A Membrane Separation Unit (MSU) and an integrated gasification combined cycle (IGCC) process and apparatus are described in which a produced synthesis gas is separated in the MSU into a hydrogen rich permeate gas and a carbon monoxide rich retentate gas, and, combusting the hydrogen rich permeate gas with air in a gas turbine-combined cycle to produce electricity and a carbon dioxide lean exhaust gas suitable for atmospheric emission, and, combusting the carbon monoxide rich retentate gas with oxygen and re-circulated exhaust gas in a gas turbine-combined cycle to produce electricity and a carbon dioxide rich exhaust gas suitable for capture.

The title of the patent application is "INTEGRATED GASIFICATION COMBINED CYCLE SYNTHESIS GAS MEMBRANE PROCESS."
INTEGRATED GASIFICATION COMBINED CYCLE SYNTHESIS GAS MEMBRANE PROCESS

Cross Reference to Related Application

This is a nonprovisional application of U.S. Application No. 60/751,998 filed on December 21, 2005, which is incorporated herein by reference in its entirety.

General Field

It is well known that fossil (hydrocarbon) fuel can be converted into a gaseous mixture of predominantly CO and H₂ in varying ratios depending on the type of fossil fuel. The produced gas known as synthesis gas is also more commonly known by the term syngas. The conversion of fossil fuel to syngas is accomplished in a gasification process called partial oxidation / steam reformation. The process unit in which gasification occurs is called a steam reformer which is also known as an air gasifier. In the gasifier, fossil fuel, water and high purity O₂ are reacted in a partial oxidation reaction to produce syngas. It is well known in the field that the partial oxidation reaction in the gasifier is exothermic proceeding forward at a high temperature of about 1,400 °C and a high pressure of about 1,000 psig. Contaminants in some fossil fuels, such as mercury and sulfur, can be subsequently removed from the syngas before further use in either a chemical conversion process or a power conversion process. Elemental mercury is removed in an activated carbon adsorption bed, and sulfur containing acid gas such as H₂S, produced in the gasifier, is removed in an Acid Gas Removal (AGR) solvent absorption unit. It is well known in the field that mercury adsorption and H₂S absorption processes occur at a lower temperature in the range of 100 °F (38 °C) to 230 °F (110 °C), much lower than the temperature of the syngas exiting the gasifier. If CO₂ capture is required, current technology requires that the syngas be further processed with steam in a unit called a Water Gas Shift (WGS) reactor to form a shift gas. The resultant shift gas is predominantly H₂ and CO₂, plus additional H₂ from the water. The CO₂ can then be stripped with steam from the Shift Gas in a solvent absorption process unit yielding a high purity hydrogen stream and a high purity CO₂ stream. The clean hydrogen can be used as a fuel to be converted to electricity in a Combined Cycle (CC) power island consisting of a Gas Turbine (GT), a Heat Recovery Steam Generator (HRS) and a Steam Turbine (ST). The high purity CO₂ extracted in the solvent absorption steam stripper can be compressed and pumped to a geologic sequestration site. The combination of a gasifier and a CC power island
is called an Integrated Gasification Combined Cycle or IGCC, with or without WGS and solvent absorption units.

Background

The growing demand for electricity combined with the high costs of petroleum and natural gas and the environmental need for clean power conversion is driving the current interest in new power plant technology. A technology of primary interest is IGCC. The present IGCC power conversion plant technology with CO₂ capture and sequestration combines the following major components:

1. A gasifier and associated Air Separation Unit (ASU) to convert hydrocarbon fossil fuel into syngas (H₂ and CO) with an associated syngas cleaning and cooling unit
2. Adsorption and absorption units, respectively, to remove mercury and sulfur containing acid gas compounds from the syngas
3. A Water Gas Shift reactor to convert syngas (H₂ and CO) to shift gas (H₂ and CO₂)
4. A solvent absorption plant to remove CO₂ from the shift gas
5. Two H₂ gas combustion turbines each connected to an electric generator to generate electricity
6. A Heat Recovery Steam Generator (HRSG) that uses the high temperature gas turbine exhaust to make high pressure steam
7. A steam turbine connected to an electric generator that uses the high pressure steam from the HRSG to generate electricity

An IGCC power plant is able to convert low cost abundant fossil fuels, such as coal, into electricity more efficiently and more cleanly than existing Pulverized Coal (PC) power plants. Combined cycle power plants in general are more efficient than PC boiler plants, typically about 45% versus about 35%, respectively, before auxiliary or parasitic power deductions.

If CO₂ Capture and Sequestration (CCS) are not required, then an IGCC power plant will be more efficient without the WGS reactor and the CO₂ absorption removal plant (3 and 4 above). If CCS is required, components 3 and 4 will be included, thus increasing the auxiliary power demand in the IGCC power plant and reducing efficiency and net power output. The
WGS reactor and the CO$_2$ removal unit represent the largest power deduction in an IGCC power plant that includes CCS.

Another demand on efficiency in an IGCC with carbon dioxide capture with current technology is fugitive hydrogen loss associated with the stripping step in the solvent absorption process. Typically a physical absorption process is used in which carbon dioxide is absorbed in the solvent under pressure followed by stripping from the solvent by pressure reduction. It has been reported by others in the field that an unacceptable amount of the hydrogen is typically carried over with the carbon dioxide when it is stripped from the solvent by pressure reduction alone. Studies by others have found that adding steam stripping to the pressure reduction stripping minimizes the hydrogen loss to 3.3%. However even this level of loss plus the additional steam demand from the power cycle, creates a significant reduction in the overall efficiency of the IGCC power plant having a WGS reactor and a solvent absorption unit.

Others have considered replacing the WGS reactor and solvent absorption unit, with high temperature ceramic or palladium membranes for separating hot syngas or hot shift gas before cooling. However, it has been found that the short life cycle of these membranes due to excessive erosion and consequent loss of separation factor of these membrane materials when exposed to the extreme conditions of high temperature and pressure of syngas and shift gas makes this approach unfeasible.

There is a need to find a less complex and a more power and capital efficient method to capture CO$_2$ in an IGCC power plant with carbon capture and sequestration (CCS).

**Summary of the Invention**

Referring to FIG.1, the process according to the invention replaces the WGS reactor unit and solvent absorption plant with a perma-selective gas separation Membrane Separation Unit (MSU) having membranes made of polymeric materials such as polysulfone, polyimide, cellulose acetate and polycarbonate. The MSU separates the cleaned cooled syngas into a CO rich retentate stream at high pressure and a H$_2$ rich permeate stream at low pressure. The CO rich retentate stream is then pre-mixed in the combined cycle power island with high purity O$_2$ from the ASU and CO$_2$ rich exhaust from the HRSG and fired in a gas turbine. The outputs of the gas turbine are:
1. Mechanical energy which is used to produce electricity in a connected electric generator
2. High temperature exhaust which is used to produce high pressure steam in the HRSG
3. Captured carbon dioxide rich exhaust which is ready for compression and sequestration after being cooled in the HRSG.

A Membrane Separation Unit (MSU) is an equipped process skid that, in addition to membranes in one or two stages, may comprise piping headers, hand valves, control valves, particle filters, pre-coolers, pressure and temperature sensors, control instrumentation, and any other process device to control or enhance the efficient performance of the membranes.

It is well known in the field that membranes separate gases by differences in permeability. Intrinsic Permeability is the actual mixed gas permeability that exists in the operating membrane under conditions of temperature, pressure, and mixed gas composition in an MSU, and, in a two stage MSU, is relatively high for the less permeable gas in the gas mixture in an MSU stage compared to the permeability of the less permeable gas in another MSU stage. Selectivity is equal to the Intrinsic Permeability of the more permeable gas divided by the Intrinsic Permeability of the less permeable gas. Relatively high selectivity is calculated for the more permeable gas over the less permeable gas under the conditions of operation in an MSU stage, compared to the selectivity for the same selectivity ratio in another MSU stage.

Advantages of the syngas membrane and carbon monoxide rich gas turbine system are:
1. Syngas from the gasifier is already at high pressure thus obviating the need for a feed gas compressor in the MSU.
2. Syngas cooled to a sufficiently low temperature range of 100°F (38°C) to 230°F (110°C) to facilitate the removal of mercury and hydrogen sulfide, permits the use of commercially available polymeric membranes such as polysulfone, polyimide, and cellulose acetate have high separation factors for H₂ over CO and high permeability for H₂.
3. The CO rich retentate is dried to a low dew point in the MSU, which is a requirement of the captured CO₂.
4. The footprint, elevation profile and parasitic power consumption is less with the Syngas Membrane compared to a WGS reactor and a solvent absorption plant.
5. Lesser quantities of CO2 or H2 that may occur in the CO rich retentate are acceptable and do not pose a subsequent CO2 capture challenge.

6. No possibility of fugitive hydrogen losses as with the solvent absorption process since all the hydrogen produced going to the permeate and the retentate streams is combusted in each respective turbine.

7. Less capital than a WGS reactor / solvent absorption system

8. No steam is required as with solvent absorption which reduces power plant efficiency

9. No solvent replacement or disposal required as with solvent absorption

10. Reduces the oxygen requirement by about half compared to combusting all the syngas with oxygen in order to capture carbon dioxide.

The H2 / CO couple is a favorable gas separation for an economic MSU. Productivity and selectivity are high, which means capital and operating costs will be within acceptable economic limits.

Below is a comparison table of single gas permeability and selectivity values for several polymeric membranes that show favorable membrane permeation and selectivity characteristics for a H2 and CO gas mixtures separation:

<table>
<thead>
<tr>
<th>Membrane</th>
<th>P_H2</th>
<th>P_CO2</th>
<th>P_CO</th>
<th>P_N2</th>
<th>(\alpha_{H2/CO2})</th>
<th>(\alpha_{CO2/N2})</th>
<th>(\alpha_{H2/CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone</td>
<td>14</td>
<td>5.6</td>
<td>0.28</td>
<td>0.25</td>
<td>2.5</td>
<td>22.4</td>
<td>50.0</td>
</tr>
<tr>
<td>Polyimide</td>
<td>14</td>
<td>2.1</td>
<td>0.11</td>
<td>0.10</td>
<td>6.7</td>
<td>21.0</td>
<td>127.3</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>12</td>
<td>4.8</td>
<td>0.17</td>
<td>0.15</td>
<td>2.5</td>
<td>32.0</td>
<td>70.6</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>n/a</td>
<td>6.5</td>
<td>0.29</td>
<td>0.26</td>
<td>n/a</td>
<td>25.0</td>
<td>n/a</td>
</tr>
</tbody>
</table>

In the comparison table, P is permeability in barrer, one barrer = 10^{-10} (cm^3-cm)/(cm^2-sec-cm Hg), and \(\alpha_{ij} = P/Pj\) is the calculated selectivity. It is well known in the field that polymeric membranes operate at lower temperatures than ceramic and metallic membranes and have an upper operating temperature limit of 230 °F (110 °C) and preferably operate in the range of 100 °F (38 °C) to 122 °F (50 °C).
**Brief Description of the Drawings**

FIG. 1 compares the main process steps of an IGCC having a syngas membrane to the main process steps of an IGCC having a Water Gas Shift (WGS) and a solvent absorption, wherein it is illustrated that a syngas membrane replaces a WGS and an solvent absorption, and carbon dioxide is captured in the combined cycle of the former and the solvent absorption of the latter.

FIG. 2 illustrates a preferred embodiment of the invention comprising a single stage Membrane Separation Unit (MSU).

FIG. 3 illustrates a preferred embodiment of the invention comprising a two stage Membrane Separation Unit (MSU) wherein the first stage permeate is fed to the second stage and the second stage retentate is recycled to the first stage.

FIG. 4 illustrates a preferred embodiment of the invention comprising a two stage Membrane Separation Unit (MSU) wherein the first stage retentate is fed to the second stage and the second stage permeate is recycled to the first stage.

FIG. 5 illustrates a preferred embodiment of the invention comprising a single stage Membrane Separation Unit (MSU).

**Detailed Description of the Invention**

Referring to Fig.2, in a preferred embodiment of the invention using a single stage Membrane Separation Unit (MSU), a mixture of a fossil fuel (e.g., coal) and water in stream 1, and high purity $O_2$ in stream 4 produced in Air Separation Unit 3, are fed into Gasifier 2. In Gasifier 2 the coal, water and $O_2$ are converted into gas stream 8 from which mercury is removed in stream 6a, and sulfur (predominantly as H$_2$S) is removed in stream 6b. The gasifier has an associated syngas particulate-matter cleaning and after-cooling unit, which is not shown, since mercury and H$_2$S removal and the membrane separation occur at temperatures between 100°F (38 °C) and 230°F (110 °C), well below the gasification partial oxidation reaction temperature. The cleaned cooled Syngas, which is at a high pressure in stream 8, is fed to Membrane Separation Unit (MSU) 9. Residual solids in the fossil fuel are removed as slag in stream 7.
Membrane Separation Unit (MSU) 9, which uses polymeric membranes that are highly selective for H₂ over CO, yields a CO rich retentate at high pressure in stream 11 and a H₂ rich permeate at low pressure in stream 10. The CO rich retentate in stream 11 is combined in a gas turbine 12 with a mixture of high purity O₂ in stream 5 and a cooled CO₂ rich stream 13, which is cooled gas turbine Exhaust Gas Recirculation (EGR) from stream 19. Stream 19 from HRSG 18 is the net cooled CO₂ in exhaust stream 14 after EGR stream 13 is recirculated. The CO rich stream 11 is combusted in gas turbine 12 to produce mechanical energy to be converted to electricity in a connected electric generator, which is not shown. The high temperature exhaust in stream 14 is fed to HRSG 18 to make high pressure steam in stream 22. The net flow of cooled high purity CO₂ in stream 19 is sent to a compression and sequestration unit, which is not shown.

The H₂ rich stream 10 is combined in a gas turbine 15 with air in stream 16, and combusted in gas turbine 15 to produce mechanical energy to be converted to electricity in a connected electric generator, which is not shown. The high temperature exhaust in stream 17 is fed to HRSG 20 to make high pressure steam in stream 22. The total flow of cooled excess moist air and a small amount of un-captured CO₂ in stream 21 is sent to a vent stack, which is not shown.

High pressure steam in stream 22 is fed to steam turbine 23 to produce mechanical energy to be converted to electricity in a connected electric generator, which is not shown. Steam condensate in stream 24 is returned to HRSG 18 and 20 to make more steam.

Referring to Fig. 3, in another preferred embodiment of the invention using a two stage Membrane Separation Unit (MSU), the cleaned cooled syngas at high pressure in stream 8 is fed to the primary stage of Membrane Separation Unit (MSU) 9 comprising a membrane having a relatively high intrinsic permeability for the less permeable gas which yields a CO rich retentate at high pressure in stream 11 and an intermediate purity H₂ permeate at low pressure in stream 10a. Stream 10a is compressed in compressor 9a yielding the secondary stage Membrane Separation Unit (MSU) feed stream 10b at a higher pressure than the primary stage feed stream 8. The secondary stage of Membrane Separation Unit (MSU) 9 comprising a membrane having a selectivity for the more permeable gas which is relatively high compared the selectivity in the primary stage membrane, yields a lowered intermediate purity H₂ retentate at high pressure in stream 11a which is recycled to syngas feed stream 8,
and a H₂ rich permeate at low pressure in stream 10. All the remaining stream flow and
process unit designations in Fig. 3 are the same as those in the detailed description of Fig. 2.

Referring to Fig. 4, in another preferred embodiment of the invention using a two stage
Membrane Separation Unit (MSU), the cleaned cooled Syngas at high pressure in stream 8 is
fed to the primary stage of Membrane Separation Unit (MSU) 9 comprising a membrane
having a relatively high selectivity for the more permeable gas which yields a H₂ rich
permeate at low pressure in stream 10 and an intermediate purity CO retentate at high
pressure in stream 10a. Stream 10a is directed to the secondary stage Membrane Separation
Unit (MSU) yielding a CO rich retentate at high pressure in stream 11 and low pressure .
intermediate purity hydrogen permeate 11a, which permeate is compressed in compressor 9a,
the discharge of which is recycled to feed stream 8. AU the remaining stream flow and
process unit designations in Fig. 4 are the same as those in the detailed description of Fig. 2.

Referring to Fig. 5, which is a preferred embodiment having a single stage MSU, coal in
stream 1, high purity O₂ in stream 4, which is produced in an air separation unit (ASU) 3, and
water in stream 4 are reacted in a partial oxidation reaction in gasifier 2 to produce syngas in
stream 8 and vitreous slag in stream 7. The syngas in stream 8 exiting gasifier 2 is generally
at a temperature of about 1,400 °C and a pressure of about 1,000 psig and comprises about
52.0% CO, 35.0% H₂, 11.0% CO₂, 1.0% N₂, 0.6% H₂S, 0.4% Ar and a trace of Hg. The hot high pressure syngas in stream 8 exiting gasifier 2 is cleaned of particulate matter and cooled
in after-cooler 6 to a temperature of about 110° to 150° C. The cooled syngas in stream 8
exiting the after-cooler has Hg removed by an adsorption in stream 6a and H₂S removed by
absorption in stream 6b yielding a cooled, high pressure syngas stream 8 containing very low
amounts of Hg and H₂S just before the Membrane Separation Unit (MSU) 9.

The MSU 9 separates the cool high pressure syngas in stream 8 entering the MSU into a high
pressure retentate stream 11 comprising about 76.0% CO, 11% H₂, 10% CO₂, 2.0% N₂ and
1.0% Ar, and, a low pressure permeate stream 10 comprising 85.0% H₂, 3.0% CO, and
12.0% CO₂. The flow in retentate stream 11 equals about 40% of the MSU feed stream 8
flow and the permeate flow in stream 10 equals about 60% of the MSU feed stream 8 flow.

High pressure retentate stream 11 is expanded in expander 11a yielding a reduced pressure
retentate in stream 11b, which pressure is equal to the fuel pressure required in gas turbine
12. Expander 11a is mechanically connected to compressor 10a and supplies power to compressor 10a. Low pressure permeate in stream 10 is compressed in compressor 10a yielding an increased pressure permeate in stream 10b, which pressure is equal to the fuel pressure required in gas turbine 15.

Retentate stream 11b is combusted in gas turbine 12 with a combined stream of O₂ in stream 5 and exhaust re-circulation (EGR) in stream 13. Gas turbine 12 is mechanically connected to electric generator 12a which generates electricity. Hot exhaust stream 14 is cooled in heat recovery steam generator (HRSG) 18 which delivers high pressure steam in stream 22 to the inlet of steam turbine 23 and receives steam condensate in stream 24 from the outlet of steam turbine 23. Steam turbine 23 is mechanically connected to electric generator 23a which generates electricity.

Cooled exhaust in stream 19e comprising predominantly CO₂ plus un-combusted O₂ and small amounts of H₂O, N₂ and Ar is compressed to about 1,000 psig in compressor 19d yielding a compressed gas and liquid exhaust mixture in stream 19c. The gas phase in stream 19c comprises predominantly un-condensed CO₂ plus the non-condensable gases O₂, N₂ and Ar. The liquid phase in stream 19c comprises most of the CO₂ as a critical fluid with a small amount of dissolved water. The gas and liquid phases of compressed gas and liquid exhaust mixture 19c is separated in gas/liquid separator 19a. Separator head pressure due to non-condensable gas build-up is controlled by bleeding small amounts of non-condensable gas through bleed valve 19b. Uncondensed exhaust gas stream 13 comprising un-condensed CO₂ plus the non-condensable gases O₂, N₂ and Ar is reduced in pressure by pressure reduction valve 13a before being mixed with O₂ in stream 5 and re-circulated to gas turbine 12.

Compressed CO₂ liquid at about 1,000 psig in stream 19 is directed to sequestration or other uses.

Permeate stream 10b is combusted with air in stream 16 in gas turbine 15. Gas turbine 15 is mechanically connected to electric generator 15a which generates electricity. Hot exhaust stream 17 is cooled in heat recovery steam generator (HRSG) 20 which delivers high pressure steam in stream 22 to the inlet of steam turbine 23 and receives steam condensate in stream 24 from the outlet of steam turbine 23. Steam turbine 23 is mechanically connected to electric generator 23a which generates electricity. Cooled exhaust in stream 21, comprising mostly
N₂ with a lesser amount of un-combusted O₂ and small amounts of CO₂, H₂O and 1% Ar, is vented to the atmosphere.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.
Claims:

1. A membrane process comprising using one or more membrane stages in a membrane separation unit to separate a synthesis gas output produced from a fossil fuel gasifier, said synthesis gas comprising predominantly carbon monoxide and hydrogen, into a carbon monoxide rich retentate stream and a hydrogen rich permeate stream.

2. A membrane process as in claim 1 wherein a single stage membrane separation unit provides a carbon monoxide rich retentate and a hydrogen rich permeate.

3. A membrane process as in claim 1 using a two stage membrane separation unit, wherein a primary stage membrane provides carbon monoxide rich retentate and intermediate purity hydrogen permeate which is recompressed and directed as feed to the secondary stage membrane which provides pressurized retentate recycled to the primary stage membrane feed and a hydrogen rich permeate.

4. A membrane process as in claim 1 using a two stage membrane separation unit, wherein the primary membrane stage comprises a membrane having a relatively high Intrinsic Permeability and the secondary membrane stage comprises a membrane having a relatively high selectivity.

5. A membrane process as in claim 1 wherein the membrane separation unit comprise one or more polysulfone, polyimide, cellulose acetate or polycarbonate polymeric membranes.

6. A process as in claim 1 wherein the carbon monoxide rich retentate stream is mixed with high purity oxygen and re-circulated carbon dioxide rich exhaust and provided to a gas combustion turbine to produce therefrom mechanical energy, heat, and a carbon dioxide rich exhaust.

7. A process as in claim 6 wherein the hydrogen rich permeate stream is mixed with air and provided to a gas combustion turbine to produce mechanical energy and heat.
8. A process as in claim 6 wherein the carbon dioxide rich exhaust from a gas combustion turbine is converted to a dense fluid and pumped to a place for sequestration from the atmosphere.

9. A process as in claim 7 wherein the gas turbines are connected to electric generators, which convert mechanical energy into electricity.

10. A process as in claim 7 wherein the heat from the gas turbines is used to generate high pressure steam, which steam is then provided to a steam turbine connected to an electric generator to generate electricity.

11. A membrane process as in claim 1 using a two stage membrane separation unit, wherein a primary stage membrane provides a hydrogen rich permeate and an intermediate purity carbon monoxide retentate which is directed as feed to the secondary stage membrane which provides carbon monoxide rich retentate and an intermediate purity hydrogen permeate which is recompressed and recycled to the primary stage membrane feed.

12. A membrane process as in claim 1 wherein a gas processing temperature range is sufficiently low to permit the use of a Membrane Separation Unit comprising polymeric membranes.
FIG. 1
FIG. 2
FIG. 4