The F-T reactor is capable of converting more than 70% syngas into a wide range of hydrocarbons ranging from methane to wax. The products from the F-T reactor are sent to a product upgrader where the high molecular weight hydrocarbons are refined into liquid fuel or naphtha while the low molecular weight fuel gas stream is sent to a power generation block to generate electricity for the air separation unit and other parasitic energy consumption. In this process, expensive gas cleanup units for sulfur and CO₂ removal are needed and the parasitic energy consumption for cooling and reheating the gas stream is very large. This parasitic energy consumption requires the off gases to be burnt in a turbine which reduces the total liquid fuel yield from the coal.

In contrast if the calcium looping process is used in the production of liquid fuels, a H₂: CO ratio of the desired level can be obtained by converting the C1-C4 hydrocarbons and unconverted syngas produced from the FT reactor and the syngas from the gasifier in an efficient manner, while achieving CO₂ and H₂S removal in the same reactor system. Since contaminant removal is achieved at high temperatures the parasitic energy requirement is greatly reduced and also the issues related to procurement and deactivation of the sulfur tolerant catalyst for the WGSR are eliminated. As shown in Figure 19 the unreacted syngas and light hydrocarbons from the FT reactor are mixed with the syngas from the gasifier and sent into the single reactor system which adjusts the ratio of the H₂:CO in the syngas stream by reforming the hydrocarbons (eqn. 1)) and shifting the syngas (eqn. 2)) in the presence of
CaO. The concomitant carbonation of the metal oxide (CaO) leading to the formation of the metal carbonate (CaCO$_3$) incessantly drives the equilibrium-limited WGSR and the reforming reaction forward by removing the CO$_2$ product from the gas mixture (eqn. (3)). The metal carbonate can then be regenerated by heating, to give back the metal oxide and a pure CO$_2$ stream (eqn. (5)). By improving the equilibrium conversion of the reforming and WGS reaction, steam addition can be greatly reduced. The reduction in steam consumption not only reduces energy consumption but also aids in the removal of H$_2$S to ppb levels by the CaO (eqn. (4)) as steam poses an equilibrium constrain to the removal of H$_2$S. Various reactions occurring in this system are as follows

\[
\text{Reforming:} \quad \text{C}_x\text{H}_y + x\text{H}_2\text{O} \rightarrow x\text{CO} + (\frac{y}{2} + x)\text{H}_2 \quad (1)
\]
\[
\text{WGSR:} \quad \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad (2)
\]
\[
\text{Carbonation:} \quad \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (3)
\]
\[
\text{Sulfidation:} \quad \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \quad (4)
\]
\[
\text{Calcination:} \quad \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (5)
\]

There are three main scenarios for the integration of the calcium looping process in coal to liquid technology. In the first scenario, the mixture of gases from the FT reactor and the gasifier are mixed and sent into a single reactor which contains a mixture of reforming catalyst and CaO. Here the steam injection rate and the calcium injection rate will be optimized such that the C1-C4 compounds are reformed and the syngas is shifted to the required extent to obtain a H$_2$:CO ratio of 2. In the second scenario, the single reactor contains a mixture of pre-reforming catalyst and sorbent which convert the C2-C4 hydrocarbons into H$_2$ and CO$_2$ due to the high selectivity of the catalyst and the CO$_2$ is removed by the CaO. Since the pre-reforming catalyst is resistant to carbon deposition, low quantities of steam injection can be used, which is beneficial for H$_2$S removal. Also since the pre-reforming catalyst operates at lower temperatures of 500-600°C, which is the optimum temperature for carbonation and sulfidation, the amount of solid circulation is very low, making this scheme very attractive in all respects. Since methane is not reformed by the pre-reforming catalyst either a purge stream can be removed and used for power generation or a fixed bed of the reforming catalyst can be used downstream in the same reactor system. In the third scenario the reactor contains only calcium oxide sorbent which accelerates the reforming and the
WGSR in the non catalytic mode, while removing the CO₂ and H₂S impurities. This option is very attractive as it obviates the need for a catalyst which simplifies the operation of the reactor system and reduces the costs associated with the deactivation of the catalyst.

**CO₂ capture testing:** Mesoporous CaCO₃ and CaO sorbents, synthesized by a wet precipitation technique under the influence of negatively charged sodium polyacrylate ions, show a 70 wt% capture capacity for CO₂ in a TGA. Carbonation experiments with commercial CaO under entrained flow conditions show a 27-55 wt% CO₂ capture in 140-160 milliseconds residence time. Multiple CCR cycle experiments reveal that our CaO sorbent retains **36 wt%** CO₂ capture capacity even after 100 cycles which is higher than that achieved by all the other sorbents as shown in Figure 2. The details about the synthesis procedure of mesoporous PCC and reactivity testing towards CO₂ capture are outlined elsewhere (Agnihothri, R. et al (1999) Ind. Eng. Chem. Res. 38:2283 and Gupta, H. et al (2002) Ind. Eng. Chem. Res. 41:4035).

**Combined WGS and carbonation reaction and H₂S removal:** The combined carbonation, WGS reaction and sulfidation for enhanced H₂ production from syngas was conducted in an integral fixed bed reactor assembly described elsewhere.

Figure 22(a) illustrates the break through curves in H₂S composition for experiments conducted at ambient pressure and 15 atm. It can be seen that in the prebreakthrough region of the curve the calcium oxide sorbent undergoes sulfidation removing H₂S to levels of less than 1 ppm at ambient pressure. At a higher pressure of 15 atm, lower levels of H₂S in the ppb range were detected in the outlet stream. This clearly shows that when stoichiometric quantity of steam is used very high H₂S removal is achieved in the system. Figure 22(b) illustrates the break through curve for H₂ composition in the same experiment. A very distinct prebreakthrough region is observed in the curve which shows that the CaO is very effective in driving the water gas shift reaction in the forward direction. At ambient pressure, 70% H₂ purity is obtained while at 15 atm, 99.97% purity of H₂ is obtained. From this it can be understood that the high reactivity of the OSU patented calcium oxide results in rapid carbonation and high conversions(80%) of the sorbent which will greatly reduce the amount of solid loading in the system.
Three different cases of steam:CO (S/C) ratios without catalyst at ambient pressures. The data is as follows:

CASE 1: (Best case of H2S removal)
For S/C ratio of 0.75/1
Lowest H2S concentration achieved is 0 ppm (the analyzer cannot read in ppb).

H2 : CO ratio in the outlet stream = 1.3

CASE 2:
For S/C ratio of 1/1
Lowest H2S concentration achieved is 8 ppm
H2 : CO ratio in the outlet stream = 2.5

CASE 3: (Best case of H2 purity)
For S/C ratio of 3/1
Lowest H2S concentration achieved is 25 ppm
Percentage of H2 in the outlet stream: 95 %

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiment(s), but on the contrary, is intended to cover various modifications and equivalent arrangements within the scope of the invention.

References and prior art:


What is claimed is:

1. A process for producing hydrogen, comprising the steps of:
   gasifying a fuel into a raw synthesis gas comprising CO, hydrogen, steam, sulfur contaminants in the form of H₂S and COS, and halide contaminants in the form of HX, where X is a halide;
   injecting the raw synthesis gas, CaO and steam into a water gas shift reactor (WGSR), wherein the raw synthesis gas transforms into a shifted gas without a catalyst;
   allowing the shifted gas to react with the CaO in the WGSR so as to remove CO₂, sulfur and halides in a solid-phase calcium-containing product comprising CaCO₃, CaS and CaX₂;
   separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and
   regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

2. The process of claim 1 additionally comprising the step of:
   recycling at least a portion of a product stream from a Fischer-Tropsch reactor, fed by the WGSR, into the WGSR so as to introduce a chemical species selected from the group consisting of: methane, C₁ - C₄ hydrocarbons, CO, hydrogen and combinations thereof back into the WGSR.
3. The process of claim 1 or 2 wherein a carbon to steam stoichiometric ratio in the WGSR is about 1 to 3.

4. The process of claim 1, 2 or 3 wherein the raw synthesis gas, CaO and steam are injected simultaneously into the WGSR.

5. The process of any one of claims 1 to 4, wherein said enriched gaseous hydrogen product has a purity in the range of from about 70% to about 99.99% H₂, a temperature in the range of from about 400 to about 1000 °C, and a pressure in the range of from about 1 to about 100 atmosphere.

6. The process of any one of claims 1 to 4, wherein said enriched gaseous hydrogen product has a purity in the range of from about 90% to about 95% H₂, a temperature in the range of from about 400 to about 1000 °C, and a pressure in the range of from about 1 to about 40 atmosphere.

7. The process of any one of claims 1 to 6, wherein the WGSR is operated at a temperature in the range of from about 550 - 750 °C and in a pressure range of from about 1 to about 60 atmosphere.

8. The process of any one of claims 1 to 6, wherein the WGSR is operated at a temperature in the range of from about 600 - 700 °C and in a pressure range of from about 20 to about 30 atmosphere.

9. The process of any one of claims 1 to 8, wherein said CaO has a surface area of at least 12.0 m²/g and a pore volume of at least 0.015 cm³/g, said CaO having a sorption capacity of at least about 70 grams of CO₂ per kilogram of CaO.
10. A process for producing hydrogen, comprising the steps of:

at least partially oxidizing a fuel into a raw gas comprising CO, hydrogen, steam, sulfur contaminants in the form of H₂S and COS, and halide contaminants in the form of HX, where X is a halide;

injecting the raw gas, CaO and steam into a water gas shift reactor (WGSR), wherein the raw gas transforms into a shifted gas without a catalyst;

allowing the shifted gas to react with the CaO in the WGSR so as to remove CO₂, sulfur and halides in a solid-phase calcium-containing product comprising CaCO₃, CaS and CaX₂;

separating the solid-phase calcium-containing product from an enriched gaseous hydrogen product; and

regenerating the CaO by calcining the solid-phase calcium-containing product at a condition selected from the group consisting of: in the presence of steam, in the presence of CO₂, in the presence of synthesis gas, in the presence of H₂ and O₂, under partial vacuum, and combinations thereof.

11. The process of claim 10, wherein a carbon to steam stoichiometric ratio in the WGSR is about 1 to 3.

12. The process of claim 10 or 11, wherein the raw gas, CaO and steam are injected simultaneously into the WGSR.

13. The process of claim 10, 11 or 12, wherein said enriched gaseous hydrogen product has a purity in the range of from about 70% to about 99.99% H₂, a temperature in the range of from about 400 to about 1000 °C, and a pressure in the range of from about 1 to about 100 atmosphere.
14. The process of claim 10, 11 or 12, wherein said enriched gaseous hydrogen product has a purity in the range of from about 90% to about 95% H₂, a temperature in the range of from about 400 to about 1000 °C, and a pressure in the range of from about 1 to about 40 atmosphere.

15. The process of any one of claims 10 to 14, wherein the WGSR is operated at a temperature in the range of from about 550 - 750 °C and in a pressure range of from about 1 to about 60 atmosphere.

16. The process of any one of claims 10 to 14, wherein the WGSR is operated at a temperature in the range of from about 600 - 700 °C and in a pressure range of from about 20 to about 30 atmosphere.

17. The process of any one of claims 10 to 16, wherein said CaO has a surface area of at least 12.0 m²/g and a pore volume of at least 0.015 cm³/g, said CaO having a sorption capacity of at least about 70 grams of CO₂ per kilogram of CaO.
FIG-2 (PRIOR ART)
✓ Linwood Carbonate (LC)
✓ 50 cycles (30 min each cycle) at 700°C
✓ Carbonation in 10% CO₂ and Calcination in pure N₂
✓ Monotonic decrease in the Wt % capture
✓ 58% in 1st cycle to 20% in 50th cycle

FIG–5 (PRIOR ART)
✓ Precipitated Calcium Carbonate: MESOPOROUS
✓ 100 cycles (30 min each cycle) at 700°C in TGA
✓ Carbonation in 10% CO₂ and Calcination in pure N₂
✓ PCC stabilizes beyond 50th cycle
✓ 68%: 1st cycle —— 40%: 50th cycle —— 36%: 100th cycle

**FIG-6** (PRIOR ART)
**FIG-10(a)**

Equilibrium H$_2$S Conc (ppm) with 30 atm total pressure

\[ \text{CaO} + \text{H}_2\text{S} \leftrightarrow \text{CaS} + \text{H}_2\text{O} \]

**FIG-10(b)**

Equilibrium COS Conc (ppm) with 30 atm total pressure

\[ \text{CaO} + \text{COS} \leftrightarrow \text{CaS} + \text{CO}_2 \]
\[ \text{CaO} + 2\text{HCl} \leftrightarrow \text{CaCl}_2 + \text{H}_2\text{O} \]

**FIG-10(c)**

- In-situ removal of H$_2$S from fuel gas from coal gasifier
- Application
  - Hot gas clean-up in IGCC's
- Reaction temperature: 800°C
- $P_T = 1 \text{ MPa}, 3 \text{ kPa}$
- Strong effect of surface area on reactivity of CaCO$_3$ particles

\[ \text{CaO} + \text{H}_2\text{S} \leftrightarrow \text{CaS} + \text{H}_2\text{O} \]

**FIG-11**
FIG-12(a)

T=600°C, 10.3% CO, 31% H₂O, Total flow=0.725 slpm

FIG-12(b)

T=600°C, 10.3% CO, 31% H₂O, Total flow=0.725 slpm (N / Steam free)
T=650°C, 10.3% CO, 31% H₂O, 20 atm

FIG-15(a)

T=650°C, 10.3% CO, 31% H₂O, 20 atm

FIG-15(b)
FIG-19 (PRIOR ART)

FIG-20
$\text{H}_2\text{S}$ concentration (ppm)

$T=600^\circ\text{C}$, 10.3\% CO, Total flow=0.725 slpm ($\text{N}_2$/Steam free)

**FIG - 22(a)**

Time (sec)

$S/C$ ratio=1:1

$<1$ ppm

0 psig

300 psig

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$\text{H}_2$ Gas Composition (%)

$T=600^\circ\text{C}$, 10.3\% CO, Total flow=0.725 slpm ($\text{N}_2$/Steam free)

**FIG - 22(b)**

Time (sec)

$S/C$ ratio=1:1

0 psig

300 psig

High purity $\text{H}_2$
**FIG-26**

**FIG-27**
FIG-28

FIG-29
FIG-32

FIG-33

T=600°C, P=0 psig, 10.3% CO, Total flow=0.725 slpm (N₂/Steam free)
Estimated: 421 in 2003 to 772 quadrillion BTU in 2030

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