1.0 EXECUTIVE SUMMARY

Project Background

The CO_2 Capture Project (CCP), a Joint Industry Project, consists of eight (8) major energy companies to develop cost effective technologies for the capture and geologic storage of carbon dioxide. CCP is commissioning work in Europe and North America with co-funding from the United States (US) Department of Energy (DOE), European Union and Norwegian Klimatek Agencies. The goals of the advanced technologies are:

- to capture at least 90% of the carbon dioxide that would be emitted by a given facility;
- to reduce the cost of carbon dioxide capture and storage by 75% for new facilities and 50% for retrofits when compared to the cost of achieving the same level of removal using currently available technologies; and
- to develop these technologies by 2003, conduct a demonstration test, and start commissioning of a large-scale operation before 2010.

The technical staff of CCP is divided into specialized teams: (i) Post-Combustion, (ii) Pre-Combustion, (iii) Oxyfuels. They have identified four scenarios, which represent existing or future planned facilities. Baseline studies shall be developed for each scenario to provide input to an economic model, which will be used to estimate the extent of cost savings for future technology development options.

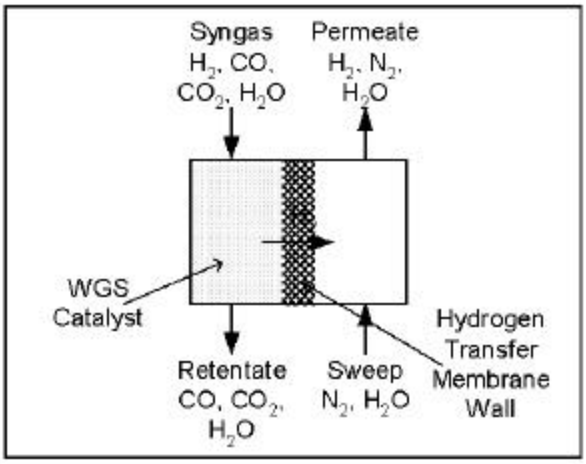
This study (Membrane Water Gas Shift Reactor Study) has been initiated by the Pre-Combustion team, which has a specific focus on the capture and separation of carbon dioxide from fuel before combustion.

Objectives of the Study

The objective of this study (Phase I) is to determine the performance of a gasification plant with a Membrane Water Gas Shift (MWGS) reactor, which separates hydrogen from syngas. This study is based on the European Refinery scenario, which consists of multiple refinery heaters/boilers fired with sulfur-containing residual fuel oil, refinery fuel gas and natural gas.

For this study, the residual fuel oil and refinery fuel gas are fed to a gasification plant to produce syngas for a MWGS reactor. The concept for the MWGS reactor is shown in Figure 1-1.

Figure 1-1
Membrane Water Gas Shift Reactor



The MWGS reactor consists of a hydrogen transfer membrane with water gas shift catalyst. The 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) is returned to the existing refinery heaters/boilers resulting in a carbon-dioxide free flue gas. The retentate is mostly carbon dioxide and, after removal of sulfur compounds, is sent to geologic formations for storage. Electrical power required to operate the entire gasification plant is provided by a natural gas fired combined cycle.

Four different membranes were chosen by CCP to be evaluated in this study: (i) proton-conducting metal ceramic composite membrane, (ii) palladium alloy membrane, (iii) microporous silica membrane, and (iv) zeolite membrane. Sensitivity studies were first developed using a computer simulation model developed by Energy research Centre of the Netherlands (ECN) to determine the "optimum" operating conditions of the MWGS reactor in conjunction with the gasification plant. Operating parameters (e.g. syngas feed temperature and pressure) were determined.

Based on experimental tests with both sulfur-free (sweet) and sulfur-containing (sour) syngas, the membrane vendors provided permeances for both sweet and sour conditions. To compare the four membranes, each MWGS reactor was isolated from the rest of the gasification plant, and the performance for each reactor was estimated using the computer model. A membrane was selected and integrated into the gasification plant.

Facility Summary Description

The Membrane Water Gas Shift Reactor Study is based on a gasification plant fed with residual fuel oil and refinery fuel gas. The major units/systems comprising the gasification plant are:

- Air Separation Unit
- Gasification Island
- Preheating and Bulk Shift Catalyst Unit
- Membrane WGS Reactor
- Permeate Cooling Unit
- Retentate Cooling Unit
- Condensate (Ammonia) Stripper Unit
- Sulfur Recovery (Sulferox) Unit
- CO_2 Compression/Dehydration Unit
- Natural Gas Fired Combined Cycle
- Utilities and Support Systems

Key Results and Path Forward

The individual membrane performances are shown in Table 1-1. The following definitions were used to compare the membrane performances:

- Carbon Compounds = carbon in all carbon-containing compounds (i.e. CO, CO_2, CH_4 & COS)
- Carbon Recovery = (carbon compounds in retentate)/(carbon compounds in feed)
- Hydrogen Recovery = (H_2 in permeate)/(H_2 + CO in feed)
- CO_2 Purity = molar composition of CO_2 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 areas and sweep flow rates were adjusted to determine the maximum carbon recovery for a membrane with a retentate containing 90 mol% (dry) carbon dioxide and a permeate heating value of 150 Btu/SCF (LHV).

The performance results are shown in Table 1-1, which show that the H_2/CO_2 permselectivities for three membranes were inadequate. Consequently, these membranes could not meet the target carbon recovery. The metal ceramic composite was the only membrane to achieve a carbon recovery over 90%; as a result, CCP decided that the overall gasification plant performance be based on the metal ceramic composite membrane with permeances from experimental tests with sweet syngas. Therefore, for Phase I, the performance of the sulfur tolerant MWGS reactor was estimated based on permeances derived from experiments with a sweet syngas feed and is shown in Table 1-2.

Path Forward

The work for Phase II will be based on the metal ceramic composite membrane with permeances derived from experiments with a sweet syngas feed. The sulfur tolerant MWGS reactor will not be pursued due to low hydrogen flux when sulfur compounds are present. Consequently, the configuration for the gasification plant will be revised to remove the sulfur compounds to less than a 10 ppmv hydrogen sulfide and carbonyl sulfide content in the feed to the MWGS Reactor. The tasks for Phase II will include:

- Design the gasification plant for a sweet syngas feed to the metal ceramic composite membrane WGS reactor (Fluor).
- Develop a laboratory proof-of-concept MWGS reactor (Eltron Research Inc.).
- Design and estimate the cost of a commercial scale MWGS reactor (SOFCo).

Table 1-1
Membrane Water Gas Shift Reactors Performance Summary

Membrane Type	Metal Ceramic Composite		Pd-Alloy		Silica	Zeolite
Syngas Feed for Experimental Tests (to determine permeances)	Sweet	Sour	Sweet	Sour	Sour (Note 4)	Sour (Note 4)
Syngas feed temperature, C	315	450	350		315	315
Syngas feed pressure, barg	34					
Sweep gas pressure, barg	2					
Carbon recovery,%	100.0		73.5	45.6	35.1	12.4
CO2 purity, dry %	90.2	90.0	90.0	90.0	90.0	86.6
Hydrogen recovery, %	95.3	95.2	96.9	97.8	95.9	98.9
Hydrogen LHV, Btu/SCF (Note 1)	149.7	149.8	150.0	150.7	149.8	150.1
H2 flux, mol/m2-sec	0.19	0.08	0.35	0.15	0.22	0.17
H2:CO2 permselectivity at feed conditions	infinite	infinite	13.3	5.5	4.7	2.6 (Note 2)
Membrane area required, m2	17,325	39,000	9,400	21,500	15,000	19,400
Nitrogen sweep gas required, kgmol/hr	9,100	9,100	7,800	5,000	7,000	4,500
Steam sweep gas required, kgmol/hr	8,800	20,000	-	20,000	230,000	8,000

Notes:
(1) Cooling of fuel to 35°C was required to meet LHV requirement
(2) Permeance at 10 bar.
(3) n/a = not applicable
(4) See preliminary sensitivity studies for performance of the silica and zeolite membrane with sweet syngas.

Table 1-2 Gasification Plant Performance Metal Ceramic Composite Membrane	
Gasifier feed (41% fuel oil/59% refinery fuel gas)	3802.8 GJ/hr (LHV)
Natural gas for power generation	755.8 GJ/hr (LHV)
Total fuel to plant	4558.6 GJ/hr (LHV)
Hydrogen fuel return to existing boilers	2800.1 GJ/hr (LHV)
Overall thermal efficiency for hydrogen fuel	61%
Pure carbon dioxide to sequestration	2.02 million tonnes/yr
Power Generation	MWe
Combustion Turbine	72
Steam Turbine	34
Auxiliary Power Consumption	69
Net Power Export	37

2.0 INTRODUCTION

2.1 Project Background

Eight energy companies (British Petroleum, ChevronTexaco, ENI, Norsk Hydro, EnCana, Shell, Statoil, and Suncor Energy) have joined together to form the CO_2 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. This economic model will be used to prioritize and measure the extent of cost savings for future technology development options.

2.2 Scope of Work

The scope of this study (Phase I) is to determine the performance of a gasification plant with a Membrane Water Gas Shift (MWGS) reactor, which separates hydrogen from 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, after removal of sulfur compounds, is sent to geologic formations for storage. Electrical power required to operate the plant is provided by a natural gas fired combined cycle.

Membranes from four vendors were chosen by CCP to be evaluated in this study:

- 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

To compare the four membranes, each Membrane WGS reactor was isolated from the rest of the gasification plant, and the performance for each reactor was estimated using a computer simulation model provided by CCP and developed by ECN. The membrane with the "best" performance was chosen and integrated into a gasification plant to determine the overall performance of the entire facility. For Phase I, it is assumed that the MWGS reactor is sulfur tolerant (sour syngas feed).

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

- Develop design basis for the project
- Use the computer simulation model to determine the performance for each Membrane WGS reactor with the different membranes
- Based on CCP's input, develop a process design for the overall gasification plant

The results of the study effort are presented in the following deliverables:

- Design basis
- Membrane comparison table
- Summary block flow diagram
- Brief process descriptions
- Process flow schematics
- Heat and material balance
- Overall plant performance

2.3 Scope of Facilities

The gasification plant consists of the following units:

- Air Separation Unit
- Gasification Island
- Preheating and Bulk Shift Catalyst Unit
- Membrane WGS Reactor
- Permeate Cooling Unit
- Retentate Cooling Unit
- Condensate (Ammonia) Stripper Unit
- Sulfur Recovery (Sulferox) Unit
- CO_2 Compression/Dehydration Unit
- Natural Gas Fired Combined Cycle
- Utilities and Support Systems

3.0 MEMBRANE WATER GAS SHIFT REACTOR

3.1 Concept

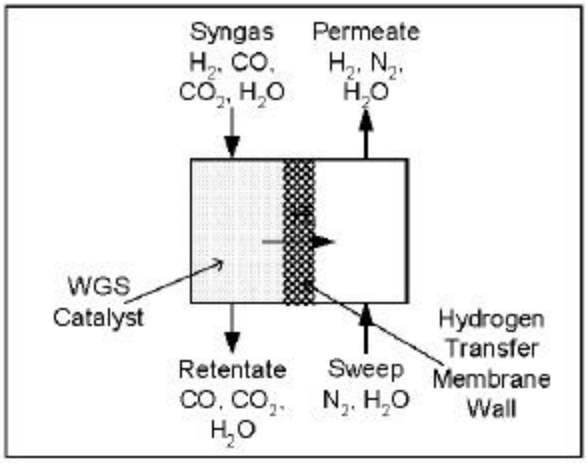
The Membrane Water Gas Shift (MWGS) Reactor concept involves a hydrogen transfer membrane inside a MWGS reactor. The membrane technology involves the separation of the hydrogen utilizing a membrane by selective permeation of the hydrogen across the membrane. The hydrogen is dissolved into the membrane 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:

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

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 3-1.

Figure 3-1
MWGS Concept



3.2 Membrane Types

In July 2001, CCP chose four types of membrane for testing in Phase I of the project. The membrane types and vendors are shown in Table 3-1.

Table 3-1
Membrane Types and Vendors

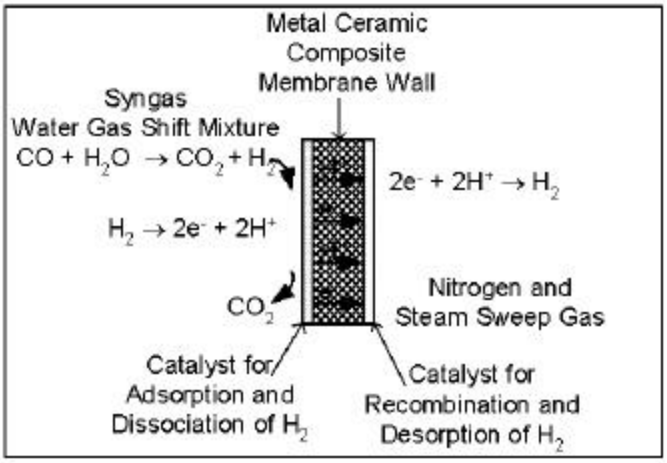
Membrane Type	Membrane Vendor
Proton-conducting metal ceramic composite	Eltron Research Inc.
Palladium alloy	Colorado School of Mines/TDA Research
Microporous silica	Energy research Centre of the Netherlands (ECN)
Zeolite	University of Cincinnati

All four membrane vendors conducted hydrogen flux tests using single and binary gases at various temperatures and pressures. Leakage due to membrane imperfections and/or seal leaks were identified by measuring the permeation of non-hydrogen compounds. Following the initial tests, each membrane developer conducted flux tests using a prescribed syngas composition, containing water and hydrogen sulfide. No WGS catalyst was present in either flux tests.

3.2.1 Proton-Conducting Metal Ceramic Composite Membrane

The proton-conducting metal ceramic composite membrane was offered by Eltron Research Inc. located in Boulder, Colorado. The hydrogen transport concept for the membrane is shown in Figure 3-2.

Figure 3-2
Hydrogen Transport for the Metal Ceramic Composite Membrane



Metal ceramic composites were made by sintering together perovskite (ceramic) and palladium (metal powder) to form dense continuous matrices of both metal and ceramic. These materials were chosen based on: high proton transport rate, cost, low toxicity, ease of synthesis, thermal and chemical stability, and catalytic properties. The palladium and perovskite 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.

The first membrane test consisted of measuring hydrogen flux through the membranes under ideal conditions using a hydrogen plus helium mixture. The mixture was streamed past one side of the membrane and pure argon carrier (sweep) gas was streamed past the opposite side of the membrane. Hydrogen and helium concentrations were measured in the argon exhaust by gas chromatography. Leaks, if any, were detected using helium; however, the membranes tested were reported to be leak-free. The performance of the membrane based on permeances derived from experimental tests with sweet syngas are shown in section 3.4.3 (Note that the actual feed basis in the computer model for the MWGS reactor is sour syngas.)

Because of anticipated reactions between palladium and the hydrogen sulfide in the syngas and concerns over the high cost of palladium, metals from Group IVB and Group V including, for example, vanadium, niobium, tantalum and zirconium 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.