

Report Title

CO₂ Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO₂ Separation, Capture and Geologic Sequestration

Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel

Report Reference

1.2.1.1.6

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1.2.1.1.6.1 Abstract

The object of the Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel is to produce a detailed design of the membrane reactor that will allow a cost estimate to be constructed.

Structural design of a membrane which can be reproduced in large scale was the first item which was addressed. In Phase 1 only lab scale membranes were tested and a scale up of several orders of magnitude is required for the commercial reactor.

Structural analysis of the support structure for a hydrogen separation membrane for the MWGS reactor design was accomplished. Finite element analysis indicates that it is structurally adequate for 41.1 bar (600 psid) pressure loading at 450°C (842°F). A feasible membrane design has been established which can support the pressure, gravity, and differential thermal expansion loadings considered.

Conceptual design of the MWGS reactor is in progress. An analysis tool to permit examination of different arrangements for the MWGS reactor was developed which showed good agreement with the model developed in Phase 1. Four different flow arrangement options have been examined and conceptually sized to meet the performance and pressure drop requirements. These include:

- 1) Counter-Flow
- 2) Baffled Counter-Flow
- 3) Cross-Flow
- 4) Multi-Pass Cross-Flow

While the Counter-Flow option has the best efficiency, the Multi-Pass Cross-Flow option may be more practical for manufacture and assembly.

After final selection of a reactor arrangement, work will continue to finalize the design of the wafer membrane package, manifolds, and reactor vessel. The materials selection for the membrane support structure as well as other reactor components is on going. A study of the manufacturing processes for the membrane and vessel will then feed into a cost estimate of the reactor design, which will proceed in parallel with the design efforts.

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1.2.1.1.6.4 Introduction

The objective of the Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel project is to integrate a H₂ transfer membrane into a WGS reactor. The two products from this reactor will be 1) a high purity hydrogen stream which could be used in boilers and furnaces and 2) a concentrated, high pressure CO₂ stream which can be sent to sequestration.

The MWGS reactor would combine the WGS and CO₂ removal steps into one process. The potential benefits are lower capex and opex, and a simplified process. In addition, since the CO₂ is produced at an elevated pressure, sequestration compression costs will be lower.

The project will produce a detailed design of the membrane reactor that will allow a cost estimate to be constructed. The effort will require the following steps:

1. Structural design of a membrane which can be reproduced in large scale. The membrane work to date has been lab scale. A several order of magnitude increase in scale is required for the commercial size unit.
2. Examination of the reactor flow configuration. In phase 1 a model was developed for use in the process model. However the model does not allow for looking at the impact of flow configuration and stream pressure drop on performance.
3. Conceptual reactor design.
4. Detailed design and engineering.
5. Cost estimating.
6. Optimization. Once the cost elements are better understood, an optimization can be performed to see if there is a more optimum configuration than what was developed.

To date, items 1 through 3 have been substantially completed, with item 4 underway.

1.2.1.1.6.5 Executive Summary

The object of the Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel is to produce a detailed design of the membrane reactor that will allow a cost estimate to be constructed. The effort will require the following steps:

1. Structural design of a membrane which can be reproduced in large scale. The membrane work to date has been lab scale. A several order of magnitude increase in scale is required for the commercial size unit.
2. Examination of the reactor flow configuration. In phase 1 a model was developed for use in the process model. However the model does not allow for looking at the impact of flow configuration and stream pressure drop on performance.
3. Conceptual reactor design.
4. Detailed design and engineering.
5. Cost estimating.
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To date, items 1 through 3 have been substantially completed, with item 4 underway.

Structural design of a membrane which can be reproduced in large scale was the first item which was addressed. In Phase 1 only lab scale membranes were tested and a scale up of several orders of magnitude is required for the commercial reactor.

Structural analysis of the support structure for a hydrogen separation membrane for the MWGS reactor design was accomplished. A feasible membrane design has been established which can support the pressure, gravity, and differential thermal expansion loadings considered. Finite element analysis indicates that it is structurally adequate for 41.1 bar (600 psid) pressure loading at 450°C (842°F).

The following additional analyses are recommended:

- 1) Re-evaluation of the membrane stress when mechanical properties of the membrane material are available.
- 2) Analysis of the differential thermal expansion between the membrane and support structure. Substituting a support material with improved thermal expansion match may be warranted.
- 3) Natural frequency analyses of the wafer assembly.

Conceptual design of the MWGS reactor is in progress. An analysis tool to permit examination of different arrangements for the MWGS reactor was developed which showed good agreement with the model developed in Phase 1. Four different flow arrangement options have been examined and conceptually sized to meet the performance and pressure drop requirements. These include:

- 1) Counter-Flow
- 2) Baffled Counter-Flow
- 3) Cross-Flow
- 4) Multi-Pass Cross-Flow

The results are summarized in Table 1.2.1.1.6.5(1). Based on this study, a selection can be made for which arrangement is best suited to meet the requirements for the MWGS Reactor study and the design further developed.

Table 1.2.1.1.6.8(1) – Summary of Results for MWGS Reactor Performance Study

| Arrangement Option | Membrane Required m ² | Permeate Flow Path m | Feed Flow Path m | Plate Pitch cm | Number of Stacks | Wafers per Stack | Stack Height m | Package Width m | Package Length m | Total Package Volume m ³ |
|-------------------------|-------------------------------------|-------------------------|---------------------|-------------------|------------------|------------------|-------------------|--------------------|---------------------|--|
| 1a) Counter Flow | 11,512 | 15.2 | 15.2 | 3.88 | 13 | 105 | 4.08 | 3.96 | 15.24 | 247 |
| 1b) Counter Flow | 11,512 | 15.2 | 15.2 | 3.23 | 12 | 114 | 3.69 | 3.66 | 15.24 | 206 |
| 2) Baffled Counter Flow | 11,512 | 15.2 | 22.9 | 1.93 | 7 | 196 | 3.78 | 3.26 | 15.24 | 188 |
| 3) Multipass Cross Flow | 12,544 | 3.0 | 15.2 | 1.93 | 50 | 150 | 2.90 | 3.05 | 22.86 | 202 |
| 4) Cross Flow | 14,062 | 3.0 | 15.2 | 1.52 | 50 | 168 | 2.56 | 3.05 | 23.47 | 183 |

While the Counter-Flow option has the best efficiency, the Multi-Pass Cross-Flow option may be more practical for manufacture and assembly.

After final selection of a reactor arrangement, work will continue to finalize the design of the wafer membrane package, manifolds, and reactor vessel. The materials selection for the membrane support structure as well as other reactor components is on going. A study of the manufacturing processes for the membrane and vessel will then feed into a cost estimate of the reactor design, which will proceed in parallel with the design efforts.

1.2.1.1.6.6 Experimental

No experimental apparatus was used in this study.

1.2.1.1.6.7 Results and Discussion

1.2.1.1.6.7.1 Structural Analysis of Hydrogen Separation Membrane

Structural analysis of the support structure for a hydrogen separation membrane was accomplished. The analysis considered pressure, gravity, and differential thermal expansion loading. Designs that satisfy stress and instability constraints for several permeate gap heights were found. The details of the structure are considered to be proprietary in nature so are not included here.

1.2.1.1.6.7.2 MWGS Reactor Performance

1.2.1.1.6.7.2.1 MWGS Reactor Performance Model

A simple model of the MWGS reactor was developed to facilitate design activities and sensitivity studies of important design parameters. The model included:

- Membrane kinetics based on Phase I results
- Catalyst kinetics for a commercially available bulk catalyst
- Heat transfer between the feed and permeate streams

A comparison of the output from this model (SOFCo) was compared to the output from the ASPEN based model developed in Phase I of the program. The results, summarized in Table 1.2.1.1.6.7(1), show the agreement is adequate for design purposes.

Improvement in catalyst activity and membrane H₂ flux rates warrant raising the inlet temperature to the MWGS reactor from the current value of 315°C up to 400°C (as shown in Table 1.2.1.1.6.7(1)). Because the temperature exiting the bulk WGS reactor is at 450°C and requires cooling to get down to 315°C, this is a simplification to the process as well. The benefit of the increased temperature would be on the order of 30% less surface area required, with even greater potential reductions in catalyst volume.

Table 1.2.1.1.6.7(1) – Comparison of SOFCo MWGS Model Output to ASPEN Model

| | Baseline 315°C | | | 400°C Case 1 | | | 400°C Case 2 | | |
|---|----------------|--------|--------------|--------------|--------|---------------|--------------|--------|---------------|
| | Aspen | SOFCo | % Diff | Aspen | SOFCo | % Diff | Aspen | SOFCo | % Diff |
| Operating Conditions | | | | | | | | | |
| Membrane Area, m ² | 17,325 | 17,325 | | 11,410 | 11,410 | | 11,780 | 11,780 | |
| Catalyst Volume to Area, m ³ /m ² | 0.100 | 0.100 | | 0.005 | 0.005 | | 0.005 | 0.005 | |
| Nitrogen Sweep Gas, kmol/hr | 9,100 | 9,100 | | 9,100 | 9,100 | | 9,100 | 9,100 | |
| Steam Sweep Gas, kmol/hr | 8,800 | 8,800 | | 8,800 | 8,800 | | 10,200 | 10,200 | |
| Feed Side Pressure, bara | 35.00 | 32.20 | | 32.20 | 32.20 | | 32.20 | 32.20 | |
| Sweep Side Pressure, bara | 3.00 | 3.35 | | 3.35 | 3.35 | | 3.35 | 3.35 | |
| Performance Comparisons | | | | | | | | | |
| Average H ₂ Flux (mol/m ² -sec) | 0.186 | 0.185 | -0.4% | 0.275 | 0.277 | 0.7% | 0.272 | 0.274 | 0.6% |
| H ₂ Recovery, % | 95.3% | 95.0% | -0.3% | 93.3% | 93.9% | 0.7% | 95.2% | 95.7% | 0.5% |
| CO ₂ Purity (dry) | 90.2% | 88.90% | -1.3% | 86.86% | 86.84% | 0.0% | 90.04% | 89.97% | -0.1% |
| CO Out, PPM | 995 | 1,000 | -0.5% | 3,000 | 4,077 | -35.9% | 2,000 | 3,063 | -53.1% |
| Permeate Outlet Temp, °C | 347.5 | 346.5 | 0.3% | 419.9 | 417.3 | 0.6% | 421.9 | 420.4 | 0.4% |
| Retentate Outlet Temp, °C | 327.7 | 329.0 | -0.4% | 421.8 | 422.7 | -0.2% | 418.0 | 418.9 | -0.2% |

1.2.1.1.6.7.2.2 Pressure Drop Performance

The reactor flow conditions are shown in Table 1.2.1.1.6.7(2). Note that the outlet conditions are dependent on the particular reactor flow configuration, shown here are for a cross-flow configuration. On the feed/retentate side of the reactor, the allowable pressure drop was specified as 2.76 bar (40 psid). On the sweep/permeate side of the reactor, the allowable pressure drop was specified as 0.34 bar (5 psid).

Table 1.2.1.1.6.7(2) – Flow Streams for MWGS Reactor

| Flow Stream | Temperature | Pressure | Constituent | Mole Flow (kmol/hr) | |
|-------------|-------------------------|------------------------------|------------------|---------------------|-----------|
| | | | | In | Out |
| Sweep Side | 400°C in 417.8°C out | 3.34 bara in 3.0 bara out | H ₂ | 0 | 11,592 |
| | | | H ₂ O | 8,800 | 8,800 |
| | | | N ₂ | 9,100 | 9,100 |
| Feed Side | 400°C in 425.3°C out | 35 bara in 32.2 bara out | CO | 908.434 | 43.711 |
| | | | H ₂ O | 10,135.650 | 9,270.927 |
| | | | H ₂ | 11,222.230 | 543.301 |
| | | | CO ₂ | 4,837.563 | 5,702.286 |
| | | | N ₂ | 34.561 | 34.561 |
| | | | CH ₄ | 3.474 | 3.474 |
| | | | Other | 8.409 | 8.409 |

1.2.1.1.6.7.2.2.1 Feed/Retentate Pressure Drop

The feed/retentate side pressure drop is a function of how catalyst is packaged in the reactor and the spacing between membrane wafers assemblies. Catalyst can be included by:

- Placing catalyst between the membrane wafer plates
- Placing catalyst between stages of reactor membranes
- Some combination of between wafers and between stages

The packaging of the membrane is conceptualized as some number of stages down the flow direction of the reactor. This determines the amount of flow per unit area, which is inversely proportional to the number of stages. As the number of stages increases, the flow per unit area increases as well as the length of the flow path. To meet the pressure drop target, the gap height must be increased as the number of stages is increased. In this initial stage, a flow path length of 15.24 meters (50 feet) was targeted while considering the different configuration options. The gap between the membranes was varied as needed to meet the pressure drop target. Additional optimization of the length will be performed after initial cost estimates are developed.

1.2.1.1.6.7.2.2.2 Sweep/Permeate Side Pressure Drop Performance

On the sweep side, the pressure drop target is met by increasing the height of the membrane support structure inside of the wafer. A reactor arrangement which accommodates counter-flow would require a flow path of 15.24 meters (50 feet).

1.2.1.1.6.7.2.3 MWGS Reactor Performance Results

Using the MWGS reactor model, a number of studies were performed to examine the required amount of membrane and catalyst for different conditions and reactor arrangements. Four different configurations have been considered:

- 1) Counter-Flow
- 2) Baffled Counter-Flow
- 3) Cross-Flow
- 4) Multi-Pass Cross-Flow

For each of these cases, the membrane configuration was based upon a premise of a .305 m (1 foot) wide membrane between 3.05 and 15.2 m (10 to 50 feet) long. The performance of each arrangement and its resulting reactor size is discussed below.

1.2.1.1.6.7.2.3.1 Counter-Flow Arrangement

A counter-flow arrangement is the baseline case studied in Phase 1. A schematic of how that would look is shown in Figure 1.2.1.1.6.7(3). The membrane wafers were assumed to be 15.2 m long (50 feet). An internal gap of 12.7 mm (0.5 in) is required on the permeate side to meet the sweep side pressure drop requirement. Two sub-cases were examined:

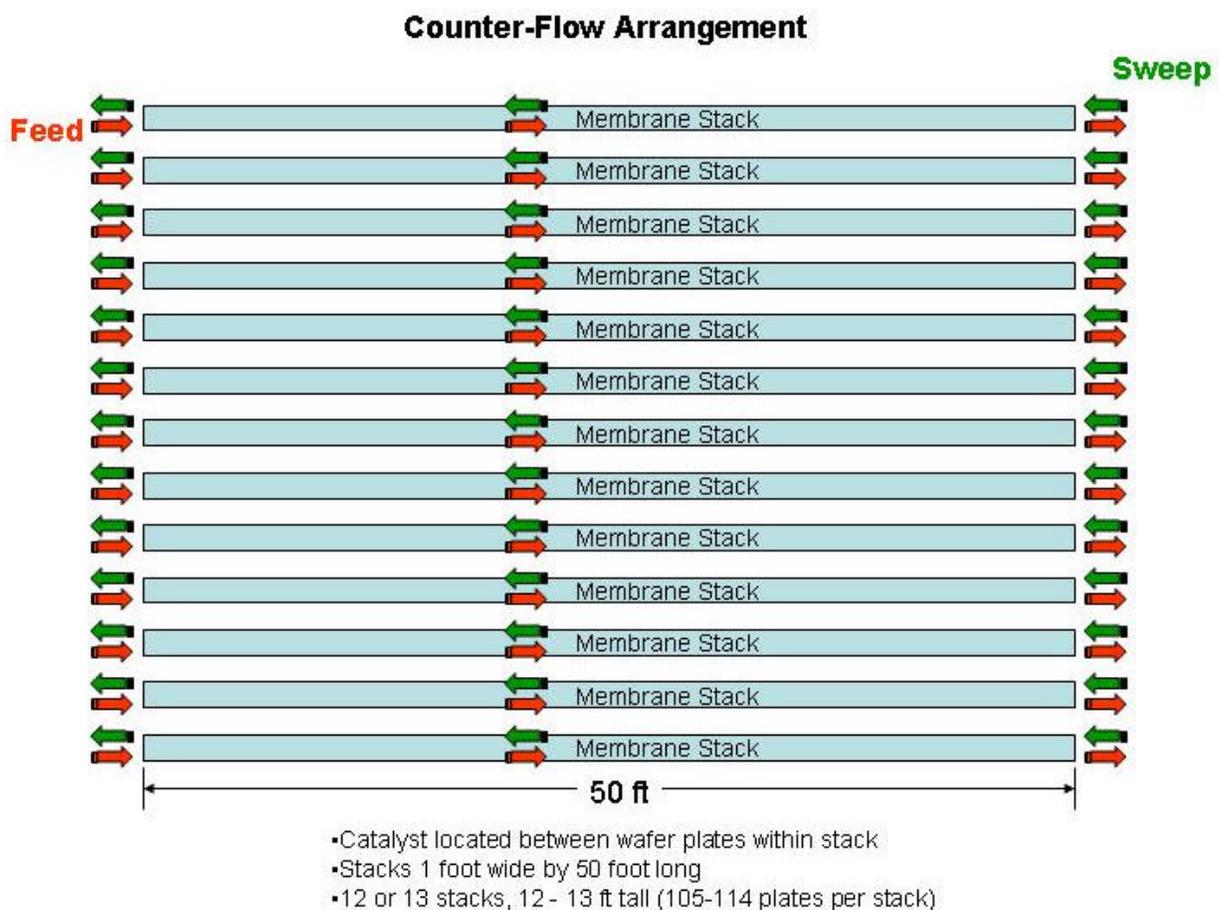


Figure 1.2.1.1.6.7(3)– Schematic of Counter-Flow MWGS Reactor Arrangement

- 1a) The gap between the plates is filled of catalyst
- 1b) The gap between the plates is partially filled with catalyst

The reason for 1b) was to only include the required amount of catalyst and thus reduce the pressure drop and plate spacing required.

The reactor performance profiles are shown for this case in Figures 1.2.1.1.6.7(4) and 1.2.1.1.6.7(5). The performance for this case was the best in terms of the amount of Vanadium required. The total active membrane surface required was 11,512 m². Due to having catalyst between the membranes, a large space is required between the membrane wafers, at 3.88 cm (1.53 inches). The package size required for the membrane and catalyst is 13 stacks wide, each 15.2 meters (50 feet) long and 4.1 meters (13.4 feet) tall. The total volume is 247 m³. The total number of wafers is 1240, each 15.2 meters long by .305 meters wide.

Advantages and Disadvantages - The counter flow arrangement is the most efficient in terms of membrane surface required. As this will likely be the primary cost driver, this is a very important item. This arrangement is the least efficiently packaged, however, because of the large space required between the plates for catalyst. It should be pointed out that the process of assembling such large quantities of membrane with catalyst between them may be challenging. This led to the idea of counter-flow concept 1b, in which the gap is not completely filled with catalyst, but only the required volume of catalyst is used. This results in a slightly smaller package at 12 stacks wide, each 15.2 meters (50 feet) long and 3.7 meters (12.1 feet) tall. The total volume is 206 m³. The total number of wafers remains 1240.

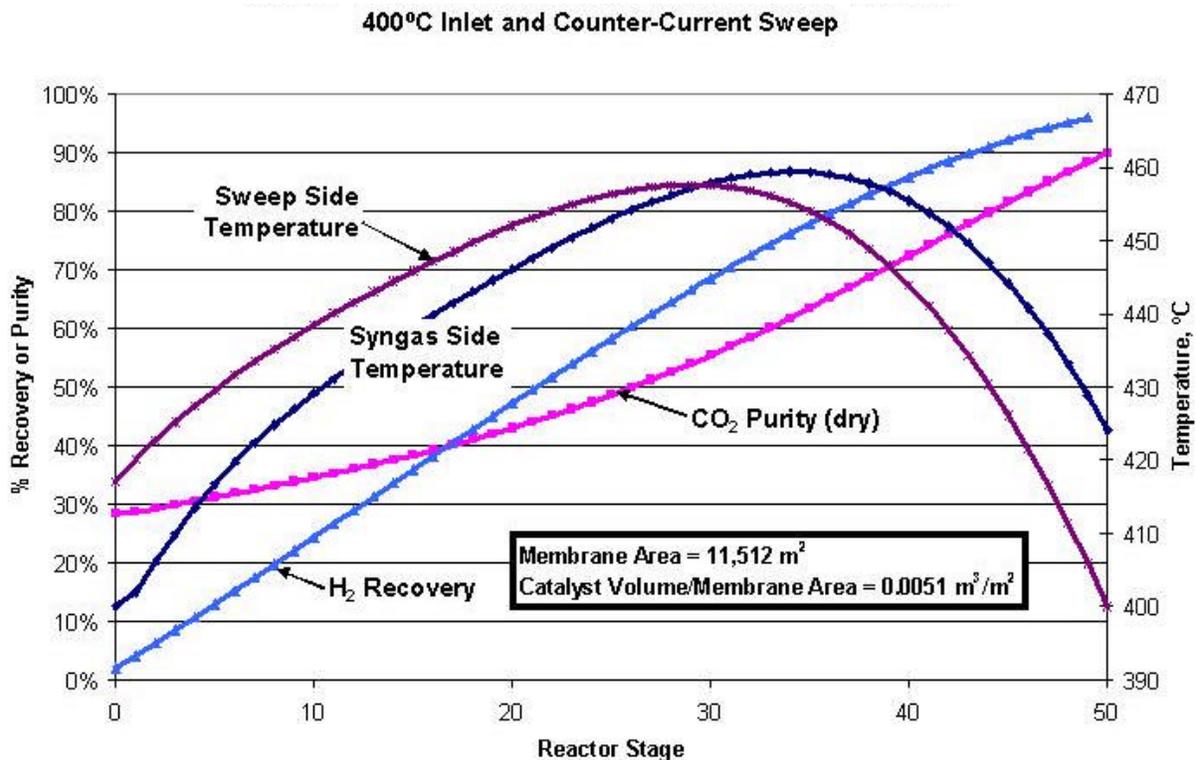


Figure 1.2.1.1.6.7(4)– Counter-Flow MWGS Reactor Temperature and Recovery Profiles

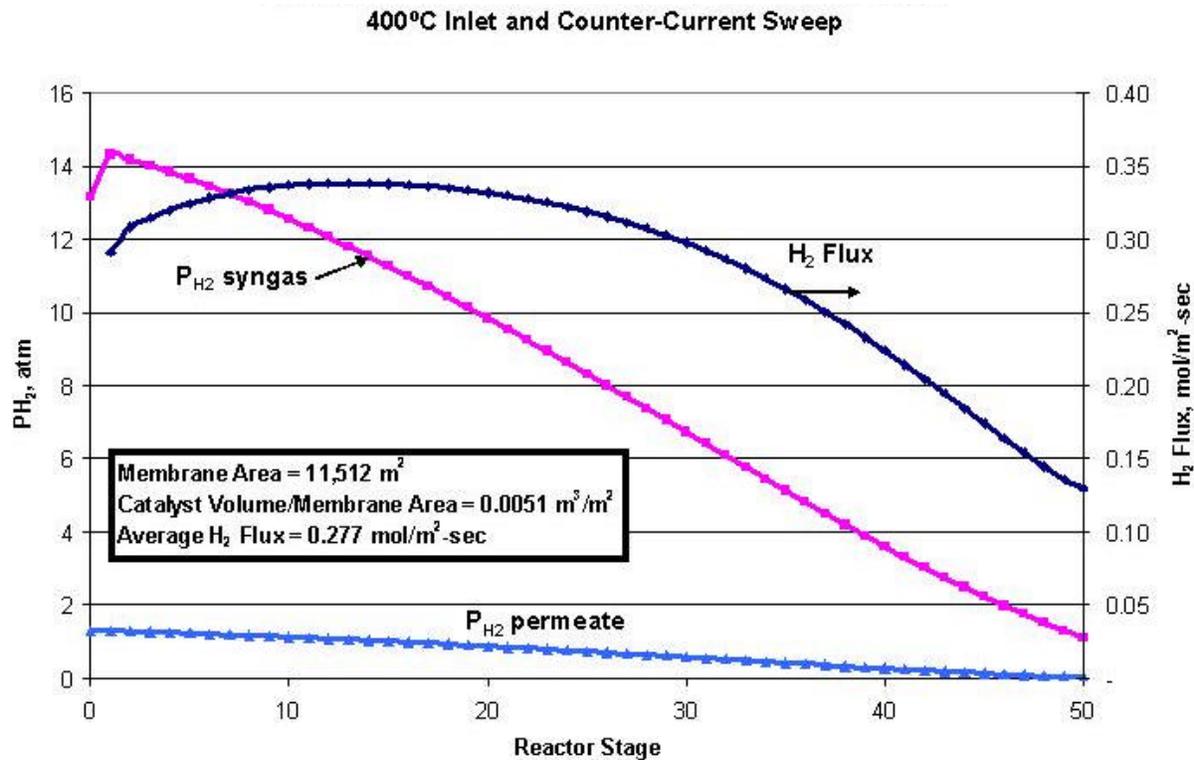


Figure 1.2.1.1.6.7(5)– Counter-Flow MWGS Reactor Partial Pressure and H₂ Flux Profiles

1.2.1.1.6.7.2.3.2 Baffled Counter-Flow Arrangement

To better facilitate catalyst placement within the reactor, an arrangement was conceived which places the catalyst outside of the membrane stacks. In order to keep a flow pattern which is still basically counter-flow, the feed flow is baffled back and forth across the membrane stacks. It was assumed that the performance would be essentially the same as that seen for the pure counter-flow case. This arrangement is shown in Figure 1.2.1.1.6.7(6).

In this arrangement, the amount of area for catalyst transverse to the flow is increased. This allows for lower velocities and shorter path length, both of which reduce the pressure drop. As such, the spacing between membranes is reduced and the overall package size is considerably smaller. The resulting package consists of 7 stacks, each 15.2 meters (50 feet) long and 3.8 meters (12.4 feet) tall. The total volume is 188 m³. The total number of wafers is 1240, each 15.2 meters long by .305 meters wide.

Advantages and Disadvantages - What this arrangement gains in practicality for catalyst placement it gives back up by adding a multitude of baffle plates. And while these would not need to be leak tight their assembly between the 1240 wafers would not be trivial.

Baffled Counter-Flow Arrangement

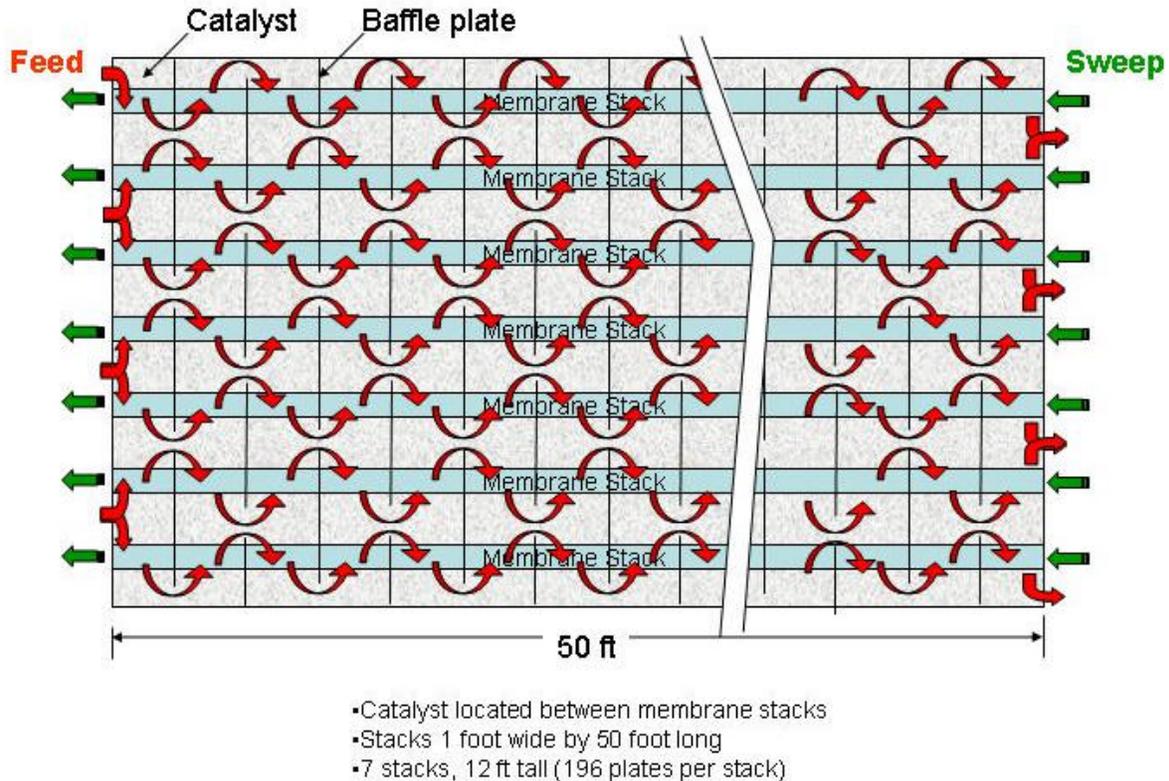


Figure 1.2.1.1.6.7(6)– Schematic of Baffled Counter-Flow MWGS Reactor Arrangement

1.2.1.1.6.7.2.3.3 Cross-Flow Arrangement

A cross-flow arrangement (Figure 1.2.1.1.6.7(7)) is likely the easiest to assemble. For this case the arrangement was assumed to consist of 50 stacks, each 3.05 meters (10 feet) long and 0.305 meters (1 foot) wide. The catalyst placement is made between wafer stacks. The manifolds for the sweep and feed sides are easily connected and distributed. Because the permeate flow path is now shortened, the size of the permeate side gap can be reduced.

The performance of this arrangement is shown in Figures 1.2.1.1.6.7(8) and 1.2.1.1.6.7(9). As shown, the required amount of membrane area increases by 22% up to 14,062 m². This is due to the lower H₂ flux caused by the reduced average P_{H₂} differential caused by the cross-flow arrangement. The resulting package (meeting all pressure drop criteria) consists of 50 stacks, each 3.05 meters (10 feet) long and 2.6 meters (8.4 feet) tall. The total volume is 183 m³. The total number of wafers is 7568.

Advantages and Disadvantages - The advantage of this arrangement is its simplicity of assembly and smallest package size. The efficient packing is possible because of the reduced permeate side gap (2.54 mm compared to 12.7 mm for the other designs).

The 22% increase in membrane area is a major concern. Because the membrane cost may be the majority of the MWGS reactor cost, minimizing this is a primary concern.

Figure 1.2.1.1.6.7(7)– Schematic of Cross-Flow MWGS Reactor Arrangement

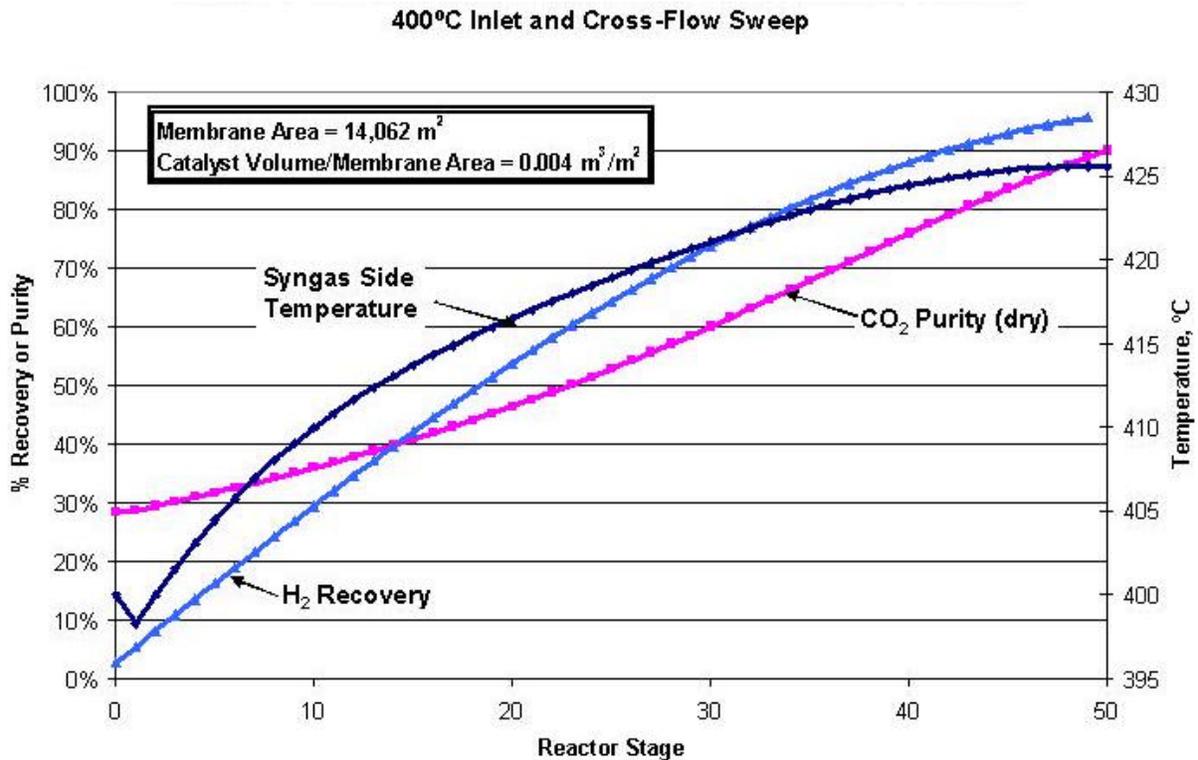
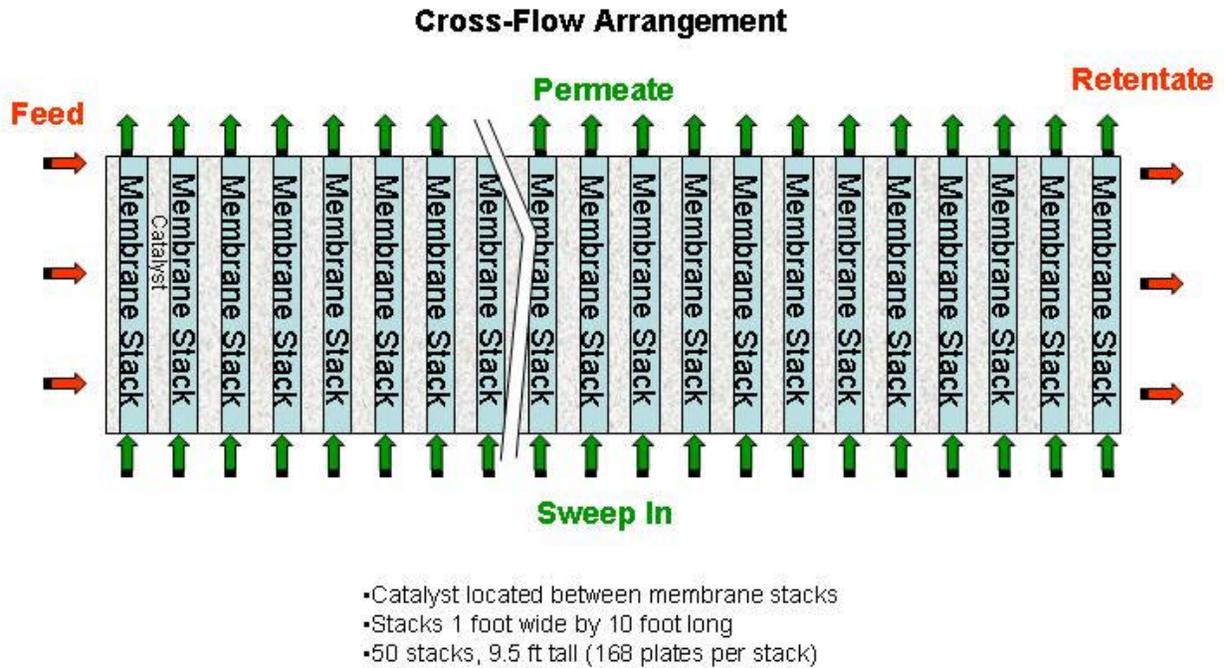


Figure 1.2.1.1.6.7(8)– Cross-Flow MWGS Reactor Temperature and Recovery Profiles

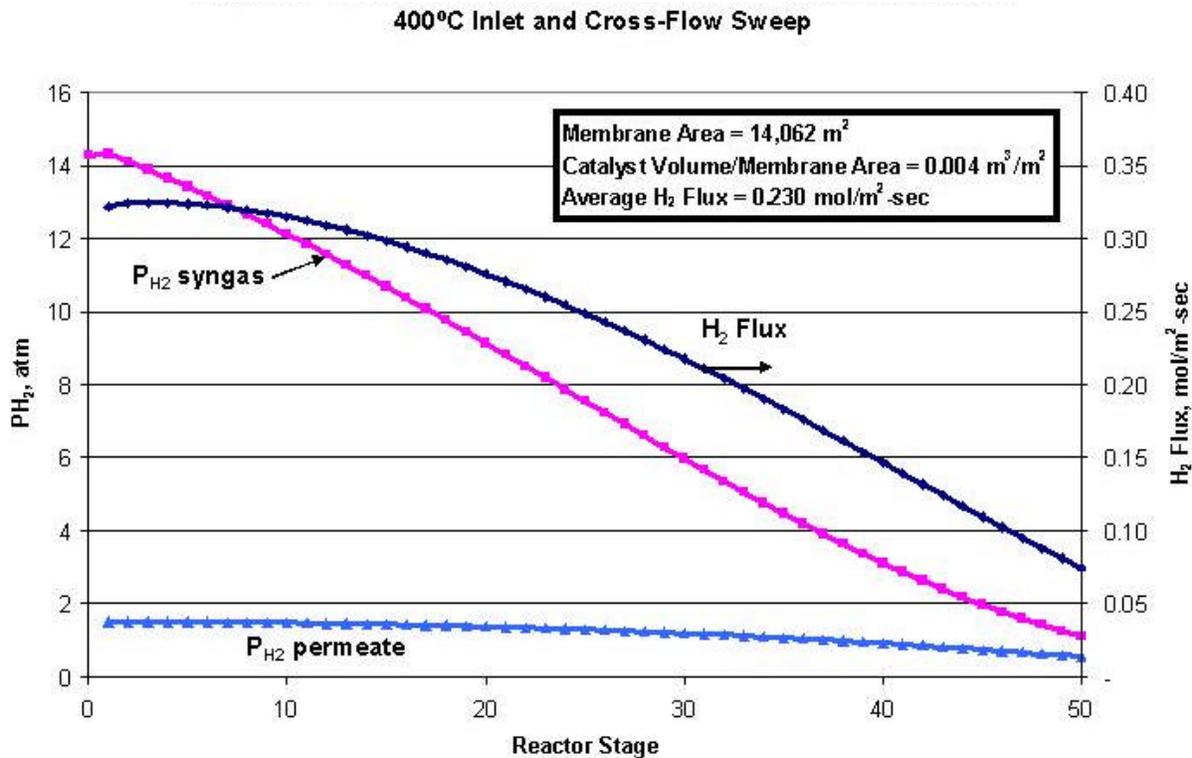


Figure 1.2.1.1.6.7(9) – Cross-Flow MWGS Reactor Partial Pressure and H₂ Flux Profiles

1.2.1.1.6.7.2.3.4 Multi-Pass Cross-Flow Arrangement

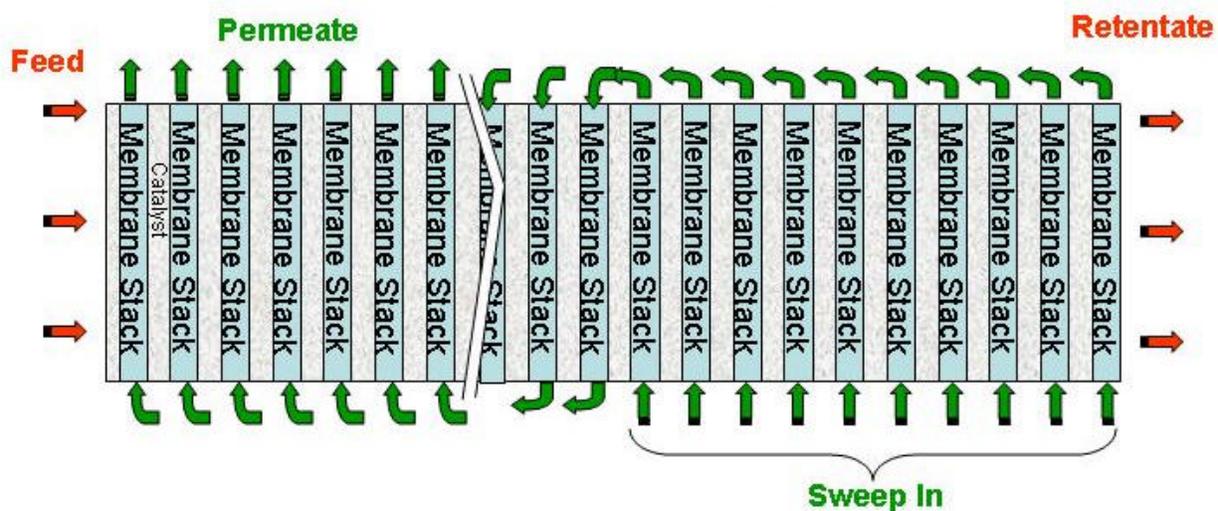
A final arrangement was examined which combined the flow direction and manifolding of the cross-flow into more of a counter flow arrangement as shown in Figure 1.2.1.1.6.7(10). Again 50 stacks are used, each 3.05 meters (10 feet) long and 0.305 meters (1 foot) wide. The catalyst placement is made between wafer stacks.

The permeate side flow gap was increased back to 12.7 mm (0.5 in) to allow the permeate flow to traverse 15.2 m (50 feet). The sweep/permeate gas makes a total of 5 passes through the membrane stacks. The result is a more efficient use of membrane area which still retains some of the packaging advantages of the cross-flow arrangement.

The performance for this arrangement is shown in Figures 1.2.1.1.6.7(11) and 1.2.1.1.6.7(12). The effects of five sweep passes can be seen distinctly in Figure 17. As shown, the required amount of membrane area increases by 9% compared to the counter-flow case up to 12,544 m². The resulting package (meeting all pressure drop criteria) consists of 50 stacks, each 3.05 meters (10 feet) long and 2.9 meters (9.5 feet) tall. The total volume is 202 m³. The total number of wafers is 6751.

Advantages and Disadvantages - The cross-flow arrangement facilitates a simpler reactor assembly and catalyst placement between membrane stacks. The multi-pass arrangement provides better efficiency in terms of membrane surface required compared to the cross-flow case. The package size is about 10% larger than the cross-flow and baffled counter-flow cases.

Multi-Pass Cross-Flow Arrangement



- Catalyst located between membrane stacks
- Stacks 1 foot wide by 10 foot long
- 50 stacks, 8.4 ft tall (150 plates per stack)

Figure 1.2.1.1.6.7(10) – Schematic of Multi-Pass Cross-Flow MWGS Reactor Arrangement

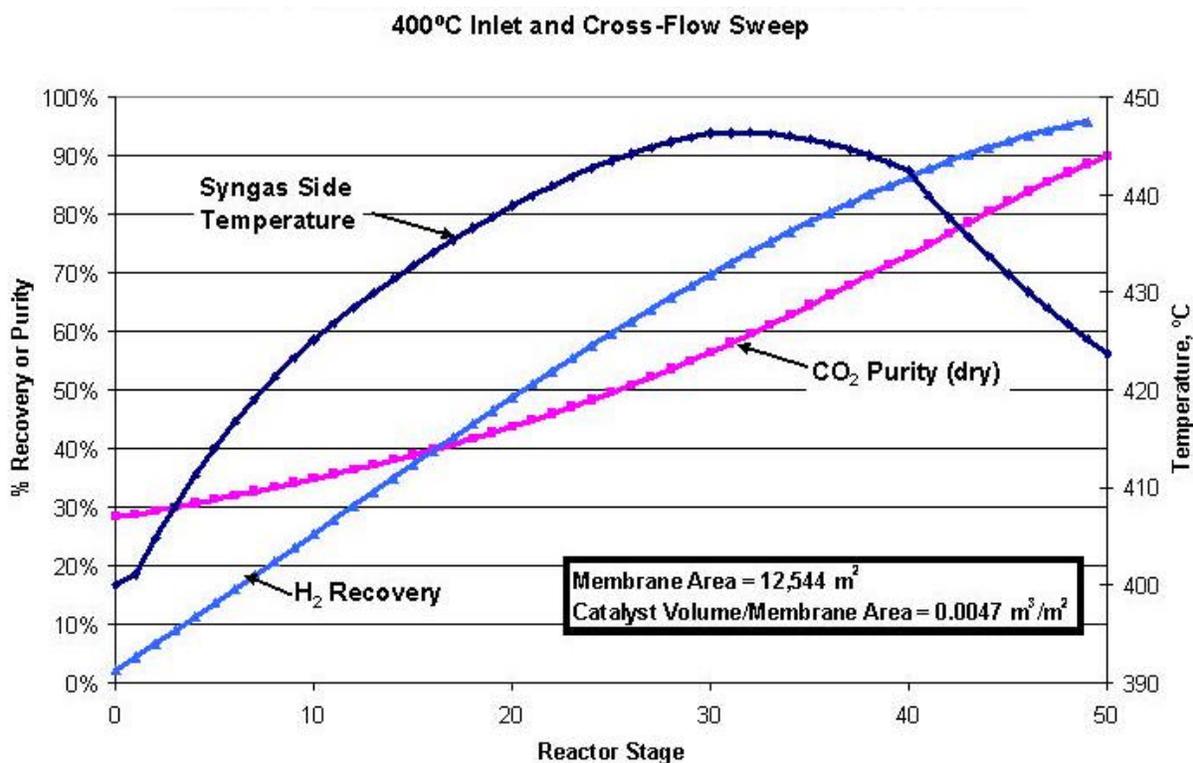


Figure 1.2.1.1.6.7(11) – Multi-Pass Cross-Flow MWGS Reactor Temperature and Recovery Profiles

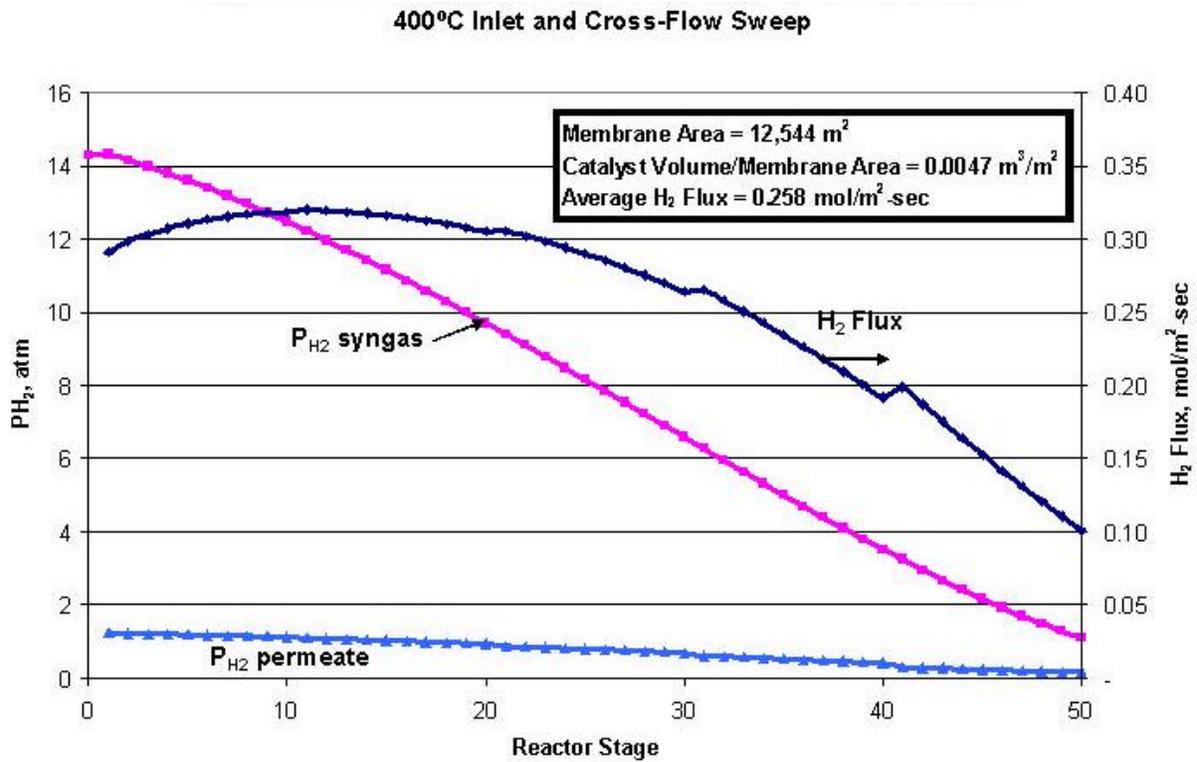


Figure 1.2.1.1.6.7(12) – Multi-Pass Cross-Flow MWGS Reactor Partial Pressure and H₂ Flux Profiles

1.2.1.1.6.7.3 Future Work

After final selection of a reactor arrangement, work will continue to finalize the design of the wafer membrane package, manifolds, and reactor vessel. The materials selection for the membrane support structure as well as other reactor components is on going. A study of the manufacturing processes for the membrane and vessel will then feed into a cost estimate of the reactor design, which will proceed in parallel with the design efforts.

1.2.1.1.6.8 Conclusion

Structural analysis of the support structure for a hydrogen separation membrane for the MWGS reactor design was accomplished. A feasible membrane design has been established which can support the pressure, gravity, and differential thermal expansion loadings considered. Finite element analysis indicates that it is structurally adequate for 41.1 bar pressure loading at 450°C.

The following additional analyses are recommended:

- 1) Re-evaluation of the membrane stress when mechanical properties of the vanadium alloy membrane material are available.
- 2) Analysis of the differential thermal expansion between the membrane and support structure. Substituting a support material with improved thermal expansion match may be warranted.
- 3) Natural frequency analyses of the wafer assembly.

Conceptual design of the MWGS reactor is in progress. An analysis tool to permit examination of different arrangements for the MWGS reactor was developed. Four different flow arrangement options have been examined and conceptually sized to meet the performance and pressure drop requirements.

The results presented above are summarized in Table 1.2.1.1.6.8(1). Based on this study, a selection can be made for which arrangement is best suited to meet the requirements for the MWGS Reactor study and the design further developed.

Table 1.2.1.1.6.8(1)– Summary of Results for MWGS Reactor Performance Study

| Arrangement Option | Membrane Required m ² | Permeate Flow Path m | Feed Flow Path m | Plate Pitch cm | Number of Stacks | Wafers per Stack | Stack Height m | Package Width m | Package Length m | Total Package Volume m ³ |
|-------------------------|-------------------------------------|-------------------------|---------------------|-------------------|------------------|------------------|-------------------|--------------------|---------------------|--|
| 1a) Counter Flow | 11,512 | 15.2 | 15.2 | 3.88 | 13 | 105 | 4.08 | 3.96 | 15.24 | 247 |
| 1b) Counter Flow | 11,512 | 15.2 | 15.2 | 3.23 | 12 | 114 | 3.69 | 3.66 | 15.24 | 206 |
| 2) Baffled Counter Flow | 11,512 | 15.2 | 22.9 | 1.93 | 7 | 196 | 3.78 | 3.28 | 15.24 | 188 |
| 3) Multipass Cross Flow | 12,544 | 3.0 | 15.2 | 1.93 | 50 | 150 | 2.90 | 3.05 | 22.86 | 202 |
| 4) Cross Flow | 14,062 | 3.0 | 15.2 | 1.52 | 50 | 168 | 2.56 | 3.05 | 23.47 | 183 |

After final selection of a reactor arrangement, work will continue to finalize the design of the wafer membrane package, manifolds, and reactor vessel. The materials selection for the membrane support structure as well as other reactor components is on going. A study of the manufacturing processes for the membrane and vessel will then feed into a cost estimate of the reactor design, which will proceed in parallel with the design efforts.

1.2.1.1.6.9 References

None applicable.

1.2.1.1.7 Development of Gasification Process Incorporating Membrane Water Gas Shift Reactor for Producing Hydrogen Fuel With CO₂ Capture

Report Title

CO₂ Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO₂ Separation, Capture and Geologic Sequestration

Development of Gasification Process Incorporating Membrane Water Gas Shift Reactor for Producing Hydrogen Fuel with CO₂ Capture

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1.2.1.1.7.1 Abstract

Phase II for this project developed a conceptual process design case for a gasification plant with a Membrane Water Gas Shift Reactor for the separation of hydrogen. This work was commissioned by the Pre-Combustion team of the CO₂ Capture Project (CCP), a consortium of eight energy companies (British Petroleum, ChevronTexaco, ENI, Norsk Hydro, EnCana, Shell, Statoil, and Suncor Energy).

The scope of this study (Phase II) is to determine the performance of a gasification plant with a Membrane Water Gas Shift (MWGS) reactor, which separates hydrogen from a sweet syngas, for an European Refinery scenario. The recovered hydrogen is sent to the existing refinery furnaces and boilers that produce a carbon dioxide-free flue gas. The remaining stream (retentate) is mostly carbon dioxide and is sent to geologic formations for storage. Electrical power required to operate the plant is provided by a natural gas fired combined cycle power plant.

The work is currently in progress and preliminary deliverables (design basis, summary block flow diagram, selected preliminary process flow diagrams and selected process descriptions) are provided in this semi-annual report.

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1.2.1.1.7.4 Introduction

1.2.1.1.7.4.1 Project Background

Eight energy companies (British Petroleum, ChevronTexaco, ENI, Norsk Hydro, EnCana, Shell, Statoil, and Suncor Energy) have joined together to form the CO₂ Capture Project (CCP). CCP intends to address the issue of reducing emissions in a manner that will contribute to an environmentally acceptable and competitively priced continuous energy supply for the world. The goals of the CCP include:

- Reduce the cost of carbon dioxide capture
- Develop methods for safe underground, carbon dioxide storage
- Participate with government and non-government organizations, and other stakeholders to deliver technology that is cost-effective and meets the needs of society.

The CCP seeks to develop technologies to the ‘proof of concept’ stage by the end of 2003. Thereafter, demonstration tests can be conducted to verify performance and cost estimates, and a large-scale application could be in operation before 2010.

In addition to CCP, support is also provided by the United States (U.S.) Department of Energy, the European Union, and Norway for the reduction of carbon dioxide emissions.

CCP is divided into the following specialized teams:

- Post-Combustion – Carbon dioxide is removed from the exhaust gas from furnaces, boilers, combustion turbines, etc. This technology is commercially proven and can be retrofitted to existing equipment.
- Pre-Combustion – Carbon is removed from the fuel gas before combustion in furnaces, boilers and combustion turbines.
- Oxyfuels – Oxygen is separated from air and is used to combust hydrocarbons to produce an exhaust containing carbon dioxide and water (no nitrogen). The water can be easily condensed, leaving a highly concentrated carbon dioxide stream for storage.

CCP has identified four different scenarios, which represent existing or future planned facilities, for carbon dioxide capture technologies. This allows the technologies to be evaluated under “real” conditions, and the suitability of a technology to a variety of situations/conditions can be identified. These scenarios are:

- Norcap – A natural gas-fired 400 MWe combined-cycle power plant
- Alaska – Multiple, distributed small/medium simple cycle combustion turbines driving process compressors
- Canadian Tar Sands Complex - Petroleum coke gasification plant supplying hydrogen, steam and electrical power.
- European Refinery – Multiple refinery heaters (furnaces) and boilers fired with sulfur-containing residual fuel oil, refinery fuel gas and natural gas.

Baseline studies shall be developed for each distinct scenario and individual site-specific requirements to provide input to an economic model. The economic model will be used to prioritize and measure the extent of cost savings for future technology development options.

1.2.1.1.7.4.2 Scope of Work

The scope of this study (Phase II) is to determine the performance of a gasification plant with a Membrane Water Gas Shift (MWGS) reactor, which separates hydrogen from a sweet syngas, for the European Refinery scenario. The recovered hydrogen is sent to the existing refinery furnaces and boilers that produce a carbon dioxide-free flue gas. The remaining stream (retentate) is mostly carbon dioxide and is sent to geologic formations for storage. Electrical power required to operate the plant is provided by a natural gas fired combined cycle power plant.

In Phase I of this study, four membrane vendors were chosen by CCP to be evaluated:

- Proton-conducting metal ceramic composite membrane provided by Eltron Research Inc.
- Palladium alloy membrane provided by Colorado School of Mines (Chemical Engineering and Petroleum Refining Department) in partnership with TDA Research, Inc.
- Microporous silica membrane provided by Energy research Centre of the Netherlands (ECN)
- Zeolite membrane provided by University of Cincinnati

The results of Phase I show that the metal ceramic composite membrane was the only membrane to meet the carbon recovery target set by the project (due to high CO₂/H₂ permselectivity). Therefore, CCP decided that Phase II will be based on the metal ceramic composite membrane fed with a sulfur-free syngas. (The sulfur tolerant MWGS reactor was not pursued due to low hydrogen flux when sulfur compounds were present.) Note that the gasification plant configuration was revised from Phase I to Phase II by incorporating a sulfur removal system upstream of the MWGS reactor in order for the hydrogen sulfide and carbonyl sulfide content in the feed to the MWGS reactor to be less than a 10 ppmv.

Following is a summary of the major activities for the Phase II of this study:

Eltron Research Inc.

- Develop a laboratory proof-of-concept MWGS reactor.

SOFCo

- Design and estimate the cost of a commercial scale MWGS reactor.

Fluor

- Develop a design basis for the project
- Design the gasification plant for a sweet syngas feed to the metal ceramic composite membrane WGS reactor.
- Incorporate design considerations into the gasification plant based on input from SOFCo.
- Develop a block flow diagram
- Estimate the plant performance.
- Develop process descriptions
- Develop process flow diagrams.
- Estimate heat and material balance of the entire plant.
- Develop sized equipment list.
- Develop utility summary.
- Prepare a report.

The results of the process design effort are/will be presented in the following deliverables:

- Design basis
- Summary block flow diagram
- Preliminary process flow diagrams

- Brief process descriptions
- Preliminary process flow diagrams
- Heat and material balances
- Preliminary equipment lists with approximate sizes
- Utility summary

1.2.1.1.7.4.3 Scope of Facilities

The IGCC plant consists of the following units:

- Air Separation Unit
- Gasification Island
- Low Temperature Gas Cooling and COS Hydrolysis Unit
- Condensate (Ammonia) Stripper Unit
- Acid Gas Removal Unit
- Sulfur Recovery (Claus) and Tailgas Treating Unit
- Fuel Gas Saturation/Sweet Shift Unit
- Membrane Water Gas Shift Reactor
- Permeate and Retentate Cooling Unit
- CO₂ Compression/Dehydration Unit
- Power Generation
- Utilities & supporting systems include:
 - Natural gas supply
 - Demineralized water package
 - Cooling water package
 - Potable water package
 - Oily water separator
 - Fire protection and monitoring systems
 - Back-up plant and instrument air package
 - Wastewater treatment package (includes drains and sewer)
 - Flare system
 - Miscellaneous material handling system
 - Electrical distribution
 - Uninterruptible power supply (UPS)
 - Generator step-up transformer
 - Continuous emissions monitoring system (CEMS)
 - Distributed control system (DCS)
 - Interconnecting piping
 - Other supporting facilities (Process analyzers; Hazardous gas detection system; Communications; Control room; Maintenance, warehouse and administration facility; Laboratory for inspection, certification and process control; Turbine building; Overhead turbine crane; Heating, ventilation and air conditioning (HVAC) systems; and Roads, parking, fencing and lighting)

1.2.1.1.7.5 Executive Summary

1.2.1.1.7.5.1 Facility Summary Description

The MWGS Reactor case is based on feeding residual oil and refinery fuel gas to produce a hydrogen rich fuel (carbon-free fuel) for the use in the existing refinery and petrochemicals furnaces and heaters at the European refinery. The syngas from the gasifier is cleaned of particulates, carbonyl sulfide (COS) and hydrocyanic acid (HCN) are removed or destroyed, and the syngas is cooled to a temperature suitable for the Acid Gas Removal (AGR) unit. Sulfur compounds are removed in the AGR and recovered as elemental sulfur product in the Sulfur Recovery unit.

The clean fuel gas is saturated with water and fed to a bulk shift catalyst where the carbon monoxide and water are converted to hydrogen and carbon dioxide. The partially shifted syngas is then fed to the membrane water gas shift (MWGS) reactor system, which provides additional conversion of the remaining carbon monoxide and separates the product hydrogen from the product carbon dioxide. The hydrogen rich stream is cooled to condense and separate the water from the gas then fired in the existing equipment producing a flue gas, which is relatively free of carbon dioxide. The carbon dioxide rich stream from the MWGS reactor is cooled, compressed and dehydrated for geologic sequestration. The target carbon dioxide purity is 90 mol%, dry.

1.2.1.1.7.5.2 Membrane Water Gas Shift Concept

The concept for the MWGS reactor is shown in Figure 1.2.1.1.7.5.2(1).

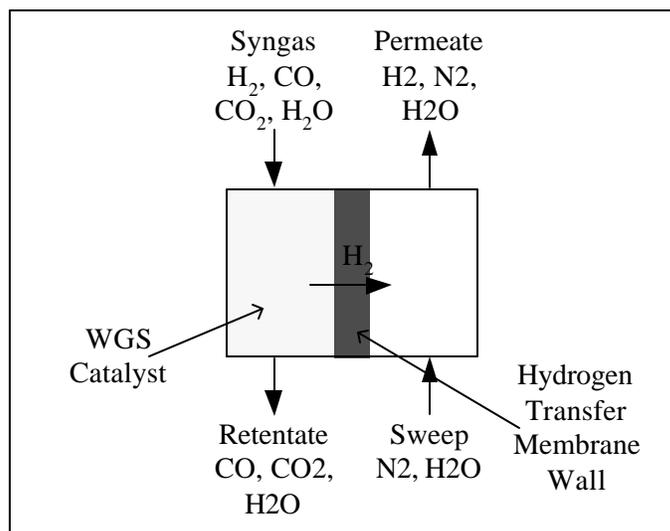


Figure 1.2.1.1.7.5.2(1) Membrane Water Gas Shift Reactor Concept

The MWGS reactor consists of a hydrogen transfer membrane with water gas shift catalyst. The sulfur-free syngas is shifted in the reactor and hydrogen is selectively transported through the membrane. The driving force for the permeation is enhanced by the use of sweep gas to lower the partial pressure of the hydrogen on the permeate side of the membrane. The remaining syngas (retentate) exits the reactor at a pressure close to the syngas pressure.

The resulting hydrogen (permeate) contains nitrogen and steam from the sweep gas; thus lowering the heating value of the fuel gas. Therefore, the permeate is cooled to condense and separate the water from the hydrogen rich stream, which is then returned to the existing refinery heaters/boilers resulting in a carbon-dioxide free flue gas.

1.2.1.1.7.5.3 Key Results

The metal ceramic composite membrane performance determined by SOFCo (a partnership between McDermott International, Inc. and Ceramatec, Inc.) is shown in Table 1.2.1.1.7.5.3(1). The following definitions were used for the membrane performance:

- Carbon Compounds = carbon in all carbon-containing compounds (i.e. CO, CO₂, CH₄ & COS)
- Carbon Recovery = (carbon compounds in retentate)/(carbon compounds in feed)
- Hydrogen Recovery = (H₂ in permeate)/(H₂ + CO in feed)
- CO₂ Purity = molar composition of CO₂ in retentate (mol%, dry basis)
- Permeate LHV = lower heating value of the hydrogen-rich fuel to the existing furnaces and boilers (permeate from the MWGS reactor).

The membrane surface area and sweep flow rate was adjusted to determine the maximum carbon recovery for the membrane with a retentate containing 90 mol% (dry) carbon dioxide and a permeate heating value of 150 Btu/SCF (LHV).

| Table 1.2.1.1.7.5.3(1) Metal Ceramic Composite Membrane Performance | |
|--|--------------------------------|
| Feeds to MWGS Reactor | |
| Syngas Type | Sweet (Sulfur-free) |
| Syngas Temperature | 400°C |
| Syngas Pressure | 34 barg |
| Sweep Temperature | 400°C |
| Sweep Pressure | 2.36 barg |
| Membrane Performance | |
| Carbon Recovery | 100% |
| CO ₂ Purity | 90 mol% (dry) |
| Hydrogen Recovery | 95.6% |
| Hydrogen LHV (after cooling) | 150.4 Btu/SCF (LHV) |
| Hydrogen Flux | 0.228 gmol/m ² -sec |
| H ₂ :CO ₂ permselectivity | infinite |
| Required Membrane Parameters | |
| Surface Area | 14,095 m ² |
| Nitrogen Sweep Gas | 9,100 |
| Steam Sweep Gas | 8,800 |

The performance of the gasification plant will be provided later in the study and will include the following:

- Gasifier feed heating value
- Natural gas feed heating value for power generation
- Hydrogen fuel return heating value
- Overall thermal efficiency for hydrogen fuel

- Carbon dioxide flow rate to sequestration
- Electrical power summary

1.2.1.1.7.6 Experimental

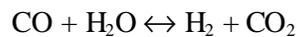
Experimental methods were used by others (e.g. Eltron Research Inc.) for this study. Fluor performed computer simulation to determine the performance of the gasification plant based on the membrane water gas shift reactor.

1.2.1.1.7.7 Membrane Water Gas Shift Reactor

1.2.1.1.7.7.1 Concept

The Membrane Water Gas Shift (MWGS) Reactor concept involves a hydrogen transfer membrane inside a MWGS reactor. The membrane technology involves the separation of the hydrogen utilizing a membrane by selective permeation of the hydrogen across the membrane. The hydrogen is dissolved into the membrane at one surface, transported across the membrane as the result of a concentration gradient (partial pressure difference between the two sides), and desorbed from the surface to the gas phase. The residue gas (retentate) leaves the MWGS reactor at a pressure close to that of the feed, while the permeate (hydrogen) product leaves at a much reduced pressure.

Catalyst is present in the reactor, which produces hydrogen from the water gas shift reaction shown below:



With the removal of hydrogen by permeation through the membrane, the WGS reaction is driven toward the products thus producing more hydrogen and carbon dioxide. To promote permeation, a sweep gas of nitrogen and steam is used to decrease the partial pressure of the hydrogen on the permeate side. The MWGS Reactor concept is shown in Figure 1.2.1.1.7.7.1(1).

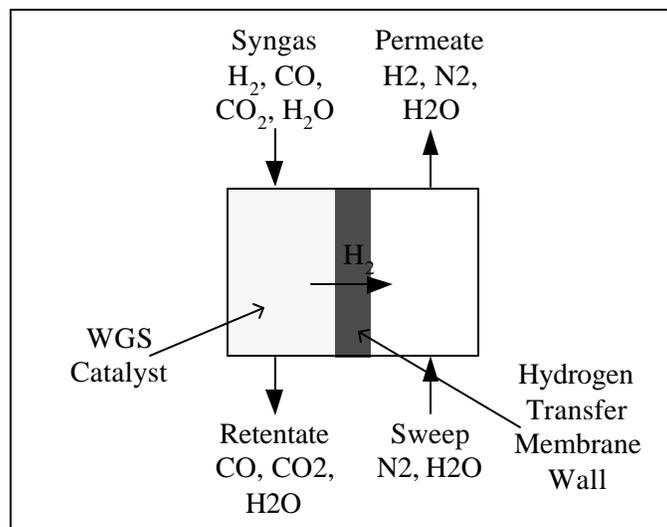


Figure 1.2.1.1.7.7.1(1) Membrane Water Gas Shift Concept

1.2.1.1.7.7.2 Proton-Conducting Metal Ceramic Composite Membrane

Phase II of the study is based on the proton-conducting metal ceramic composite membrane provided by Eltron Research Inc. The hydrogen transport concept for the membrane is shown in Figure 1.2.1.1.7.7.2(1).

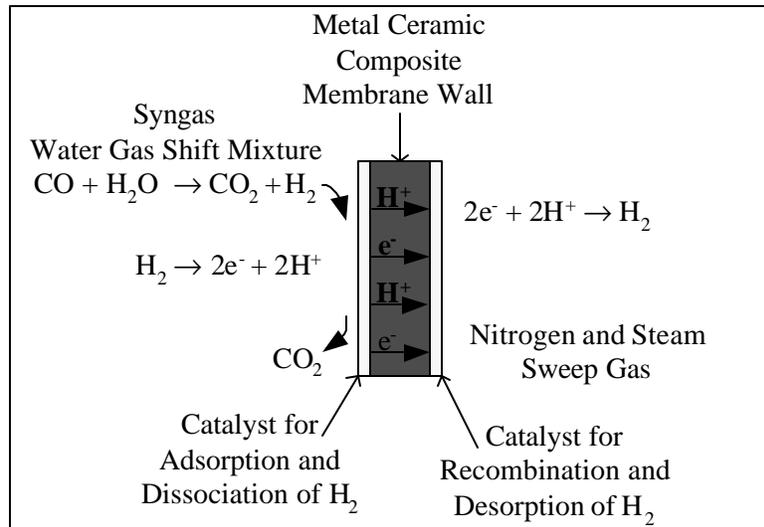


Figure 1.2.1.1.1.7.2(1) Hydrogen Transport for the Metal Ceramic Composite Membrane

Metal ceramic composites were made by sintering together ceramic and metal powder to form dense continuous matrices of both metal and ceramic. The materials chosen were based on: high proton transport rate, cost, low toxicity, ease of synthesis, thermal and chemical stability, and catalytic properties. The two materials were aligned so that their lattices matched to minimize strain and dislocations and to aid nucleation and growth of metal on the ceramic during membrane preparation.

Selected metals were tested and selected. Ceramics were identified to match the coefficients of thermal expansion of many of the metals. Eltron Research Inc.'s final choice of materials was not disclosed.

However, it was found that the catalyst for adsorption and dissociation was poisoned by hydrogen sulfide in a sour syngas feed to the MWGS reactor. The project schedule for Phase I did not permit Eltron Research Inc. to continue their efforts in troubleshooting this problem. Therefore, for Phase II, the gasification plant configuration was revised to remove the sulfur compounds upstream of the MWGS reactor. For more details on the metal ceramic composite membranes, see the reports prepared by Eltron Research Inc.

1.2.1.1.7.3 MWGS Reactor Computer Simulation Model

For Phase I, a computer model of the membrane water gas shift (MWGS) reactor was developed by Energy research Centre of the Netherlands (ECN) to determine the conditions (flow rate, composition, temperature and pressure) of the permeate and retentate for a specified membrane surface area. After consultations with the individual membrane vendors, the following hydrogen permeance equation was programmed into the model:

$$J = P_0 e^{-E/RT} (P_f^n - P_p^n)$$

- where
- J = flux of hydrogen (gmol/m²-s)
 - P₀ = pre-exponential permeance factor (gmol/m²-s-Paⁿ)
 - E = activation energy for hydrogen transport (J/gmol)
 - R = ideal gas constant (8.314 J/gmol-K)
 - T = temperature (Kelvin)
 - P = partial pressure of H₂ on the feed (f) and permeate (p) side (Pa)
 - n = exponent on driving force

Three computer, mathematical models (simplified, first version and final version) for integration into an Aspen Plus process computer simulator were developed by ECN.

However, for Phase II, the SOFCo developed a configuration for the MWGS that consisted of multiple parallel paths rather than the counter-current flow arrangement of the computer simulation model. The performance determined by SOFCo was compared to the results of the computer simulation model and the two outcomes were consistent with each other. In addition, the computer model did not take into account the pressure drop in the MWGS reactor. Therefore, the SOFCo MWGS reactor performance was used to determine the performance and size of the gasification plant.

1.2.1.1.7.8 General Design Criteria

1.2.1.1.7.8.1 Introduction

This section presents the General Design Criteria for the Membrane Water Gas Shift (MWGS) Reactor Study for CO₂ Capture Project. The scope of this conceptual study is to develop a process design for the gasification of residual fuel oil and refinery fuel gas to produce a hydrogen rich fuel for the use in the existing refinery and petrochemical furnaces and heaters and a carbon dioxide stream for sequestration.

The purpose of this section is to ensure a degree of uniformity of criteria for the design of the plant.

1.2.1.1.7.8.1.1 Brief Project Facilities Description

The following is a brief description of the MWGS reactor plant. The residual oil and refinery fuel gas is gasified with oxidant (99.5 mol% oxygen) from the Air Separation Unit (ASU) to produce a raw syngas. The syngas from the gasifier is cleaned of particulates, carbonyl sulfide (COS) and hydrocyanic acid (HCN) are removed or destroyed, and the syngas is cooled to a temperature suitable for the Acid Gas Removal (AGR) unit. Sulfur compounds are removed in the AGR and recovered as elemental sulfur product in the Sulfur Recovery unit. The clean fuel gas is saturated then fed to a bulk shift catalyst where the carbon monoxide and water are converted to hydrogen and carbon dioxide. The shifted syngas is then routed to the MWGS reactor, which provides additional conversion of the remaining carbon monoxide then separates the product hydrogen from the product carbon dioxide. The hydrogen rich stream is cooled to remove the water in the stream and fired in the existing equipment producing a flue gas, which is relatively free of carbon dioxide. The carbon dioxide rich stream from the MWGS reactor is cooled then compressed for geologic sequestration. The target carbon dioxide purity is 90 mol%, dry.

The electrical power for the plant is provided by a natural gas fired combined cycle.

1.2.1.1.7.8.1.2 General Criteria and Philosophy

- a) The plant is designed to recover two (2) million tonnes per year of CO₂ (100% basis and 330 days per year operation with a carbon recovery of 100% for the membrane WGS reactor). This target quantity reflects the overall aims of the Grangemouth site, i.e. to capture 50% of the CO₂ from across the complex.
- b) The plant is designed to be self sufficient in most utilities including electrical power. The firewater is assumed to be provided by the existing site infrastructure. (This assumption for the firewater is the same as the design in the BP Grangemouth CO₂ Capture Report.)

1.2.1.1.7.8.1.3 Battery Limits Definition

The following commodities are supplied to the plant at the battery limits:

- Residual oil feed
- Refinery fuel gas
- Natural gas
- Make up water
- Ambient air

- Firewater
- Water treatment chemicals
- Chemicals for the gasification unit

The following commodities are produced from the plant at the battery limits:

- Dry carbon dioxide product
- Hydrogen rich stream to existing fuel gas system
- Electrical power
- Sulfur product
- Treated wastewater suitable for disposal
- Filter waste
- Sulfur recovery vent
- Air Separation Unit vent
- Flue gas
- Cooling tower evaporation
- Cooling tower drift (water droplets carried by the wind)
- Sewage
- Storm Drains

The firewater is the only integration of the new plant with the existing utility systems.

1.2.1.1.7.8.2 Site Data

1.2.1.1.7.8.2.1 Location

The case is based on a typical European refinery and is modeled after BP's facilities at Grangemouth. Site information was taken from Exhibit E – Technical Specification: BP Grangemouth (Scenario A), Revision C dated October 1, 2001 (PC-RFP-006).

BP Grangemouth collects oil and gas from fields across the Central Area of the North Sea. The complex is made up of a series of business units, including:

- a) Kinneil – gas and liquids collected from the Forties system are stabilized, separated and processed.
- b) Refinery – crude oil collected from the Forties Pipeline system is refined to produce LPG, Alkylate, Petrol, Diesel Jet Fuel, Kerosene and Fuel Oil.
- c) Chemicals – gases and light distillate feedstocks from the refinery are converted to petrochemical products.
- d) Power Station – power and steam are produced for users in the complex.

BP Grangemouth is located between the estuaries of the Rivers Carron and Avon in Scotland, United Kingdom. The exact plot location of the gasification plant in the existing plant is to be determined; however, it is assumed that the plot is clean, level and free of any underground obstructions.

The elevation of the plot is 3.5 meters above sea level. The associated barometric pressures are shown in Table 1.2.1.1.7.8.2.1(1).

| Table 1.2.1.1.7.8.2.1(1) Barometric Pressures (mbara) | |
|--|------|
| Estimated mean | 1015 |
| Maximum | 1030 |
| Minimum | 970 |

1.2.1.1.7.8.2.2 Meteorological Data

1.2.1.1.7.8.2.2.1 Site Temperatures

The dry bulb temperatures are summarized in Table 1.2.1.1.7.8.2.2.1(1).

| Table 1.2.1.1.7.8.2.2.1(1) Ambient Air Dry Bulb Temperatures, °C | |
|---|-----|
| Estimated mean | 7 |
| Maximum | 30 |
| Minimum | -12 |
| Design temperature for winter | -15 |

1.2.1.1.7.8.2.2.2 Relative Humidity

The relative humidity for the site is shown in Table 1.2.1.1.7.8.2.2.2(1). The average relative humidity of 78.5% is estimated using the mathematical average of the two humidities reported in the morning (0700) and the afternoon (1500).

| Table 1.2.1.1.7.8.2.2.2(1) Relative Humidity, % | |
|--|------|
| Average | 78.5 |
| At 0700 | 87 |
| At 1500 | 70 |

1.2.1.1.7.8.2.2.3 Rainfall

The annual average rainfall is 815 mm with a one (1) hour maximum of 6.5 mm.

1.2.1.1.7.8.2.2.4 Wind

The maximum wind velocity is 50 m/s.

1.2.1.1.7.8.3 Process Design Basis

1.2.1.1.7.8.3.1 Feedstocks

There are a wide range of existing process furnaces and heaters, distributed across the BP Grangemouth complex. These units are fired with fuel gas from the refinery or chemical plants and refinery fuel oil. In the CO₂ Capture Report, Grangemouth developed by Fluor, the flue gases from these furnaces and heaters were routed to a proposed plant for the post combustion recovery of carbon dioxide. There were approximately twenty (20) points of source emissions for the carbon dioxide, which added up to twice the amount required for recovery for the Grangemouth site. Therefore, sources were eliminated based on the following:

- a) Size of source.
- b) Distance from the proposed carbon dioxide recovery plant.
- c) Potential difficulties in making ties ins between the carbon dioxide plant and existing flue gas ducting.
- d) Operational status in the future.

The remaining sources fell into three natural groupings:

- a) BP refinery group
- b) Power plant group
- c) BP Chemicals ethylene plant source group

The final selection consisted of refinery sources F, G, H & I, power plant sources K, L & M and finally the ethylene plant sources S & T. For this MWGS Reactor Study, the feed usually fed to these existing furnaces and heaters will be routed to the proposed gasification plant. The hydrogen rich fuel gas from the membrane WGS reactor will be fed to the existing furnaces and heaters. Any deficiency of fuel for the existing equipment will be augmented by natural gas. The amount of fuel available to the gasification plant is set by the BP Grangemouth Technical Specification (Exhibit E). The feed will be adjusted so that two (2) million tonnes of carbon dioxide per year is recovered from the plant (based on 330 days per year operation and a carbon recovery of 100%). The feed is supplied to the gasifier in the following priority:

- a) Fuel oil,
- b) Refinery fuel gas,
- c) Fuel gas from the chemicals plant, and
- d) Natural gas.

The summary of the annual fuel consumption of the existing equipment is shown in Table 1.2.1.1.7.8.3.1(1).

| Table 1.2.1.1.7.8.3.1(1) Annual Fuel Consumption for Existing Equipment | | | | | |
|--|-----------------|------------------|----------------|---|---------------|
| | | Tonnes/yr | | kg/hr (based on 330 days per year operation) | |
| | Source | Gas | Oil | Gas | Oil |
| Refinery Site Stacks | | | | | |
| F | CCR | 63,972 | 2,324 | 8,077 | 293 |
| G | HCU | 52,117 | - | 6,580 | - |
| H | VDU | 26,676 | 7,797 | 3,368 | 984 |
| I | H2U | 35,039 | - | 4,424 | - |
| Total | | 177,804 | 10,121 | 22,449 | 1,277 |
| Power Plant Stacks | | | | | |
| K | Boiler 9/10 | 45,614 | 79,612 | 5,759 | 10,052 |
| L | Boiler 11/12/13 | 81,502 | 114,218 | 10,291 | 14,421 |
| M | Boiler 14/15 | 104,559 | 107,970 | 13,202 | 13,633 |
| Total | | 231,675 | 301,800 | 29,252 | 38,106 |
| BP Chemicals Stacks | | | | | |
| S | KG (36F1A/F) | 136,200 | - | 17,197 | - |
| T | Boilers | 49,100 | - | 6,199 | - |
| Total | | 185,300 | - | 23,396 | - |
| | | | | | |
| Overall Total Fuel Oil | | | 311,921 | | 39,384 |
| Overall Total Refinery Fuel Gas | | 409,479 | | 51,702 | |
| Overall Total Fuel Gas from Chemicals Plant | | 185,300 | | 23,396 | |

The quality of the Fuel Oil varies significantly. Therefore, the ultimate analysis for the Fuel Oil to the gasifier was estimated as an average and is shown in Table 1.2.1.1.7.8.3.1(2) (reference: CCP Membrane Water Gas Shift Reactor Invitation for Proposals).

| Table 1.2.1.1.7.8.3.1(2) Fuel Oil Ultimate Analysis | |
|--|------------|
| | wt% |
| Carbon | 87.2 |
| Hydrogen | 9.9 |
| Nitrogen | 0.7 |
| Oxygen | 0.8 |
| Sulfur | 1.4 |
| Total | 100.0 |
| Flow rate available, kg/hr (Note 2) | 39,384 |

Notes:

- 1) Ash content is assumed to be zero.
- 2) Based on 330 days per year operation

The quality of the fuel gas varies significantly across the Grangemouth site. Therefore, an analysis of the refinery and chemicals plant fuel gas was estimated as an average and is shown in Table 1.2.1.1.7.8.3.1(3) (reference: BP Grangemouth Technical Specification).

| Table 1.2.1.1.7.8.3.1(3) Fuel Gas Typical Analysis | | |
|---|--------------------------|---------------------------|
| | Refinery Fuel Gas | Chemicals (Site 1) |
| | mol% | mol% |
| Methane | 67.80 | 58.0 |
| Ethane | 9.42 | 0.1 |
| Ethene | 0.02 | 0.1 |
| Propane | 7.42 | 0.0 |
| Propene | 0.01 | 0.0 |
| Iso-Butane | 1.07 | 0.0 |
| N-Butane | 3.12 | 0.0 |
| Iso-Butene | 0.05 | 0.0 |
| Methyl-1-Butenes | 0.15 | 0.0 |
| n-Pentane | 0.04 | 0.0 |
| Iso-Pentane | 0.16 | 0.0 |
| Hydrogen | 7.87 | 40.8 |
| Oxygen | 0.03 | 0.0 |
| Nitrogen | 0.75 | 1.0 |
| Carbon Monoxide | 0.00 | 0.0 |
| Carbon Dioxide | 2.01 | 0.0 |
| Hydrogen Sulfide | 0.08 | 0.0 |
| Total | 100.00 | 100.0 |
| Flow rate available, kg/hr* | 51,702 | 23,396 |

*Note: Based on 330 days per year operation.

1.2.1.1.7.8.3.2 Products

The products of the plant are a hydrogen rich stream to the existing furnaces and heaters and a carbon dioxide rich stream for sequestration. In the CCP Membrane Water Gas Shift Reactor Invitation for Proposals, the target production rate of the hydrogen is 700,000 Nm³/hr. However, CCP has directed Fluor that recovering the amount of hydrogen corresponding to two million tonnes per year of carbon dioxide captured is sufficient for this project. Therefore, the design of the plant was not constrained by a hydrogen production rate of 700,000 Nm³/hr. The specifications for the product streams are shown in Table 1.2.1.1.7.8.3.2(1).

| Table 1.2.1.1.7.8.3.2(1) Product Specifications | | |
|--|-----------------------|---|
| | CO₂ | H₂ |
| Production Rate, million tonnes/yr (100% basis with carbon recovery of 100% (Note1)) | 2 | Governed by amount of fuel to gasifier and extent of shift conversion |
| kg/hr (Note 2) | 252,525 | To be determined |
| Nm ³ /hr (Note 2) | 128,609 | To be determined |
| Target design carbon recovery, % (Note 1) | 90 | - |
| Minimum purity, mol%, dry | 90 | - |
| Minimum heating value, Btu/SCF (LHV) | - | 150 |
| Temperature at battery limits, °C | 45 | 45 |
| Minimum pressure at battery limits, bara | 80 | 3 |

Notes:

- 1) Carbon recovery = carbon compounds in retentate/carbon compounds in feed
- 2) Based on 330 days per year operation.

1.2.1.1.7.8.3.3 Make-up Water

Make-up water is available as Towns Water from the local water supplier (reference: BP Grangemouth Technical Specification). It is possible that chemically treated cooling water and demineralized water may be provided by the existing facilities. However, at this phase of the project, it is assumed the new plant requires facilities for water treating. In the event, demineralized water is imported from the existing facilities, the feedwater is accessible at 150 barg \pm 4 bar and 126°C. The parameters for the feedwater quality from the existing plant are shown in Table 1.2.1.1.7.8.3.3(1) and are based on a steam drum pressure of 140 barg.

| Table 1.2.1.1.7.8.3.3(1) Demineralized Water Quality (Potentially Available from Existing Facilities) | | |
|--|-----------|-------|
| Normal Conductivity | 2.5 – 6 | μS/cm |
| pH | 8.5 – 9.5 | |
| Silica as SiO ₂ | < 0.02 | mg/kg |
| Iron | < 0.02 | mg/kg |
| Aluminum | - | mg/kg |
| Sulfate as SO ₄ | - | mg/kg |
| Sodium | - | mg/kg |
| Copper | < 0.003 | mg/kg |
| Hardness as CaCO ₃ | < 0.15 | mg/kg |
| Oxygen | < 0.01 | mg/kg |

For the majority of the time, the make-up water is supplied by the Towns Water. A typical water quality is shown in Table 1.2.1.1.7.8.3.3(2).

| | | |
|--------------------------------|----------------|-------|
| Conductivity | 68 – 128 | µS/cm |
| pH | 7.2 – 10.0 | |
| Turbidity | 0.12 – 1.17 | FTU |
| Iron as Fe | < 2 – 272 | µg/l |
| Aluminum as Al | 17 – 170 | µg/l |
| Sulfate as SO ₄ | 4.7 – 19.3 | mg/l |
| Sodium as Na | 3.6 – 5.8 | mg/l |
| Copper as Cu | 1.8 – 52.6 | µg/l |
| Dry Residues | 57 – 61 | mg/l |
| Calcium as Ca | 5.7 – 9 | mg/l |
| Magnesium as Mg | 0.97 – 1.6 | mg/l |
| Chlorides as Cl | 6.4 – 10.4 | mg/l |
| Ammonium as NH ₄ | 0.004 – 0.0019 | mg/l |
| Total Organic Carbon as C | 1.03 – 1.22 | mg/l |
| Alkalinity as HCO ₃ | 9.8 – 18.3 | mg/l |
| Manganese as Mn | < 0.5 – 24.2 | µg/l |
| Phosphorus as P | < 8 – 162 | µg/l |
| Barium as Ba | 15 – 18 | µg/l |
| Lead as Pb | < 0.4 – 37.8 | µg/l |
| Nickel as Ni | 1.5 – 6.2 | µg/l |
| Mercury as Hg | < 0.05 – 0.36 | µg/l |
| Chromium as Cr | < 0.8 – < 1.0 | µg/l |
| Zinc as Zn | 5 – 315 | µg/l |
| Cadmium as Cd | < 0.4 – < 0.5 | µg/l |

1.2.1.1.7.8.3.4 Environmental Criteria

The level of pollutants in the plant emissions should be below those of the current operating environmental discharges. Environmental limits for the new plant are to be determined. The existing emissions for NO_x and SO₂ are provided in Table 1.2.1.1.7.8.3.4(1).

| Stack | Fuel Fired | Total Flue Gas Flow Rate, kg/hr | NO _x , ppm (Note 1) | SO ₂ , ppm |
|-------|------------|---------------------------------|--------------------------------|-----------------------|
| F | Oil/Gas | 188,616 | 300 | 37 |
| G | Gas | 155,762 | 100 | 27 |
| I | Gas | 105,639 | 100 | 27 |
| K | Oil/Gas | 322,778 | 300 | 211 |
| L | Oil/Gas | 514,604 | 300 | 192 |
| M | Oil/Gas | 558,474 | 300 | 171 |
| S | Gas | 402,257 | 100 | 0 |
| T | Gas | 146,437 | 100 | 0 |

Notes:

- 1) NO_x emissions are estimated.
- 2) No emissions were provided for Stack H.

The plant emission/effluent points are as follows:

- Flue gas,
- Sulfur recovery vent
- Air Separation Unit vent
- Cooling tower evaporation/drift
- Waste water
- Sewage
- Storm Drains
- Sulfur product,
- Cooling tower evaporation/drift,
- Waste water, and
- Filter waste.

Noise limitations at the site boundary are < 55 dB.

1.2.1.1.7.8.3.5 Utility Information

The following utilities are provided for the plant:

- Steam
- Boiler Feedwater
- Condensate
- Cooling Water
- Demineralized Water
- Plant Water
- Potable Water
- Firewater
- Drains and Blowdown
- Plant and Instrument Air
- Nitrogen
- Natural Gas
- Flare
- Electrical Power

Conditions for steam are shown in Table 1.2.1.1.7.8.3.5(1).

| Table 1.2.1.1.7.8.3.5(1) Selected Steam Conditions | | | |
|---|---------------------------|--|---|
| Commodity | Pressure, barg | Saturation Temperature °C | Superheat Temperature °C |
| Extra High Pressure Steam | 127 | 330 | 520 |

| Commodity | Pressure, barg | Saturation Temperature °C | Superheat Temperature °C |
|--------------------------------|-----------------------|----------------------------------|---------------------------------|
| High, High Pressure Steam | 43 | 256 | 400 |
| High Pressure Steam | 33 | 241 | 400 |
| Medium Pressure Steam | 12.8 | 194 | 245 |
| Low Pressure Steam (typically) | 1 | 120 | 240 |

The cooling water system is a stand-alone unit. The cooling water supply temperature is set to 23°C, which results in a 5°C approach temperature to the assumed design wet bulb temperature of 18°C. The maximum temperature rise is 26°C.

The cooling tower blowdown is calculated such that the cooling towers operate at five (5) cycles of concentration. The design of the cooling towers (e.g. supply temperature, design wet bulb temperature, maximum temperature rise and cycles of concentration) were set to be the same as the design in the BP Grangemouth CO₂ Capture Report.

It is assumed that firewater is provided from the existing site infrastructure. (This is the same as the design in the BP Grangemouth CO₂ Capture Report.)

Plant and instrument air and utility nitrogen are supplied by the Air Separation Unit.

Natural gas is supplied to the new gas turbine for the production of electrical power.

1.2.1.1.7.8.3.6 Unit Numbering

The unit numbering is shown in Table 1.2.1.1.7.8.3.6(1).

| Unit | Number |
|---|---------------|
| Air Separation Unit | 001 |
| Gasification Island | 102/202 |
| Low Temperature Gas Cooling and COS Hydrolysis | 003 |
| Condensate (Ammonia) Stripper | 004 |
| Acid Gas Removal | 005 |
| Sulfur Recovery (Claus) and Tailgas Treating Unit | 006 |
| Fuel Gas Saturation/Sweet Shift/Nitrogen Saturation | 007 |
| Membrane Water Gas Shift Reactor/Permeate and Retentate Cooling | 008 |
| CO ₂ Compression/Dehydration | 009 |
| Power Generation | 010 |
| Utilities | 011 |

1.2.1.1.7.8.3.6.1 Equipment Identification

The equipment identification system is based on Fluor standards. The equipment will be numbered using the following system.

AAA-B-CCC D/D

AAA - Unit number

B - Equipment Identification Letter Symbol (See Table 1.2.1.1.7.8.3.6.1(1))

CCC - Equipment number (starting with 001 for each type of equipment)

D/D - If equipment is spared (i.e. A/B)

| Table 1.2.1.1.7.8.3.6.1(1) Equipment Identification Symbols | |
|--|---------------------------|
| Letter Symbol | Equipment |
| B | Burner |
| C | Compressor |
| CT | Combustion Turbine |
| DA | Deaerator |
| E | Heat exchanger and cooler |
| EA | Air Cooler |
| EX | Expander |
| F | Filter |
| G | Eductor |
| ME | Mechanical package |
| P | Pump (including motor) |
| S | Stack |
| SG | Steam generator |
| ST | Steam turbine |
| SU | Sump |
| TK | Tank |
| V | Vessel/Column |

1.2.1.1.7.8.3.6.2 Units of Measurement

The design incorporates SI units. The specific units to be used on this project for each type of measurement are shown in Table 1.2.1.1.7.8.3.6.2(1).

| Measurement | Unit |
|--------------------------------------|---|
| Temperature | °C |
| Pressure | barg, bara |
| Vacuum | mbar |
| Mass | kg |
| Volume, liquids | m ³ |
| Volume, gases (actual) | m ³ |
| Volume, gases (standard) | Nm ³ |
| Density | kg/m ³ |
| Flow, liquids | m ³ /h |
| Flow, gases | Nm ³ /h, m ³ /h, kg/h |
| Flow, solids | kg/h, kg/s |
| Heat | kJ/h |
| Power | MW, kW |
| Equipment dimensions and pipe length | m |
| Nominal pipe diameter | mm |
| Velocity | m/s |

The following prefixes in Table 1.2.1.1.7.8.3.6.2(2) may be used.

| Multiplication Factor | Prefix | Symbol |
|------------------------------|---------------|---------------|
| 10 ⁶ | Mega | M |
| 10 ³ | Kilo | k |
| 10 ⁻² | Centi | c |
| 10 ⁻³ | Milli | m |

1.2.1.1.7.9 Results and Discussion

The deliverables for the Membrane Water Gas Shift Reactor Study, Phase II are the following:

- General Design Criteria
- Summary Block Flow Diagram
- Process Descriptions
- Preliminary Process Flow Diagrams
- Heat and Material Balances
- Preliminary Equipment Lists with Approximate Sizes
- Utility Summary (for major utilities)

The project is currently in progress; therefore, this section contains the deliverables (results) completed to date, which consist of the following:

- General Design Criteria (provided in previous section)
- Summary Block Flow Diagram
- Selected Process Descriptions
- Selected Preliminary Process Flow Diagrams

Any issue specific to a process unit is discussed in the process descriptions.

1.2.1.1.7.9.2 Selected Process Descriptions

The process descriptions completed to date for the Membrane Water Gas Shift, Phase II are provided below. Note that all these process descriptions and process flow schemes are “work in progress.”

1.2.1.1.7.9.2.1 Gasification Island

The purpose of the Gasification Island (GI) is to produce raw syngas from residual fuel oil and refinery fuel gas gasified with high purity oxygen in a low pressure gasifier with convective cooling. The process configuration for the Gasification Island is shown in the Process Flow Diagram (102-PFD-001) in Figure 1.2.1.1.7.9.3(1). This unit consists of two 50% trains and is considered a package unit. The following is a process description for a typical Gasification Island.

Residual fuel oil and refinery fuel gas with Intermediate Pressure (IP) steam are fed to the GI where they are partially oxidized with high purity oxygen supplied by the Air Separation Unit. The resulting raw syngas is primarily a mixture of hydrogen and carbon monoxide with smaller quantities of nitrogen, water vapor, carbon dioxide, hydrogen sulfide, carbonyl sulfide, methane, and argon. The raw syngas is then cooled by producing high pressure steam in the convective cooling section of the gasifier. Low temperature, high pressure boiler feedwater (BFW) is also preheated in the convective cooling section of the gasifier then combined with high temperature, high pressure BFW for steam production.

Particulates entrained in the raw syngas are removed via wet scrubbing, and the syngas is routed to the Low Temperature Gas Cooling and COS Hydrolysis unit. The particulates exit the GI as fines for disposal and wastewater from the unit is also sent offsite for disposal.

Flashed gas from the water treating area in the GI is routed to the Sulfur Recovery Unit. Process condensate from the condensate stripper unit is returned to the GI for syngas scrubbing, and make-up water is supplied to maintain the GI water balance.

1.2.1.1.7.9.2.2 Low Temperature Gas Cooling and COS Hydrolysis Unit

The purpose of the Low Temperature Gas Cooling (LTGC) and COS Hydrolysis Unit is two-fold. The first is to convert most of the carbonyl sulfide (COS) and hydrocyanic acid (HCN) in the syngas feed to hydrogen sulfide (H₂S) and ammonia (NH₃) via catalytic hydrolysis reactions. The second is to cool the syngas to a suitable temperature for the Acid Gas Removal (AGR) Unit. The AGR unit removes most of the sulfur containing compounds from the syngas to meet the membrane water gas shift (MWGS) reactor constraint of 10 ppmv hydrogen sulfide plus carbonyl sulfide in the reactor feed. Hydrogen sulfide is removed more readily than carbonyl sulfide in the AGR Unit; therefore, the carbonyl sulfide in the syngas is converted to hydrogen sulfide to maximize sulfur removal from the raw syngas. The hydrocyanic acid is also converted to ammonia, which is removed along with the condensate produced from the cooled syngas. The AGR unit operates more efficiently at lower temperatures and thus the syngas is cooled to 35°C in the LTGC Unit.

The process configuration for the LTGC and COS Hydrolysis unit is shown in the Process Flow Diagrams (003-PFD-001/002) in Figures 1.2.1.1.7.9.3(2)/(3). This unit consists of one 100% train.

The feed to the LTGC is a particulate-free, raw syngas from the Gasification Island (GI). The raw syngas enters the LTGC saturated with water at 167°C and 44.0 barg.

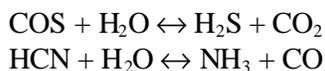
Optimal conversion of the hydrocyanic acid occurs at temperatures close to 195°C; however, this is not the optimal temperature for the conversion of the carbonyl sulfide (optimal temperature is ~150°C). Therefore, the conversion of COS is not maximized in order that the hydrocyanic acid content is

minimized in the syngas. This approach is acceptable as the amount of hydrogen sulfide removed in the AGR is able to meet the MWGS reactor feed requirements.

A degree of superheat of the reactor feed is also required to avoid condensation in the catalysts. Therefore, the raw syngas feed from the GI is first preheated to 193°C immediately prior to the COS Hydrolysis reactors.

The saturated, raw syngas from two gasification trains is combined and is first preheated to 170°C in a COS Hydrolysis Feed/Effluent Exchanger (003-E-001) against hot syngas from the reactors. Further superheat to 193°C is supplied by Medium Pressure (MP) steam at 26.3 barg in the COS Hydrolysis Feed Heater (003-E-002). The flow rate of the MP steam is controlled with a reset from the temperature controller on the syngas to the reactors at 193°C. During start-up, it is assumed that this exchanger will provide the necessary heat to preheat the gas to the desired temperature of operation of the catalyst during start-up for partial flow rates of syngas. The condensate formed from the cooling of the steam is collected in a MP Condensate Pot (003-V-003) and routed back to the steam system. The flow rate of steam condensate is varied to maintain a set liquid level in the condensate pot.

The preheated syngas at 193°C enters the top of the Guard Bed (003-V-001) which provides protection for the main reactor from dust and soot in the syngas. The syngas then enters the top of the COS Hydrolysis Reactor (003-V-002) where the carbonyl sulfide and hydrocyanic acid are reduced by the following catalytic reactions:



COS analyzers are provided at the inlet and outlet of each reactor to measure the performance of the catalysts. The syngas can be by-passed around either reactor for catalyst replacement.

The temperature rise over the Guard Bed and COS/HCN Hydrolysis Reactor is normally small (less than 1°C) as long as side reaction activity is negligible. The reactor effluent at 193°C is routed to the feed/effluent exchanger and cooled to 182°C against the raw syngas feed to the COS hydrolysis reactors.

The syngas is then cooled to 156°C in the Saturator Water Heater #1 (003-E-003) against circulating fuel gas saturator water. Condensate in the cooled syngas is separated from the gas in LTGC Knock-out Drum #1 (003-V-004), which is on level control. The syngas is further cooled to 52°C in the Vacuum Condensate Heater (003-E-004) against vacuum condensate from the surface condenser in the steam system. Condensate in the cooled syngas is separated from the gas in LTGC Knock-out Drum #2 (003-V-005), which is on level control.

The final cooling of the syngas to 35°C is in the Syngas Trim Cooler (003-E-005) against cooling water. Condensate formed in the cooled syngas is separated from the gas in the LTGC Wash Column (003-V-006), which scrubs out any ammonia present in the cooled syngas. The condensate from LTGC knock-out drums #1, #2 and wash column are routed to the stripper feed drum.

The cooled syngas is routed to the Acid Gas Removal unit for sulfur removal.

1.2.1.1.7.9.2.3 Condensate (Ammonia) Stripper Unit

The purpose of the Condensate (Ammonia) Stripper Unit is to remove ammonia, carbon dioxide and hydrogen sulfide present in the condensate produced in the Low Temperature Gas Cooling (LTGC) and COS Hydrolysis Unit. The water is recycled back to the Gasification Island (GI) to minimize fresh water

make-up to the system. Condensate stripping is provided to prevent the build up of ammonia in the syngas scrubbing section of the GI.

The process configuration for the Condensate Stripper Unit is shown in the Process Flow Diagram (004-PFD-001) in Figure 1.2.1.1.7.9.3(4). The unit consists of one 100% train.

The feed to the condensate stripper is the condensate from LTGC Knock-out Drums #1 and #2 and LTGC Wash Column and are collected in the Stripper Feed Drum (004-V-003). Minor (normally no flow) streams from the Sulfur Recovery Unit are also routed to the feed drum. Flash gas from the feed drum is combined with the condensate stripper overhead and routed to the Sulfur Recovery Unit. The pressure in the feed drum is controlled by varying the flow rate of the flash gas stream from the vessel.

The condensate from the feed drum is routed to the top section of the Condensate Stripper (004-V-001) (trayed column) where it is stripped by steam from the Condensate Stripper Reboiler (004-E-002). The liquid level in the feed drum is controlled by a reset on the flow of the condensate feed. The stripped condensate exits the condensate stripper and is routed by the Stripper Bottoms Pump (004-P-002A/B) to the Gasification Island.

The stripper reboiler uses LP (Low Pressure) steam to generate stripping steam at 125°C for the column. The flow rate of the steam is controlled with a reset from the temperature controller on the bottom of the stripper. The condensate formed at XXX°C from the cooling of the steam is routed to the LP Condensate Pot (004-V-004) and then returned to the steam system. The flow rate of the LP condensate is varied to control the liquid level in the condensate pot.

Most of the dissolved gases are removed from the condensate and sent overhead in the column. The overhead is cooled against cooling water in the Condensate Stripper Condenser (004-E-001), and the non-condensing sour gas is routed to the Sulfur Recovery Unit. A by-pass around the condenser is provided to control the temperature of the condensed overhead to the Condensate Stripper Overhead Accumulator (004-V-002) at XX°C. The pressure in the drum is controlled to a back pressure of 1.0 barg by varying the flow rate of the sour gas from the accumulator. The liquid from the drum is routed by the Condensate Stripper Reflux Pump (004-P-001A/B) to the top of the stripper. The liquid level in the accumulator is controlled by a reset on the flow rate of the reflux.

1.2.1.1.7.9.2.4 Acid Gas Removal Unit

The purpose of the Acid Gas Removal (AGR) Unit is to remove the sulfur containing compounds from the syngas. The solvent for the AGR unit is Selexol, a physical solvent designed to absorb hydrogen sulfide and carbonyl compounds. The unit is designed to minimize the overall removal of carbon dioxide from the syngas. The resulting clean syngas is also free of mercaptans, nickel and iron carbonyls. Selexol is a solvent consisting of dimethyl ether of polyethylene glycol and is non-corrosive, non-foaming, non toxic and biodegradable.

The process configuration for the Acid Gas Removal Unit is shown in the Process Flow Diagrams (005-PFD-001/002) in Figures 1.2.1.1.7.9.3(5)/(6). The unit consists of one 100% train.

Cooled syngas from the Low Temperature Gas Cooling (LTGC) Unit is combined with recycled flash gas and fed to the Absorber (005-V-001). Chilled Selexol at 0°C enters the absorber at the top of the column through an internal liquid distributor and flows down through the packed beds in the column, absorbing the hydrogen sulfide, carbonyl sulfide, carbon dioxide, water and other components from the syngas flowing counter current to the solvent. The clean syngas exits the absorber with a total sulfur compound content of 22 ppmv and is routed to the Fuel Gas Saturation unit and Sulfur Recovery unit (small amount) at a pressure controlled to 38.5 barg.

As the solvent flows down through the absorber, acid gases are absorbed from the upward flowing feed gas. The resultant heat of absorption causes rich Selexol solvent to exit the bottom of the column at a temperature of 24°C. A solvent reservoir is maintained in the bottom of the absorber by a level control valve in the rich solvent line downstream of the lean/rich exchanger.

The rich solvent from the absorber is heated to 135°C against lean solvent in the Lean/Rich Exchanger (005-E-001) where hydrogen sulfide, carbonyl sulfide, carbon dioxide and other components in the liquid are vaporized. The pressure of the rich solvent is reduced in the level control valve for the absorber and routed to the Rich Flash Drum (005-V-003) where the flashed gases are separated.

The flash drum serves several purposes: reduces the amount of acid gas from the stripper and thereby the stripper reboiler duty; minimizes the amount of inerts to the Sulfur Recovery Unit thereby decreasing the capital cost of the unit; and increases the hydrogen sulfide partial pressure in the feed to the absorber thereby decreasing the solvent circulation rate.

The pressure of the drum is maintained at 9.3 barg by varying the flow rate of the flash gas. The flash gas is cooled to 35°C against cooling water in a Flash Gas Cooler (005-E-004). The gas temperature is controlled by a by-pass around the cooler.

Condensate is produced when cooling the flash gas and is separated from the gas in the Flash Gas KO Drum (005-V-004). The dry gas is compressed in the Flash Gas Compressor (005-C-001A/B) to 40.2 barg and cooled to 35°C in an aftercooler (included in compressor package) against cooling water. The cooled flash gas is recycled to combine with the syngas feed from the LTGC unit and both are routed to the absorber.

The solvent from the rich flash drum is combined with the condensate from the flash gas knockout drum and routed to the Stripper (005-V-002). The flow rate of the solvent from the rich flash drum is varied to maintain the liquid level in the rich flash drum.

The rich solvent enters the top of the stripper and flows down the packing releasing the dissolved gases after contact with the stripping steam generated at 148°C in the Selexol Reboiler (005-E-006). The stripper reboiler uses LP (Low Pressure) steam to generate stripping steam for the column, and the LP steam flow rate is controlled with a reset from the temperature controller on the bottom of the stripper. The reboiler condensate at 164°C is routed to the LP Condensate Pot (005-V-006) and then returned to the steam system. The flow rate of the LP condensate is adjusted to maintain a liquid level in the condensate pot.

Most of the dissolved gases are removed from the solvent and sent overhead in the column. The overhead is cooled against cooling water in the Stripper Condenser (005-E-005), and the non-condensing acid gas is routed to the Sulfur Recovery Unit. A by-pass around the condenser is provided to control the temperature of the condensed overhead at 49°C to the Stripper Overhead Accumulator (005-V-005). A small amount of water is added to the accumulator to maintain the water balance in the system. The pressure of the drum is maintained at 1 barg by adjusting the flow rate of the acid gas from the accumulator. The liquid from the drum is routed by the Reflux Pump (005-P-003A/B) to the top of the stripper. The liquid level in the accumulator is controlled by a reset of the flow rate of the reflux.

The hot, lean solvent exiting the bottom of the stripper is routed by the Lean Solvent Pump (005-P-001A/B) to the lean/rich exchanger where it is cooled to 39°C. Solvent make-up (when required) is injected into the suction of the lean solvent pump.

A small portion of the cooled lean solvent is diverted to the Solvent Filter (005-F-001) to remove any particulate matter present in the system. The flow rate of this slip stream is controlled to 10% of the circulating solvent flow. The filtered solvent recombines with the circulating solvent and is further

cooled to 35°C in the Lean Solvent Cooler (005-E-003) against cooling water. The cooled gas temperature is controlled by a by-pass around the cooler. Final chilling of the lean solvent to 0°C is provided by the Lean Solvent Refrigeration Exchanger (005-E-002). The chilled solvent is routed to the top of the absorber by the Lean Solvent Booster Pump (005-P-004A/B). The liquid level in the stripper is controlled by a reset of the flow rate of the chilled, lean solvent to the absorber.

Solvent storage is included for the AGR unit. All sample points, purges, drains, etc. from the Selexol unit enter a drain header, which discharges, to the Solvent Sump (005-SU-001). The solvent is routed from the sump by the Solvent Sump Pump (005-P-005A/B) as make-up to the AGR unit (flow is normally no flow). A Selexol Storage Tank (005-TK-001) with a Selexol Storage Tank Heater (005-E-007) is provided for fresh make-up of the solvent provided by tank trucks. Two pumps are provided for the fresh solvent make-up; Solvent Make-up Pump (005-P-002A/B) for small make-up flow rates and Solvent Charge Pump (005-P-006A/B) for the initial filling of the system (both are normally no flow).

The two main process streams exiting from the AGR unit are the clean fuel gas to the fuel gas saturator and sulfur recovery unit (small amount for fuel to the thermal oxidizer) and acid gas to the sulfur recovery unit.

1.2.1.1.7.9.2.5 Fuel Gas Saturation/Sweet Shift/Nitrogen Saturation

The purpose of the Fuel Gas Saturator/Sweet Shift/Nitrogen Saturation Unit is two-fold. This unit “preshifts” the syngas to the membrane water gas shift (MWGS) reactor by first saturating the syngas with water and then shifting the gas in order that the carbon monoxide is converted to hydrogen via the shift reaction shown below:



The nitrogen for sweep gas for the MWGS reactor is also saturated with water to facilitate hydrogen permeation in the reactor.

Moisturization of the syngas and nitrogen is preferable to steam injection as low level heat can be used for saturation versus the higher level of steam required for steam injection (thus increasing the plant efficiency). The amount of water added to the syngas was such that the ratio of moles of steam to moles of carbon monoxide was 2.8 per requirements of the shift catalyst vendor. The amount of water added to the nitrogen was dependent on the amount of low level heat available for recovery.

The process configuration for the Fuel Gas Saturation/Sweet Shift/Nitrogen Saturation Unit is shown in the Process Flow Diagram (007-PFD-001) in Figure 1.2.1.1.7.9.3(7). The unit consists of one 100% train.

The syngas from the Acid Gas Removal Unit enters the Fuel Gas Saturator (007-V-001) and is contacted counter currently with heated water over packing. The gas, saturated with water vapor, is preheated in the Shift Feed/Retentate Exchanger (007-E-001) to 288°C against retentate from the MWGS reactor. A Start-up Heater (007-E-002) is provided (during normal operation, the exchanger is by-passed), which heats the shift feed against superheated High Pressure (HP) steam. The flow rate of the steam is controlled with a reset from the temperature controller on the feed to the shift. The steam condensate is collected in the HP Condensate Pot (007-V-007) and returned to the steam system.

The preheated syngas is fed to the Shift Reactor (007-V-002) where the carbon monoxide is shifted to hydrogen. As the shift reaction is exothermic, the syngas exits the reactor at 451°C. The syngas is then routed to the MWGS Reactor unit. Hydrogen and carbon monoxide analyzers are installed at the inlet and outlet of the reactor to measure the performance of the catalyst.

The water exiting the bottom of the column is routed to the Low Temperature Gas Cooling (LTGC) Unit and Permeate and Retentate Cooling Unit by the Saturator Bottoms Pump (007-P-001A/B). Blowdown, which is equivalent to 2% of the water evaporated in the column, is extracted from the suction of the pump. The flow rate of the water from the bottoms of the column is controlled with a reset from the temperature controller on the saturated gas. Make-up water from the steam system is added to the bottoms water to compensate for the water evaporated in the column and the blowdown. The flow rate of this water is adjusted to control the liquid level in the column.

The combined bottoms and make-up water is heated in four exchangers (some in parallel and others in series): from 138°C to 246°C in the Saturator Water Heater (Permeate) (008-E-003), from 138°C to 215°C in the Saturator Water Heater (Retentate) (008-E-005), and from 138°C to 171°C in the Saturator Water Heater #1 (003-E-003). The water from the last two exchangers was then heated to 246°C in the Saturator Water Heater (BFW) (007-E-003) combined with the remaining heated water and fed to the top of the Fuel Gas Saturator.

The nitrogen from the Air Separation Unit enters the Nitrogen Saturator (007-V-004) and is contacted counter currently with heated water over packing. The saturated nitrogen is routed to the MWGS Reactor unit for sweep gas.

The water exiting the bottom of the column is routed to the Permeate and Retentate Cooling Unit by the Nitrogen Saturator Bottoms Pump (007-P-002A/B). Blowdown, which is equivalent to 2% of the water evaporated in the column, is extracted from the suction of the pump. The flow rate of the water from the bottoms of the column is controlled with a reset from the temperature controller on the saturated gas. Make-up water from the steam system is added to the bottoms water to compensate for the water evaporated in the column and the blowdown. The flow rate of this water is adjusted to control the liquid level in the column.

The combined bottoms and make-up water is heated in two exchangers in parallel: from 79°C to 172°C in the Nitrogen Saturator Water Heater #1(008-E-007) and from 79°C to 121°C in the Nitrogen Saturator Water Heater #2 (008-E-008). The combined, heated water is fed to the top of the Nitrogen Saturator.

1.2.1.1.7.9.2.6 CO₂ Compression/Dehydration

The purpose of the CO₂ Compression/Dehydration system is to compress the product carbon dioxide stream to 79 barg for sequestration. The process configuration for the CO₂ Compression/Dehydration system is shown in the Process Flow Diagram (009-PFD-001) in Figure 1.2.1.1.7.9.3(8). The unit consists of one 100% train.

The cooled retentate stream from the Membrane Water Gas Shift (MWGS) is compressed in the CO₂ Product Compressor (009-C-001) to the required 79 barg and 45°C product specifications. At an interstage pressure of XX barg, the compressed carbon dioxide is sent to the Dehydration Package (009-ME-002), which reduces the moisture level down to a –40°C dew point. The dryer package uses a natural gas fired heater during its regeneration cycle. An intercooler and after cooler utilizing cooling water are provided in the compressor package.

1.2.1.1.7.9.3 Selected Preliminary Process Flow Diagrams

The process flow diagrams completed to date for the Membrane Water Gas Shift, Phase II is shown in the following figures. All these drawings are “work in progress.”

| Membrane Water Gas Shift, Phase II | | |
|---|-----------------------|---|
| Figure Number | Drawing Number | Title |
| 1.2.1.1.7.9.3 (1) | 102-PFD-001 | Gasification Island |
| 1.2.1.1.7.9.3 (2)/(3) | 003-PFD-001/002 | Low Temperature Gas Cooling and COS Hydrolysis Unit |
| 1.2.1.1.7.9.3 (4) | 004-PFD-001 | Condensate (Ammonia) Stripper Unit |
| 1.2.1.1.7.9.3 (5)/(6) | 005-PFD-001/002 | Acid Gas Removal Unit |
| 1.2.1.1.7.9.3 (7) | 007-PFD-001 | Fuel Gas Saturation/Sweet Shift/Nitrogen Saturation |
| 1.2.1.1.7.9.3 (8) | 009-PFD-001 | CO ₂ Compression/Dehydration |

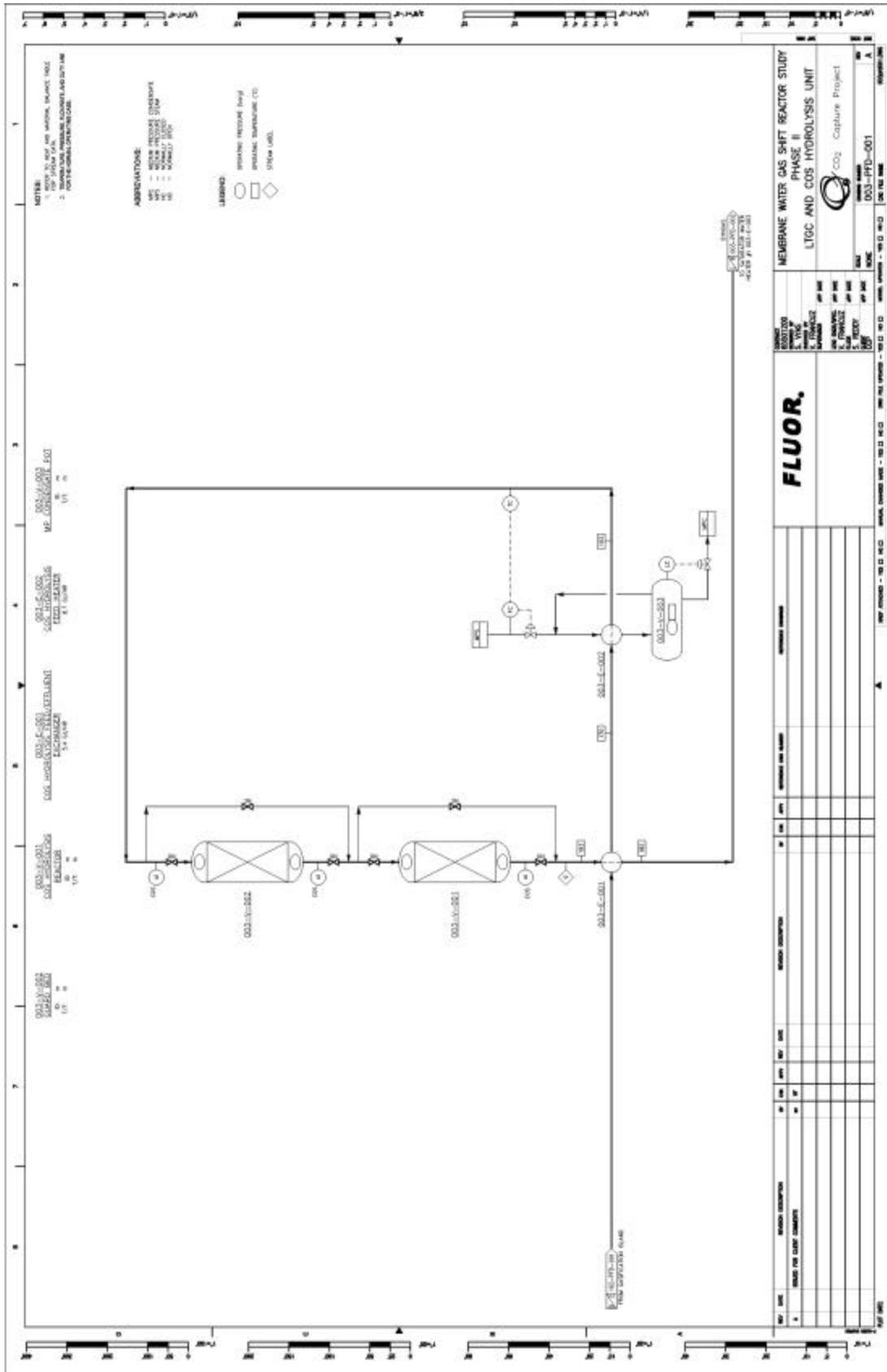


Figure 1.2.1.1.7.9.3(2) Low Temperature Gas Cooling (Sheet 1 of 2)

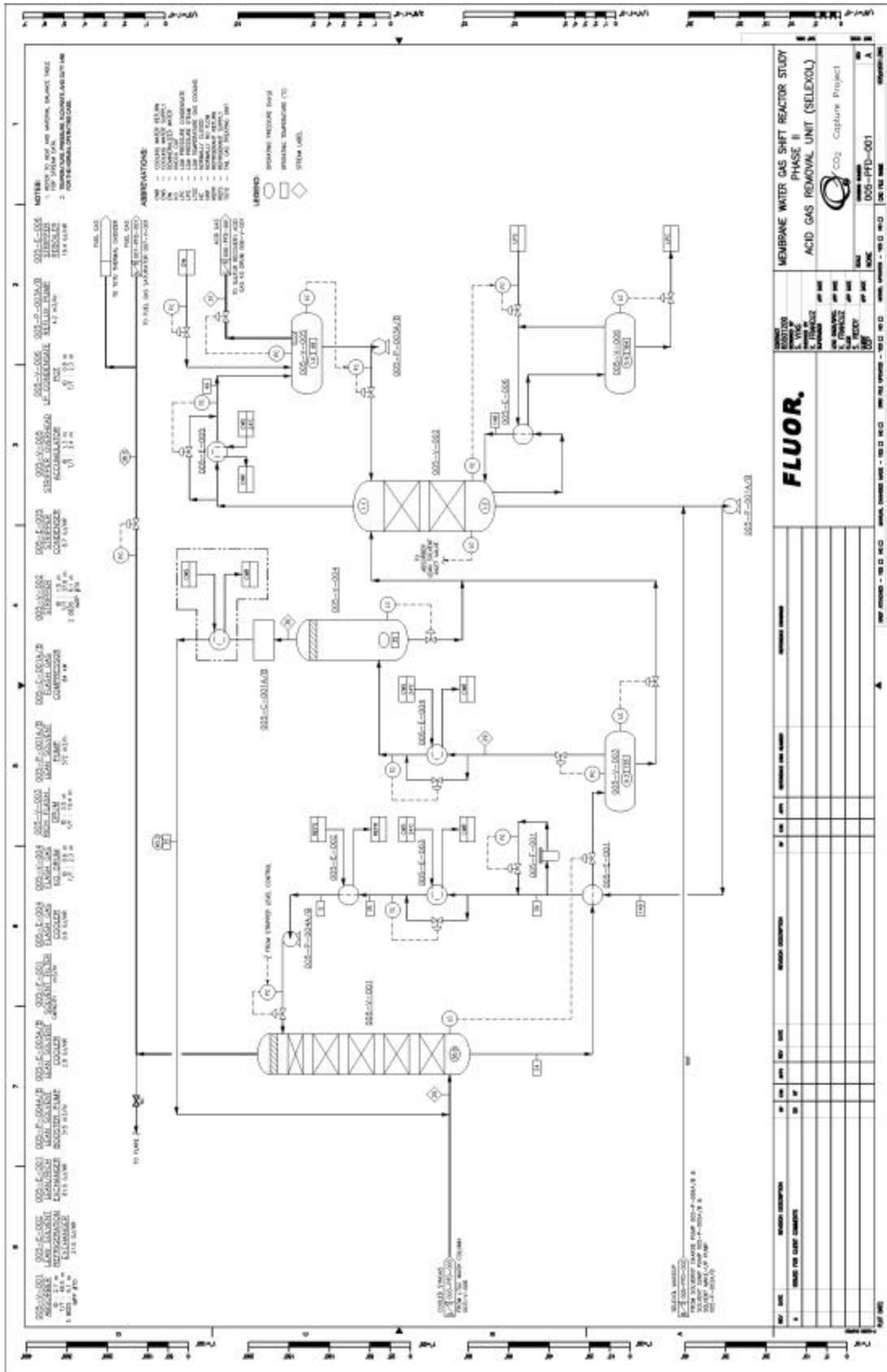


Figure 1.2.1.1.7.9.3(5) Acid Gas Removal Unit (Sheet 1 of 2)

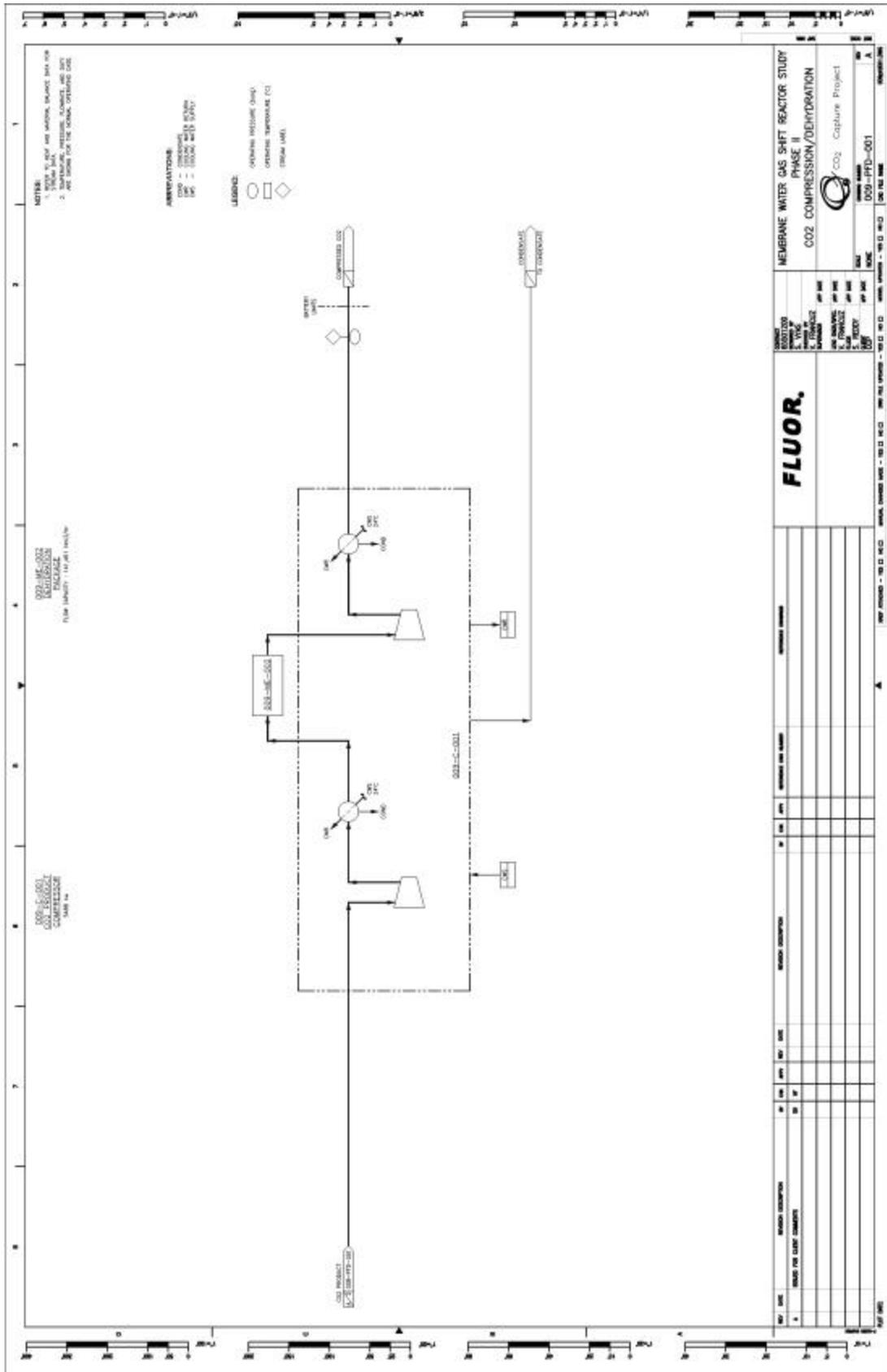


Figure 1.2.1.1.7.9.3(8) CO₂ Compression/Dehydration

1.2.1.1.7.10 Conclusion

The Membrane Water Gas Shift Reactor Study, Phase II, is continuing in developing the performance for the overall gasification plant. An equipment list with approximate sizes will be produced in addition to the deliverables listed in Section 1.2.1.1.7.9.

1.2.1.1.7.11 List of Acronyms and Abbreviations

ASU – Air Separation Unit

bara – bar absolute

barg – bar gauge

BFW – Boiler Feedwater

BL – Blower

BTU – British Thermal Unit

C – Compressor

°C – Degrees Celsius

CA – Corrosion Allowance

CCP – CO₂ Capture Project

CEMS – Continuous Emissions Monitoring System

CH₄ – Methane

CO – Carbon monoxide

CO₂ – Carbon dioxide

Cond – Steam condensate

COS – Carbonyl sulfide

CT – Combustion Turbine

CVX - ChevronTexaco

DA – Deaerator

dB – Decibels

DCS – Distributed Control System

DOE – Department of Energy

DP – Design Pressure

DT – Design Temperature

E – activation energy

E – Heat exchanger or cooler

ECN – Energy research Centre of the Netherlands

EOR – Enhanced Oil Recovery

F – Filter

Fe – Iron

Fe-Cr – Iron Chromium

FV – Full Vacuum

GE – General Electric

GI – Gasification Island

gmol – gram mole

h or hr – Hour

H₂ – Hydrogen

H₂O – Water

H₂S – Hydrogen sulfide

HCN – Hydrocyanic acid

HP – High Pressure

HRSG – Heat Recovery Steam Generator

HVAC – Heating, Ventilation and Air Conditioning

ID – Inside Diameter
IGCC – Integrated Gasification Combined Cycle
IP – Intermediate Pressure

J – Joule
J – flux

K – Kelvin
kg – Kilogram
kgmol – Kilogram moles
kJ – Kilojoules
KO – Knock-out
kV – Kilovolts
kW – Kilowatt

LHV – Lower Heating Value
LP – Low Pressure
LTGC – Low Temperature Gas Cooling

m – Meter
 m^2 – Square meters
 m^3 – Cubic meters
mbar – Millibar
ME – Mechanical package
mm – Millimeter
Mol% – Molar percent
mt/d – Metric Tons per Day
MW – Molecular Weight
MW – Megawatt
MWe – Megawatt electric
MWGS – Membrane water gas shift

n – exponent on driving force
 N_2 – Nitrogen
 NH_3 – Ammonia
 Nm^3 – Normal cubic meter

O_2 – Oxygen
OPER – Operating
OT – Operating Temperature

P – partial pressure
P – Pump
 P_0 – pre-exponential permeance factor
P&I – Plant and Instrument
Pa – Pascal
PFD – Process flow diagram
ppmv – Parts Per Million (volume basis)
ppmvd – Parts Per Million (volume and dry basis)

R – ideal gas constant

s or sec – Second

SOFCo – partnership between McDermott International, Inc. and Ceramtec, Inc.

SRU – Sulfur Recovery Unit

ST – Steam Turbine

SU – Sump

SWS – Sour Water Stripper

T – Temperature

TGTU – Tailgas Treating Unit

TK – Tank

T/T – Tangent to Tangent Length

UPS – Uninterruptible Power Supply

US – United States

V – Vessel/Column

WGS – Water Gas Shift

Wt% – Weight percent

1.2.1.1.7.12 Appendix A - MWGS Reactor Phase 1

CO₂ CAPTURE PROJECT



MEMBRANE WATER GAS SHIFT REACTOR

PHASE I

PREPARED BY

FLUOR,

CONTRACT: 65501200

JUNE 2003

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ABBREVIATIONS/ACRONYMS

| | |
|---|--|
| ASU – Air Separation Unit | IGCC – Integrated Gasification Combined Cycle |
| bara – bar absolute | J – Joule |
| barg – bar gauge | J – flux |
| BFW – Boiler Feedwater | K – Kelvin |
| BTU – British Thermal Unit | kg – Kilogram |
| °C – Degrees Celsius | kgmol – Kilogram moles |
| CCP – CO ₂ Capture Project | kJ – Kilojoules |
| CEMS – Continuous Emissions Monitoring System | LHV – Lower Heating Value |
| CH ₄ – Methane | LP – Low Pressure |
| CO – Carbon monoxide | m – Meter |
| CO ₂ – Carbon dioxide | m ² – Square meters |
| Cond – Steam condensate | m ³ – Cubic meters |
| COS – Carbonyl sulfide | mbar – Millibar |
| CSM – Colorado School of Mines | mm – Millimeter |
| CT – Combustion Turbine | Mol% – Molar percent |
| Cu – Copper | mt/d – Metric Tons per Day |
| dB – Decibels | MW – Molecular Weight |
| DCS – Distributed Control System | MWe – Megawatt electric |
| DOE – Department of Energy | MWGS – Membrane water gas shift |
| E – activation energy | n – exponent on driving force |
| ECN – Energy research Centre of the Netherlands | N ₂ – Nitrogen |
| EOR – Enhanced Oil Recovery | NAG – Numerical Algorithm Group Ltd |
| Fe – Iron | NH ₃ – Ammonia |
| Fe-Cr – Iron Chromium | Nm ³ – Normal cubic meter |
| GE – General Electric | O ₂ – Oxygen |
| GI – Gasification Island | P – partial pressure |
| gmol – Gram mole | P ₀ – pre-exponential permeance factor |
| h or hr – Hour | P&I – Plant and Instrument |
| H ₂ – Hydrogen | Pa – Pascal |
| H ₂ O – Water | Pd – Palladium |
| H ₂ S – Hydrogen sulfide | ppmv – Parts Per Million (volume basis) |
| HCN – Hydrocyanic acid | ppmvd – Parts Per Million (volume and dry basis) |
| HP – High Pressure | R – ideal gas constant |
| HRSG – Heat Recovery Steam Generator | s or sec – Second |
| HVAC – Heating, Ventilation and Air Conditioning | |

SOFCo – partnership between
McDermott International, Inc.
and Ceramatec, Inc.

SRU – Sulfur Recovery Unit

T – Temperature

TDA – TDA Research, Inc.

UPS – Uninterruptible Power Supply
US – United States

WGS – Water Gas Shift

Wt% – Weight percent