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Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane

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Abstract

Capture of carbon dioxide from an advanced integrated gasification combined-cycle (IGCC) process offers several technical and economic advantages over the conventional coal-combustion systems. The pre-combustion gas stream is at high pressure, has low volumetric flow rates and is capable of producing relatively pure hydrogen for conversion into electricity by gas turbines or fuel cells without generating additional carbon dioxide.
Polybenzimidazole (PBI) polymer shows promise as a high temperature membrane material for pre-combustion-based capture of CO_2 from IGCC gas streams. We are developing a process that is based on PBI membrane to achieve a capture of 90% CO_2 as a high pressure stream with about 10% increase in the cost of energy. A significant advantage of the PBI membrane compared to other sorbent-based technologies and conventional polymeric membranes is that PBI membrane is capable of operating at over a broader temperature range (~100 – 400°C). In contrast, solvent-based processes such as Selexol require syngas cooling prior to treatment, followed by reheating the processed fuel gas stream.
In this paper, we are presenting the preliminary results of a process simulation using the ASPEN program under several scenerios including the IGCC with no CO_2 capture, IGCC with Selexol, and IGCC with PBI membrane separator. The high temperature membrane-based CO_2 capture method compares favorably against the Selexol-based CO_2 capture method. If H_2S remains with the CO_2 stream and can be sequestered, then the cost of electricity appears to be lower than Selexol-bsed separation systems.

Keywords: Type your keywords here, separated by semicolons ; Carbon Capture; Polybenzimidazole; IGCC; Membrane

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1. Introduction

Capturing carbon dioxide from mixed-gas streams is a first and critical step in carbon sequestration. To be technically and economically viable, a successful separation method must be applicable to industrially relevant gas streams at realistic temperatures, and be compatible with large gas volumes.. Polymer-based membrane separations are less energy intensive, requiring no phase change in the process, and typically provide low-maintenance operations.

Previous work has demonstrated that polybenzimidazole (PBI) shows promise as a membrane material for pre-combustion-based capture of CO_2. PBI possesses excellent chemical resistance, a very high glass transition temperature (450°C), good mechanical properties and excellent material processing ability. A significant advantage of the PBI membrane compared to the Selexol "base-case," and conventional polymeric membranes is that PBI membrane is capable of operating at higher temperatures (200 – 400°C). This high temperature operation preserves the heat associated with steam in the IGCC gas streams. If steam is permeated along with H_2 in the permeate stream, the mass of gas feed to the gas turbine is increased significantly thereby improving the turbine efficiency. In contrast, processes such as Selexol require syngas cooling prior to treatment, followed by reheating the processed fuel gas stream and these operations reduces the efficiency of power generation.

A second significant advantage of PBI membrane technology is the ability to provide the concentrated CO_2 stream at elevated pressures, typically 600 to 800 psig depending on gasifier type, process location, and other process variables) than that possible with Selexol absorbers. This high pressure recovery reduces the energy for compressing CO_2 for pipeline transportation.

2. Results and Discussion

The process simulation was performed in several steps. An Enerfex membrane simulation was used to simulate H_2 and CO_2 separation performance data. An Aspen program was used to simulate the various unit processes in the IGCC process. A GT-Pro program was used to simulate the gas and steam turbine performances. The results from these simulations are presented below.

2.1. Membrane Simulation

We performed an engineering analysis for a membrane process design based on previous work conducted at the Los Alamos National Laboratory (LANL). An Enerfex membrane simulation was used to simulate H_2 and CO_2 separation performance data. The PBI membrane developed by LANL has been shown to separate H_2 and CO_2 at high temperatures, similar to those that will be encountered in shifted syngas in an IGCC power plant.

The feed composition tested at LANL was: 55% H_2, 1% CO, 41% CO_2, 1% H_2O and 1% $N_2/CH_4/H_2S$. The feed conditions were: 250ºC and 715 psia. The membrane dense layer effective thickness was 0.5 μ. The analysis basis assumed a permeate pressure of 71.5 psia, giving a feed to permeate pressure ratio of 10.

Simulations of the LANL performance yielded GPU values which were consistent with the GPU values reported by LAN, within 20% of the values.

The LANL GPU performance and simulated GPU performance at 98% H_2 recovery and 90% CO_2 recovery are compared in the Table 2 below:

Table 1. Comparison of Observed and Simulated Membrane Performances

	Feed flux Ft^2/10k scfh	Retentate CO2			Permeate H_2		
		Pressure	Purity	Recovery	Pressure	Purity	Recovery
LANL Performance (GPU)	285	715	90.0%	90.0%	N.A.	92.0%	98.0%

Simulated Performance (GPU)	286	715	87.7%	90.0%	71.5	91.4%	98.0%

The simulated GPU and simulated performance in general compared well with the LANL data. The differences in the simulated and reported purities may be due to a difference in permeate pressure.

The simulated LANL performance results for four data points of H_2 and CO_2 purity and recovery are summarized in the two charts below.

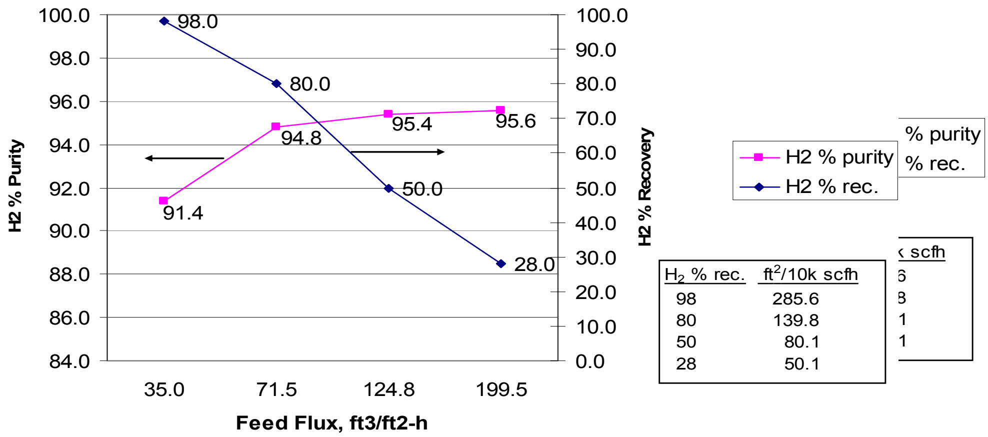

Figure 1. Simulated performance of PBI membrane with respect to hydrogen purity and recovery as a function of feed flux.

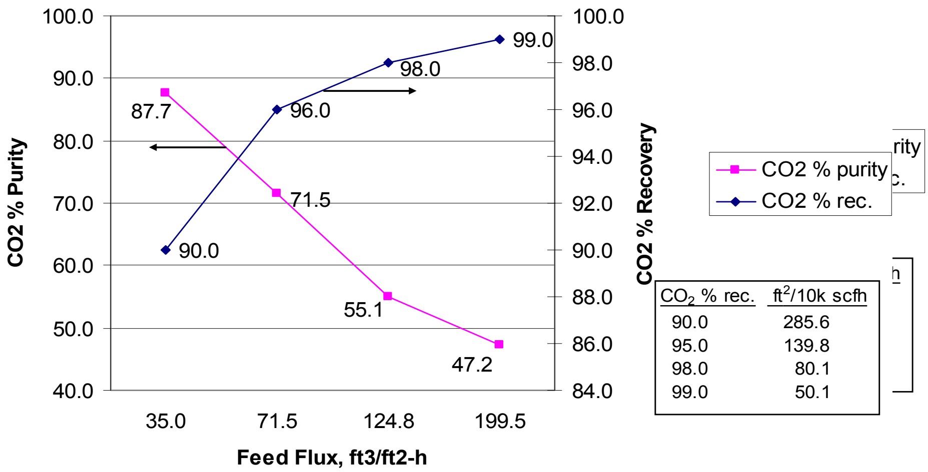

Figure 2. Simulated performance of PBI membrane with respect to carbon dioxide purity and recovery as a function of feed flux.

Since 90% CO_2 capture is the acknowledged NETL CO_2 capture goal, the most advantageous operating point would be that point that gives 90% CO_2 recovery and the highest H_2 recovery, which in the present case is 98% H_2 recovery.

2.2. Process Modeling

Process modeling was performed to evaluate the location and performance effects that the PBI membrane system will have on the overall power plant performance. The effort is aimed at optimizing the overall plant to take advantage of the beneficial characteristics of the membrane system. The initial assumption is that the membrane unit will be located downstream from the water gas shift reactors.

Five different scenarios were explored:

- Scenario 1: Base case IGCC plant with no CO_2 capture
- Scenario 2: IGCC plant equipped with CO_2 capture. Selexol units are used to separate CO_2 from H_2 and also to remove H_2S from the CO_2 stream
- Scenario 3: PBI membrane used to remove CO_2. H_2S passes through the PBI membrane with the H_2. Selexol is used on the hydrogen rich stream to remove H_2S from the H_2 stream
- Scenario 4a: PBI membrane used to remove CO_2. H_2S remains with the CO_2 and is co-sequestered
- Scenario 4b: PBI membrane used to remove CO_2. H_2S remains with the CO_2 and is removed using a Selexol unit prior to sequestration

Preliminary data has been developed for Scenarios 1, 2, 4a, and 4b. Results of the scenario 3 will be reported later. The results from the four scenarios were compared and additional efforts were made to makes sure that the process conditions were as consistent as possible with the NETL results presented in 2007.

An Aspen/GT-Pro model was used to simulate the various scenarios. In all scenarios the IGCC plant uses a GEE (Texaco) radiant only gasifier and two GE F-class gas turbines which produce 232 MW each. The two gas turbines dictate the sizing of the entire IGCC plant as they require a specific amount of fuel depending on the fuel's composition. For this reason, both the total power output and the coal feed rate vary based on the particular parameters of each scenario. The syngas fuel composition determined in the Aspen program is entered into GT-Pro model. The input parameters to GT-Pro include the composition of the fuel gas, the particular gas turbine, flow rate and composition of diluents, and any inputs or bleeds of steam or hot water. The program then designs an optimal energy recovery system. Both GT-Pro and Aspen calculate a required syngas fuel flow rate to the gas turbines. Once both programs are in agreement, heat integration was performed where heating and cooling streams required within the Aspen model can be accounted for in the GT-Pro model. Given these heating and cooling inputs along with the syngas composition, GT-Pro calculates the steam turbine power output.

2.2.1. No CO2 Capture (Scenario 1)

In this scenario the IGCC plant operates without CO_2 capture to establish a baseline of performance. Figure 1 illustrates the block flow diagram of an IGCC process in which there is no CO_2 capture. A bituminous coal is gasified in an oxygen-blown, slagging gasifier at about 2400°F. An air separation unit (ASU) is used to supply the necessary O_2 to the gasifier and to the Claus unit combustor. Nitrogen from the ASU is used in the gas turbine as a diluent. The syngas leaving the gasifier is cooled and the COS in the gas stream is hydrolyzed to H_2S to assist the capture of S compounds. A Selexol solvent absorber is used to capture the H_2S in the coal gas and the captured H_2S is sent to a Claus unit for producing elemental sulfur. The clean syngas is combusted in a gas turbine to generate electricity. Additional electricity is produced in the bottoming steam cycle. The gas and steam turbines produce about 464 and 303 MW of electricity respectively. The total auxiliary power requirement is 144 MW, resulting in a net power output of 629 MW.

The input parameters to GT-Pro include the composition of the fuel gas, the particular gas turbine, flow rate and composition of diluents, and any inputs or bleeds of steam or hot water. The program then designs an optimal energy recovery system. In Scenario #1, low pressure steam is drawn from the first low pressure super heater to provide heating in several unit operations. There are also three large energy inputs to the steam cycle which are generated by cooling processes from the gasifier portion of the plant. High pressure water is drawn from the final high pressure economizer and used to provide steam cooling, predominately in the radiant cooler. This high pressure water is vaporized and returned to the first high pressure super heater. There is also water removed from the low pressure boiler and the low temperature economizer to provide cooling to successively cooler unit operations.

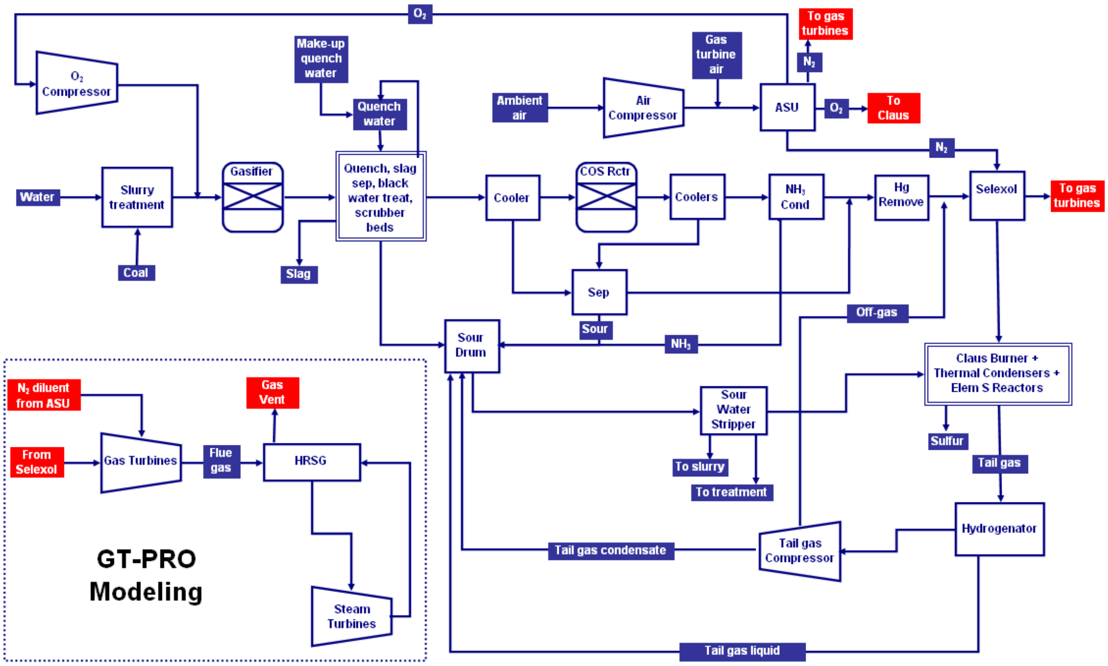

Figure 3. Block flow diagram of scenario 1

2.2.2. CO_2 Capture Using Selexol (Scenario 2)

In this scenario, the CO_2 is captured using Selexol solvent as shown in the block flow diagram in Figure 4. The CO in the syngas is converted to H_2 and CO_2 using two water gas shift reactors in series. To convert the desired amount of CO, it is necessary to feed steam into the syngas prior to the first water gas shift reactor. We have assumed that the water gas shift reaction will take place in the presence of H_2S (sour gas shift) using a sulfur tolerant catalyst at an inlet temperature of 450°F for both reactors. The gas stream leaving the second water gas shift reactor contains about ~1wt% CO and passes through a series of coolers and separators which remove water, ammonia, and mercury. The syngas then enters the two stage Selexol unit which is operated such that is separates the feed gas into three streams. The H_2S rich stream is sent to the Claus unit as in Scenario 1. The CO_2 rich stream is sent to a series of compressors and compressed to 2215 psia for sequestration. The syngas leaves the Selexol unit and is expanded in a turbine before being mixed with diluent nitrogen prior to being combusted in the gas turbines.

The firing temperature of the gas turbines is reduced from Scenario 1 in order to maintain the life of the parts in the gas turbines. This is necessary as the water content of the fuel gas increases significantly in the CO_2 capture cases. This also reduces the temperature of the flue gas being fed to the heat recovery steam generator (HRSG) and therefore the temperature of the steam being fed into the steam turbines.

The net plant output in Scenario 2 is significantly smaller then the output in Scenario 1. The gas turbines still have an output of 464 MW but the steam turbine output is 277 MW and the auxiliary power requirements are 231 MW. The net power output for the plant is 516 MW which is approximately 18% less then Scenario 1. Additionally, the Scenario 2 plant requires about 6% more coal. The largest parasitic losses related to the capture of CO_2 are associated with the compression of the CO_2 from approximately 30 psia to 2215psia and the additional pumping, chilling, and compressing requirements of operating the Selexol unit. The heat produced by the water gas shift reaction can be recovered but a large portion of it is used to produce the steam that is added to the water gas shift reactors in order to improve the equilibrium of the reaction.

In the GT-Pro simulation for Scenario 2, high pressure steam is drawn from the first high pressure super heater to be mixed into the gasifier product stream just before the water gas shift reactors. A saturated high pressure steam is drawn from the stream leaving the high pressure steam turbine to provide the required heating to the Selexol unit. A final heating stream is withdrawn from the low pressure superheater to provide heating to various unit operations throughout the plant. There are also three large energy inputs to the steam cycle which are generated by cooling processes from the gasifier portion of the plant. High pressure water is drawn from the final high pressure economizer and used to provide steam cooling, predominately in the radiant cooler. This high pressure water is vaporized and returned to the first high pressure super heater. There is also water removed from the low pressure boiler and the low temperature economizer to provide cooling to successively cooler unit operations.

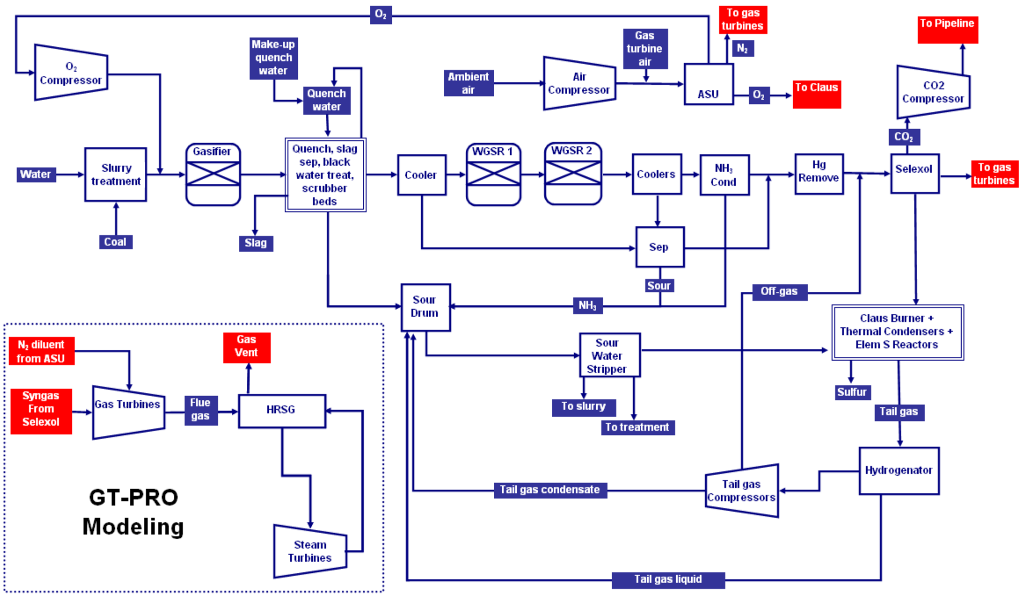

Figure 4. The block flow diagram of scenario 2

2.2.3. CO_2 and H_2S Capture Using High Temperature PBI Membrane (Scenerio #4A)

In this scenario, a PBI membrane is used to separate the hydrogen from the carbon dioxide and the H_2S is sequestered with the CO_2. Figure 5 is the block flow diagram for Scenario 4A. The CO in the syngas is converted to H_2 and CO_2 using two water gas shift reactors in series. We have assumed again that the water gas shift reaction will take place in the presence of H_2S (sour gas shift) using a sulfur tolerant catalyst at an inlet temperature of 450°F for both reactors. The gas stream leaving the second water gas shift reactor contains about ~1wt% CO and then enters the high temperature membrane separator.

The details of the CO_2 separation and H_2 recovery were simulated using the membrane module simulator described earlier. We assumed that in the membrane separator, most of the steam and hydrogen mixture permeates through the membrane whereas CO, H_2S and CO_2 remain mainly in the retentate. Nitrogen gas from ASU, after compression, is passed through the permeate side of the membrane which is kept at 250 psia. The H_2 recovery is estimated to be 91%. The permeate and sweep gases are compressed from 250 psia to 455 psia to meet the gas turbine design specification. After the water, ammonia, and mercury have been removed, the retentate stream is pressurized to 2215 psia.

The gross plant output in Scenario 4A is slightly smaller then the output in Scenario #2 while the coal feed rate is 16% higher. The gas turbines still have an output of 464MW but the steam turbine output is 273 MW and the auxiliary power requirements are 194 MW. The net power output for the plant is 543 MW which is approximately 5% greater then Scenario 2. The net efficiencies of the plants are similar with Scenario 4A having a lower heating value (HHV) efficiency of 29.03% while Scenario 2 has an HHV efficiency of 30.35%.

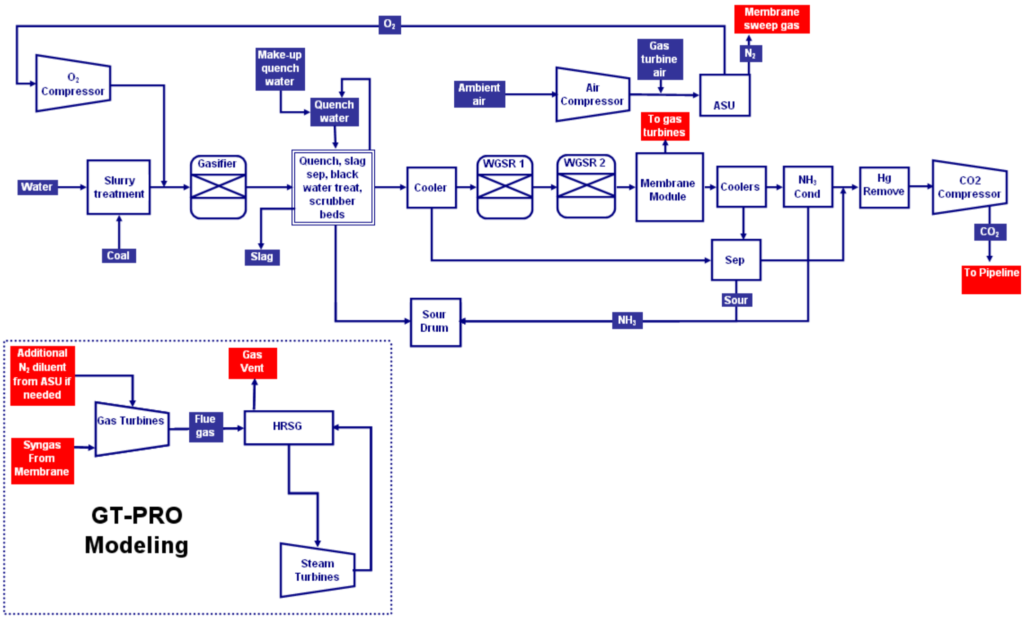

Figure 5. The block flow diagram of scenario 4a.

2.2.4. CO_2 Capture Using High Temperature PBI Membrane and H_2S Capture Using Selexol (Scenario 4B)

In this scenario a PBI membrane is used to separate the hydrogen from the carbon dioxide and the H_2S is captured with Selexol and sent to a Claus unit. Figure 6 is the block flow diagram for Scenario 4B. The CO in the syngas is converted to H_2 and CO_2 using two water gas shift reactors in series. We have assumed that the water gas shift reaction will take place in the presence of H_2S (sour gas shift) using a sulfur tolerant catalyst at an inlet temperature of 450°F for both reactors. The gas stream leaving the second water gas shift reactor contains about ~1wt% CO and then enters the high temperature membrane separator.

The details of the CO_2 separation and H_2 recovery were simulated using the membrane module simulator described earlier. We assumed that in the membrane separator, most of the H_2O, H_2, and H_2S mixture permeates through the membrane whereas CO and CO_2 remain mainly in the retentate. After the water, ammonia, and mercury have been removed, the retentate stream the CO_2 is compressed to 2215 psia. Nitrogen gas from ASU, after compression, is passed through the permeate side of the membrane which is kept at 250 psia. The H_2 recovery in the permeate is estimated to be 91%. The permeate and sweep gas enter the Selexol unit where the H_2S is captured and sent to the Claus unit. The remaining H_2 and sweep gas are compressed from 250 psia to 455 psia to meet the gas turbine design specification.

The gross plant output in Scenario 4B is slightly smaller then the output in Scenario #2 while the coal feed rate is 11% higher. The gas turbines still have an output of 464MW but the steam turbine output is 272MW and the auxiliary power requirements are 215MW. The net power output for the plant is 521MW which is approximately 1% greater then Scenario 2. Scenario 4B having a HHV efficiency of 27.57% while Scenario 2 has an HHV efficiency of 30.35%.

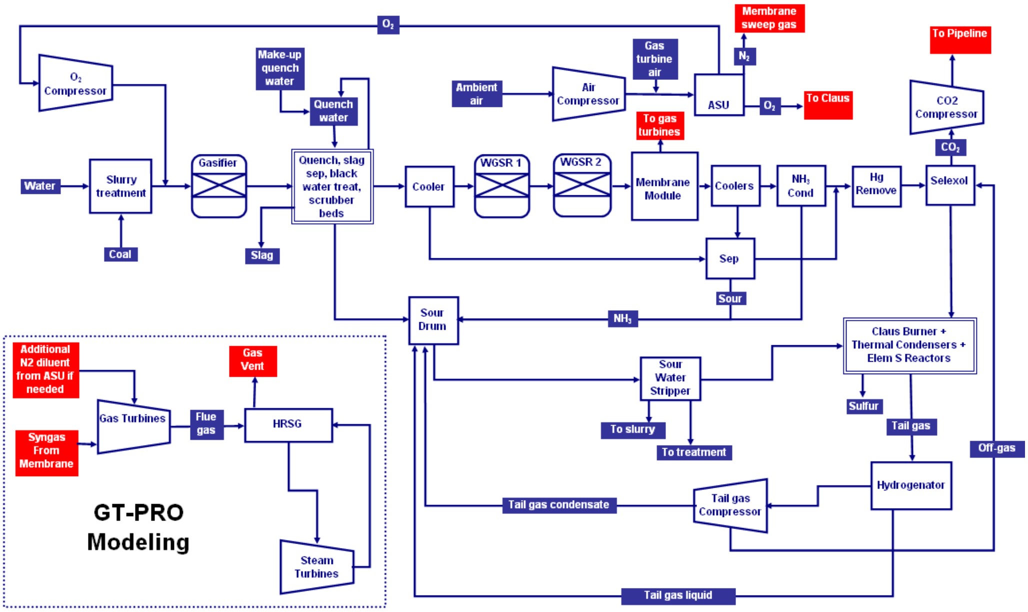

Figure 6. The block flow diagram of scenario 4b.

2.2.5. Plant Performance Summary

The plant performance summary data is shown in Table 9. The gas turbine output is kept constant in the different scenerios by chaning the coal feed rate. The gross output of both steam and gas turbines is comparable between Scenarios 2, 4A and 4B. In comparing the auxiliary load requirements, the membrane-based separation has a lower power load and a higher net plant output power than the selexol-based separation system. The net plant efficiency based on HHV is comparable between both systems.

The economic summary of the various scnarios is shown in Table 3. In the three CO_2 capture scenarios, the simultaneous CO_2 and H_2S capture using the high temperature membrane appears to have the lowest cost of electricity. This mode of capture will require the development of membranes that are not permeable to H2S, as we expect PBI-based membranes to be. If H2S is permeates through the membrane and it needs to be captured using a solvent such as Selexol, then the estimated costs of electricity between the membrane- and Selexol-based systems are very similar. However, this result is based on preliminary membrane data while the operation of Selexol has been optimized over many years. Additionally, no steps have been taken to optimize the membrane separation parameters.

Table 2. Power Plant Performance Summary

Gross Plant Power Output		**Scenario 1**	**Scenario 2**	**Scenario 4A**	**Scenario 4B**
Gas Turbine Gross Power	kWe	464,000	464,000	464,000	464,000
Sweet Gas Expander Gross Power	kWe	6,600	6,440	0	0
GT-PRO Steam Turbine Gross Power	kWe	302,855	276,977	273,126	271,796
Total Gross Power	kWe	**773,455**	**747,417**	**737,126**	**735,796**
Auxiliary Load					
Coal Handling	kWe	432	457	503	508
Coal Milling	kWe	2,187	2,316	2,547	2,574
Coal Slurry Pumps	kWe	713	755	831	840
Slag Handling and Dewatering	kWe	1,126	1,193	1,312	1,326
Air Separation Unit Auxiliaries	kWe	1,000	1,000	1,000	1,000
ASU Main Air Compressor	kWe	68,180	72,190	77,170	80,010
Oxygen Compressor	kWe	10,810	11,440	12,590	12,720
Nitrogen Compressor	kWe	31,897	34,271	23,519	23,347
Selexol	kWe	2,896	29,756	0	3,697
Tail Gas Recycle Compressor	kWe	2,350	5,490	0	2,100
Fuel Compression/Expansion	kWe	0	0	40,030	48,330
CO2 Compressor	kWe	0	50,393	12,550	15,555
Flash Bottoms Pump	kWe	200	200	200	200
Scrubber Pumps	kWe	420	420	420	420
GT-PRO Auxillary Power Requirements	kWe	18,782	18,686	18,657	18,776
Claus Plant Auxiliaries	kWe	200	200	0	200
Miscellaneous Balance-of-Plant	kWe	3,000	3,000	3,000	3,000
Total Auxiliary	**kWe**	**144,193**	**231,766**	**194,327**	**214,603**
Net Plant Power	**kWe**	**629,262**	**515,651**	**542,799**	**521,193**
Net Plant Efficiency (HHV)		39.2%	30.3%	29.0%	27.6%
Net Plant Heat Rate (HHV)	Btu/kWhr	8,707	11,251	11,754	12,372
Coal Feed Flow Rate	lb/hr	469,630	497,286	546,883	552,757
Thermal Input	kWe	1,605,650	1,700,204	1,869,776	1,889,857
Oxygen Flow Rate	lb/hr	400,438	423,938	457,774	469,915
CO2 Captured	lb/hr	0	1,023,964	1,126,092	1,136,804
CO2 Removal (%)		0.0	89.7	89.9	89.9

3. Conclusions

An ASPEN based process model has shown that a high temperature membrane separation system is competitive with the Selexol-based system. The advantages of the PBI membrane system is the preservation of the CO_2 stream at elevated pressures reducing the energy needed for compression to pipeline pressures. If H_2S remains with the CO_2 stream and can be sequestered, then the cost of electricity appears to be lower than Selexol-bsed separation systems.

4. Acknowledgements

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Table 3. Summary of Economic Estimates

Power Plant Cost Summary		**Scenario 1**	**Scenario 2**	**Scenario 4A**	**Scenario 4B**
Capacity Factor		80%	80%	80%	80%
Capital Charge Factor		17.5%	17.5%	17.5%	17.5%
20-year Levelization Factors					
Fuel		1.2022	1.2022	1.2022	1.2022
Non-Fuel Variable O&M		1.1568	1.1568	1.1568	1.1568
Fixed O&M		1.1568	1.1568	1.1568	1.1568
Plant Operating Life	years	30	30	30	30
Power Production @ 100% Capacity	GWh/yr	5,455	4,461	4,755	4,566
CO2 Captured (millons metric tonnes/year)		0.0	3.3	3.6	3.6
Power Plant Capital	c/kWh	4.50	6.19	5.53	6.26
Power Plant Fuel	c/kWh	1.90	2.47	2.54	2.68
Variable Plant O&M	c/kWh	0.78	1.00	0.95	0.98
Fixed Plant O&M	c/kWh	0.60	0.79	0.74	0.77
Power Plant Total	c/kWh	7.78	10.44	9.76	10.69
CO2 Transport	c/kWh	0.00	0.29	0.28	0.29
CO2 Storage	c/kWh	0.00	0.04	0.04	0.04
CO2 Monitoring	c/kWh	0.00	0.08	0.09	0.09
BOTTOM LINE TOTAL	c/kWh	**7.78**	**10.86**	**10.16**	**11.11**
Increase in COE (Over NETL Base)		-0.2%	39.3%	30.3%	42.4%
CO_2 Emissions	lb/MWh	1713	228	232	244
CO_2 Captured	$/Ton	n/a	30	23	30
Carbon Captured	$/Ton	n/a	112	84	111
CO_2 Avoided	$/Ton	n/a	50	39	54
Carbon Avoided	$/Ton	n/a	182	141	200

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