Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO$_2$ Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

Edited by

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Chapter 23

GRACE: PRE-COMBUSTION DE-CARBONISATION HYDROGEN MEMBRANE STUDY

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ABSTRACT

This chapter details the GRangemouth Advanced CapturE (GRACE) project to develop new membrane technology to preferentially permeate hydrogen as part of a pre-combustion de-carbonisation process to capture CO_2. The project forms part of the wider CO_2 Capture Project (CCP) that aims to develop a range of technology options to capture CO_2 via either pre-combustion de-carbonisation, the use of oxygen-rich combustion systems or post-combustion CO_2 recovery.

In addition to developing a new hydrogen membrane, the remit of the GRACE project includes applying the new technology to a specific scenario to evaluate installation costs and the amount of CO_2 emissions that could be avoided if the technology were to be implemented. In this study, the capture of 2 million tonnes/year of CO_2 from BP's Grangemouth complex in Scotland has been selected as the "real-life" scenario.

Previous study work completed by the GRACE project identified a Palladium/Silver metal membrane, developed by SINTEF, as the best membrane technology for hydrogen permeation. This study is based on the use of the SINTEF membrane coupled to conventional hydrogen production technology.

The results of this study are that:

- the option of using conventional hydrogen production technology and the SINTEF hydrogen membrane to capture CO_2 and produce hydrogen suitable for combustion is technically feasible;
- a SINTEF membrane module design has been developed;
- the fabrication cost of each membrane module is estimated to be $3.12 million;
- the total cost to capture 2 million tonnes of CO_2 from the Grangemouth complex using pre-combustion de-carbonisation technology that incorporates the SINTEF membrane is estimated to be $251 million;
- this cost represents the lowest cost of any technology developed in the CCP programme, and represents a 28% cost reduction compared to the CCP baseline technology (post-combustion amine absorption);
- the selected process incorporates a high degree of self-sufficiency in terms of power demand. However, a certain amount of electrical power will have to be imported from local sources. Assuming that conventional gas turbines are used to generate this shortfall, this reduces the amount of CO_2 emitted to atmosphere that is avoided by implementing the selected process scheme to about $1\frac{1}{2}$ million tonnes per year.

INTRODUCTION

The CO_2 Capture Project (CCP) is a joint project being undertaken by eight major energy companies to develop new and novel technologies that significantly reduce the cost of capturing and storing CO_2. The project is split into three distinct elements:

Abbreviations: ASU, Air separation unit; ATR, Autothermal reactor; CCP, CO_2 capture project; GRACE, Grangemouth advanced capture project; LHV, Lower heating value; OOM, Order of magnitude; SINTEF, Norwegian Petroleum Research Institute; WGS, Water gas shift.

- pre-combustion de-carbonisation;
- the use of oxygen-rich combustion systems; and
- post-combustion CO_2 recovery.

For each element, technologies will be developed in the context of certain scenarios that relate to combustion sources and fuels common to the operations of the CCP participants. Four scenarios are considered:

- large gas-fired turbine combined cycle power generation;
- small or medium sized simple cycle gas turbines;
- petroleum coke gasification; and
- refinery and petrochemical complex heaters and boilers.

The GRangemouth Advanced CapturE (GRACE) project forms part of the wider CCP programme and is funded partly by the CCP partners and partly by the European Commission. Its remit is to develop pre-combustion de-carbonisation and oxy-fuel options to capture CO_2 using BP's Grangemouth complex as the case study—representative of the "refinery and petrochemical complex heaters and boilers" scenario listed above. Post-combustion technology is not part of the GRACE project scope.

As implied by the name, pre-combustion de-carbonisation technology relates to the removal of carbon from fuel gas upstream of a combustion chamber. Typically, methane-rich fuel gas is converted into CO_2 and hydrogen. Separation of these two components yields two process streams, a hydrogen-rich stream for use as combustion fuel and a CO_2-rich stream that can then be compressed and transported to a suitable location for subsurface storage. The GRACE project is concerned with developing membrane technology to preferentially permeate hydrogen and thus deliver the required separation.

Three different hydrogen membrane technologies have previously been considered—a Palladium/Silver metal membrane from SINTEF (Norway), a Silica-based membrane developed by the University of Twente (Netherlands) and a Zeolite option from a joint development between Zaragoza University (Spain) and the Royal Technical University of Stockholm (KTM, Sweden). Each membrane was tested by the Institute for Membrane Research—an associate of the University of Calabria, Italy—and it was concluded that the preferred option is the Palladium/Silver SINTEF membrane.

This report summarises a study to capture CO_2 from BP's Grangemouth complex using conventional hydrogen production technology coupled with the SINTEF membrane. The tasks undertaken in this study are:

to develop a process design incorporating a hydrogen membrane unit;
to propose a membrane design;
to evaluate the operating efficiency, level of CO_2 capture and utility demand; and
to size equipment and derive order of magnitude (OOM) costs for the BP Grangemouth case.

PROCESS DESIGN SCREENING AND EVALUATION

Design Basis
This section outlines the design basis for the study, the selected hydrogen production process, and the schemes considered to separate hydrogen and optimise the overall process. The design basis for the study is as follows:

- To capture 2 million tonnes/year of CO_2 from BP's Grangemouth complex, meeting the following specification:
  - CO_2 to contain at least 90% of the carbon present in the methane-rich feed gas;
  - CO_2 purity to be at least 97 mol%;
  - water content of the CO_2 stream to be less than 50 ppmv;

- ○ CO$_2$ to be delivered to the Grangemouth Battery Limits at a pressure of 220 barg—this is linked to the intent to transport the captured CO$_2$ to a suitable location for subsurface storage and is consistent with all CCP studies, thus allowing comparison of costs on an equal footing.
- The hydrogen-rich product stream must have minimum hydrogen content of 60 mol%.
- A single process train.
- Utility supply to be included in the equipment design and costing:
  - ○ oxygen to be supplied from an air separation unit (ASU) at 30 barg and 30 °C;
  - ○ nitrogen available from the ASU at 4 barg and 25 °C;
  - ○ cooling medium to be an indirect water system with supply temperature of 27 °C and return temperature of 45 °C;
  - ○ heating medium to be steam;
  - ○ power demand to be met, as far as possible, by steam raised by recovering heat from the process. This steam is then to be used in steam turbines either to provide direct mechanical shaft power or to generate electrical power. Any shortfall must then be taken from the local electrical grid.

Feed gas to the process is a fuel gas typical of the Grangemouth complex. Table 1 outlines the compositions of three such fuel gas streams and their relative contribution to the process feed gas considered by the study.

TABLE 1
TYPICAL GRANGEMOUTH COMPLEX FUEL GAS COMPOSITIONS

Component	Fuel gas A	Fuel gas B	Fuel gas C
Contribution to feedstock			
Mol%	63	0	37
Composition (mol%)			
Methane	67.8	58.0	69.7
Ethane	9.5	0.1	0.9
Ethene	0.02	0.1	0.1
Propane	7.4	0	0
Propene	0.01	0	0
iso-Butane	1.1	0	0
n-Butane	3.1	0	0
iso-Butene	0.05	0	0
Methyl-1-Butenes	0.1	0	0
iso-Pentane	0.16	0	0
n-Pentane	0.04	0	0
Hydrogen	7.9	40.8	29.1
Oxygen	0.03	0	0
Nitrogen	0.75	1.0	0.2
Carbon monoxide	0	0	0
Carbon dioxide	2.0	0	0
Hydrogen sulphide	0.005	0	0
Total	100	100	100
Lower heating value			
LHV (MJ/kg)	46.5	54.3	53.2
Pressure			
bara	2.5	2.5	2.5
Temperature			
°C	20	20	20

Various process schemes are evaluated by the study. The preferred option is selected based on the following metrics:
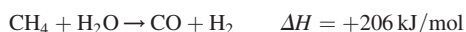
- *Lower heating value (LHV) efficiency*—a measure of the heat content of the recovered hydrogen stream, relative to the methane-rich feed gas.
- *Power deficit*—the additional electrical power that must be supplied from external sources.
- *CO_2 captured*—the amount of carbon present in the methane-rich feed gas that is captured as CO_2.
- *CO_2 purity*—the CO_2 content of the captured CO_2-rich stream (mol%).
- *Hydrogen purity*—the hydrogen content of the hydrogen-rich stream (mol%).

The selected case is then taken forward to more detailed design, costing and evaluation. This is covered in the section on "Review of the Selected Design Option" of this report.

Hydrogen Production

The process selected by this study to produce hydrogen and carbon dioxide from methane-rich fuel gas consists of an autothermal reformer (ATR) coupled to a water gas shift (WGS) reactor. This option is considered typical of the available processes and representative of best-in-class technology.

Autothermal reforming consists of a combination of steam reforming and partial oxidation of the fuel gas feed. Steam reforming is a highly endothermic reaction, typically undertaken over a Nickel catalyst in a tubular reactor:

$$CH_4 + H_2O \rightarrow CO + H_2 \qquad \Delta H = +206\,kJ/mol$$

or, more generally:

$$C_xH_y + H_2O \rightarrow xCO + (x + \tfrac{1}{2}y)H_2 \qquad \Delta H + ve$$
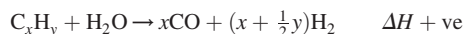
A high conversion of methane/hydrocarbon to hydrogen is achieved at high temperatures of $800-900\,°C$.

Partial oxidation involves reacting the light hydrocarbon feed in a sub-stoichiometric oxygen atmosphere in a catalytic or non-catalytic reactor. In contrast with the steam reforming reaction, the partial oxidation process is exothermic:

$$C_xH_y + \tfrac{1}{2}O_2 \rightarrow xCO + \tfrac{1}{2}yH_2 \qquad \Delta H - ve$$
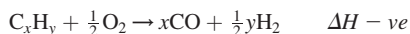
Autothermal reforming uses both the above reaction mechanisms and seeks to efficiently convert hydrocarbons by providing the endothermic steam reforming heat of reaction, in part, by the heat generated by the partial oxidation reaction.

The gas mixture produced by the ATR is predominantly hydrogen and carbon monoxide, and is often termed synthesis gas or "syngas". Higher hydrogen conversion rates can be achieved by further converting the carbon monoxide to carbon dioxide and hydrogen using the WGS reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -410.25kJ/mol$$

Process Scheme Options

Six process schemes are considered:

Case A   Base Case Option
Case B   Base Case + Hydrogen-Powered Gas Turbine
Case C   Base Case + Membrane Retentate Combustion
Case D   Base Case + Discrete WGS Reaction and Membrane Separation
Case E   Base Case + Nitrogen Sweep Gas
Case F   Base Case + Discrete Reaction/Membrane Separation + Nitrogen Sweep Gas

Case A is a simple application of the ATR and WGS processes outlined in the previous section coupled with a SINTEF Palladium/Silver membrane to separate the hydrogen. Alternative process scheme options include variations in reactor arrangement, the use of different membrane sweep gases and varying degrees of waste heat recovery to raise additional steam and thereby reduce the net import of electrical power from the local grid.

Case A: base case
A schematic process flow sheet for Case A is provided in Figure 1.
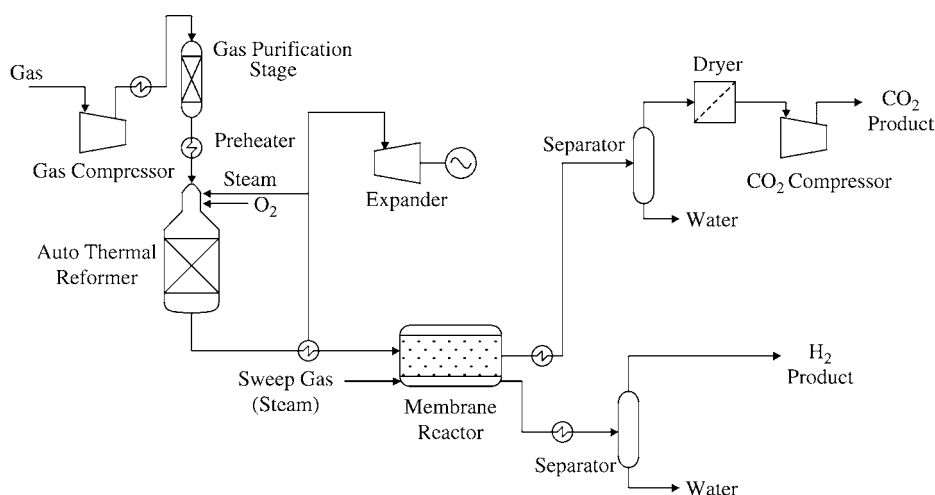
Figure 1: Case A: base case schematic process design.

Feed gas pre-treatment. The fuel gas feed is initially compressed to 30 bar and then heated to 300 °C. Any sulphurous components must be removed prior to the ATR to avoid deactivating the catalyst. This is achieved by initially converting all sulphurous components to H_2S in a Cobalt–Molybdenum catalyst bed, and then removing the H_2S with a Zinc Oxide bed. Desulphurised feed gas is then further heated to about 550 °C and then fed to the ATR.

Autothermal reformer (ATR). Both steam and oxygen are fed to the ATR to convert the light hydrocarbon feed into syngas by the reaction mechanisms outlined in the section on "hydrogen production" (steam reforming and partial oxidation).

The ATR is operated with an exit gas temperature of up to 1000 °C to ensure acceptable methane conversion is achieved without the need for excessive oxygen consumption. The exit gas is then cooled to around 200 °C by heating the fuel gas feed to the process and by raising high-pressure steam, which is, in turn, fed to steam turbines and used to provide direct mechanical shaft power and to generate part of the electrical power consumed by the process.

Water gas shift/hydrogen separation. The base case option incorporates a single membrane reactor unit, within which the WGS reaction and hydrogen separation take place simultaneously. The concept, shown in Figure 2, comprises a reaction zone containing a catalyst that promotes the WGS reaction. High-pressure gas from the ATR passes through this reaction zone producing carbon dioxide and additional hydrogen from the carbon monoxide in the feed gas. Hydrogen permeates through the membrane and is removed from the unit either by sweep gas or simply by maintaining the permeate stream at a low pressure—steam sweep gas is considered in this case. Removal of the hydrogen helps drive the WGS reaction equilibrium position in favour of hydrogen production, thus increasing the overall conversion rate.

Figure 2: Conceptual design for a membrane reactor unit in which the water gas shift reaction and hydrogen separation take place simultaneously.
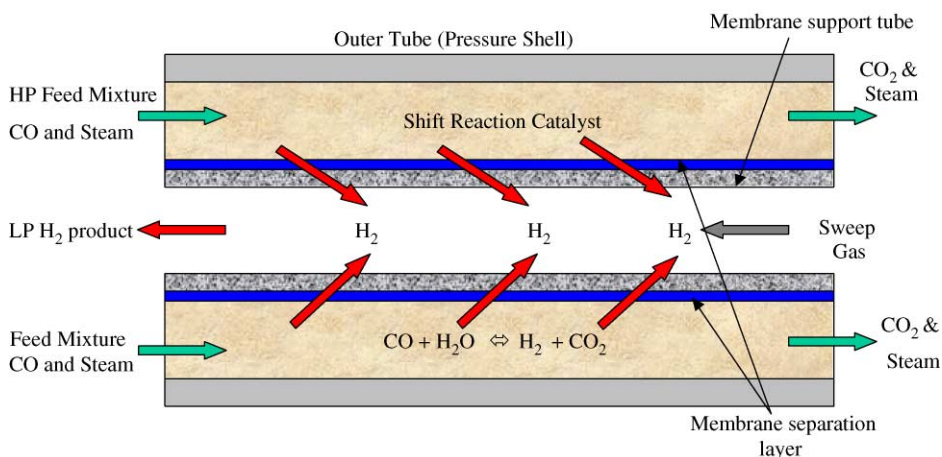
There are several possible physical layouts of the system. The option considered in this study is a concentric tube arrangement with the high-pressure catalyst filled reaction zone in the annular space around a membrane tube, within which is the low-pressure permeate stream.

The membranes developed by the GRACE project are extremely thin in order to maximise the mass transfer flux. A porous support is then needed to provide mechanical strength and avoid damage to the membrane.

The gas leaving the membrane reactor is predominantly carbon dioxide and steam, but also contains small quantities of unreacted methane and carbon monoxide. The gas is then cooled to about 25 °C by heat integration with the ATR feedstock and by heating process water. The recovered hydrogen is cooled to about 40 °C with cooling water.

CO$_2$ drying and compression. The cooled retentate stream from the membrane reactor is fed to a separator to remove condensed water. A molecular sieve is then used to dry the CO$_2$ product stream and meet the water specification of less than 50 ppmv. The CO$_2$ is then compressed to 220 barg with a 4-stage electric motor driven centrifugal compressor.

Hydrogen drying and compression. The permeation mechanism of the Palladium/Silver membranes is such that only hydrogen can pass through. Consequently, contamination of the hydrogen product stream can only result from the presence of residual sweep gas. For a steam sweep gas, simply cooling and then separating the condensed water is sufficient to deliver an acceptable hydrogen product stream for use as a fuel gas.

Some downstream compression of the hydrogen stream is required to meet the demands of the Grangemouth complex. This is not covered here, but is consistently applied to all cases from a cost perspective.

Power generation. Heat recovery from the various process streams is maximised to meet process demands and to raise steam that is, in turn, used to either generate electrical power or used in steam turbines to provide direct mechanical drive shaft power. Additional electrical power not generated from within the process is imported from the local grid.

Case B: base case + hydrogen power gas turbine
This option, shown schematically in Figure 3, is identical to the base case, but incorporates a gas turbine, fired by hydrogen, to generate the power deficit imported in case A.
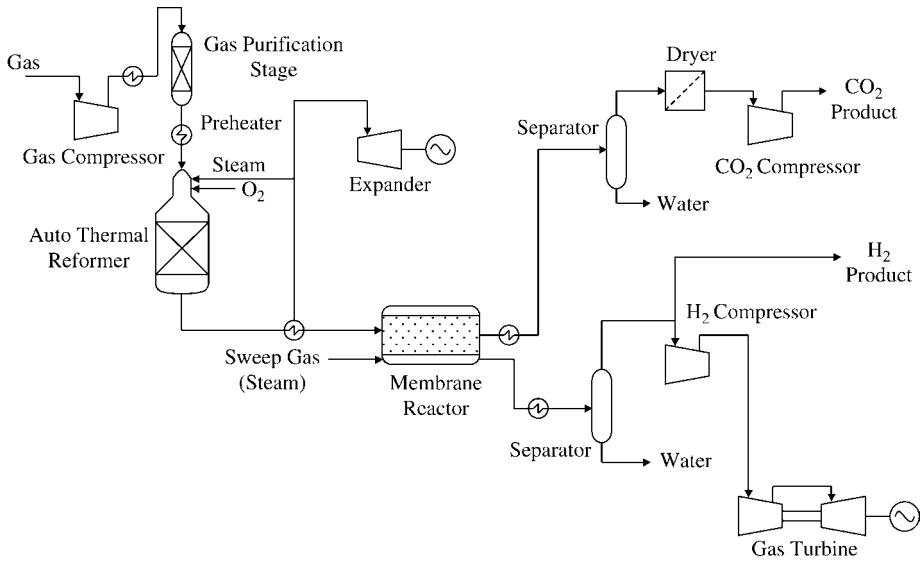
Figure 3: Case B: base case option with an added hydrogen-powered gas turbine.

Case C: base case with membrane retentate combustion

The option, shown schematically in Figure 4, is again similar to the base case (Case A), but includes a step to burn the membrane retentate stream and thereby convert the remaining hydrocarbons (essentially methane) and carbon monoxide to carbon dioxide. In this way, the CO_2 recovery and purity increase and additional steam can be raised by recovering heat from the outlet of the combustor and thereby cut the power deficit.
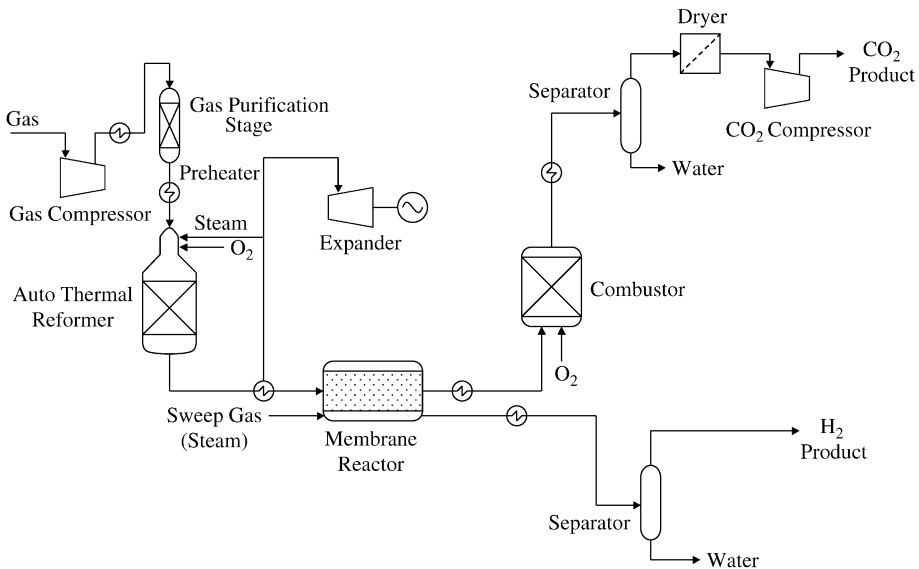
Figure 4: Case C: base case with addition of membrane retentate combustion.

The membrane retentate stream is cooled to about 170 °C by heating high-pressure boiler feed water. The retentate stream is then fed to the combustor with sufficient oxygen to fully convert all hydrocarbons and carbon monoxide to carbon dioxide. This produces an exit gas temperature of about 950 °C, which is cooled by raising high pressure steam, heating the fuel gas feedstock to the process, superheating medium pressure steam, raising low pressure steam and heating process water.

Case D: base case with discrete water gas shift reaction and membrane separation
Case D, shown schematically in Figure 5, is identical to Case C, but with discrete reaction and membrane separation stages rather than a single membrane reactor unit. This gives flexibility in the membrane arrangement, permitting tubular or planar schemes and allowing a higher surface area per unit volume. In addition, the combined membrane reactor has an inherent risk that the membranes will be damaged during change-out of the catalyst.
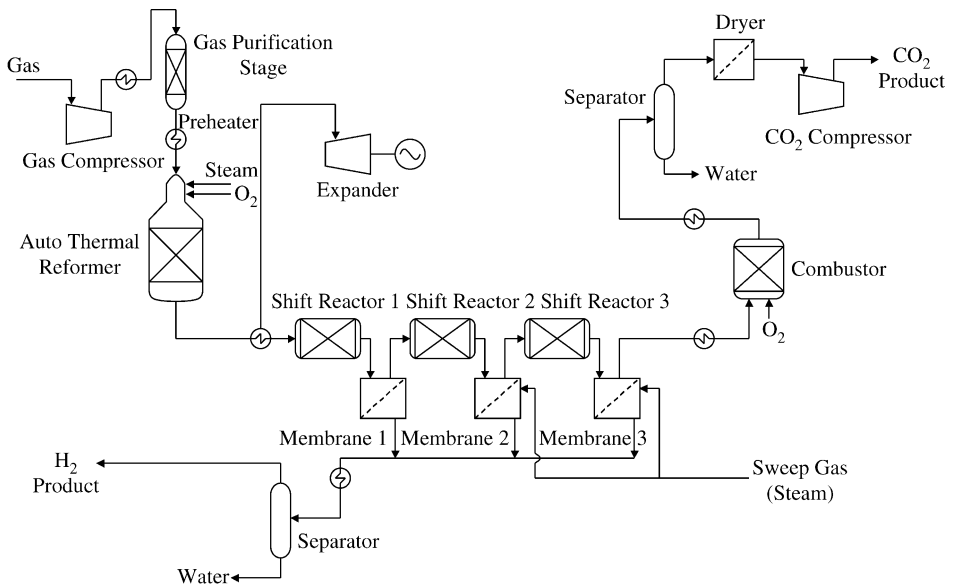
Figure 5: Case D: base case with discrete water gas shift reaction and membrane separation.

The use of discrete membrane stages also allows some optimisation of the sweep gas. For example, in the case considered, sweep gas is only used in the second and third membrane stages.

Case E: base case with nitrogen sweep gas
Case E, shown schematically in Figure 6, is identical to Case C, but uses nitrogen as the membrane sweep gas instead of steam. This adversely affects the purity of the hydrogen product stream, as no additional processing is included to separate nitrogen from hydrogen.

Case F: base case with discrete reaction membrane separation and nitrogen sweep gas
The final case is identical to Case D, but uses nitrogen as the sweep gas instead of steam.

Hydrogen Membrane Process Option Comparison
Table 2 summarises the performance metrics of each of the six options considered here.
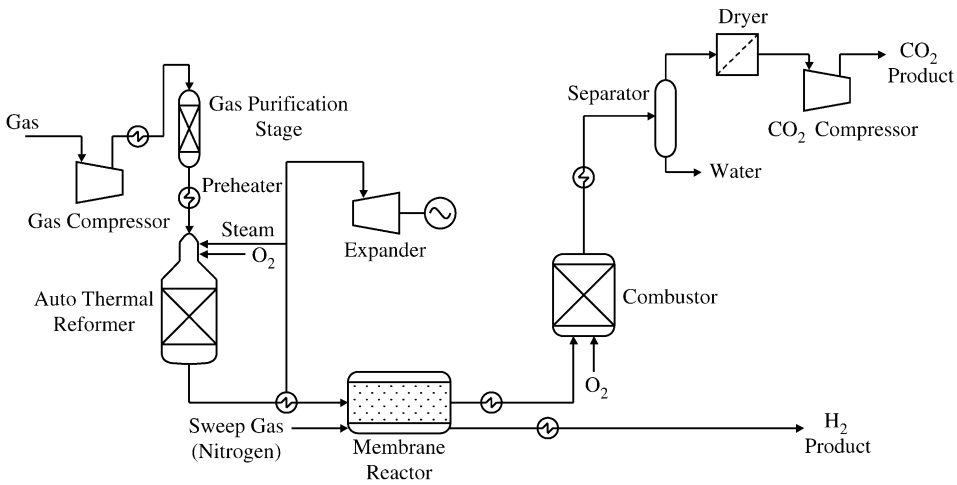
Figure 6: Case E: base case with membrane retentate combustion and nitrogen sweep gas.
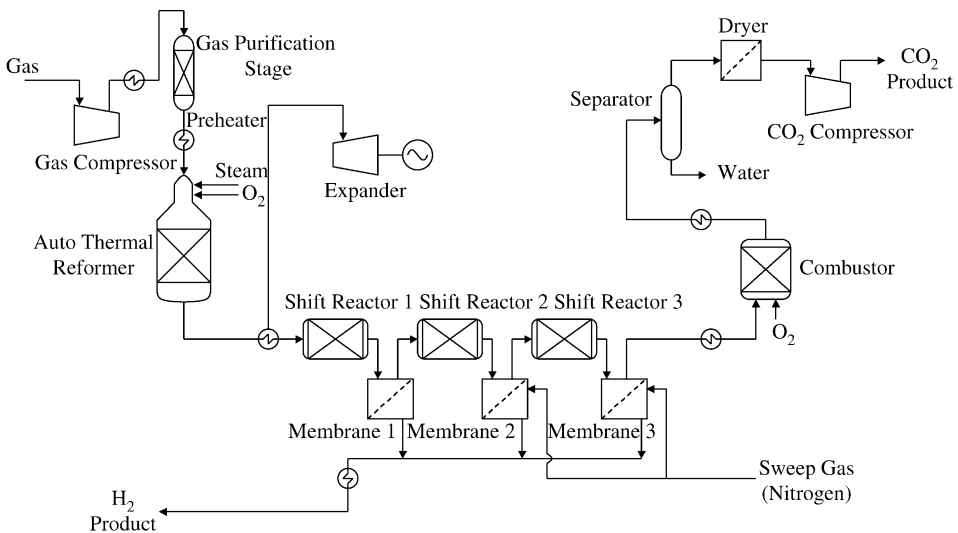
Figure 7: Case F: base case with discrete reaction/membrane separation and nitrogen sweep gas.

Considering each option in turn:

- Case A is the base case and provides a baseline for the comparison of other options.
- Case B differs from Case A in that it uses some of the recovered hydrogen to generate the power that cannot be generated as a result of heat recovery from the process stream. The use of some of the hydrogen product stream inevitably means that the heat content of the hydrogen stream exported to the Grangemouth complex is lower than that in Case A, and hence the LHV efficiency is lower.
- Cases A and B both fail to meet the minimum CO_2 product stream purity specification of 97 mol%.

TABLE 2

CONSOLIDATED PERFORMANCE METRICS FOR THE SIX HYDROGEN MEMBRANE DESIGNS

Case	A	B	C	D	E	F
LHV efficiency (%)	80	71	78	78	78	78
Power deficit (MW)	47	0	23	21	19	18
CO_2 captured (%)	91	91	99	99	99	99
CO_2 purity (mol%)	91	91	99	99	99	99
Hydrogen purity (mol%)	100	100	100	100	71	86

- Cases C to F each include a combustor to convert residual levels of methane and carbon monoxide in the exit gas stream from the membrane unit into CO_2. Consequently, in each of these options, both the amount of CO_2 captured and the purity of the CO_2 product stream increases. The rise in CO_2 purity is particularly relevant as these cases now meet the required CO_2 purity product specification.
- The heat generated by the exothermic reaction in the combustor also means that more steam is raised in Cases C to F and hence more power can be generated from within the process scheme—steam raised by heat recovery is used either to generate electrical power or to provide direct mechanical shaft power via steam turbines. Consequently, in each of these options, the power deficit is lower than Case A.
- The discrete WGS reactor and membrane option of Case D has a lower total sweep gas demand than Case C as sweep gas is not fed to the first membrane stage. Consequently, more steam is available for electrical power generation or direct mechanical drive and the overall power deficit of Case D decreases relative to that of Case C.
- Changing the sweep gas to nitrogen reduces the power deficit even further, as shown by the performance metrics of Case E. No steam is required for membrane sweep gas and hence additional steam is available to generate electrical power or to provide direct mechanical shaft power.
- Case F combines the benefits outlined above for Cases D and E. The use of discrete membrane units minimises the demand for permeate sweep gas and the use of nitrogen as the sweep gas maximises the available steam for electrical power generation and mechanical drivers.

Screening Study Conclusions

The conclusions drawn from the screening study are as follows:

- Cases A and B are discounted on the basis that neither meets the required CO_2 purity specification of 97 mol%.
- Cases C, D, E and F each meet the required hydrogen and CO_2 specifications detailed in the "Design basis" section.
- Case F is selected on the basis that it meets the required product specifications and has the lowest power deficit (or additional power import from the local grid).
- The discrete WGS reactor/membrane stage option represented in Cases D and F offers advantages in that it permits the permeate sweep gas demand to be optimised. In addition, the construction of the units is less complex and greater flexibility of membrane module design is possible as both tubular and planar membrane configurations can be accommodated.

REVIEW OF THE SELECTED DESIGN OPTION

This section outlines the results of applying the preferred process scheme which is application of ATR and WGS with a SINTEF developed Palladium/Silver membrane for hydrogen separation in a discrete reaction and membrane separation process using nitrogen as a sweep gas. The process is shown schematically in Figure 7.

A membrane unit design is proposed and costs derived both for the membrane unit itself and for the installation of a pre-combustion de-carbonisation process using the selected process scheme that is capable

of capturing 2 million tonnes per year from the Grangemouth complex. Finally, a review of the CO_2 emissions resultant from this process design and the utility demand is included.

Membrane Unit Design

The process screening study discussed above provides the basis for selecting Case F. This design incorporates discrete membrane stages, which offers advantages over the combined WGS membrane reactor in terms of reduced design complexity and a lower risk of membrane damage during catalyst change-out.

The design of each membrane unit is based on discussions with the membrane supplier, SINTEF, and the manufacturer of the support material, Pall. The outcome of these discussions is the following design basis for each membrane module:

- A tubular membrane design is preferred to the alternative planar design on the basis that Pall has a greater level of experience of manufacturing tubular membrane units. There is, therefore, greater confidence in the integrity of membrane module.
- In order to maximise the membrane separation area per unit volume, the smallest practicable tube size should be selected—$\frac{1}{2}$ inch nominal bore.
- The membrane support should have a minimum pore size of 2 μm to minimise resistance to both the flow of hydrogen through the membrane, and to the flow of sweep gas through the support. Allowing sweep gas to penetrate the support with minimum resistance will help to remove hydrogen from close to the membrane surface and thereby maximise the hydrogen partial pressure differential over the membrane.
- Each module should be 2 m in diameter and 3 m in length. This maximises the available membrane area per module whilst remaining within the bounds of construction feasibility. The membrane tubes are manufactured in 1 or $1\frac{1}{2}$ m lengths and this configuration will require 1 or 2 internal couplings per module. For the purposes of this study, 1 m membrane tube lengths have been assumed.
- A system design pressure of up to 30 barg.

Given the above physical dimensions for each membrane module and a triangular tube pitch, 6792 membrane tubes are installed in each module. This gives a mass transfer surface area of 800 m^2 per module. A diagram of the proposed membrane module design is shown in Figure 8.

Material of Construction—The membrane system is designed to operate in a temperature range of 270–320 °C with a pressure on the feed gas side of approximately 30 barg. The feed gas contains up to 60 mol% hydrogen, thus giving a hydrogen partial pressure of up to 20 bar. Under these conditions, alloy steel with resistance to hydrogen embrittlement is required for both the module shell and tubesheet—steel containing 1% Chromium and $\frac{1}{2}$% Molybdenum is, therefore, specified. This is in accordance with the Nelson chart indicating safe operating regions for materials from the perspective of hydrogen attack. The same material is specified for the WGS reactor vessels and internals. The permeate stream is at low pressure (approx 3 barg) and well below the range of hydrogen embrittlement. Carbon steel is, therefore, selected.

Optimum Permeation per Membrane Stage—Figure 9 demonstrates the influence of membrane permeation within each module on the operating costs, power demand and LHV efficiency.

From a cost perspective, the optimum permeation rate per membrane stage is about 70%. Both below and above this permeation rate, a cost penalty will occur. It should also be noted that this corresponds to the minimum power demand of the process and that above this permeation rate, the improvement in LHV efficiency starts to tail off.

It is, therefore, concluded that each membrane stage should be designed to permeate 70% of the hydrogen in the gas phase. Given the fact that the selected process scheme has three stages of membrane separation, this gives an overall hydrogen recovery of about 97.3%.

Number of Membrane Modules per Stage—The membrane design outlined previously has been modelled by SINTEF to evaluate the impact of permeate pressure and the number of modules per stage. Figure 10 details the impact on hydrogen recovery (or permeation) that results from changing these parameters

Hydrogen
Product
Outlet

Compression Fittings
to Tubesheet

Membrane Tubes

Shifted Syngas
Feed Gas Inlet

Baffles
30% Cut

Membrane Section
Connections and
Supports

Tie Rods

CO₂ Rich
Product Outlet

Compression Fitting
to Tubesheet

Lower Tubesheet
Freely Supported
by bundle & Tie
Rods

Expansion Sliders

Sweep Gas
Distribution Plenum

Sweep Gas Feed
Expansion Bellows

Support Skirt

Sweep Gas Feed

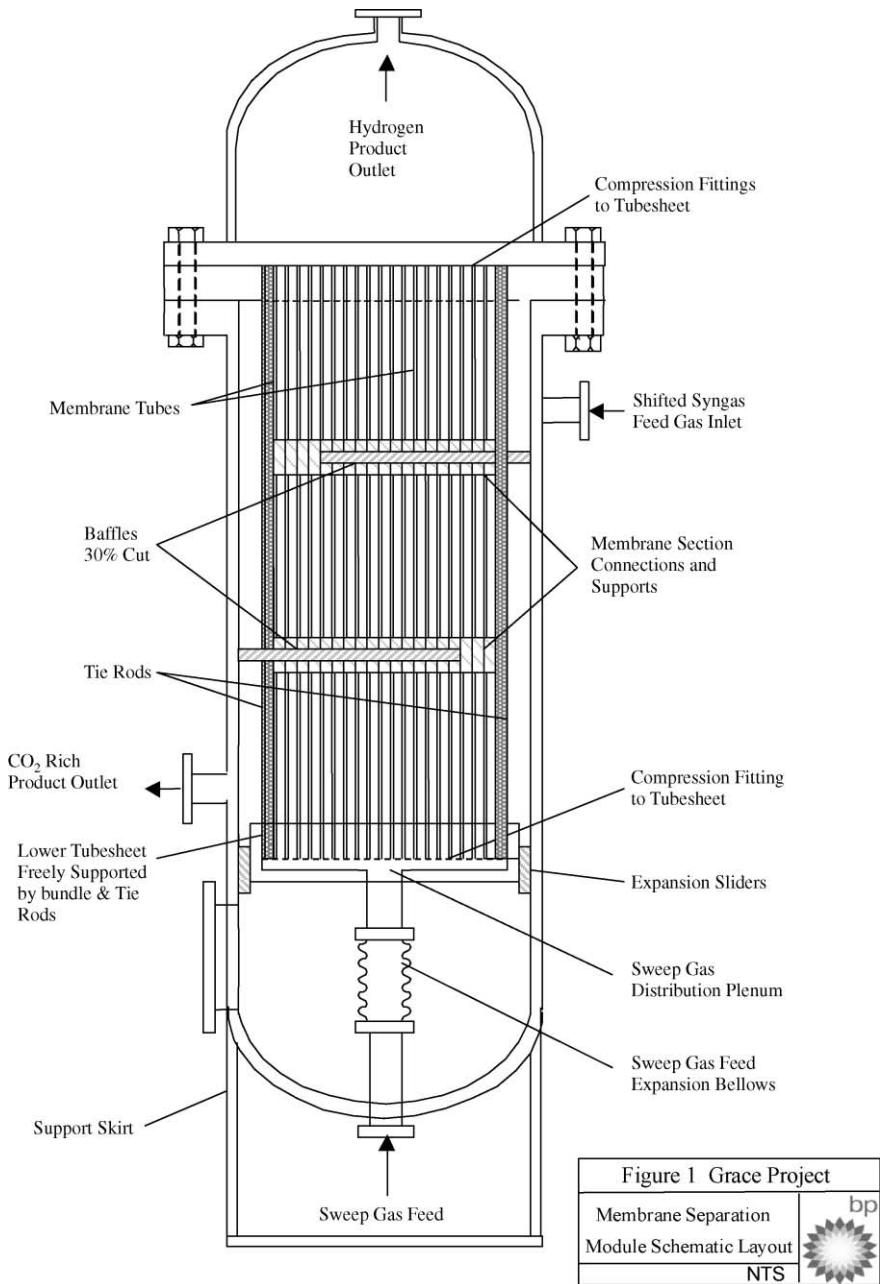| Figure 1 Grace Project	
Membrane Separation Module Schematic Layout	bp
NTS	

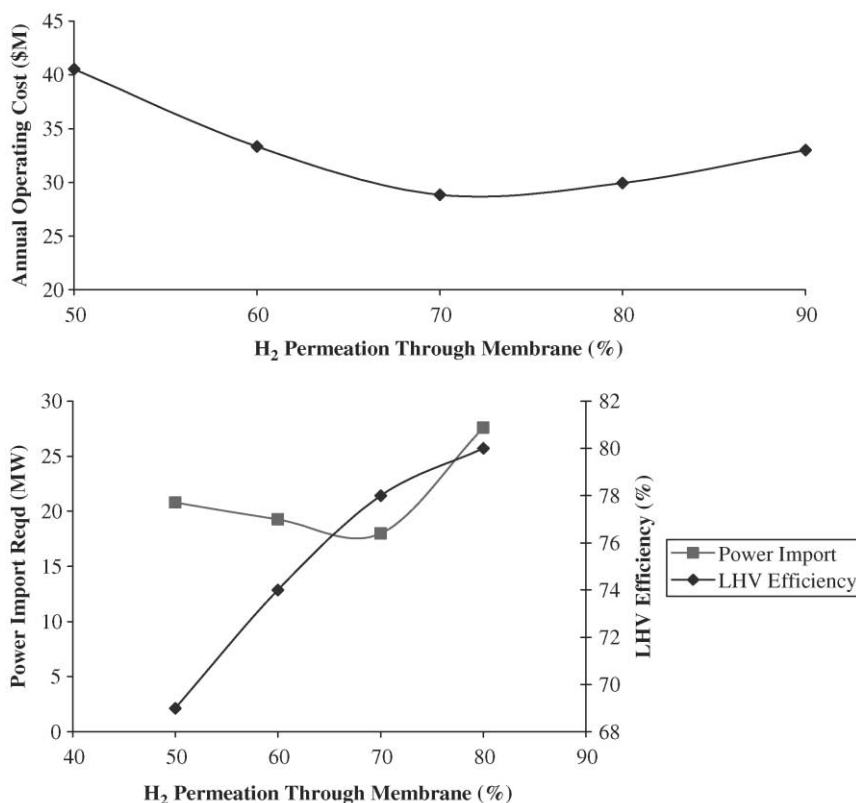**Figure 8:** Proposed hydrogen membrane separation unit.

Figure 9: Optimum membrane separation efficiency relationship to operating costs and power needs.

of the first membrane stage—note that the physical design (membrane area, tube diameter) of each module is fixed.

From Figure 10, and given the physical membrane module design outlined previously, at least five parallel modules are required to recover 70% of the hydrogen in the feed gas into the permeate stream. It is also concluded form the above chart, that increasing the permeate pressure to 3 barg has a limited impact on the overall membrane performance. A similar evaluation is shown in Figure 11 for the second and third membrane stages—note that this figure assumes a permeate pressure of 3 barg.

The conclusion drawn for stages 2 and 3 is that two parallel modules are required to deliver the required hydrogen recovery.

Hydrogen Membrane Pre-combustion De-Carbonisation Process Costs
Overall process costs
The total cost of installing a hydrogen membrane based pre-combustion de-carbonisation process at BP's Grangemouth complex to capture 2 million tonnes per year of CO_2 is estimated to be *$251 million*. This estimate has been developed using a cost basis consistent with all CCP-related studies. A full breakdown of this cost estimate is given in Table 3.
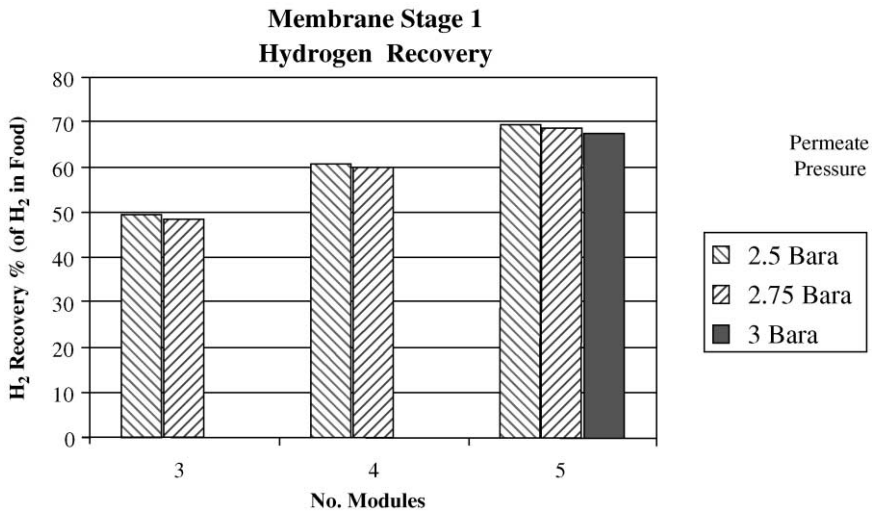
Membrane Stage 1
Hydrogen Recovery

Figure 10: Effects of operating pressure and module numbers on hydrogen recovery efficiency.
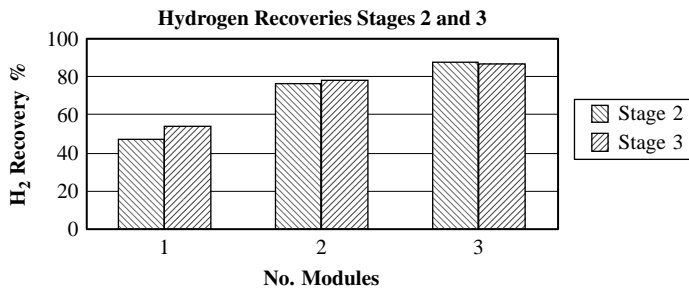
Figure 11: Hydrogen recovery for multiple stage membrane modules.

This cost compares very favourably with other technology developments pursued by the CCP. It is the lowest capital cost option developed by the CCP for the Grangemouth complex and offers a 28% cost reduction when compared to the CCP baseline option of using amine technology to capture CO_2 from low pressure flue gas sources.

Membrane unit
The cost of fabricating each membrane module is estimated at $3.12 million. This has again been prepared using a basis common to all CCP technology studies and with the assistance of the membrane manufacturer, SINTEF. A breakdown of this cost estimate is given in Table 4.

CO_2 Emissions/Utility Demand
CO_2 emissions
Table 5 outlines the impact on CO_2 emissions of implementing the selected CO_2 capture process based on the SINTEF hydrogen membrane. Two cases are considered; the first assuming that the fuel gas is burnt in conventional gas-fired turbines, and the second assuming the design outlined in this report is adopted.

TABLE 3

INSTALLATION COSTS FOR A HYDROGEN MEMBRANE-BASED
PRE-COMBUSTION DE-CARBONISATION PROCESS AT BP'S
GRANGEMOUTH COMPLEX TO CAPTURE
2 MILLION TONNES/YEAR OF CO_2

Process unit	Cost (%)	Costs ($ million)
Feed conditioning	10	25.1
CO_2 compression	8	20.1
Autothermal reformer	5	12.6
Retentate combustion	1	2.5
Steam and condensate system	8	20.1
Membrane shift reactor	16	40.2
Utilities	14	35.1
Air separation unit	21	52.7
First catalyst fills	2	5.0
Location cost premium	15	37.7
Totals	100	251.1

TABLE 4

ESTIMATED HYDROGEN MEMBRANE SEPARATION MODULE COST

Component	Cost (%)	Cost ($ million)
Pressure vessel	5	0.156
Support tube and connectors	36	1.123
Palladium	5	0.156
Membrane preparation	5	0.156
Tube assembly and leak test	9	0.281
bundle assembly	9	0.281
Contingency	14	0.437
Profit	17	0.530
Totals	100	3.12

Note that although 2 million tonnes per year of CO_2 is captured, a certain amount of CO_2 will be emitted to generate the additional electrical power required by the process. This gives a *total amount of CO_2 emissions that are avoided* as a result of implementing the selected process scheme of approximately $1\frac{1}{2}$ million tonnes of CO2 per year.

Power demand
Table 6 lists the power requirements for the selected process scheme.

Cooling water demand
Table 7 details the cooling water demand of the selected process scheme.

CONCLUSIONS

The conclusions drawn from this study are as follows:

- Post-combustion de-carbonisation of fuel gas by conversion to hydrogen and recovery using a hydrogen membrane-based process scheme is technically and practically feasible. The selected process can

TABLE 5
EXPECTED CO_2 EMISSIONS AND CAPTURE FROM THE PROPOSED PROCESS

		Hydrocarbon fuel gas combustion	H_2 combustion/CO_2 capture
CO_2 emissions from			
Fuel gas	tonnes/hr	228.1	1.2[a]
Additional power generation	tonnes/hr	–	59.4[b]
Total CO_2 emissions	tonnes/hr	228.1	60.5
CO_2 emissions avoided	tonnes/hr		167.5
CO_2 captured	tonnes/hr	0	226.8
Avoided/captured	%		73.9
Annual CO_2 emissions avoided[c]	tonnes/yr		1,467,388
Annual CO_2 captured[c]	tonnes/yr		1,986,505

[a] CO_2 emission from the de-aerator vent. Hydrogen fuel is carbon free.
[b] CO_2 arising from additional gas used to generate the power deficit of the selected process scheme.
[c] Annual operation assumed to be 365 days, and 100% availability.

TABLE 6
PROPOSED PROCESS ELECTRIC POWER REQUIREMENTS

Equipment	Power consumption (kW)	Drive
Feed gas compressor	10,832	Gas turbine
CO_2 compressor	8982	MP steam turbine
HP boiler feed water pump	1328	MP steam turbine
LP condensate pump	20	Electric motor
De-aerated water pump	82	Electric motor
Air separation unit	46,191	HP/MP/LP steam turbine (single shaft)
Cooling water pumps	1765	MP steam turbine
Electrical power generation	1000	MP steam turbine

Notes: Total power delivered by steam turbines is: HP steam turbine, 15,685 kW; MP steam turbines, 20,446 kW; LP Steam turbine, 24,439 kW. Gas turbine power output, 10,832 kW.

TABLE 7
COOLING WATER REQUIREMENTS FOR THE SELECTED
PROCESS SCHEME

Equipment	Cooling water consumption (m^3/h)
Feed gas compressor intercooler	298
CO_2 compressor intercoolers	1340
Steam turbine condenser	8862
CO_2 drier package	58
Total	10,549

Notes: Cooling water supply temperature 27 °C, return 45 °C.

achieve a high conversion efficiency (75.6% following completion of the detailed design) and can be designed to incorporate a high degree of self-sufficiency in terms of power demand.

- The cost of installing the selected process scheme at BP's Grangemouth complex and sized to capture 2 million tonnes of CO_2 per year is estimated at *$251 million*.
- The fabrication cost of each hydrogen membrane module is estimated to be $3.12 million.
- The above cost for the selected hydrogen membrane-based scheme offers the lowest capital cost option developed by the CCP for the Grangemouth complex. With reference to the CCP baseline technology of post-combustion CO_2 capture using an amine unit, the hydrogen membrane option is approximately 28% cheaper.
- Sequential WGS reactor and hydrogen separation is preferred to a combined unit. Although the combined unit requires a smaller membrane area and catalyst volume, the discrete and sequential option offers greater flexibility in terms of membrane unit design and avoids the inherent risk of damaging the membrane during periodic catalyst change-outs.
- A 3-stage reactor/membrane option will deliver the required product specifications.
- The SINTEF Palladium/Silver membrane is considered to be the best membrane option for hydrogen permeation of those reviewed by the GRACE project, based on permeability, selectivity towards hydrogen and stability under operating conditions.
- Tubular membrane modules are preferred at this stage to planar membranes by the manufacturer based on their current experience. Planar membranes generally lead to a higher surface area per unit volume and thus could prove attractive.
- The optimum hydrogen recovery in each membrane stage is about 70%. However, the increase in operating costs as the recovery is either increased or reduced is fairly minimal, suggesting that recoveries in the range 67–77% would have a limited cost impact.
- A recovery of 70% in each membrane stage will be achieved with the developed SINTEF module using five parallel modules for the first stage and two parallel modules for stages 2 and 3.
- Combustion of the membrane retentate stream with oxygen provides usable high-grade heat for the process and increases both the recovery and purity of the CO_2 product stream.