Report Title:

A Novel Membrane Reactor for Direct Hydrogen Production from Coal

Type of Report: Quarterly Report

Reporting Period Start Date: 4/1/2005

Reporting Period End Date: 6/30/2005

Principal Authors:
Shain Doong, Estela Ong, Mike Atroshenko, Francis Lau, Mike Roberts

Date Report Issued: July 29, 2005

DOE Award Number: DE-FC26-03NT41851

Submitting Organization:
Gas Technology Institute
1700 South Mount Prospect Road
Des Plaines, IL 60018

DISCLAIMER

ABSTRACT

Gas Technology Institute is developing a novel concept of membrane reactor coupled with a gasifier for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal-derived synthesis gases. The objective of this project is to determine the technical and economic feasibility of this concept by screening, testing and identifying potential candidate membranes under high temperature, high pressure, and harsh environments of the coal gasification conditions. The best performing membranes will be selected for preliminary reactor design and cost estimates.

Hydrogen permeation data for several perovskite membranes BCN ($BaCe_{0.9}Nd_{0.1}O_{3-x}$), SCE ($SrCe_{0.9}Eu_{0.1}O_3$) and SCTm ($SrCe_{0.95}Tm_{0.05}O_3$) have been successfully obtained for temperatures between 800 and 950^oC and pressures from 1 to 12 bar in this project. However, it is known that the cerate-based perovskite materials can react with CO_2. Therefore, the stability issue of the proton conducting perovskite materials under CO_2 or H_2S environments was examined. Tests were conducted in the Thermo Gravimetric Analyzer (TGA) unit for powder and disk forms of BCN and SCE. Perovskite materials doped with zirconium (Zr) are known to be resistant to CO_2. The results from the evaluation of the chemical stability for the Zr doped perovskite membranes are presented.

During this reporting period, flowsheet simulation was also performed to calculate material and energy balance based on several hydrogen production processes from coal using high temperature membrane reactor (1000^oC), low temperature membrane reactor (250^oC), or conventional technologies. The results show that the coal to hydrogen process employing both the high temperature and the low temperature membrane reactors can increase the hydrogen production efficiency (cold gas efficiency) by more than 50% compared to the conventional process. Using either high temperature or low temperature membrane reactor process also results in an increase of the cold gas efficiencies as well as the thermal efficiencies of the overall process.

TABLE OF CONTENTS

Abstract

LIST OF GRAPHICAL MATERIALS

INTRODUCTION

The objective of this project is to develop a novel membrane reactor for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. This concept has the potential of significantly increasing the thermal efficiency of producing hydrogen, simplifying the processing steps and reducing the cost of hydrogen production from coal. The specific objective of the project is to determine the technical and economic feasibility of using the membrane reactor to produce hydrogen from coal. GTI and our project team (Arizona State University, University of Florida and American Electric Power (AEP)) have identified potential membranes (ceramic and metal) suitable for high temperature, high pressure, and harsh coal gas environments. The best performing membranes will be selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with other hydrogen production technologies from coal.

To evaluate the performances of the candidate membranes under the gasification conditions, a high temperature/high pressure hydrogen permeation unit has been constructed. The unit was designed to operate at temperatures up to 1100^{o}C and pressures to 60 atm for evaluation of ceramic membranes such as mixed ionic conducting membrane. Hydrogen permeation data for several perovskite membranes BCN ($BaCe_{0.9}Nd_{0.1}O_{3-x}$), SCE ($SrCe_{0.9}Eu_{0.1}O_3$) and SCTm ($SrCe_{0.95}Tm_{0.05}O_3$) have been successfully obtained for temperatures between 800 and 950^{o}C and pressures from 1 to 12 bar in this project.

A particularly notable issue with the proton conducting perovskites is their tendency to react with CO_2 or H_2S in the syngas under the high temperature and pressure conditions of coal gasification. During this reporting period, Thermo Gravimetric Analyzer (TGA) unit was used to study the reactions of perovskite powders and membrane disks with CO_2 or H_2S. Literature survey shows that the Zr doped perovskite materials have improved stability for CO_2. Samples of Zr doped barium cerate perovskite were acquired and evaluated in the TGA unit.

The feasibility of configuring a membrane module within a gasifier was investigated in the previous quarter. The preliminary conceptual design considered a 1000 TPD coal gasifier using the fluidization bed technology and tubular membrane module. The performance of the membrane reactor was calculated using the modeling approach with the experimental hydrogen flux data. In this quarter, several hydrogen from coal gasification processes with and without the membrane reactors were developed and evaluated by flowsheet simulation. The advantages of using the membrane reactors in the hydrogen from coal gasification processes are demonstrated in terms of the hydrogen cold gas efficiency and the thermal efficiency.

EXECUTIVE SUMMARY

During this reporting period, the stability issue of the proton conducting perovskite materials under CO_2 or H_2S environments was examined. The tests were conducted in the Thermo Gravimetric Analyzer (TGA) unit for powder and disk forms of BCN. The tests were conducted at 950C and 10 atm with 10% CO_2 in He. When the perovskite material encountered CO_2, the weight of the sample increased due to the formation of carbonate compounds. As expected, the BCN disk has better chemical stability than the BCN powder. The powder form of BCN reacted with CO_2 very quickly and reached complete conversion equilibrium in a few minutes. On the other hand, the disk form of BCN reacted with CO_2 much slower. Only about 15% of BCN was converted in about 2 hours.

Both the powder and the disk forms of BCN were also tested in TGA in a H_2S environment. The tests were conducted at 950C and 10 atm with 0.1% H_2S in H_2. The disk form of BCN reacted with H_2S much slower than the powder form, similar to the reaction with CO_2.

Literature survey shows that the Zr doped perovskite materials have improved stability for CO_2. Therefore, the Zr and Yb doped barium cerate perovskite powder, $BaCe_{0.5}Zr_{0.4}Yb_{0.1}O_{3-x}$ (BCZY), was fabricated into dense membrane disks and tested in the TGA unit for the chemical stability in a CO_2 or H_2S environment. It was confirmed that the Zr doped perovskite or BCZY has better stability with respect to CO_2 or H_2S than BCN or SCE.

Flowsheet simulation was also performed to calculate material and energy balance based on several hydrogen production processes from coal using high temperature membrane reactor (1000^{o}C), low temperature membrane reactor (250^{o}C), or conventional technologies. The commercial HYSYS process simulator was used for the task. The results show that the coal to hydrogen process employing both the high temperature and the low temperature membrane reactors can increase the hydrogen production efficiency (cold gas efficiency) by more than 50% compared to the conventional process. Using either high temperature or low temperature membrane reactor process also results in an increase of the cold gas efficiencies as well as the thermal efficiencies of the overall process.

EXPERIMENTAL

Thermo Gravimetric Analyzer (TGA) Unit

A schematic diagram of the high-pressure/high-temperature TGA unit used in this project is presented in Figure 1. This state-of-the-art TGA unit is capable of operation at 1850°F and 70 bar. All the hot wetted parts of the unit are made of quartz to eliminate reaction with corrosive and reactive gases, which would result in the loss of the reactant species in the gas phase.

The TGA unit is capable of continuously weighing a sample that is undergoing reaction in a gaseous environment of desired composition at constant pressure. The temperature can be kept constant or varied at a desired rate. In a typical TGA test, about 20 mg of membrane powders or disks is placed inside a wire mesh basket, which is then lowered to the heated zone of the reactor tube. The desired temperature and pressure conditions are then established in the lower, heated section of the reactor in the presence of flowing inert gas. The reactant gas mixtures with the desired composition are also prepared and initially bypassed to the reactor. When the reactor temperature and pressure have reached the desired values, the test is initiated by switching from the inert gas to the reactant gas mixture. The sample weight is continually monitored and recorded as the solid sample reacts with the gas. The test is terminated when the sample weight reaches a constant value (no weight loss or gain).

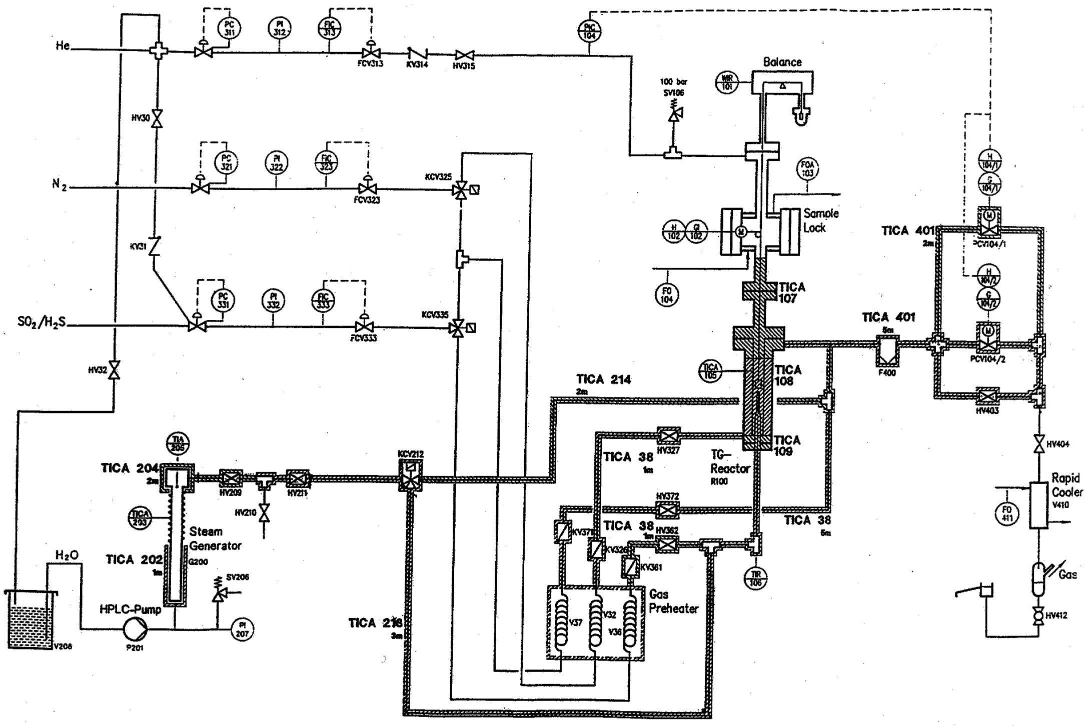

Figure 1. High-pressure/high-temperature Thermo Gravimetric Analyzer

RESULTS AND DISCUSSION

Reaction of Perovskite with CO_2

The BCN powders were in the size range of 250 to 400 micron. The disk form of BCN was of irregular shape of 2-3 mm in dimensions and about 0.5 mm in thickness. The tests were conducted at 950C and 10 atm with 10% CO_2 in He. When the perovskite material encountered CO_2, the weight of the sample increased due to the formation of carbonate compounds. The TGA results are shown in Figure 2 in terms of moles of CO_2 per mole of BCN sample versus time. As can be seen, the powder form of BCN reacted with CO_2 very quickly and reached complete conversion equilibrium. On the other hand, the disk form of BCN reacted with CO_2 much slower. Only about 15% of BCN was converted in about 2 hours. The slow reaction of the membrane form of the perovskite material with CO_2 could be due to the smaller areas available to the CO_2 molecules in the membrane than in the powder. It is also possible that the sintered membrane disk has stronger structure than the powder.

The formation of barium carbonate was confirmed by the XRD analysis for the reacted samples.

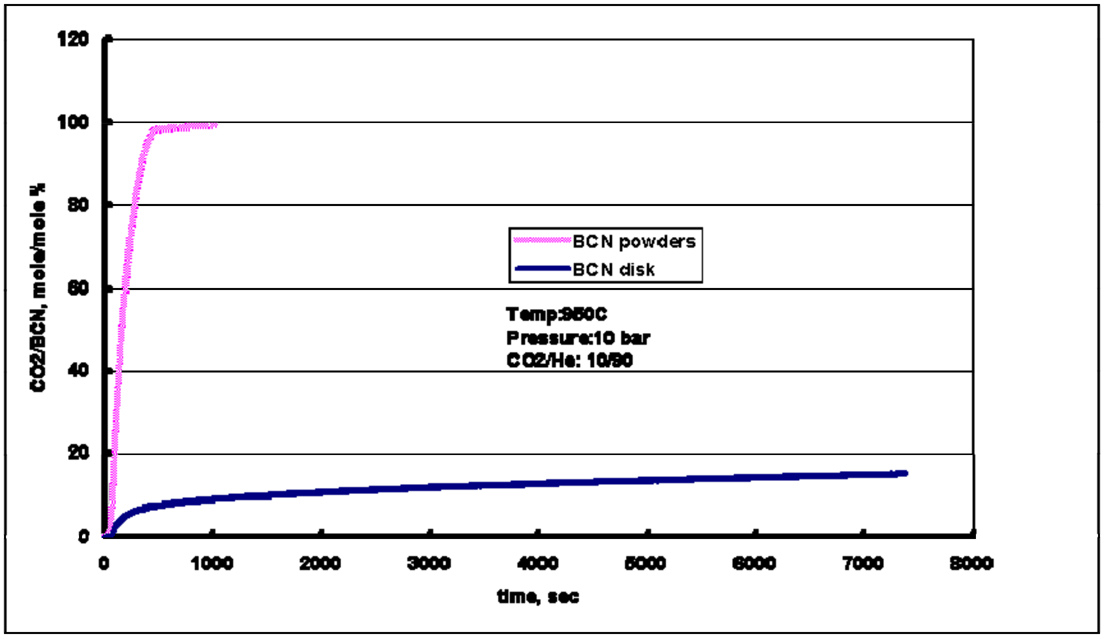

Figure 2. Thermo gravimetric results for the reaction of CO_2 with BCN powder and disk

Reaction of Perovskite with H_2S

The tests were conducted at 950°C and 10 atm with 0.1% H_2S in H_2. The TGA results are shown in Figure 3 in terms of the moles of H_2S per mole of the BCN sample versus time. As can be seen, the disk form of BCN reacted with H_2S much slower than the powder form, similar to the reaction with CO_2. When the perovskite material encountered H_2S, the weight of the sample increased, perhaps due to the adsorption of the H_2S molecules on the perovskite surface. XRD analysis of the reacted sample indicated the presence of the perovskite structure with the formation of neodymium oxide sulfide, Nd_2O_2S and barium sulfide, BaS. Presumably, H_2S was adsorbed chemically on the surface of the membrane, forming the above sulfide compounds.

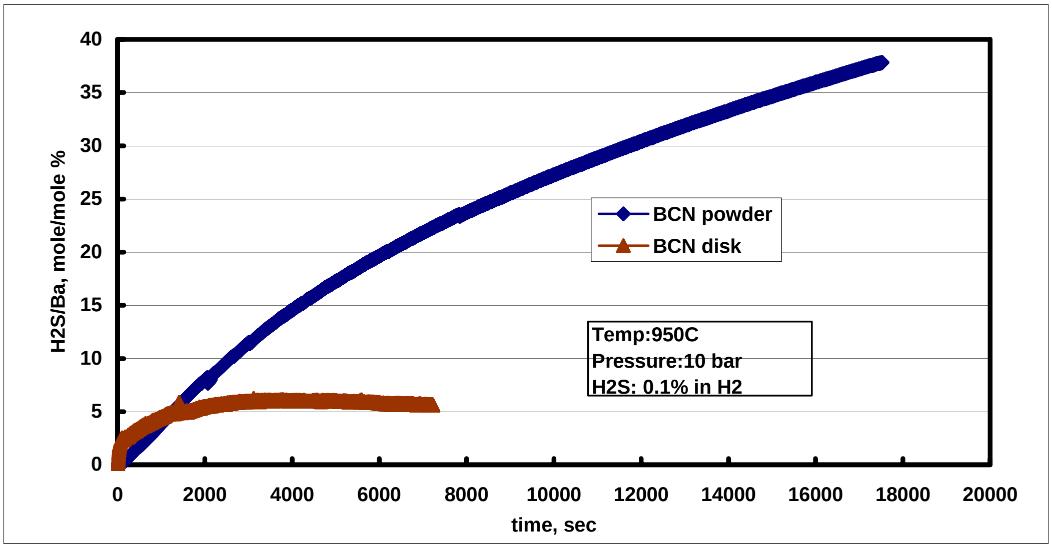

Figure 3. Thermo gravimetric results for the reaction of H_2S with BCN powder and disk

<u>Zr-doped Perovskite</u>

Literature survey indicates that the Zr doped perovskite materials have improved stability for CO_2 [1,2,3]. In particular, the Yb-doped perovskite shows little reduction of the conductivity by the introduction of Zr [1]. Therefore, the Zr and Yb doped barium cerate perovskite powder, $BaCe_{0.5}Zr_{0.4}Yb_{0.1}O_{3-x}$ (BCZY), which was made by Praxair, was fabricated into dense membrane disks and tested in the TGA unit for the chemical stability with respect to CO_2 and H_2S. The reaction of BCZY disk with CO_2 is shown in Figure 4 in comparison with the BCN and SCE membranes. As can be seen, the Zr doped perovskite or BCZY has better stability with CO_2 than BCN or SCE. BCZY in the form of powders was also tested in the TGA and showed better CO_2 stability than the powder form of the BCN or SCE (data not shown here).

The chemical stability of BCZY with respect H_2S is shown in Figure 5. The tests were conducted at 950°C and 10 atm with 0.1% H_2S in H_2. In comparison with the BCN powder and the BCN membrane disks, the BCZY shows improved resistance to H_2S.

The Zr-doped perovskite is expected to have lower conductivity, hence lower hydrogen flux. Material development in increasing the conductivity and reducing the membrane thickness will be required to raise the flux of the Zr-doped materials.

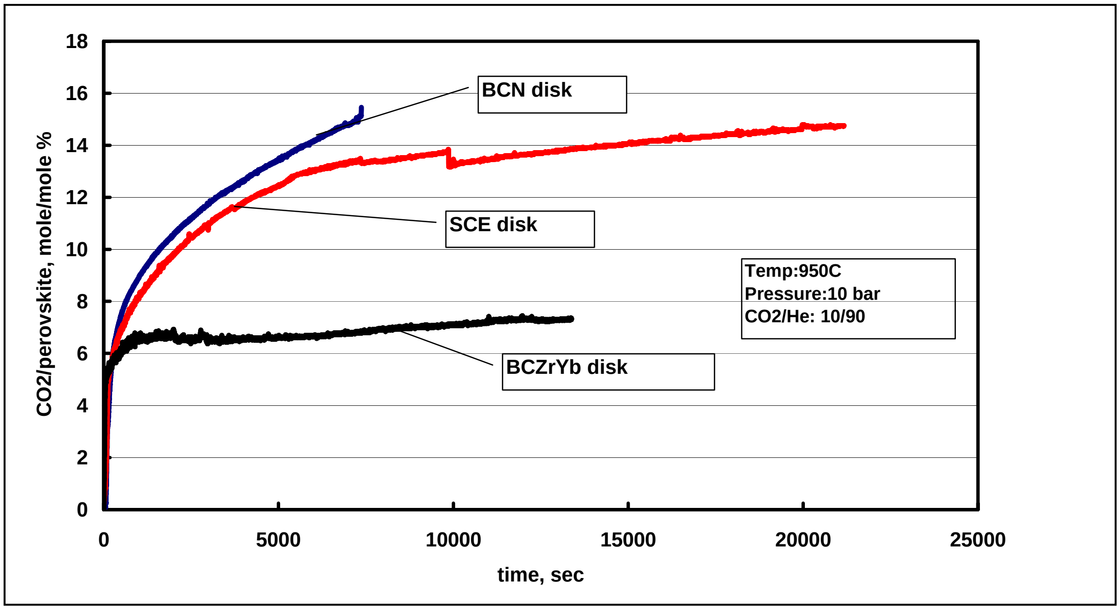

Figure 4. Thermo gravimetric results for the reaction of CO_2 with Zr-doped BCZY, BCN and SCE membrane disks

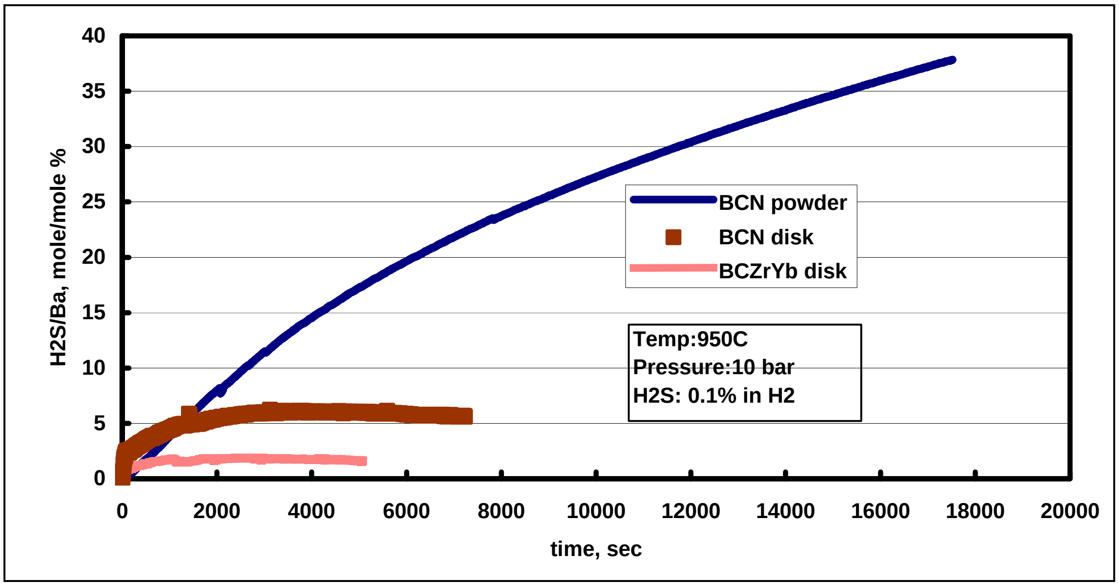

Figure 5. Dense membrane of Zr doped perovskite shows stronger resistance to H_2S than BCN membrane or powder

Flowsheet simulation for hydrogen production from coal based on membrane processes

Flowsheet simulation was performed to calculate material and energy balance based on several hydrogen production processes from coal using high temperature membrane reactor (1000°C), low temperature membrane reactor (250°C), or conventional technologies. The commercial HYSYS simulator was used for the task. As shown in

Figure 6, Process A is the conventional coal to hydrogen process, where a Pressure Swing Adsorption (PSA) is used for hydrogen separation unit. Process B combines the low temperature shift reaction and hydrogen separation into a single membrane shift reactor unit. Process C is one of the membrane gasification reactor concept, where hydrogen is directly extracted from the coal gasifier and the non-permeable gas, after clean up, is used for power generation. If the non-permeable gas stream is further processed by a low temperature membrane shift reactor to increase the overall hydrogen product, this option of the membrane gasification reactor concept is designated as Process D as shown in Figure 6.

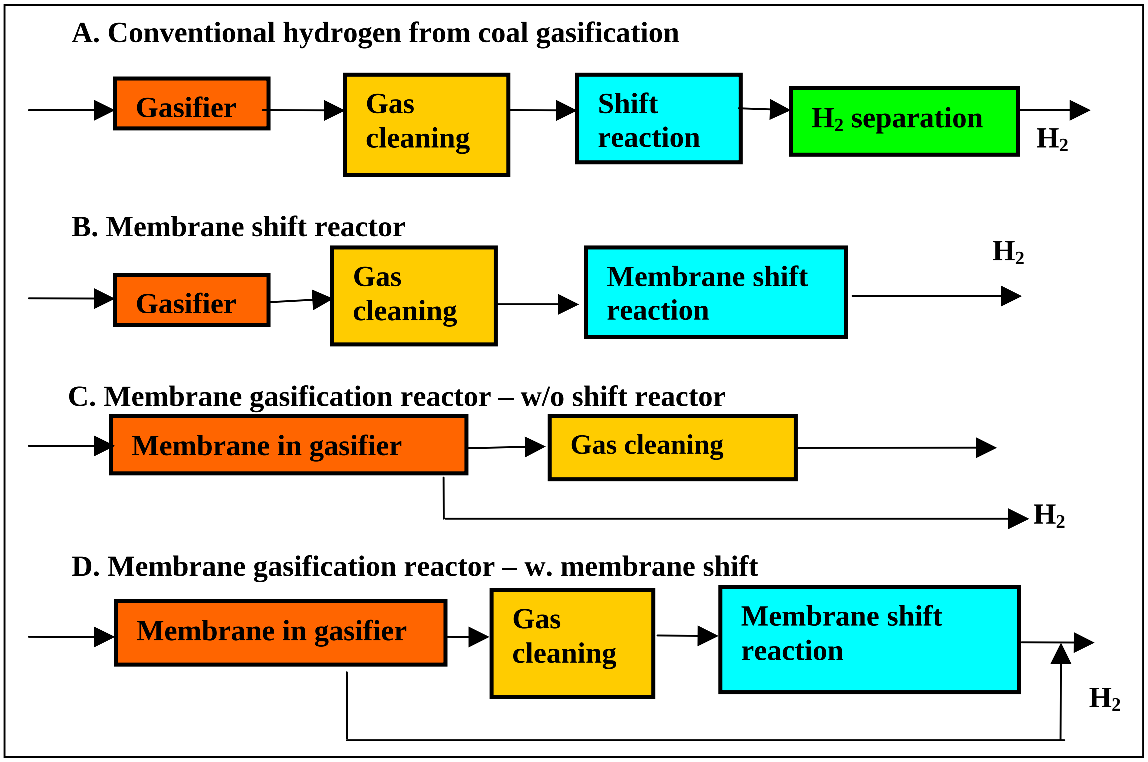

Figure 6. Comparison of process options for hydrogen from coal gasification

Design Basis

The design was based on a coal feed of 1000 TPD (Tons Per Day) using Illinois #6 coal. GTI's U-GAS® fluidized bed was used for the gasifier, operating at 60 bar and 1100°C. Oxygen, instead of air, was used for the gasifier oxidant. Air separation was based on the conventional cryogenic process. In addition to the gasifier, oxygen was also used for the combustion of the waste gas for steam or power generation. The simulation also focused on the heat recovery to generate additional power from the steam cycle. For the membrane processes, gas turbines were used to recover the heating value of the high pressure nonpermeate stream. For comparison purpose, the hydrogen product was generated at 50 bar, with the required hydrogen compression for the membrane processes.

Process A

For the coal to hydrogen process using the conventional technologies, a block flow diagram is shown in Figure 7, with the calculated stream information listed in Table 1. The hot syngas from the gasifier passes through a HRSG (Heat Recovery Steam Generation) unit to cool to below 300^{o}C. After the fine particulates are removed by a filter, the syngas stream is added with steam before entering the water-gas-shift reactor. Because the shift reactor is located upstream of the acid gas removal unit, a sulfur tolerant catalyst has to be used for the shift reactor unit. The shift reaction is assumed to reach equilibrium at the reactor adiabatic temperature, which results in a CO conversion greater than 80%. Although the acid gas removal unit is not defined in this simulation, conventional process such as Selexol can be used in this low temperature range. All of the H_2S and 80% of CO_2 are removed in the acid gas removal unit. The hydrogen recovery for the PSA unit is assumed to be 80%. The PSA tail gas, which still contains CH_4, H_2 and CO, is sent to a boiler for steam generation, which is then used for power generation in this case.

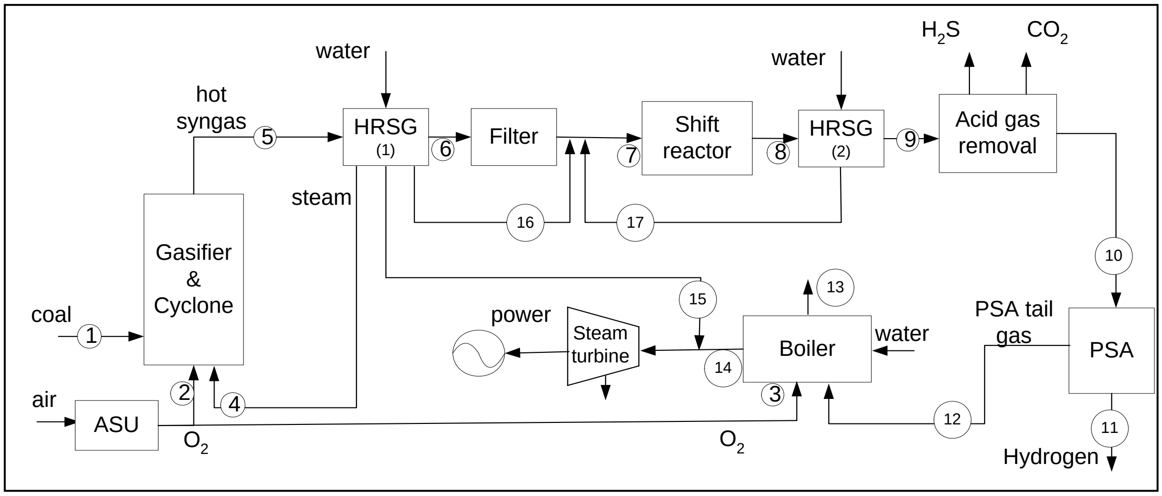

Figure 7. Block flow diagram for the coal to hydrogen process based on the conventional technologies, Process A

Table 1. Major gas streams of Process A, conventional coal to hydrogen process

stream number	1	2	3	4	5	6	7	8	9
stream description	coal feed	oxygen to gasifier	oxygen to combustor	steam to gasifier	hot syngas	cool syngas	syngas to shft	syngas from shift	cool shifted gas
stream composition, %									
CH4					4.13	4.13	3.39	3.39	3.39
CO					29.72	29.72	24.37	3.48	3.48
CO2					14.55	14.55	11.93	32.82	32.82
H2					27.99	27.99	22.95	43.84	43.84
H2O				100	22.06	22.06	36.08	15.19	15.19
O2		97.5	97.5		0	0	0	0	0
N2		2.5	2.5		0.69	0.69	0.57	0.57	0.57
H2S					0.86	0.86	0.71	0.71	0.71
total					100	100	100.00	100.00	100.00
molar flow, kgmole/hr		779	680	1377	4270	4270	5207	5207	5207
mass flow, kg/hr	41667	24920	21760	24781	87170	87170	104000	104000	104000
pressure, atm	60	60	1.7	60	58	54	53	52	51
temperature, C	25	30	30	276	1040	270	266	331	265

stream number	10	11	12	13	14	15	16	17
stream description	syngas to PSA	hydrogen product	PSA tail gas	boiler flue gas	steam from boiler	steam to turbine from HRSG(1)	steam to shift from HRSG(1)	steam to shift from HRSG(2)
stream composition, %								
CH4	6.2	0	17.28	0	0	0	0	0
CO	6.37	0	17.78	0	0	0	0	0
CO2	5.99	0	16.7	38.23	0	0	0	0
H2	80.18	100	44.73	0	0	0	0	0
H2O	0.23	0	0.63	59.04	100	100	100	100
O2	0	0	0	0.6	0	0	0	0
N2	1.03	0	2.88	2.13	0	0	0	0
H2S	0	0	0	0	0	0	0	0
total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
molar flow, kgmole/hr	2847	1826	1021	1383	5366	705	637	300
mass flow, kg/hr	20960	3682	17278	39033	96662	12700	11469	5340
pressure, atm	50	50	1.7	1.6	87	87	51	51
temperature, C	40	40	35	375	510	510	267	262

Process B

The block flow diagram for the Process B, which utilizes a low temperature (<350^{o}C) membrane shift reactor to replace the shift reactor and the PSA unit, is shown in Figure 8. The stream information is listed in Table 2.

The low temperature membrane shift reactor in process B is modeled as a shift reactor and a hydrogen separation unit with part of its non-permeate or retentate stream recycled to the shift reactor as shown in Figure 9. The hydrogen recovery for the separation unit is assumed to be 80%, and 70% of the retentate is recycled back to the shift reactor. The hydrogen partial pressure in the permeate side is maintained at about 2 bar. The final hydrogen product is compressed to 50 bar, which is at about the same pressure from the PSA unit of the Process A.

Because the sulfur tolerance of the membrane material (such as palladium) has not been proven, a warm gas clean up unit is placed upstream the membrane shift reactor. This gas clean up unit is mainly for the H_2S removal.

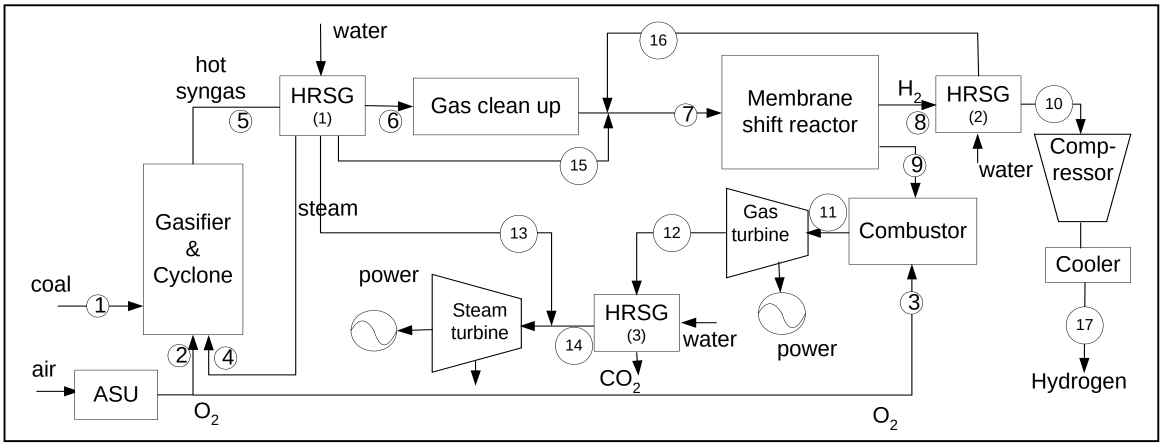

Figure 8. Block flow diagram for the coal to hydrogen process using a low temperature membrane shift reactor, Process B.

Table 2. Major gas streams of Process B, low temperature membrane shift reactor

stream number	1	2	3	4	5	6	7	8	9
stream description	coal feed	oxygen to gasifier	oxygen to combustor	steam to gasifier	hot syngas	cooled syngas	syngas to membran	hydrogen from mem	syngas to combustor
stream composition, %									
CH4					4.13	4.13	3.54	0	6.28
CO					29.72	29.72	25.44	0	4.29
CO2					14.55	14.55	12.46	0	62.95
H2					27.99	27.99	23.96	100	5.81
H2O				100	22.06	22.06	34.01	0	19.62
O2		97.5	97.5		0	0	0	0	0
N2		2.5	2.5		0.69	0.69	0.59	0	1.05
H2S					0.86	0.86	0	0	0
total					100	100	100	100	100
molar flow, kgmole/hr		779	680	1377	4270	4270	115	0	2177
mass flow, kg/hr	41667	24920	21760	24781	87170	86300	2066	0	4390
pressure, atm	60	60	1.7	60	58	57	55	2	52
temperature, C	25	30	30	276	1030	270	110	0	348

stream number	10	11	12	13	14	15	16	17
stream description	cooled hydrogen	gas turbine inlet	gas turbine outlet	steam from HRSG(1)	steam from HRSG(3)	steam to shift from HRSG(1)	steam to shift from HRSG(2)	compressed hydrogen
stream composition, %								
CH4	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
CO2	0	65.22	65.22	0	0	0	0	0
H2	100	0	0	0	0	0	0	100
H2O	0	33.69	33.69	100	100	100	100	0
O2	0	0.16	0.16	0	0	0	0	0
N2	0	0.93	0.93	0	0	0	0	0
H2S	0	0	0	0	0	0	0	0
total	100	100	100	100	100	100	100	100
molar flow, kgmole/hr	2177	3169	3169	706	2559	640	115	2177
mass flow, kg/hr	4390	111171	111171	12723	46101	11526	2066	4390
pressure, atm	1.8	52	1.4	87	87	57	57	50
temperature, C	270	1053	573	510	510	277	277	40

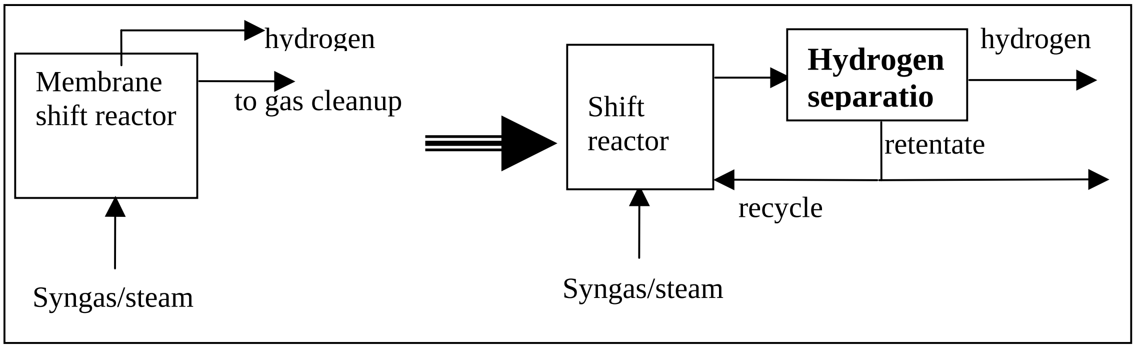

Figure 9. Modeling of membrane shift reactor

The non-permeable gas from the membrane, which is at high pressure, ~50 bar, is sent to a gas turbine for power generation. Oxygen combustion at the high pressure is used to facilitate the CO_2 capture process. High pressure steam produced in the system is sent to a steam turbine for additional power generation.

Process C

Process C employs a high temperature H_2-selective membrane such as the perovskite membranes evaluated in this project. A block flow diagram of the Process C is shown in Figure 10 and the accompanied stream information is listed in Table 3.

The performance of the high temperature membrane reactor is based on the conceptual design and modeling of the tubular membranes, as reported in the last quarter. Although the membrane module can be configured within the freeboard region of the fluidized bed gasifier, it can also be closely coupled with the gasifier, as shown in Figure 10. Because no low temperature shift reactor is used in this process option, additional steam is added to the membrane module to facilitate reforming and shift reactions in the membrane reactor. Similar to the low temperature membrane shift reactor case in Process B, the hydrogen is produced at about 2 bar. Both hydrogen product and the non-permeable gas streams go through a HRSG and are cooled to about 270^{o}C. After further cooling, the hydrogen product is compressed to about 50 bar.

The cooled non-permeable gas, after cleaned up for the removal of sulfur and other particulates, is sent to a combustor for power generation in a combined cycle, similar to the Process B.

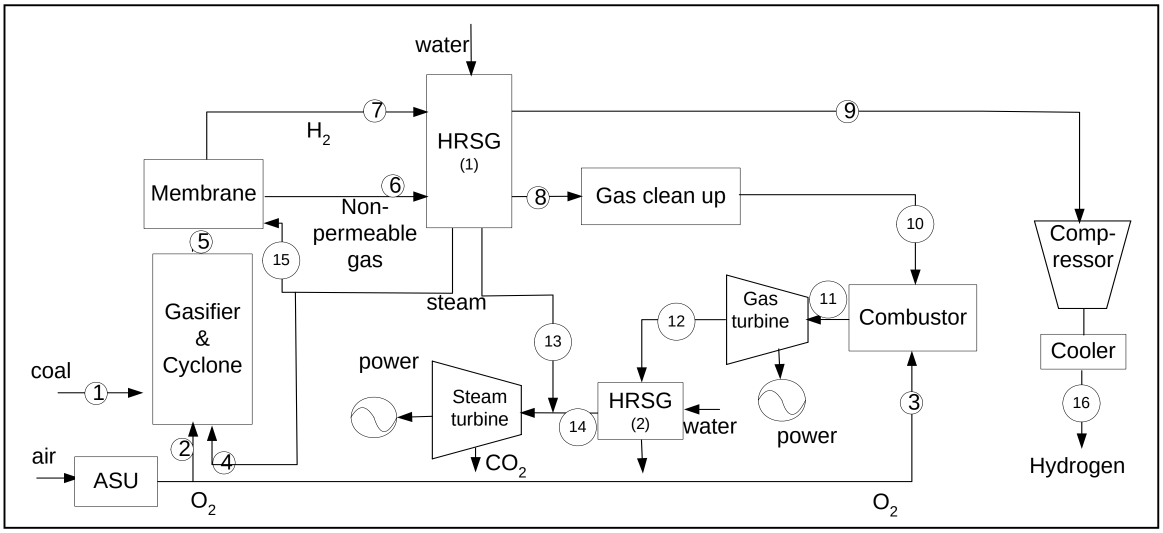

Figure 10. Block flow diagram for the coal to hydrogen process using a high temperature membrane reactor, Process C

Table 3. Major gas streams of Process C, high temperature membrane shift reactor

stream number	1	2	3	4	5	6	7	8
stream description	coal feed	oxygen to gasifier	oxygen to combustor	steam to gasifier	hot syngas	nonpermeable syngas	hydrogen from HT mem	cooled syngas
stream composition, %								
CH4					4.13	0.84	0	0.84
CO					29.72	25.68	0	25.68
CO2					14.55	38.35	0	38.35
H2					27.99	5.35	100	5.35
H2O				100	22.06	27.69	0	27.69
O2		97.5	97.5		0	0	0	0
N2		2.5	2.5		0.69	0.93	0	0.93
H2S					0.86	1.16	0	1.16
total					100	100	100	100
molar flow, kgmole/hr		779	550	1377	4270	3156	2070	3156
mass flow, kg/hr	41667	24920	17600	24781	87170	94547	4173	94547
pressure, atm	60	60	52	60	59	58	2	53
temperature, C	25	30	30	276	1030	1030	1030	270

stream number	9	10	11	12	13	14	15	16
stream description	cooled hydrogen	syngas to combustor	gas turbine inlet	gas turbine outlet	steam from HRSG(1)	steam from HRSG(2)	steam to membrane	compressed hydrogen
stream composition, %								
CH4	0	0.85	0	0	0	0	0	0
CO	0	25.98	0	0	0	0	0	0
CO2	0	38.8	64.39	64.39	0	0	0	0
H2	100	5.41	0	0	0	0	0	100
H2O	0	28.02	34.46	34.46	100	100	100	0
O2	0	0	0.23	0.23	0	0	0	0
N2	0	0.94	0.92	0.92	0	0	0	0
H2S	0	0	0	0	0	0	0	0
total	100	100	100	100	100	100	100	100
molar flow, kgmole/hr	2070	3119	3180	3180	1256	4060	642	2070
mass flow, kg/hr	4173	93299	110898	110898	22624	73140	11550	4173
pressure, atm	2	52	52	1.4	87.5	87.5	60	50
temperature, C	262	190	911	469	510	510	277	40

Process D

Process D combines the high temperature membrane reactor in Process C and the low temperature membrane reactor in Process B to maximize the hydrogen production from coal gasification. The block flow diagram and the stream information are shown in Figure 11 and Table 4 respectively.

Again, the performance of the high temperature membrane reactor is based on the conceptual design reported in the last quarter. The non-permeable gas from the high temperature membrane gasification reactor, after cooling and clean up is sent to a low temperature membrane reactor to further convert CO and separate H_2. The non-permeable gas from the low temperature membrane reactor is sent to a combustor for power generation in a combined cycle.

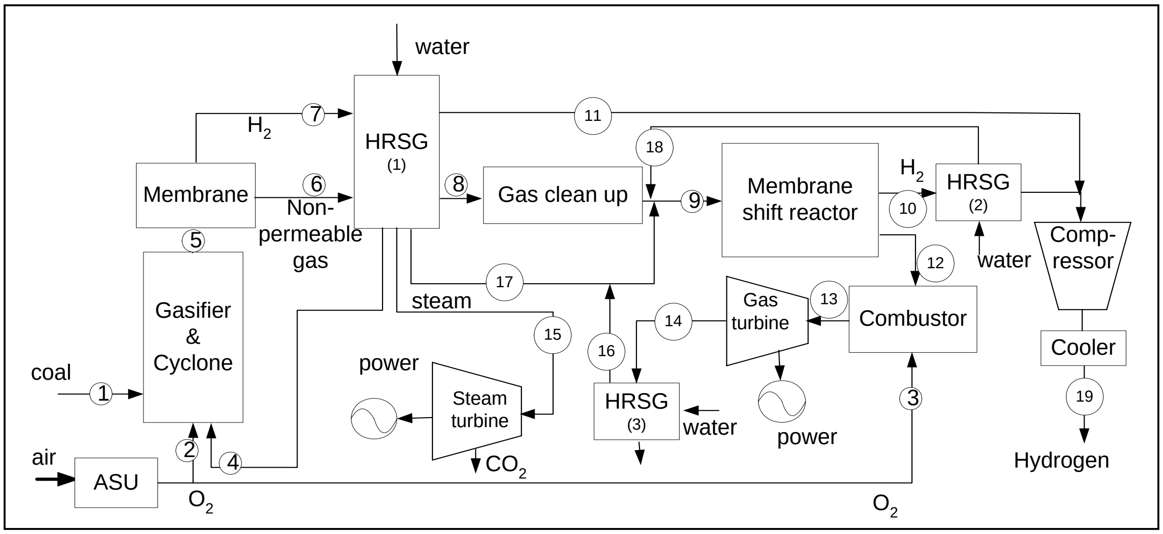

Figure 11. Block flow diagram for the coal to hydrogen process using a high temperature and a low temperature membrane reactors, Process D

Table 4. Major gas streams of Process D, with a high temperature and a low temperature membrane reactors

stream number	1	2	3	4	5	6	7	8	9	10
stream description	coal feed	oxygen to gasifier	oxygen to combustor	steam to gasifier	hot syngas	nonpermeable syngas	hydrogen from HT mem	cooled syngas	syngas to LT membrane	hydrogen from LT mem
stream composition, %										
CH4					4.13	0.71	0	0.71	0.56	0.00
CO					29.72	38.27	0	38.27	30.24	0.00
CO2					14.55	38.76	0	38.76	30.63	0.00
H2					27.99	3.74	100	3.74	2.96	100.00
H2O				100	22.06	16.05	0	16.05	34.74	0.00
O2		97.5	97.5		0	0	0	0	0	0.00
N2		2.5	2.5		0.69	1.1	0	1.1	0.87	0.00
H2S					0.86	1.37	0	1.37	0	0.00
total					100	100	100	100	100	100.00
molar flow, kgmole/hr		779	150	1377	4270	2630	1975	2630	3328	921.00
mass flow, kg/hr	41667	24920	4800	24781	87170	83188	3982	83188	95180	1857.00
pressure, atm	60	60	1.7	60	59	58	2	54	53	2
temperature, C	25	30	30	276	1030	1030	1030	270	203	348

stream number	11	12	13	14	15	16	17	18	19
stream description	hydrogen from HRSG(1)	syngas to combustor	gas turbine inlet	gas turbine outlet	steam to turbine from HRSG(1)	steam to shift from HRSG(3)	steam to shift from HRSG(1)	steam to shift from HRSG(2)	compressed hydrogen
stream composition, %									
CH4	0	0.78	0	0	0	0	0	0	0
CO	0	4.75	0	0	0	0	0	0	0
CO2	0	79.44	82.96	82.96	0	0	0	0	0
H2	100	2.87	0.00	0.00	0	0	0	0	100
H2O	0	10.96	15.02	15.02	100	100	100	100	0
O2	0	0.00	0.85	0.85	0	0	0	0	0
N2	0	1.20	1.17	1.17	0	0	0	0	0
H2S	0	0	0	0	0	0	0	0	0
total	100	100	100	100	100	100	100	100	100
molar flow, kgmole/hr	1975	2406	2464	2464	1779	451	283	48	2896
mass flow, kg/hr	3982	93317	98117	98117	32043	8120	5101	866	5839
pressure, atm	1.8	52	51.8	1.4	87.5	57	57	57	50
temperature, C	260	349	853	445	510	277	275	275	40

Process Performance Comparison

For comparative purpose, the performances of the different coal to hydrogen processes are evaluated by the cold gas efficiency and the effective thermal efficiency, both of which are defined below [4]:

$$\text{Cold gas efficiency} = \frac{\text{hydrogen product heating value (HHV)}}{\text{coal heating value (HHV)}}$$

$$\text{Effective thermal efficiency} = \frac{\text{hydrogen product heating value + net power produced}}{\text{coal heating value}}$$

Table 5 summarized the amounts of hydrogen produced, power generated from the turbines, power consumption from the major equipment, the effective thermal efficiencies, the cold gas efficiencies and other parameters for the four processes evaluated in this work. In all four processes, CO_2 can be readily captured due to the use of oxygen. However, compression of CO_2 is excluded in the power calculation.

As can be seen, less amount of oxygen would be required in the combustor to burn the waste gas when more hydrogen is produced in the process. Less power is produced when more hydrogen is generated. For the process employing both the high temperature and the low temperature membrane reactors (Process D), the hydrogen production can be increased by more than 50% relative to the conventional coal to hydrogen process (Process A), with a negative power output of 1 MW for a 1000 TPD plant. The conventional process has a net power output of 7 MW. For the process employing only the high temperature membrane reactor process (Process C), the hydrogen production is increased by about 10% relative to the conventional process, with a net power output of 15 MW. For the process employing only the low temperature membrane reactor process (Process B), the hydrogen production is increased by about 20%, with a net power output of 10 MW.

Process C or D also shows one advantage of the reduced syngas flows from the gasifier or the high temperature membrane reactor to the first HRSG (1), in comparison with Process A or Process B, which could potentially reduce the sizes of the downstream equipment such as gas clean up or shift reactor.

Apparently, the overall economics depends on the capital cost and the value of hydrogen versus the electrical power. Preliminary economic evaluation will be conducted in the next quarter.

Table 5. Summary of performance for different coal to hydrogen processes

Process	A	B	C	D
coal feed, TPD	1000	1000	1000	1000
oxygen feed, kmole/hr	1459	1278.9	1329	929
gasifier	779	778.9	779	779
combustor	680	500	550	150
hydrogen product, kmole/hr	1826	2177	2070	2896
syngas to HRSG(1), kmole/hr	4270	4270	3156	2630
steam turbine power, MW	22	12	20	7
gas turbine power, MW		21	19	14
oxygen compressor, MW	3	5	5	4
ASU power, MW	11	10	10	7
hydrogen compressor, MW		8	7	10
water pumps, MW	0.5	0.4	0.4	0.2
net power, MW	7	10	15	-1
effective thermal efficiency, %	46.3	55.6	54.4	69.8
cold gas efficiency, %	44.1	52.6	50	69.9

CONCLUSION

For the chemical stability issues of the perovskite materials, the zirconium-doped proton conducting perovskite has been identified as one potential material to be chemically stable under the coal-derived syngas environment. We have tested the reaction of Zr-doped barium-cerate perovskite materials with CO_2 and H_2S in a TGA unit. We found that the Zr-doped material was more resistant to CO_2 or H_2S than the undoped one. Also, the perovskite in a membrane or disk form was more chemically stable than in a powder form. Further work is needed to increase the flux of the Zr-doped materials.

Flowsheet simulation for the different hydrogen from coal gasification processes show that the process employing both the high temperature and the low temperature membrane reactors can increase the hydrogen production efficiency (cold gas efficiency) by more than 50% compared to the conventional process. Using either high temperature or low temperature membrane reactor process also results in an increase of the cold gas efficiencies as well as the thermal efficiencies of the overall process.

PLAN FOR NEXT QUARTER

- Conduct preliminary cost analysis for the different hydrogen from coal gasification processes.
- Complete project final report

REFERENCES

1. S. M. Haile, G. Staneff and K. H. Ryu, “Non-stoichiometry, grain boundary transport and chemical stability of proton conducting perovskites”, J. of Materials Science, 36, p1149-1160 (2001)
2. K. H. Ryu and S.M. Haile, “Chemical stability and proton conductivity of doped $BaCeO_3$-$BaZrO_3$ solid solutions” Solid State Ionics, P355-367,125 (1999)
3. K. Katahira, Y. Kohchi, T. Shimura and H. Iwahara, “Protonic conduction in Zr-substituted $BaCeO_3$” Solid State Ionics, P91-98,138 (2000)
4. Parsons Infrastructure and Technology Group, Inc. “Hydrogen Production Facilities Plant Performance and Cost Comparisons”, Final Report DOE Contract DE-AM26-99FT40465, March 2002