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Combustion-assisted CO_2 capture using MECC membranes

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ABSTRACT

Mixed Electron and Carbonate ion Conductor (MECC) membranes have been proposed as a means to separate CO_2 from power plant flue gas. Here a modified MECC CO_2 capture process is analyzed that supplements retentate pressurization and permeate evacuation as a means to create a CO_2 driving force with a process assisted by the catalytic combustion of syngas on the permeate side of the membrane. The combustion reactions consume transported oxygen, making it unavailable for the backwards transport reaction. With this change, the MECC capture system becomes exothermic, and steam for electricity production may be generated from the waste heat. Greater than 90% of the CO_2 in the flue gas may be captured, and a compressed CO_2 product stream is produced. A fossil-fueled power plant using this process would consume 12% more fuel per unit electricity produced than a power plant with no CO_2 capture system, and has the potential to meet U.S. DOE's goal that deployment of a CO_2 capture system at a fossil-fueled power plant should not increase the cost of electricity from the combined facility by more than 30%.

1. Introduction

Mixed Electron and Carbonate ion Conductor (MECC) membranes [1] have been proposed as a means to perform post-combustion CO_2 capture [2] from fossil-fueled power plant flue gas. A MECC membrane is composed of a porous metal support infiltrated with a carbonate salt mixture (i.e., lithium carbonate (Li_2CO_3), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3)). The metal support is conductive to the flow of electrons, and the carbonate salt, when molten, is conductive to the flow of carbonate ions. The transport of carbon dioxide (CO_2) across the membrane requires oxygen (O_2) at the retentate side and the transport driving force depends on the difference in CO_2 and O_2 partial pressures across the membrane. Fig. 1 shows a schematic of an MECC cell and the half-cell reactions that occur on each side of the membrane.

Because the pores of the metal support structure are filled with molten carbonate, membranes of this type tend to have high $CO_2 + O_2$ selectivity and very low permeability to substances that are not soluble in the carbonate. High CO_2 selectivity, in addition to high permeance, has been identified as a prerequisite for a successful membrane-based CO_2 separation system [3].

According to Chung et al. [1], CO_2 permeance is determined by the following expression.

$$F_{CO_2} = \frac{9RT}{16F^2L}\sigma_{ion}\ln\left(\frac{P'_t}{P''_t}\right)\frac{\varepsilon}{\tau}\left[\frac{1}{P'_t - P''_t}\right] \quad (1)$$

In Eq. (1), F_{CO_2} is the CO_2 permeance, R is the ideal gas constant, T is the temperature in K, F is Faraday's constant, L is the thickness of the membrane, σ_{ion} is the membrane ionic conductance, P'_t and P''_t are the $CO_2 + O_2$ total pressure on the retentante and permeate sides of the membrane, ε is the porosity of the membrane, and τ is the membrane tortuosity. The electrical conductance of the membrane, signified by σ_{elec} is usually much greater than the ionic conductance, σ_{ion}, under normal operating conditions, and therefore F_{CO_2} is not assumed to be a function of σ_{elec} in Eq. (1). Permeance increases when the ionic conductance of CO_2 across the membrane increases, the pressure difference of $CO_2 + O_2$ across the membrane increases, when the membrane porosity increases, and when the membrane tortuosity decreases. In this case, membrane porosity and tortuosity refer to the characteristics of the metal support structure since the molten carbonate component is liquid at operating temperature.

The permeance of MECC membranes at atmospheric pressure and over a range of temperatures has been measured. Fig. 2 shows a plot of permeance data from Chung et al. [1] and permeance values that were calculated from CO_2–O_2 flux data (ml/min cm^2) from

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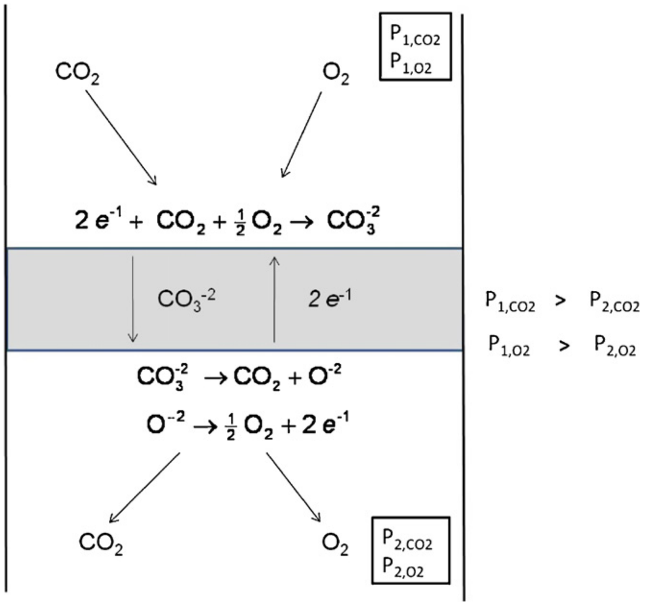

Fig. 1. MECC membrane CO_2 transport half-cell reactions.

Xu et al. [4] for sintered stainless steel membranes having the same thickness ($L = 1.57$ mm), porosity ($\varepsilon = 0.25$), tortuosity ($\tau = 5.94$), and prepared using similar Li, Na, and K carbonate mixtures. In [1], a pressure driving force of 1 atm across the membrane was created by drawing a vacuum on the permeate side of the membrane, while in [4], a helium sweep gas at 1 atm was used to remove the permeate and create a partial pressure driving force of 1 atm across the membrane. In [1], a Li/Na/K carbonate mixture was used to prepare the membrane, while in [4], two membranes were tested, one membrane infiltrated with a Li/Na carbonate salt, and another membrane infiltrated with a Li/K carbonate salt.

In Fig. 2, the permeance measurements from [1] rise to a maximum of 250×10^{-10} mol/s m^2 Pa at 650 °C and then falls at higher temperatures. In [4], the measured permeance varies with temperature, and with the type of salt used to prepare the membrane. When a Li/Na carbonate salt was used to prepare the membrane, the permeance increased monotonically with temperature, and was lower in value at all temperatures than that measured in [1]. When a Li/K carbonate salt was used to prepare the membrane, the permeance behaved in a similar manner as measured in [1], reaching a maximum value of about 270×10^{-10} mol/s m^2 Pa at 650 °C. In [1], the drop in membrane performance above 650 °C was attributed to the reaction of Li in the molten carbonate with Fe in the metal membrane support, leading to the formation of $LiFeO_2$. $LiFeO_2$ is electrically non-conductive, and formation of this substance in the membrane would increase the electrical resistance of the membrane and decrease membrane permeance. Under these circumstances, σ_{elec} becomes an important factor in limiting CO_2 transport, and Eq. (1) must be changed to include σ_{elec}.

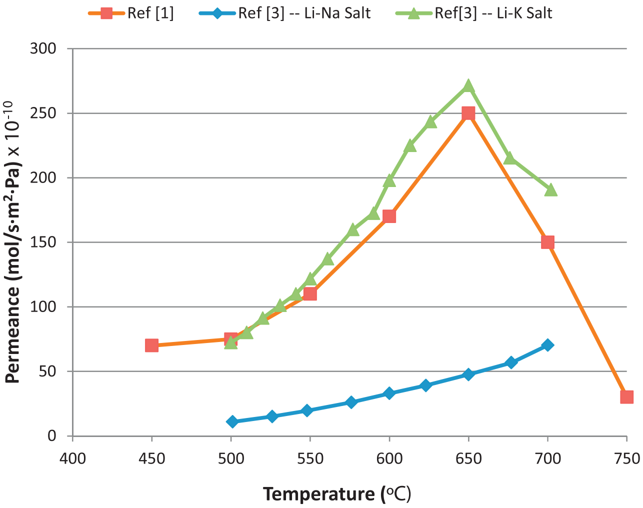

Fig. 2. MECC membrane permeance versus temperature.

MECC membranes are similar in construction to carbonate-ceramic dual-phase membranes as described by Anderson and Lin [5], except that the metal support structure found in MECC membranes is replaced by a mixed conducting oxide ceramic. Replacement of the support structure by a mixed oxide conducting ceramic allows CO_2 to permeate the membrane even when oxygen is absent in the retentate, but at a lower rate than when oxygen is available in the retentate [6].

For MECC-based membranes, stoichiometric amounts of O_2 must be present in the flue gas to facilitate CO_2 transport, and additional air or O_2 may need to be mixed with the flue gas to remove the desired amount of CO_2. A partial pressure difference must be established across the membrane, which usually requires deployment of energy-intensive gas compression on the retentate side of the membrane, and gas evacuation on the permeate side of the membrane. The permeate is a mixture of CO_2 and O_2, and further gas separation steps are needed to produce a pure CO_2 stream. Since the MECC membranes operate at higher temperatures ($T > 450$ °C), there are also safety concerns in handling high-temperature oxygen-enriched permeates.

A modified MECC process may be designed to mitigate some of these concerns. A reactive gas such as syngas (mixture of hydrogen (H_2) and carbon monoxide (CO)) or H_2 may be used as a sweep gas on the permeate side of the membrane. The sweep gas, aided by a combustion catalyst, reacts with O_2 in the permeate to make CO_2 and water vapor (H_2O), which reduces the O_2 partial pressure in the permeate. Additional CO_2 is produced by the combustion of CO, but the CO_2 produced by combustion of CO is on the “correct” side of the membrane to achieve capture. The heat released by the combustion reactions may be used to maintain membrane temperature, preheat feed streams, and to make steam for additional electricity production.

In this work, the mole balances of several combustion-assisted MECC CO_2 capture processes are compared in order to determine whether natural gas or coal are suitable feed stocks. The implications of selecting syngas or H_2 as the reactive gas are explored. Then, a detailed process flow sheet, along with its mass and energy balances, is developed that uses a syngas sweep stream produced from methane. Process energy costs are determined from the detailed process flow sheet and compared to a base case power plant with no CO_2 capture. Some information on the cost of the membranes is also determined.

2. Process mole balances

Syngas, which is a mixture of CO and H_2, or H_2 produced from syngas, are initially proposed as reactive gas inputs for a combustion-assisted MECC CO_2 capture process. Nearly all syngas streams produced industrially [7] are made from the steam reforming of coal (51%), petroleum (26%), or natural gas (21%), and about 95% of H_2 produced industrially in the United States is purified from syngas produced from natural gas [8]. The selection of the reactive gas (syngas or H_2) and the reactive gas feedstock (coal, petroleum, natural gas) affects operational costs and the amount of CO_2 generated by the CO_2 capture process. To minimize operational costs, the feedstock must be inexpensive, and the syngas H_2:CO ratio must

Table 1
Case descriptions.

	Case #1	Case #2	Case #3	Case #4
Feed type	Methane	Methane	Coal	Coal
Feed formula $C_xH_yO_z$, (x,y,z)	(1,4,0)	(1,4,0)	(1,0.7,0.1)	(1,0.7,0.1)
Water-gas shift unit deployed?	No	Yes	No	Yes
Reformer thermal efficiency	70%	70%	70%	70%
Molar conversion of feedstock in the reformer	100%	100%	100%	100%
Water-gas shift molar conversion	–	75%	–	75%
H_2 purification efficiency	–	89%	–	89%
Moles CO_2 captured per mole feed	2.1	1.4	0.45	~0.3

be maximized to reduce the amount of CO_2 generated by the CO_2 capture process itself.

Four cases are considered that span the range of potential feedstock and reactive gas types. The feedstock types and assumptions for each case are shown in Table 1.

In Case #1, methane (CH_4), is used as a feedstock, and syngas is used as the reactive gas in the MECC CO_2 capture module, as shown in Fig. 3.

In the figure, CH_4 and water (H_2O) are fed to a steam–methane reformer, where it is catalytically transformed into syngas having a 3:1 H_2:CO ratio [9]. The steam–methane reformer is heated using a methane-fired furnace. The reformer exhaust is mixed with the power plant flue gas so that CO_2 in the reformer exhaust may be captured. Full conversion of CH_4 into syngas results in the creation of 3 mol H_2 and 1 mol CO for every mole of CH_4 feed. According to the process mole balance, up to 3.4 mol of CO_2 in the power plant flue gas may be captured for every 1.6 mol of CH_4 consumed by the CO_2 capture process, or about 2.1 mol CO_2 in the power plant flue gas for every mole of CH_4 consumed.

In Case #2, the syngas stream produced by the steam–methane reformer is further transformed by the water-gas shift reaction [10] to make H_2. The water-gas shifted syngas stream is then purified, and pure H_2 is used as the reactive gas in the MECC CO_2 capture module, and the impure gas stream from the H_2 purification unit containing CO, H_2, and CO_2 is recycled back to the steam reformer furnace to be burned. A diagram of Case #2 is shown in Fig. 4. According to the process mole balance, about 2.4 mol of CO_2 from the power plant flue gas are captured for every 1.4 mol of CH_4 consumed, or about 1.7 mol of CO_2 are captured from the power plant flue gas for every mole of CH_4 consumed.

In Case #3, coal is substituted for methane in Case #1. If it is assumed that coal is represented by the hypothetical compound $CH_{0.7}O_{0.1}$, which corresponds to the approximate molar composition of bituminous coal minus moisture and other impurities [11], then only about 1.0 mol of CO_2 from power plant flue gas may be captured for every 2.2 mol of coal consumed by the steam reformer (1.0 mol coal for the steam reforming reaction, 1.2 mol coal for the reformer furnace), or about 0.45 mol of CO_2 captured for every mole of coal consumed by the reformer.

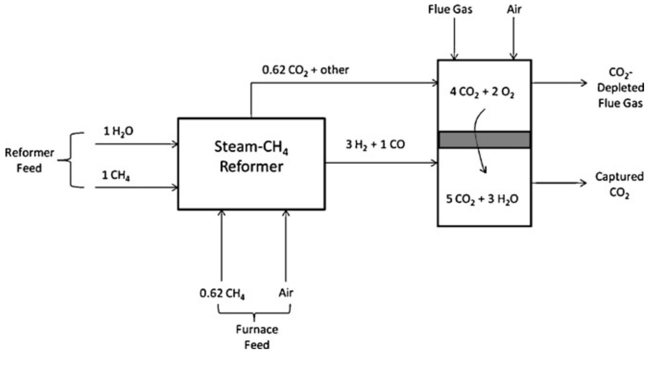

Fig. 3. Simple schematic of syngas combustion-assisted CO_2 capture system.

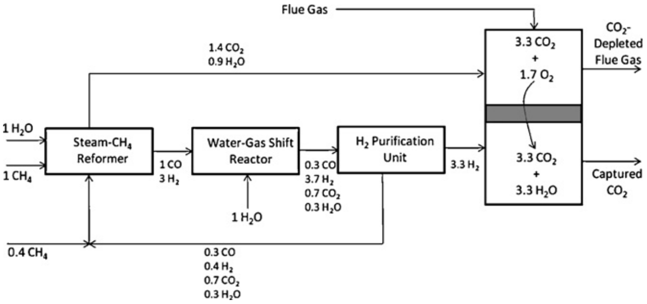

Fig. 4. Block flow diagram of Case #2.

Case #4 is similar to Case #3 except that the syngas stream produced by the steam reforming of coal is further converted into a pure hydrogen stream using a water-gas shift unit, and the results are even worse. Only about 0.3 mol of CO_2 may be captured for every mole of coal consumed.

Among the cases considered, using CH_4 as a process feedstock and syngas having a 3:1 H_2:CO ratio as the reactive gas appears to be the most desirable option. Up to 2.1 mol of CO_2 in power plant flue gas may be captured for every mole of CH_4 consumed, which is higher than the other cases. The use of a purified H_2 stream produced from methane might be considered as a back-up option, however, if the increased feedstock costs might be offset by potential operational advantages associated with combusting only H_2 in the MECC CO_2 capture units (e.g., lower CO_2 partial pressure in the permeate). Using coal as a feedstock for this process is not at all feasible because the CO_2 capture plant would consume more fuel and generate more CO_2 than the original power plant.

3. Detailed process modeling

Even in the best case, the feedstock requirements for the CO_2 capture process are high. For a natural gas-powered electrical plant of fixed size, for example, the amount of natural gas needed to operate the CO_2 capture process on a molar basis would increase the amount of fuel supplied to the combined facility by about 52%, with the additional amount of natural gas used to make syngas to drive the CO_2 capture process. That is, for every mole of methane burned at the electrical power plant, about 0.52 mol of methane are needed to drive the CO_2 capture process if 100% of the CO_2 generated by the overall plant is to be captured. Alternatively, if the natural gas feed molar rate were fixed, then the amount of power generated by the power plant would have to be reduced by 32% because a portion of the natural gas provided to the power plant complex would need to be diverted to the steam–methane reformer to make syngas instead of burning it to make steam for electricity production. At these feedstock consumption rates, the parasitic load of the CO_2 capture plant exceeds the 20% target established by the U.S. DOE for CO_2 capture processes [11,12], and the process would not be acceptable.

The utility of the proposed CO_2 capture system may be greatly improved, however, if the CO_2 capture system also serves as a supplemental power plant. The combustion of syngas in the MECC CO_2 capture units releases copious quantities of heat, and the heat may be used to make steam for electricity production. In this manner, some of the thermal value of methane fed to the CO_2 capture plant may be recovered as electrical power, and the fuel penalty associated with operating the CO_2 capture plant may be lessened.

Calculating how much supplemental power the CO_2 capture plant might generate requires a more detailed process model than previously discussed. Mass and energy balances are needed, and integration of thermal flows will be required to determine how much energy is needed to operate the CO_2 capture process, and how much excess thermal energy is available for steam production. In building a process model, physical and chemical constraints must also be recognized, so that the modeled conditions are not overly optimistic compared to what might be possible in an actual process.

3.1. Process assumptions and constraints

3.1.1. Process chemistry

The following chemical compositions, conditions, and constraints are used in the detailed process model.

- A simplified list of chemical species is used – Ar, O_2, CH_4, CO, CO_2, H_2, H_2O, and N_2.
- The power plant flue gas is assumed to contain [13]: 13% CO_2, 16% H_2O, 3% O_2, and 68% N_2; and is delivered to the CO_2 capture plant at 150 °C at 1 atm.
- The CO_2 capture plant uses CH_4 as a power source and a syngas feedstock, regardless of the fuel used to generate electricity in the electrical power plant (coal, oil, or natural gas).
- The following chemical reactions are assumed. Eqs. (1)–(3) are the H_2, CO, and CH_4 combustion reactions. Eq. (4) is the steam reforming reaction of methane. All are assumed to go to completion.

$$O_2 + 2H_2 \rightarrow 2H_2O \tag{2}$$

$$O_2 + 2CO \rightarrow 2CO_2 \tag{3}$$

$$O_2 + CH_4 \rightarrow CO_2 + 2H_2O \tag{4}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{5}$$

- Heated air is used as an O_2 source for the MECC CO_2 capture units, and is mixed at a flow rate sufficient to facilitate 100% transport of CO_2 in the power plant flue gas and the steam reformer furnace exhaust.
- Combustion of H_2 and CO in the MECC CO_2 capture modules is catalyzed, and requires at least 2 mol% excess O_2 to proceed.
- The steam–methane reformer is assumed to operate at ~20.5 atm and 850 °C [14,15].

3.1.2. Physical constraints and requirements

The following physical constraints and requirements are assumed:

- The membranes are assumed to be 100% selective for CO_2 and O_2, and are impermeable to N_2 and other gases.
- The CO_2 capture process is sized to remove 90% of the CO_2 in the combined flue gas stream (i.e., power plant flue gas + reformer furnace exhaust gas + make-up air). 100% removal is not performed because a CO_2 + O_2 partial pressure driving force must be maintained across the separation membranes in order to achieve separation.
- The fuel requirements and power output of the electrical power plant are fixed, and the CO_2 capture plant is assumed to be an add-on to an existing facility. Therefore, the CO_2 capture plant requires a dedicated fuel feed stream separate from the power plant fuel feed stream.
- The entry temperature of gases into the MECC membrane units is 500 °C on both sides of the membrane to facilitate effective CO_2 transport, and the maximum allowable exit temperature of gases from the MECC membrane units is 700 °C to avoid changes in the chemical and physical properties of the membranes [1]. Although membrane degradation in [1,4] occurred above 650 °C, it is assumed for this analysis that good membrane performance could be extended to 700 °C (or beyond) without large changes to membrane materials and construction.
- There is 10% loss of thermal energy to the environment from the steam methane reformer. All other thermal energy is available for driving the steam reforming reaction (Eq. (4)) and for preheating feed streams.
- The MECC CO_2 capture units are well insulated and operate adiabatically.
- Thermal energy released by the CO and H_2 combustion reactions is shared between the retentate and permeate streams in the MECC CO_2 capture units, but the permeate exit temperature is assumed to be 10 °C warmer than the retentate exit temperature due to heat transfer limitations.
- Excess heat not used to preheat unit feed streams is used to make high-pressure superheated steam (~20.5 atm, 426 °C) or lower pressure superheated steam (~5 atm, 155 °C) for electrical power production.
- No pressure drop through the MECC CO_2 capture units is assumed, and the cells are assumed to operate at atmospheric pressure on both sides of the MECC membrane.
- The high-pressure and lower-pressure steam turbines have a 0.8 isentropic efficiency and an exit pressure of 1 atm.
- All process compressors have an isentropic efficiency of 0.8 and a thermal efficiency of 1.0.
- All process pumps have a volumetric efficiency of 0.8 and a mechanical efficiency of 1.0.

3.2. Process simulation

Process flow sheets were developed using the process simulator ProSimPlus version 3.1.2.1.2. Initially, the basic process steps were established in the simulator, and then the feed and product streams were linked by heat exchangers, as needed, to preheat unit feed streams. The flow sheet configuration was then adjusted to ensure that the MECC CO_2 capture modules did not overheat as a result of the CO and H_2 combustion reactions. Simplified block flow diagrams of the process sections were drawn using SmartSketch 2007 version 05.02.03.09 Service Pack 3 by Intergraph Corporation.

4. Results and discussion

A high-level block flow diagram of the CO_2 capture process is shown in Fig. 5.

In the diagram, the significant process sections are the Fossil-Fueled Power Plant; the Steam–CH_4 Reformer; CO_2 Capture Modules #1 and #2; CO_2 Capture Modules #3, #4, and #5; CO_2-Depleted Flue Gas Post-Processing; and Captured CO_2 Post-Processing. The individual unit operations are grouped into process sections according to function and thermal flows. The process sections are described below.

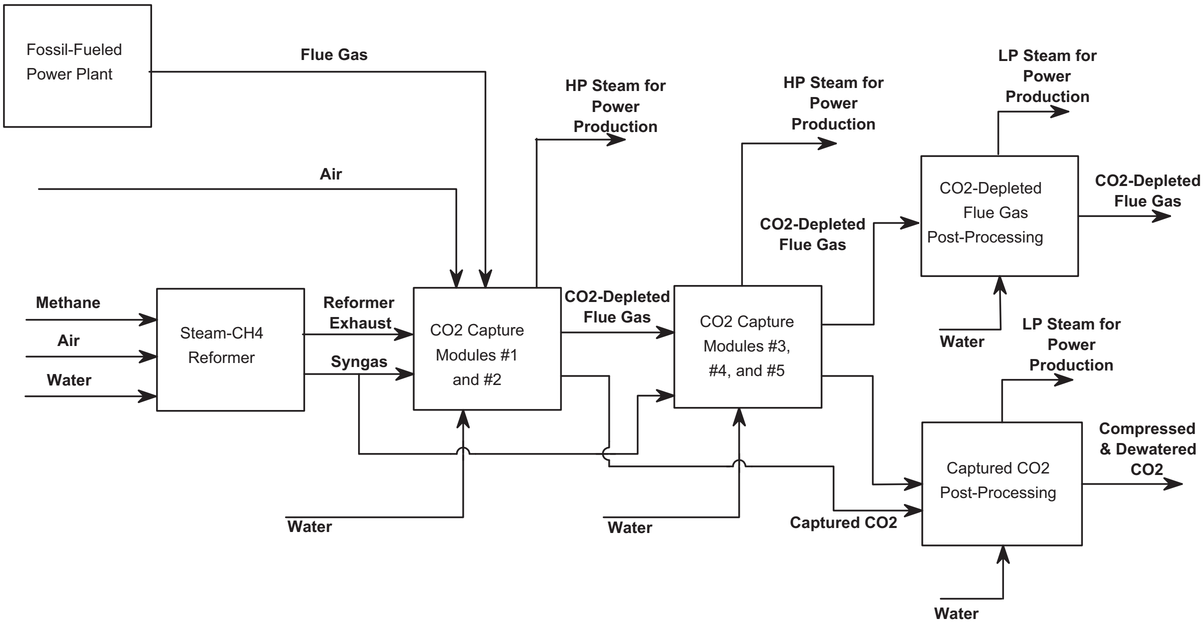

Fig. 5. Block flow diagram of proposed combined power plant/CO_2 capture facility.

4.1. Steam–CH_4 reformer process section

The Steam–CH_4 Reformer process section consists of a direct-fired steam–CH_4 reformer unit and heat exchangers that are used to recuperate heat from the furnace exhaust and syngas product streams. Fig. 6 shows a detailed block flow diagram of the Steam–CH_4 Reformer process section.

The heat exchangers are arranged to preheat reformer feed streams to the greatest extent possible, and to cool the syngas and furnace exhaust streams to 500 °C, the entry temperature of the MECC CO_2 capture units. Heat exchangers HX-1 and HX-2 cool syngas from 825 °C to 304 °C, preheat CH_4 for the reformer furnace from 25 °C to 300 °C, and preheat water at 25 °C and 20.4 atm to make superheated steam at 400 °C and 20.4 atm. Heat exchanger HX-3 cools the reformer furnace exhaust from 950 °C to 500 °C and preheats the furnace air stream from 25 °C to 607 °C. The preheated reformer furnace air stream warms the syngas stream to 500 °C in heat exchanger HX-4, while the preheated air stream is cooled from 607 °C to 363 °C before it enters into the Steam–CH_4 Reformer furnace. Compressor C-1 and pump P-1 pressurize the reformer CH_4 and water streams to 20.4 atm, and expander E-1 reduces the syngas pressure from 20.4 atm to 1 atm while recovering some of the mechanical energy to make electricity. The mechanical action of compressor C-1 preheats the CH_4 reformer stream from 25 °C to 404 °C.

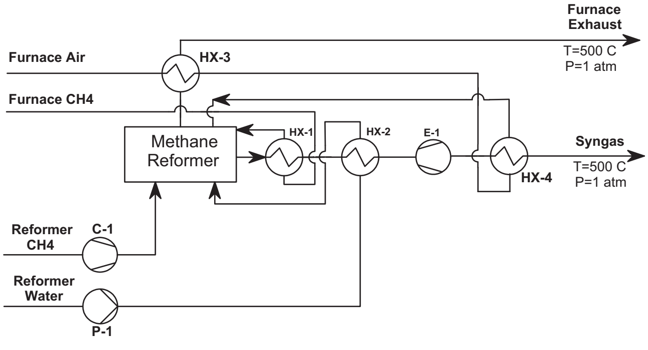

Fig. 6. Detailed block flow diagram of "Steam–CH_4 Reformer" process section.

A stream table for the Steam–CH_4 Reformer Section is shown in Table 2.In the simulation, the steam and methane feed rates is set at 90 mol/h, while the feed rate of methane to the steam reformer furnace is adjusted to 54 mol/h to ensure that enough combustion heat is available to drive the steam reforming reactions and to preheat the reformer feed streams. 10% excess air is supplied to the furnace to achieve efficient CH_4 combustion.

4.2. MECC CO_2 capture modules

For the simulation, the CO_2 capture process is divided into five stages with intercooling between each stage. The first four stages capture 80% of the CO_2 available in the combined power plant flue gas stream, while the last stage captures 10% of the available CO_2. The intercoolers remove the heat of combustion between each stage. More stages with smaller capture fractions could be deployed, but capturing more than 20% of the CO_2 inventory in each stage was found to cause overheating of the membranes in the process simulation. Heat removed between each stage, and at the end of the last stage, is used to preheat unit feed streams and to make steam for electricity generation. The first and second CO_2 capture stages are grouped in the process section "CO_2 Capture Modules #1 and #2." The third, fourth, and fifth CO_2 capture stages are grouped in the process section "CO_2 Capture Modules #3, #4, and #5." Syngas from the steam reformer section is divided into five parallel streams, and each sub-stream is sent to a CO_2 capture module (i.e., Syngas Stream #1 to Module #1, Syngas Stream #2 to Module #2, etc.). The flow rate of syngas to each module is not evenly divided, and 2/9 of the total syngas stream is each provided to Module #1 through #4, and 1/9 of the total syngas flow is provided to Module #5. The flue gas stream is maintained as a single stream, and it flows through each MECC CO_2 capture module in serial fashion (i.e., first Module #1, then Module #2, etc.). This flow arrangement was chosen to maximize the CO_2 driving force in each membrane module while minimizing the volumetric flow rate on the CO_2 capture side of the membranes.

Other flow configurations are possible. Serial flow of both the flue gas stream and the syngas stream was analyzed, but serial flow of the flue gas stream and parallel flow of the syngas stream allowed for a smaller membrane surface area. Initially, parallel distribution

Table 2
Partial stream table, reformer section.

	Steam–CH_4 reformer, reforming section		Steam–CH_4 reformer, furnace section		Output, syngas (mol/h)	Output, furnace exhaust (mol/h)
	Input, CH_4 stream (mol/h)	Input, H_2O stream (mol/h)	Input, CH_4 stream (mol/h)	Input, air (mol/h)		
Ar				6		6
O_2				132		12
CH_4	100		60			
CO					100	
CO_2	2		1	0.2	2	61
H_2					300	
H_2O		100		11		131
N_2	2		1	486	2	487

of flue gas and syngas was also pursued, but was abandoned in this analysis due to complications in managing membrane temperatures. In the dual parallel flow arrangement, the flue gas stream and the syngas stream are divided, and each CO_2 capture module operates as an independent unit. Each module therefore had to achieve 90% CO_2 capture on its own in order for the combined system to reach the CO_2 capture target. While this arrangement would minimize membrane surface area, it does not solve the problem of managing membrane temperature, and the membranes would quickly overheat without some means of cooling. In the serial flow arrangements, intercoolers are used to remove the heat of combustion, but in a completely parallel arrangement, some other means of cooling the membrane modules would be needed. For example, a pumped fluid such as water or steam could be used to cool the membrane modules. A more complex membrane module must then be constructed that contains flow paths for flue gas, syngas, a cooling fluid, and this could increase module capital costs if membrane costs are not the dominate contributor to the cost of the CO_2 capture modules. Certainly more work is needed on analyzing these alternative flow arrangements before heavy investment is made into any single flow arrangement.

A partial stream table of the CO_2 capture stages is shown in Table 3. In the table, input retentate and permeate streams and output streams are listed. The retentate input Flue Gas stream is the power plant flue gas stream that is provided to the CO_2 capture process. The retentate input Make-up Air stream is the flow of air that is mixed with the flue gas in order to oxygenate it. The permeate input Syngas Feed is the flow of syngas provided individually to each of the five MECC CO_2 capture modules in the flow sheet. The permeate output Captured CO_2 shows the flow rate of captured CO_2 from each MECC CO_2 capture module. The retentate output Flue Gas streams show the flow rates of the constituents in the depleted flue gas after emerging from each MECC CO_2 capture module in series, and the final state of the CO_2-depleted flue gas is shown in the rightmost column.

4.2.1. CO_2 capture Modules #1 and #2

The detailed configuration of this process section is shown in Fig. 7. In this section, power plant flue gas, reformer furnace exhaust, and make-up air are blended in mixer MIX-1 to make a combined stream containing CO_2 and O_2. The heat exchangers HX-5, HX-6, HX-7, and HX-9 are used to set the input temperature of the retentate and permeate streams to approximately 500 °C for each module, and to preheat the flue gas and make-up air streams using heat captured from hot exit streams. After preheating the flue gas and make-up air streams to 500 °C, some excess heat is available, and this excess heat is used to make high-pressure superheated steam using a steam generator, HX-8. A pump P-2 provides water at 25 °C to the steam generator, and a blower C-2 provides make-up air for the capture process.

Pure syngas enters the capture process as the permeate in MECC #1 and MECC #2, and it becomes diluted with captured CO_2 and water vapor as the capture process progresses. In this flow arrangement, the combustion process is syngas-limited, and the extent of combustion is limited by the supply of syngas to the membrane surfaces.

4.2.2. CO_2 capture Modules #3, #4, and #5

The detailed configuration of this process section is shown in Fig. 8. In this section, three CO_2 capture modules are used to capture the rest of the CO_2 in the retentate stream. Since all of the process streams have already been preheated at this point in the process, the excess heat from the combustion process is used to make steam for electricity generation. Steam generators HX-10 through HX-15 are used to boil water to make superheated steam for power production. The exit temperature of the retentate stream (“CO_2-Depleted Flue Gas”) and the permeate stream (“Captured CO_2”) from this process section is 500 °C, and the streams must be further cooled downstream to facilitate safer handling.

4.3. CO_2-depleted flue gas post-processing

This process section is labeled in Fig. 5 as “CO_2-depleted flue gas post-processing.” The CO_2-depleted flue gas stream was cooled from 500 °C to 106 °C before being released from the process. The heat recovered from the CO_2-depleted flue gas stream is used to generate low-pressure steam at 155 °C and 5 atm using a steam generator. The low-pressure steam then drives an electrical turbine to generate electricity.

4.4. Captured CO_2 post-processing

This process section is labeled in Fig. 5 as “captured CO_2 post-processing.” The captured CO_2 stream is first cooled from 500 °C to 77 °C in order to condense water vapor from the captured CO_2. Liquid water is then separated from CO_2 using a gas–liquid separator. The purified CO_2 stream is compressed to approximately 100 atm using a multi-stage compressor, making it suitable for sequestration, transportation, or other uses. The compression step heats the CO_2 stream to about 220 °C, but no recovery of heat from this stream is assumed.

The CO_2 stream produced by this process still contains small amounts of O_2, H_2, CO, N_2, and H_2O, and may require further purification, depending upon its use.

4.5. Electrical power production

Electricity may be generated from a number of sources in the process. High-pressure steam (426 °C, 20.4 atm) is generated from excess heat generated in the CO_2 capture Modules #2, #3, #4, and #5, and this may be used to drive electrical turbines. Low-pressure steam (155 °C, 5 atm) is generated from the heat removed from the hot CO_2-depleted flue gas and captured CO_2 streams, and this may

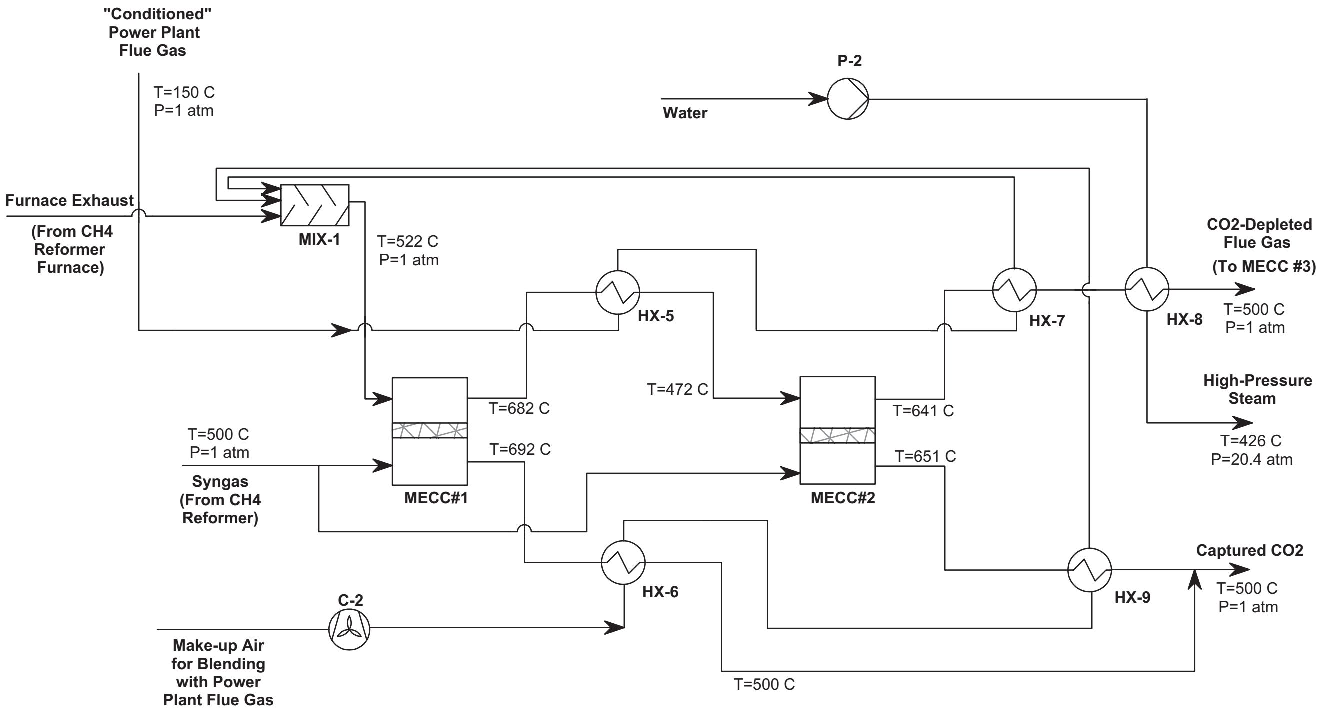

Fig. 7. Detailed block flow diagram of "CO_2 Capture Modules #1 and #2" process section.

be used to drive a lower-pressure electrical turbine, albeit with less efficiency than a high-pressure turbine.

There are also significant electrical power sinks in the process that cannot be neglected when considering the electrical power production capacity of the CO_2 capture process. These draws include the compressor used to pressurize the CH_4 flow to the Steam–CH_4 Reformer, the compressor used to generate a compressed CO_2 product stream, and the liquid water pumps used to supply water to the reformer and the process steam generators.

A summary of the electrical power generators and electrical power sinks in the CO_2 capture process is shown in Table 4.

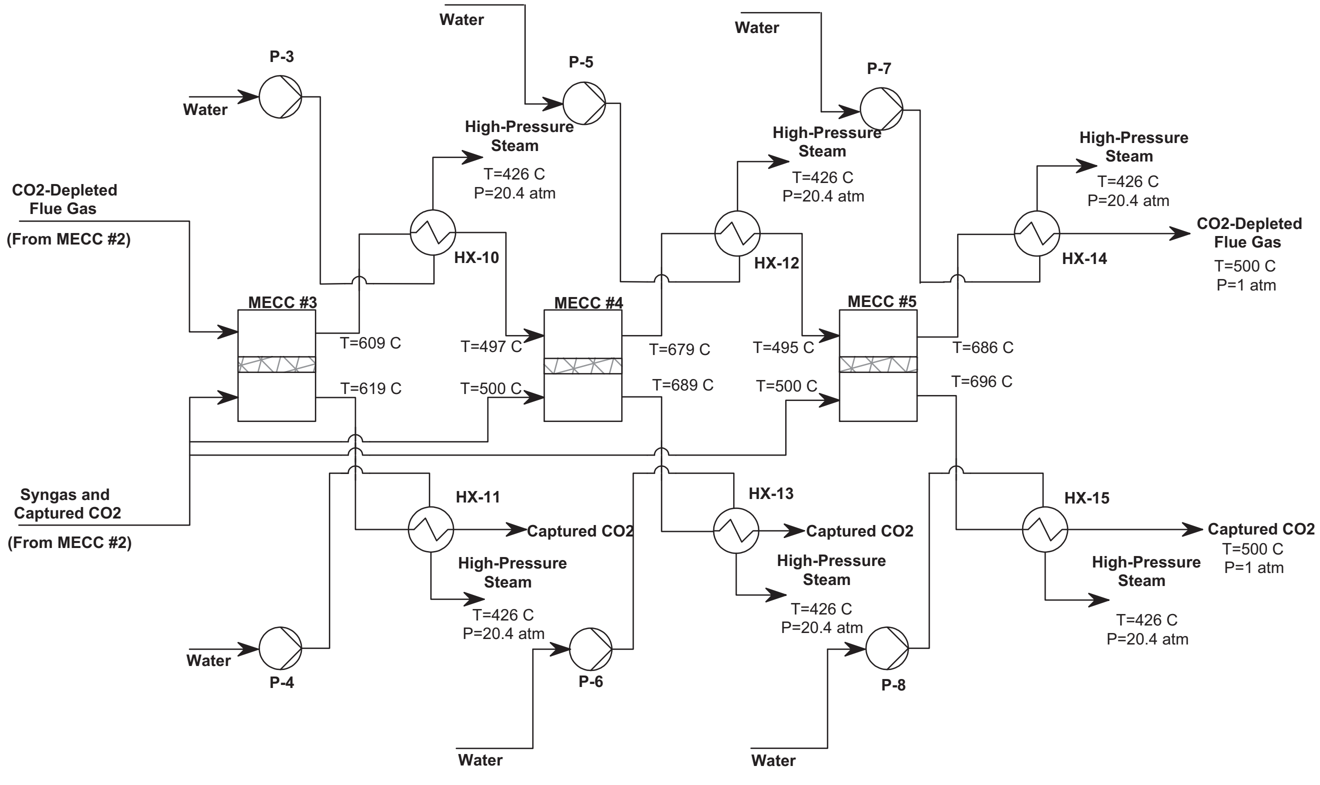

Fig. 8. Detailed block flow diagram of "CO_2 Capture Modules #3, #4, and #5" process section.

Table 3
Partial stream table, CO_2 capture section.

	Retentate input (total)	Retentate input (total)	Retentate input (total)	Permeate input (each) to Modules 1, 2, 3, and 4 (for Module 5, multiply by 0.5)	Permeate output (each) from Modules 1, 2, 3, and 4 (for Module 5, multiply by 0.5)	Retantate output (from MECC Module #1)	Retentate output (from MECC Module #2)	Retentate output (from MECC Module #3)	Retentate output (from MECC Module #4)	Retentate output (from MECC Module #5)
	Flue gas (mol/h)	Furnace exhaust (mol/h)	Make-up air (mol/h)	Syngas feed (mol/h)	Captured CO_2 (mol/h)	Flue gas (mol/h)	Flue gas (mol/h)	Flue gas (mol/h)	Flue gas (mol/h)	Flue gas (mol/h)
Ar		5	5			10	10	10	10	10
O_2	79	11	116		2	165	123	82	41	21
CH_4										
CO				20	0.4					
CO_2	342	55	0.2	0.3	101	318	238	159	80	40
H_2				60	1.2					
H_2O	427	118	10		59	555	586	586	586	586
N_2	1827	438	433	0.3	0.3	2699	2747	2747	2747	2747

Table 4
Significant electrical sources and loads.

Description	Sources (W)	Sinks (W)
H.P. steam, CO_2 Module #2	825	
H.P. steam, CO_2 Module #3	690	
H.P. steam, CO_2 Module #4	1044	
H.P. steam, CO_2 Module #5	1154	
L.P. steam, CO_2-depleted flue gas	890	
L.P. steam, captured CO_2	245	
Syngas expander, reformer	875	
CH_4 compressor, reformer		−388
CO_2 compressor, post-processing		−2726
Liquid water pumps		−25
Sub-totals	5723	−3139

Net power generation = +2584 W.

According to the table, the CO_2 capture process is capable of generating approximately 2400 W, given the material flow rates shown in Tables 1 and 2. No electrical power is generated from the heat removed from CO_2 Module #1 because the excess heat is used to preheat syngas and make-up air streams. Likewise, some excess heat from CO_2 Modules #2 and #3 are used to preheat syngas and make-up air streams, and less heat is available to make steam for power production. For CO_2 Modules #4 and #5, the full amount of excess heat is available to make steam for electricity production, and so the power output for these modules is greater than is obtained from the first three. The other electrical power outputs are produced by extracting heat and mechanical energy from other flow streams.

The ability of the CO_2 capture process to become a net generator of electricity reduces the parasitic energy load of the CO_2 capture plant. If it is further assumed that the electrical power plant burns CH_4 to make steam for electricity production; that the steam produced at the power plant is at the same temperature and pressure as the steam produced in the CO_2 capture plant (426 °C, 20.4 atm); that the electrical turbines in the power plant have the same efficiency as those used in the CO_2 capture plant; and that the CO_2 capture process, as described above, is sized to capture 100% of the CO_2 produced by the electrical power plant, then the power output of the electrical power plant is 9700 W, which results from the combustion of approximately 340 mol/h CH_4. Therefore, the combined power output of the electrical power plant and the CO_2 capture process is 9700 W + 2402 W = 12,102 W.

There is an energy cost associated with operating the CO_2 capture process, however. The CO_2 capture plant consumes 144 mol/h CH_4 in order to perform its purpose. The CH_4 used to drive the CO_2 capture process could instead have been used to make electricity in the power plant at greater efficiency. If the fuel feed rate to the electrical power plant were simply increased by this amount to 484 mol/h, then an additional 4108 W could be generated, giving a total potential power output of 13,808 W. The difference between what might have been produced by a larger electrical power plant (13,808 W) and what is produced by the combined power plant/CO_2 capture facility (12,102 W) is the energy penalty associated with operating the CO_2 capture process. In this case, the energy penalty is about 1706 W, which is an energy loss of about 12%. Presented another way, the CO_2 capture process consumes 1706 W to capture 306 mol/h CO_2 from the electrical power plant, which is equivalent to an energy penalty of 0.41 GJ/metric ton CO_2 captured.

This energy penalty is less than the U.S. DOE upper limit of 20% for parasitic energy losses [13] for CO_2 capture processes and is comparable to energy penalties calculated for other advanced post-combustion CO_2 capture processes. Merkel et al. [16] examined polymeric membrane-based CO_2 capture processes, and developed a process flow sheet for a two-step countercurrent sweep membrane process having a 16% energy penalty. Lively et al. [17]

examined a number of proposed post-combustion CO_2 capture processes, and found that the energy penalty (parasitic load) for best-case amine-based absorption systems varied between 26 and 41%, and the energy penalty for chilled ammonia processes varied between 1 and 24%, with the smallest energy penalties associated with full thermal integration of the CO_2 capture plant with the electrical power plant.

4.6. Costs

In addition to the 20% upper limit for parasitic energy losses, the U.S. DOE has also established a cost target – operation of a CO_2 capture facility should not increase the cost of electricity from a combined power plant/CO_2 capture facility by more than 30%, as compared to a power plant where no CO_2 capture is performed [3,10].

Evaluation of this criterion for the proposed process is more difficult and will require a great deal more research and development (R&D) before it can be fully addressed. The MECC membranes on which this concept is based are not yet commercially available, and a reliable cost per unit membrane area cannot yet be assigned. Also, the design of the MECC module hardware has not yet been developed.

Some order-of-magnitude calculations can be performed at this stage, however, that will provide some information on the material cost of the membranes. Although the detailed temperature and $CO_2 + O_2$ partial pressure profiles within the membrane modules are unknown at this stage of development, some average membrane conditions can be calculated for each module, thus allowing for a determination of required membrane surface area. Assuming that the membrane modules operate between 500 and 700 °C, the membrane permeance may be calculating by taking the temperature-weighted average of the permeance data shown in Fig. 2 from Ref. [1]. The average partial pressure of CO_2 and O_2 in the retentate of each membrane module may be approximated by taking the arithmetical average of the CO_2 and O_2 partial pressures at the inlet and outlet of each membrane module. If it is then assumed that the CO_2 and O_2 partial pressures are zero on the permeate side of the membrane due to the action of the syngas sweep gas, then the sum of the CO_2 and O_2 partial pressures becomes the partial pressure driving force for transport across the membrane. The required membrane surface area within each module is then determined by dividing the total molar capture rate of CO_2 and O_2 (mol/h) in each module by the molar flux rate (mol/h m^2). The molar flux rate is calculated by multiplying the temperature weighted average permeance (150 mol/s m^2 Pa) times the partial pressure driving force. Table 4 shows membrane surface areas for each module that were calculated using the above algorithm.

According to Table 5, the total membrane surface area required is 1442 m^2. Assuming the structural component of the membrane is composed of porous stainless steel having a thickness of 1.58 mm and a porosity of 0.25, then the mass of stainless steel required for this surface area is $1442\ \text{m}^2 \times 0.00158\ \text{m} \times 0.75 \times 8000\ \text{kg/m}^3 = 13{,}670\ \text{kg}$. Then, if stainless steel costs $4/kg, then the cost of metal for the membranes is approximately $54,680.

The membranes will not last for the lifetime of the plant, and the membranes are expected to be replaced at defined time intervals. For the purposes of this calculation, it is assumed that the membrane designs are mature and durable, and will survive at least 20,000 h in-service before needing replacement. If the power plant has a capacity factor of 0.9, then the CO_2 capture plant will operate 90% of the time, and the membranes will accumulate approximately 8000 h of service per year. Over the lifetime of the membranes, the membrane modules will collect about 266 tons CO_2 from the power plant flue gas, according to the process flow sheet described above. At this capture rate, the membrane material costs alone are $54,680/266 tons CO_2, or $210/ton CO_2.

The next question to answer is to determine whether this cost is tolerable, or whether it is too high to have any hope of attaining the U.S. DOE goal of not increasing the cost of electricity by 35% or more above the baseline. In the simulated plant, a 35% increase in the cost of electricity translates to an allowance of up to about $42/ton CO_2 captured, so the total yearly cost of operating the CO_2 capture plant must be less than $35/ton CO_2 captured in order to be viable. The cost of the membrane materials alone greatly exceeds this limit, and the process will not achieve its cost target.

The membrane costs could be brought within the cost limit if the membrane permeance were increased. Calculations performed in Ref. [1] indicate that the theoretical membrane permeance increases monotonically with increasing temperature, and that a permeance of 800×10^{-10} mol/s m^2 Pa or greater could be achieved at a membrane operating temperature of 700 °C for the same membrane thickness and porosity. If the membrane permeance were increased to 800×10^{-10} mol/s m^2 Pa, then the membrane material costs would be reduced by a factor of 5 to about $38/ton CO_2. More work is needed, however, to understand the chemistry of the membranes at higher temperatures, so that membrane performance is not degraded above 650 °C. High membrane permeance may only be achieved if the membranes remain stable, and the membrane constituents do not react with each other to make non-conducting by-products. A potential new direction in fashioning such membranes may be to replace the metal support structure with a ceramic material, as is described in Rui et al. [6], so that the support structure does not react with the carbonate salt at high temperature. If, in the short term, such advanced membrane types prove to be difficult to make on a large scale or are too expensive, then the maximum operating temperature of the membranes may need to be lowered to 650 °C instead of 700 °C, and greater membrane surface area and additional intercooling steps may be required to operate the process. Both changes would result in higher system costs.

More likely, multiple factors will need to be adjusted in the membrane design in order to reduce the membrane cost to tolerable levels. Improvements might be made in understanding membrane chemistry, which may allow actual membrane performance to approach the theoretical performance. A cheaper or less dense support material might be used. Thinner membranes might be used, which would also reduce membrane material costs. Using

Table 5
Calculated membrane surface areas.

Module #	$CO_2 + O_2$ capture rate (mol/h)	Membrane permeance (mol/s m^2 Pa)	Average $CO_2 + O_2$ driving force (Pa)	Membrane surface area (m^2)
1	120.7	150×10^{-10}	14,400	155
2	120.7	150×10^{-10}	11,600	193
3	120.7	150×10^{-10}	8540	262
4	120.7	150×10^{-10}	5290	423
5	60.3	150×10^{-10}	2730	409
Total membrane surface area (m^2)				1442

a thinner membrane would likely increase membrane permeance, and this would have a multiplying effect on membrane cost reduction. The actual membrane lifetime in service is unknown, and it is possible that the membranes could survive 40,000 h, for example, instead of the arbitrary 20,000 h that was used in the membrane cost calculations, and this would reduce membrane costs by a factor of 2. The partial pressure driving force across the membranes might also be increased in order to decrease membrane area, but this would require adding a compressor to the flue gas stream, and the energy cost associated with this change would be excessive.

5. Conclusions

The proposed combustion-assisted CO_2 capture process, at the conceptual level, appears capable of meeting at least two of the U.S. DOE's requirements for CO_2 capture processes. With recovery of excess process heat for electricity generation, the proposed process has an energy penalty of about 12%, which is less than DOE's expectation that any successful CO_2 capture process should have a parasitic energy load no greater than 20%. Also, the process is likely capable of capturing at least 90% of the CO_2 generated by the electrical power plant.

DOE's last criterion, that the cost of electricity from the combined power plant/CO_2 capture facility not be increased by more than 35%, will require a great deal more work before it can be fully addressed. The initial cost of the stainless steel for the membranes is calculated to be about \$210/ton CO_2 captured, which greatly exceeds the U.S. DOE cost target. More laboratory and development work is needed to improve membrane performance and reduce membrane costs before the membranes will be ready for deployment in commercial CO_2 capture applications.

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