Energy Technology Innovation Strategy
Brown Coal Research and Development

Final report for
Brown Coal Innovation Australia (BCIA)

Pre-Combustion Carbon Dioxide Capture Technologies for Brown Coal Power Generation

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The results are however, relevant to the gasification processes being pursued by HRL but are in no way representative of any specific projects. For the avoidance of doubt, use of the term CO2CRC Modelled Plant in this report refers to the CO2CRC model of the HRL IDGCC process. Interpretation of the data and resources referred to concerning the CO2CRC Modelled Plant does not refer to any specific proposed project configuration of IDGCC by HRL. Neither CO2CRC nor HRL will be liable for any consequences, including but not limited to all losses, damages and costs, arising directly or indirectly from using any information or material contained in this publication.

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1. Executive Summary

The CO2CRC/HRL Mulgrave Capture Project (Mulgrave Capture Project) represents a world first in demonstrating pre-combustion capture using three different separation technologies (solvents, membranes and adsorption) in parallel in a real gasifier setting. The work, led by the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), in partnership with HRL Developments Pty Ltd (HRL), was funded under the Victorian Government's ETIS program for three years commencing in 2007. The learning associated with operation of such a facility linked to the R&D from evaluating three novel capture techniques is unique.

Key objectives of the project were to:

a) Test solvent, adsorbent and membrane pre-combustion capture techniques with real gasifier syngas
b) Reduce the technical risk and cost of capturing CO_2 from pre-combustion sources
c) Identify the most cost effective capture technologies for Victorian use
d) Provide large scale designs for all capture technologies and compare their technical and economic performance and large scale design for a CO2CRC Modelled Plant

The project met its objectives and produced valuable new insights into the pre-combustion CO_2 capture opportunities from syngas. New methodologies and techniques to optimise the flowsheet performance for pre-combustion capture process were developed and used to produce feasible large scale integrated designs. These designs covered a range of recoveries of carbon dioxide and resulted in the technical performance noted in the table below. The most energy efficient design (14.5% energy penalty) is that based on the CO2CRC solvent IP, referred to as UNO, which uses a potassium carbonate solvent for pre-combustion capture. The adsorption based capture process (15.1% energy penalty) was next best in energy efficiency, followed by the membrane process.

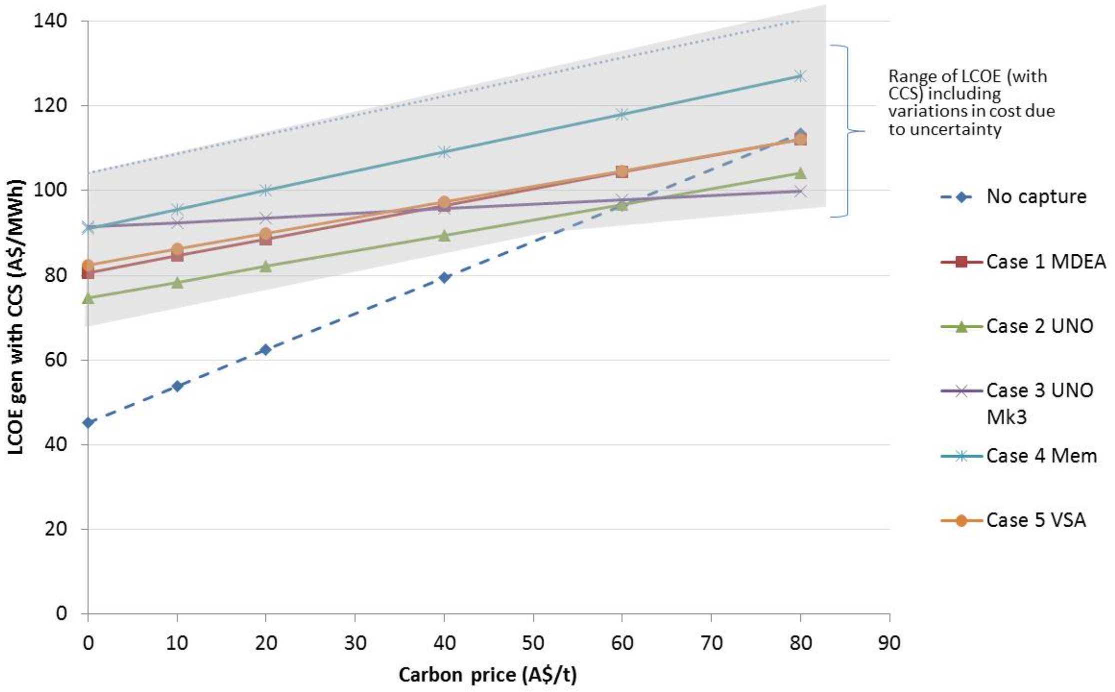
The current configuration of the CO2CRC Modelled Plant offers the prospect of a CO_2 capture rate of approximately 64% using pre-combustion techniques. This report outlines methods by which this can be increased. A post-combustion (PCC) concept design for the CO2CRC Modelled Plant by treating gas turbine and char burner exhaust gases was developed to provide a higher CO_2 capture rate (90%). This option is based on CO2CRC PCC IP, referred to as UNO Mk 3. This concept results in a 16.9% energy penalty, close to that of the better pre-combustion alternatives. While introducing larger post combustion based equipment, it may provide savings through potential removal of equipment normally associated with pre-combustion capture, such as the water gas shift reactor.

Summary of the CO2CRC Modelled Plant process with CO_2 capture.

	Units	Base Case	UNO Process (Pre)	Membrane	Adsorption	UNO Mk3 Process (Post)
Net Power	MW	550	470	405	467	457
Net Efficiency (HHV)	%	44.7	38.2	32.9	37.9	37.2
CO_2 emissions	kg/MWh	771	342	394	327	93
Energy Penalty	%	-	14.5	26.3	15.1	16.9
Net Water Required	t/MWh	1.02	1.52	2.11	1.61	1.82

These initial designs offer valuable comparisons between the capture technologies but further optimisation is required. The solvent design for pre-combustion is the most well developed whereas the membrane, adsorbent and post combustion designs offer considerable improvement potential. A further point to note is water usage. All capture designs resulted in increased water usage however, these rates represent lower consumption per MWh than current Latrobe Valley boiler based power plants without CO_2 capture. As part of the economic analysis the three alternative capture technologies are compared to a commercial solvent option for nitrogen laden syngas stream similar to that of the CO2CRC Modelled Plant process, namely N-methyl-diethanolamine or MDEA. The estimated costs per tonne avoided to capture CO_2 from that gas stream produced by a pre-CO2CRC Modelled Plant cost range from about A$47 to over A$92 per tonne CO_2 avoided. The technology with the lowest specific cost of CO_2 avoided ($47/t) is solvent absorption based post combustion capture using the potassium carbonate based UNO Mk 3 process applied to the turbine/char burner exhaust gas. The low estimate for this technology arises because of the low energy penalty, coupled with the moderate capture plant capital cost (A$365 million) compared to the other technologies. The technology with the highest estimated unit cost is membrane separation at $92 per tonne CO_2 avoided. This higher cost estimate for the membrane technology is primarily due to the high energy consumption of the process and the high additional capital costs of the capture plant (over A$355 million). The solvent based processes resulted in lower capture unit costs than the base MDEA case while the adsorbent option is similar.

The results show the capital costs for the majority of the capture technologies to be in the range of A$300 to A$350million, with the exception of the VSA process (estimated at A$440million).



Cost of CO2CRC Modelled Plant electricity generation (LCOE) with CCS (A$/MWh) against carbon price

The graph above indicates the relative performance of all the capture technologies in terms of LCOE and how that changes with increasing carbon price. The LCOE includes estimates of transportation and storage costs for a Latrobe Valley/offshore Gippsland source-sink match based on other studies. It should be noted that these costs are highly project specific and should be treated as indicative only.

Below $50-60/t carbon price, the results show that paying the price on unabated carbon dioxide would result in lower LCOE than implementing any of the capture technologies reviewed in this project. Above this carbon price, implementation of capture results in lower LCOE than paying the price for unabated carbon dioxide. This is because of the low base cost of the electricity from the CO2CRC Modelled Plant and its relatively low base emission rate. Should the base price for the CO2CRC Modelled Plant power be greater than that used for the modelling the cross over point is likely to reduce.

Of the low recovery capture cases, Case 2 (the UNO pre-combustion option) is the lowest cost alternative at all carbon prices and represents a better option than MDEA. The base case and Case 5 provide almost identical outcomes across the carbon price spectrum. The high recovery case 3 is relatively insensitive to carbon price but due to the greater avoided carbon dioxide, produces a higher LCOE at low carbon prices. The studies show that low emissions CO2CRC Modelled Plant configurations can provide a range of LCOE outcomes at various recovery rates. These LCOE's are at the low end of a range of studies for future Australian low emission power costs.

It is important to note that the conclusions of this study are largely indicative and based on well thought out but un-optimised designs.

R&D Outcomes

The specific outcomes from the three experimental campaigns at HRL are:

- Achieved successful management of a complex multi-party, multi-technology, multi-objective carbon capture demonstration project.
- Accumulated IP and confidence in construction, commissioning and operation of capture plants for a real gasifier.
- Gathered valuable information to facilitate technology development for three pre-combustion techniques (solvent absorption, membranes and adsorption), resulting in substantial reduction in technical risk and cost for all three technologies.
- Created a large scale base for future CO_2 capture at commercial scale

The specific learning achieved for each of the research areas were:

Solvent absorption: Operation of solvent absorption was successfully demonstrated for pilot scale pre-combustion capture using the CO2CRC solvent. This work, together with laboratory and process simulation, enabled the development of the robust large scale plant design presented.

Membrane: Results enabled the identification of suitable membrane materials and process designs that can attain the degree of CO_2 recovery and purity required for effective storage. For gas separation membranes, the best performing CO_2-selective membrane was poly dimethyl siloxane (PDMS). Under the process conditions this was able to achieve high CO_2 permeability while having good CO_2/H2 and CO_2/N2 selectivities. A porous polytetrafluoroethylene (PTFE) contactor with 30 wt% monoethanolamine (MEA) as the solvent, achieved the highest overall mass transfer coefficients for the membrane gas-solvent contactor.

Adsorption: Zeolite 13X and calcium chabazite showed good results at temperatures of less than 200°C due to reasonably high adsorption capacity and fast kinetics. Preliminary tests of novel adsorbents such as PEI and double salt materials showed encouraging results for CO_2 capture at higher temperature.

Heat integration: New methodologies and software were developed to optimise heat and process integration for carbon capture and storage applications. These techniques were used to establish large scale integrated flowsheets for analysis and further development. Energy penalties could be further reduced by an optimisation procedure that maximises the net power generated from the process plant. The optimisation should include not only the capture process but also variables within the CO2CRC Modelled Plant process that could not be considered as part of this study. The multi-objective optimisation tool for CO_2 capture developed by the CO2CRC could be useful for further optimisation of CO_2 capture for the power industry.

Economics: The CO2CRC economic methodologies developed at UNSW were further extended to encompass the CO2CRC Modelled Plant. The sensitivity analysis shows that cost estimates are strongly affected by the discount rate and energy penalty estimates. Doubling the discount rate increases the capture cost by up to 30% of the baseline cost. The effect of increasing the energy penalty also has a significant impact, increasing the estimate of capture cost by 10% to 30%. The effect of increasing the capital cost and cost of electricity by 20% has less than a 10% impact on the capture cost.

Intellectual Property: Intellectual property has been developed/tested in the following areas:

- Knowledge in designing and operating plant & processes for removing CO_2 from gas streams using
- Solvents
- Gas-liquid membrane contactors
- Gas separation membranes
- CO_2 adsorption systems and adsorbents
- Large scale designs for these systems
- Heat & Process Integration methodologies for reducing parasitic load.

Communications: Communications, publications, awards, collaborations, and skills development have been an important component of this project, and this area resulted in significant outcomes.

The project has been visited by more than ten groups from Australia and overseas, raising the profile of all CO_2 capture researchers and industry collaborators involved.

At least 62 publications including journal articles, book chapters, media releases, news/web articles, interviews and public lectures have been produced related to this project. They have enhanced public and scientific knowledge, and awareness of CO_2 capture options and issues.

More than 18 researchers and 6 higher degree research students were involved in the project. Their involvement with the industrial partners has assisted in developing high calibre R&D skills for the Brown Coal industry in Victoria. The capabilities of our researchers has been formally acknowledged by the awarding of a Fulbright scholarship to one of our post-doctoral fellows, Dr Colin Scholes in 2009. This provided him the opportunity to collaborate with one of the leading international gas separation membrane researchers at The University of Texas at Austin, USA.

At least one new international collaboration has been established with Forschungszentrum Jülich GmbH in Germany.

Recommendations

As a result of this work a number of recommendations to continue various studies have been made to HRL.

2. Introduction

2.1 ETIS Brown Coal Research and Development Grants Program under Victorian DPI

Victoria is facing significant environmental challenges to the economic advantages it derives from utilisation of its very low-cost brown coal resources. The State accounts for 22% of Australia's greenhouse gas emissions, and approximately 52% of these arise from the use of brown coal for electricity generation in the State. The Victorian Government has committed to a substantial reduction in greenhouse gas emissions by 2020. Its Department of Primary Industry (DPI) initiated the Energy Technology Innovation Strategy (ETIS) that has provided more than $12 million to low emissions coal research and development projects. These projects covered a broad range of research topics including carbon capture, combustion, gasification and dewatering and involved working with researchers and industry to ensure successful progression of new, low-emission energy technologies through their innovation processes.

The single objective of ETIS is to drive prospective sustainable energy technologies down their respective cost curves and, in so doing, ensure that a portfolio of low cost, low emissions technologies are available for commercial deployment to minimise the economic impact of a cost on carbon. A key feature of initiatives under ETIS is that Victoria's investments support those technologies that industry would choose as the most practical, commercial, cost effective and attractive to Australian Government and private investment.

Investment in R&D in any sector plays a major role in maintaining, retaining and growing the skills and knowledge base. The ETIS Brown Coal Research and Development Grants Program builds on the significant achievements of the brown coal industry and academia over several decades, continuing the Victorian Government's commitment to investing in brown coal science, technology and innovation.

This current project was the result of DPI's grant under the ETIS program of $2.06 million to the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) to test pre-combustion carbon dioxide (CO_2) capture technologies for brown coal-fired power generation. The objective of the project is to reduce the cost of existing pre-combustion CO_2 capture technologies and investigate other capture technologies that are likely to prove cheaper in the long term. Following the success of the ETIS Brown Coal R&D Grants program, Brown Coal Innovation Australia (BCIA) was established in 2009 with $16 million funding from the Victorian Government to continue to fund new low emissions coal research and development in Victoria. BCIA is an independent company that has a clear mandate to co-invest with industry and research entities in skills development and R&D projects in new high quality brown coal technologies and in the adaptation of existing low-emissions technologies to Victorian brown coal. BCIA co-ordinates all brown coal R&D in Australia in conjunction with the Commonwealth's Australian National Low Emissions Coal (ANLEC) R&D organisation. This project has been funded by BCIA since July 2010 with an extension grant of $0.374 million.

This report covers the research completed under funding from both the original ETIS grant and the BCIA extension grant.

2.2 Overview on Technology options for CO_2 capture: commercial and R&D

It is now well accepted that carbon capture and storage (CCS) is an essential part of the portfolio of technologies that is needed to achieve substantial global emissions reduction [*www.co2crc.com.au*]. IEA reported that in the absence of CCS, the overall cost to achieve a 50% reduction in CO_2 emissions by 2050 will increase by 70% [*IEA, 2010*]. As a result, R&D activities and interests in the CCS area are increasing around the world.

Reducing the cost of the three main elements in the CCS chain (CO_2 capture, CO_2 transport, and CO_2 storage) is critical to the effective demonstration and large-scale deployment of CCS. Among them, capture has the most potential for cost reduction due to its sheer size in the chain in terms of cost of deployment (60% to 80% of total). Various capture technologies have been tested and deployed at a range of scales around the world. The main challenges faced by the capture technologies are:

- Reducing the capital cost of the equipment,
- Reducing the energy penalty (i.e., the additional power generation required to compensate for the losses in output due to the capture load),
- Reducing the total cost by heat and process integration, and
- Addressing scale up issues

There are four main areas where capture technologies are applicable. These are:

1. Post-combustion capture (PCC): CO_2 is separated out from flue gases after combustion of fossil fuels where the CO_2 concentration in the flue gases from coal combustion is usually around 10 – 12 %.
2. Pre-combustion capture: fossil fuel gasification plants produce syngas which is a mixture of hydrogen (H_2), carbon dioxide (CO_2) and carbon monoxide (CO) under high pressure and temperature. The syngas is shift reacted with water to convert CO into additional H_2 and CO_2, which is separated from the mixture. The relatively pure H_2 is combusted in the turbine in an Integrated Gasification Combined Cycle (IGCC) plant. The CO_2 concentration in the gases sent to the capture unit after shift can be up to 60% on a dry basis.
3. Oxyfuel combustion capture: combustion of fossil fuels occurs in the presence of pure (or enriched) oxygen leading to the production of CO_2 and steam from which the CO_2 can then be separated. Because combustion occurs in a stream with low nitrogen, the concentration of CO_2 in the resulting flue gas is higher, typically 92-98%.
4. Other industrial process gas capture: this includes capturing CO_2 from process streams that contain significant concentrations of CO_2 such as in the purification of natural gas; production of synthesis gas for manufacturing ammonia, alcohols and synthetic liquid fuels; cement manufacture; steel production; and fermentation processes for food and drink production. CO_2 could be captured from all these streams using techniques that are common to post-combustion capture, pre-combustion capture and/or oxyfuel combustion capture.

Technologies that have been trialled for one or more of these applications include:

i. Solvent absorption
ii. Membrane separation
iii. Adsorption
iv. Cryogenics
v. Hydrate formation
vi. Chemical Looping
vii. Mineralisation via aqueous precipitation
viii. Enzyme-based capture
ix. Algae-based capture

Details of these technologies are readily available in the published literature, e.g., the IPCC Special Report [IPCC, 2005], Global CCS Institute [GCCSI-a, 2010], Electric Power Research Institute [EPRI, 2007], the RECCS study by the Wuppertal Institute [WI 2010], and the International Energy Agency's "Technology Roadmap – Carbon capture and storage" [IEA, 2010]. Since this project deals only with pre-combustion capture, only technologies suited for this application are summarised below. A compiled document [Appendix 1] shows the current status of worldwide commercial scale pre-combustion capture facilities [GCCSI-b, 2010].

In pre-combustion capture, the CO_2 is separated, typically utilising a physical, and, possibly, a chemical absorption process. One of the drawbacks to developing pre-combustion capture technologies compared to those in post-combustion capture is that the total IGCC installed capacity is less than 1% of the total installed electricity generation capacity worldwide. The high initial investment requirement is another hurdle. However, there are an increasing number of IGCC plants either at the implementation stage or on the drawing board as reflected in the number of planned projects listed in Appendix 1. Also, a recent publication suggests that there is a very promising future for pre-combustion capture [Linder et al.]. It shows that an IGCC plant with pre-combustion CO_2 capture was found to offer the best profit for power plant operators and significantly lower life cycle emissions of CO_2 for the three options considered: an IGCC plant with pre-combustion capture, a pulverised coal plant with post-combustion capture, or a pulverised coal plant with oxyfuel combustion carbon capture.

For pre-combustion capture, the high concentration of CO_2, typically 15 to 60% by volume, and the high pressures used in IGCC systems, typically 4.0 MPa, are favourable for CO_2 separation. In particular, the high pressure can potentially reduce the amount of compression required (and hence the cost) for transportation prior to storage.

In the case of this project, the gasification of Latrobe Valley brown coal is to be performed using a modelled HRL's Integrated Drying Gasification Combined Cycle (IDGCC) technology plant (CO2CRC Modelled Plant). The IDGCC technology has been specifically developed by HRL over many years, to deal with the peculiarities of the local coal, in particular the high moisture content.

The CO2CRC Modelled Plant is air blown and this creates additional capture challenges with syngas containing N_2. Compared to the oxygen blown gasifiers typical of IGCC plants which invariably use physical solvents, the high N_2 content of IDGCC syngas leads one to consider chemical solvents, more typically used in PCC. Also note: IDGCC operates at lower pressure than conventional IGCC plants.

While solvents are already available for pre-combustion capture, more research is needed to develop solvents with improved characteristics particularly given the process conditions of the CO2CRC Modelled Plant. The main challenges lie in identifying solvents that require less energy for regeneration, have lower solvent loss rates and lower corrosion rates. Furthermore, the management of the water content in the gas to the gas turbine is critical to maintaining power output. With these challenges in mind, the research reported here involves a hot potassium carbonate process patented by the CO2CRC. Details can be found in Section 5.1.

Membrane separation technologies are usually suitable for high-pressure gas or liquid streams. While gas separation membranes are already available for natural gas and oxygen separation, membranes suited to pre-combustion separation are only now receiving attention. The challenge is to find or develop a membrane with high CO_2 selectivity and permeability that can also withstand high temperatures typical of gasification systems. This research involves testing of a range of membranes at both the laboratory and pilot scale. Details can be found in Section 5.2.

New cycles for the CO_2 removal are under development in the CO2CRC, as well as materials development that has mainly focussed on the use zeolites due to their high porosity and a crystalline molecular structure that displays a relatively high selectivity for CO_2.

General overviews of the CO2CRC’s capture technologies are given in the next section.

2.3 CO2CRC Research Activities and Background on the Mulgrave Capture Project

2.3.1 CO2CRC Research Activities

As shown in figure 2.1, the CO2CRC has, since 2003, pursued research into capture technologies that can be applied to electricity generation as well as producing gas fields or liquefied natural gas (LNG) facilities. The aim is to develop new capture technologies and improve existing capture technologies to significantly reduce the cost of CO_2 capture. An important part of the strategy is to ensure that the research does not duplicate work elsewhere. To achieve its aim, the CO2CRC partners with leading international companies and the leading researchers in Australian and International Universities to develop, operate and maintain world-class capture capabilities and facilities.

Figure 2.1 CO2CRC Capture research at a glance

The university laboratory facilities together with the pilot scale industrial demonstration facilities and the large scale design resources provide a unique multi-scale, multi-technology, multi-site capture R&D capability to drive research outcomes towards commercialization. More details of these capabilities are provided on the pages that follow.

2.3.1.1 Solvent absorption

Solvent absorption (Fig 2.2) is the traditional method for removing CO_2 from syngas. After gasification, feed gas enters the absorption column it contacts the solvent and the CO_2 is absorbed. The other gases leave the absorption column, and the “rich” solvent containing the CO_2 is pumped to another column, variously called a desorber, a stripping column, or a regenerator. The “rich” solvent is heated to release the CO_2 from the solvent. The CO_2 emerges at the top of the desorber where it is cooled to remove water and then captured. The water is returned to the desorber and the “lean” solvent is pumped back to the absorber. On the way, the hot, lean solvent passes through a heat exchanger, the rich solvent leaving the absorber column. This exchange cools the lean solvent and heats the rich solvent on its way to the desorber.

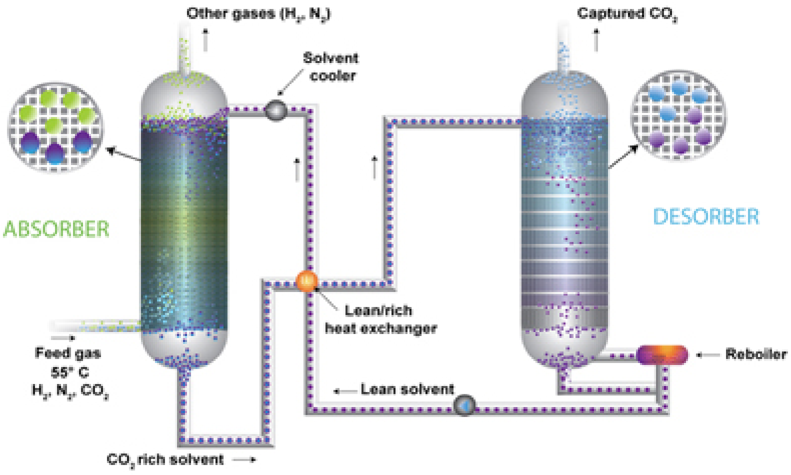


Figure 2.2 Schematic Diagram of Solvent Capture Process

2.3.1.2 Membranes

Relative to absorption or adsorption technologies, membrane technology is a ‘new’ technology that has the potential to provide significant capture cost reductions. Membranes can be used to separate CO_2 from other gases (gas separation membranes) or to allow CO_2 to be absorbed from a gas stream into a solvent (membrane gas absorption).

Gas separation membranes

CO_2 can selectively pass through gas separation membranes (Fig. 2.3), for removal from the feed gas. These membranes separate gases based on their molecular sizes. They are better suited for separations at higher pressures and higher CO_2 concentrations.

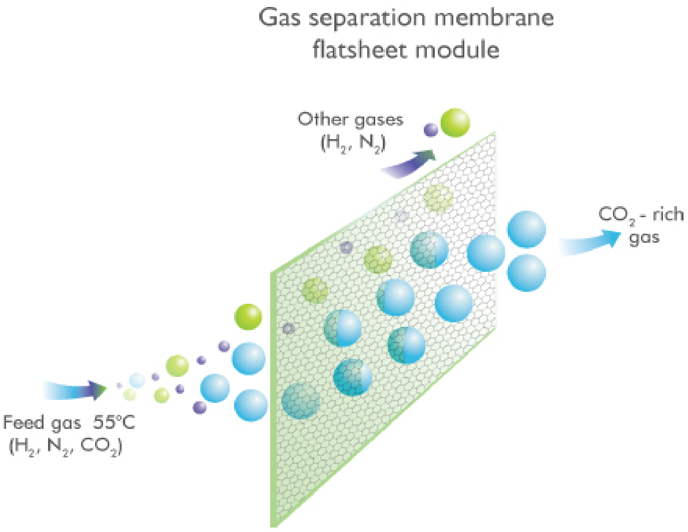


Figure 2.3 Gas Separation Membranes

Membrane gas absorption

In membrane gas absorption a membrane separates the feed gas from the liquid solvent (Fig 2.4). The CO_2 is absorbed into the solvent via pores in the membrane, while the other gases are not. The CO_2 is removed from the solvent as for solvent absorption.

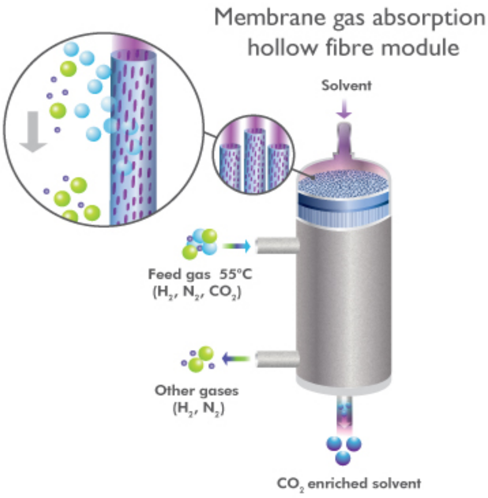


Figure 2.4 Membrane Gas Absorption

2.3.1.3 Adsorption technology

Adsorbents are solids that have the capacity to capture CO_2 on their surface and can be reused in a cyclical process. When the CO_2 is released from the adsorbent by reducing the pressure, this is known as Pressure Swing Adsorption (PSA) (Fig 2.5). Alternatively, the CO_2 can be released using Vacuum Swing Adsorption (VSA) usually for post-combustion capture, or Temperature Swing Adsorption (TSA), or in a combination mode. A multi-layered adsorption column (Fig. 2.6) can provide staged separation of five gas components.

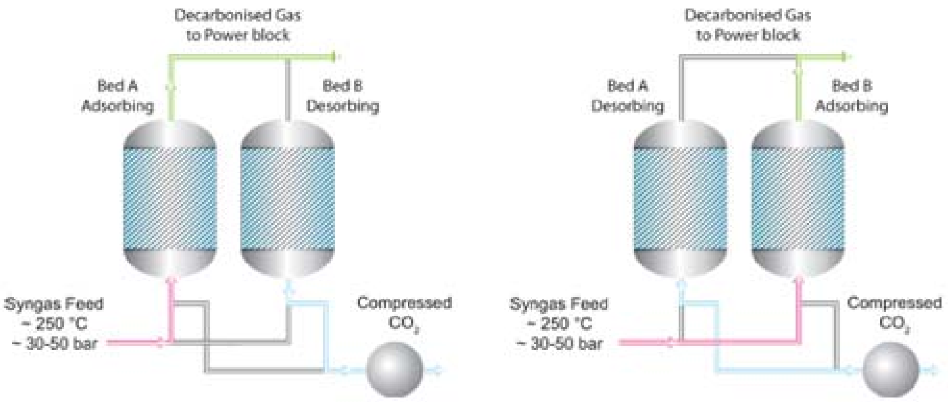


Figure 2.5 Adsorption Process (as general only, parameters are not representatives of this project)

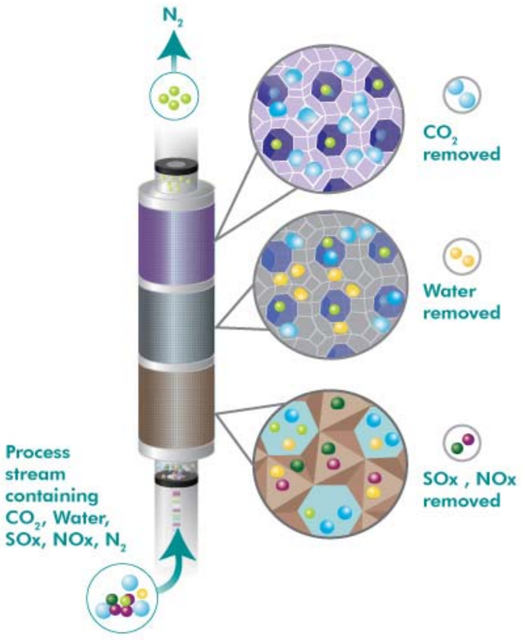


Figure 2.6 Multi-layer Adsorption Column

2.3.1.4 Cryogenics/hydrates systems

Cryogenic/hydrate systems, though not investigated as part of the ETIS/BCIA funded research, are believed to be attractive for pre-combustion capture and are being pursued in the wider CO2CRC capture research portfolio. The process requires pressures above 2.1 MPa (300 psia) at temperatures of approximately -55°C.

2.3.1.5 Capture demonstration facilities

With the help of BCIA/ETIS funding, the CO2CRC established pilot plants for three capture technologies (solvent, membrane, and adsorption) for pre-combustion at Mulgrave (HRL).

2.3.1.6 Engineering development / process integration for CO_2 capture

The translation of CO2CRC IP from research through to large scale commercial application is critical. The Engineering team undertakes studies particularly in relation to heat and energy integration, and practical equipment issues likely to lead to significant reductions in CO2 capture costs for large-scale plant.

2.3.1.7 Economic evaluation

A major decision metric for large-scale engineering projects is their commercial viability. The CO2CRC economics team is at the forefront of international efforts to develop evaluation methodologies for CCS.

2.3.2 Background on the Mulgrave Capture Project

The research summarised in this report is a three year project jointly funded by the Victorian State Government, HRL, and CO2CRC through the ETIS/BCIA program and undertaken cooperatively by the CO2CRC and HRL Development Pty Ltd. It is commonly referred to as the “CO2CRC/HRL Mulgrave Capture Project” (Mulgrave Capture Project).

HRL has a track record of progress in advanced brown coal utilisation, combustion and gasification technologies. The R&D size (0.5MW) air blown gasifier at HRL’s Mulgrave site in Victoria was considered ideal for capture tests in an industrial gasifier environment. In this project, HRL provided syngas from their R&D size (0.5MW) air blown gasifier at Mulgrave in Victoria to three different CO2CRC capture pilot plants (solvent, adsorbent and membrane) on-site at Mulgrave.

In view of the global significance of the Victorian brown coal resource, and the availability of significant close storage locations in the Gippsland Basin, the aims of the project were to:

- Design, install, commission and test three capture technologies in a real gasifier (pre-combustion) setting for brown coal
- Advance the knowledge base regarding the capabilities of pre-combustion capture for brown coal
- Evaluate the suitability of existing and emerging technologies for pre-combustion capture for brown coal at different points in the process chain
- Evaluate the opportunities to significantly drive down the cost of pre-combustion capture for brown coal through capture technology improvements, and heat and process integration

CO2CRC's selection of the three capture technologies trialled in the facility was based on the fact that the work would not only focus on traditional solvent options but also on the emerging membrane and adsorbent technologies. All three capture plants were commissioned and remained in full operation until 2010. The outcomes of this research are not only vital to the brown coal sector in Victoria but are also relevant to exploitation of brown coal elsewhere in the world. The findings and methodologies developed are readily applied to other syngas applications with other fuels, including oxygen blown gasifiers.

2.3.2 Aspects of Mulgrave gasifier/capture plant interface

The HRL Mulgrave gasifier is an 8 bar, 0.5MW capacity, air blown, fluidized bed gasifier with dried brown coal as feed. It does not have the integrated drying step of the HRL IDGCC technology. The contract to supply syngas for this capture project was for syngas “from the pipe” ie. with variable composition and conditions applying to a commercial capture situation. Most of these interface implications were accommodated in the capture plant design, others had to be reacted to in actual operation eg., variations in the syngas water content, the presence of trace hydrocarbons or other possible contaminants. The absence of full automatic controls on the solvent plant (a budget limitation) at times also complicated responses to interface difficulties that arose during trials. But this added to the learning achieved.

The confidential nature of the IDGCC technology meant that HRL staff were constrained in what technical information could be shared during the trial. Even though HRL staff assisted to the maximum degree, this constraint influenced the approach adopted, and the results that could be generated.

These plant and staff interface limitations encouraged a maximum use of simulation and technical software modelling, like ASPEN, to bridge technical gaps or differences between expected and actual conditions. As this is a normal part of technology development, it should be seen as a strength of this project and its results, rather than as a weakness ie. it is the path to real world operations rather than a substitute for them.

2.4 References

1. Appendix 1 (attached at the end of this report), “Large Scale Integrated Projects with Pre-combustion Capture” extracted from Global CCS Institute web page
2. CO2CRC webpage (www.co2crc.com.au)
3. EPRI (Electric Power Research Institute), *Assessment of Post-Combustion Technology Developments*, Paolo Alto, 2007
4. GCCSI-a (Global Carbon Capture and Storage Institute), *Webpage – Capture* under *Carbon Capture and Storage* http://www.globalccsinstitute.com/ccs/what-is-ccs/capture
5. GCCSI-b (Global Carbon Capture and Storage Institute), *Webpage – Large Scale Integrated Projects, 17 Nov 2010* under *Status of CCS Projects Database,* http://www.globalccsinstitute.com/resources/data/status-ccs-project-database
6. IEA (International Energy Agency), *Technology Roadmap – Carbon capture and storage*, 2010
7. IPCC (Intergovernmental Panel on Climate Change), *Special Report on Carbon Capture and Storage*, 2005
8. Lindner, S., Peterson, S., Windhorst, W. (2010) An economic and environmental assessment of carbon capture and storage (CCS) power plants: a case study for the City of Kiel. Journal of Environmental Planning and Management. 53: 1069-1088.
9. WI (Wuppertal Institute for Climate, Environment and Energy), *Final Report, RECCS plus - Comparison of Renewable Energy Technologies with Carbon Dioxide Capture and Storage (CCS)*, 9 August, 2010

3. Overview on Pre-Combustion CO_2 Capture Demonstration Activities under ETIS

3.1 Mulgrave gasifier: opportunity and limitations

As outlined in Section 2.3.2, the Mulgrave Capture Project has been developed to capture CO_2 from synthesis gas produced from the gasification of Victorian brown coal at the Mulgrave gasifier facility. Having been purpose-built as an R&D gasifier and commissioned approximately 15 years ago, the Mulgrave (0.5 MW capacity) gasifier did operate at different conditions to a IDGCC process gasifier. The conditions of the synthesis gas produced by the Mulgrave gasifier are presented in Table 3.1.

Table 3.1 Typical conditions of syngas from the 0.5 MW capacity Mulgrave gasifier.

Gas Flow rate	707 kg/hr 657 Sm^3/h (106 Am^3/h)
Pressure	700 kPag
Temperature	50-100 °C
Composition mol %	**(wet basis)**
H_2	11
N_2	47
CH_4	2
CO	12
CO_2	12
H_2O	13
NH_3	<2000 ppm (dry basis)
H_2S	<500 ppm (dry basis)
Heavy hydrocarbons	Trace amounts

As well as lower pressure and temperature conditions than a commercial IDGCC gasifier (700 kPag as opposed to ~ 3000 kPag; 50-100°C as opposed to over 200 °C), the Mulgrave gasifier did not include a water-gas shift reactor which would be used for industrial-scale coal gasification with capture. As such, the carbon monoxide (CO) concentration was higher than that of a traditional synthesis gas produced from IGCC coal gasification. Another feature is that the Mulgrave gasifier is an R&D plant in itself and runs in campaigns. For this study each campaign consisted of 6 run days of 8 hrs (or more often 2-4 hours). Unfortunately, while access to syngas from this gasifier allowed this project to proceed, the age and reliability of the gasifier did result in downtime of the synthesis gas supply and an overall reduction in the operating time of the capture pilot plants.

The original plan was for three campaigns with the potential of a fourth over the 3-year research program. Due to repairs, preparation and technical issues with the Mulgrave gasifier and capture plants themselves, each campaign period extended up to a couple of months. Three campaigns were eventually completed, short of a couple of days.

3.2 Objectives of the Mulgrave Capture Project

The key objective of this project was to reduce the technical risk and cost of pre-combustion capture for Victorian coal-fired stations with new coal burning technologies employing gasification. The program was executed in line with the agreed annual plans. For each of the three capture technologies (solvent absorption, membrane and adsorption), the more specific objectives were to:

- Identify and quantify the impact of realistic pre-combustion gas contaminants (H_2S, CH_4, CO) and water on the performance of each capture technology;
- Identify and quantify the impact of pre-combustion gas temperature and concentration variations on the performance of the capture medium and capture process;
- Optimise capture process operating parameters;
- Develop engineering solutions at a scale at which confidence can be established for full scale capture plant design and assessment;
- Assess the pre-combustion capture process and energy integration options;
- Review the technical and economic viability of the commercial use of pre-combustion capture for new Victorian brown-coal power stations using the gasification process route; and
- Conduct a desk-top conceptual study for post-combustion capture from the CO2CRC Modelled Plant and compare the results with pre-combustion capture (this objective was added as part of the BCIA extension process).

3.3 Background to solvent trials

The high N_2 content of the syngas from the Mulgrave gasifier suggests a chemical solvent capture option. Traditional solvents such as amines (eg: ethanolamine) being volatile and sensitive to degradation by oxygen and other impurities, are operated at low temperatures (40 – 50°C) to reduce operating costs. Despite these absorption conditions, corrosion and degradation still occur as part of the regeneration process. These low temperatures create thermodynamic inefficiencies and alter the water content in the treated syngas significantly, which in turn reduces power output of the gas turbine. Recognizing this phenomena, the CO2CRC had developed, and is in the process of patenting, a high temperature absorption process based on Potassium Carbonate (K_2CO_3) scrubbing that would address this problem for syngas streams and provide reduced parasitic load for pre-combustion. This process is known internally as the UNO process. Hot potassium carbonate solutions have been used commercially for acid gas absorption for many years. The process is commonly known as the Benfield process [Benson et al.] and was originally developed by the U.S. Bureau of Mines in 1954 to reduce the costs of synthesis gas purification for the production of liquid fuel from coal. The process was designed for gas process streams with CO_2 partial pressures. Over the years newer solvents have been introduced to the acid gas treatment market but the Benfield Process remains the process of choice in several chemical applications, globally.

In seeking solutions to CCS related CO_2 capture applications, the CO2CRC identified potassium carbonate as a strong candidate solvent due to its oxygen and impurity tolerance and low volatility. The process developed by the CO2CRC for pre-combustion application operates at temperatures above that of the Benfield Process exploiting the benefits of high temperature processing in the overall combined cycle used in both the IDGCC and IGCC gasification processes.

Additional research was introduced to the project as part of the BCIA extension, namely, the concept of applying CO2CRC's UNO Mk 3 process to the CO2CRC Modelled Plant in a post-combustion mode, removing CO_2 from the turbine exhaust rather than on the syngas. While not strictly a pre-combustion application, it was considered potentially beneficial given the air blown nature of the CO2CRC Modelled Plant, and need to increase the overall CO_2 capture rate. These desk-top conceptual studies provided an important comparison of pre- and post-combustion capture on the same gasification process: work that could be globally significant.

3.4 Background to membrane trials

There is a range of membranes with considerable potential for pre-combustion capture. The key selection criteria are suitably high permeability and selectivity with high resistance to compaction, plasticization and contamination. This project focused on polymeric membranes.

Polyimide and cellulose acetate membranes are currently used commercially for the removal of CO_2 from natural gas streams and are likely to be suitable as gas separation membranes for pre-combustion capture. Surface treated polypropylene membranes are likely to be a cheap alternative for pre-combustion membrane gas absorption because of their ability to retain hydrophobicity on exposure to solvent solutions. These membranes warranted assessment at the pilot scale.

3.5 Background to adsorption trials

Greater thermodynamic efficiency can be achieved by operating CO_2 renewal at higher temperatures. Pre-combustion adsorption capture processes are limited by the relatively low CO_2 loading capacity at high temperature of most commonly used adsorbents. The adsorbent selection criteria are therefore the ability to retain high adsorption capacity at high temperature while also retaining high selectivity, mechanical stability after a number of cycles, adequate kinetics, etc. Various adsorbent materials such as zeolites, hydrotalcites, alumina, layered double hydroxides have been studied for capturing CO_2 at elevated temperature. However, most research has focused on the basic material characteristics and little is known about the applicability of the materials at large-scale and for different operating modes e.g., pressure swing adsorption (PSA), vacuum swing adsorption (VSA), pressure vacuum swing adsorption (PVSA) and temperature swing adsorption (TSA). Work is needed on cycle development for such large scale CO_2 removal applications.

3.6 References

1. Benson, H. E. et al., "Carbon dioxide absorption employing hot potassium carbonate solutions," *Chem. Eng. Prog.,* vol. 50, pp. 356-64, 1954.

4. Project Management and Related Issues

4.1 Management structure and collaboration

CO2CRC was the proponent for the project with the Victorian Government. Participating organisations in this project were CO2CRC, HRL Developments Pty Ltd (HRL) , The University of Melbourne, Monash University, the University of New South Wales (UNSW), Process Group and Pilot Plant Management and Services (PPMS). Although the project was managed by CO2CRC, it was the collaborative effort by all participating bodies that made this project successful. Fig 4.1 shows the project management structure.

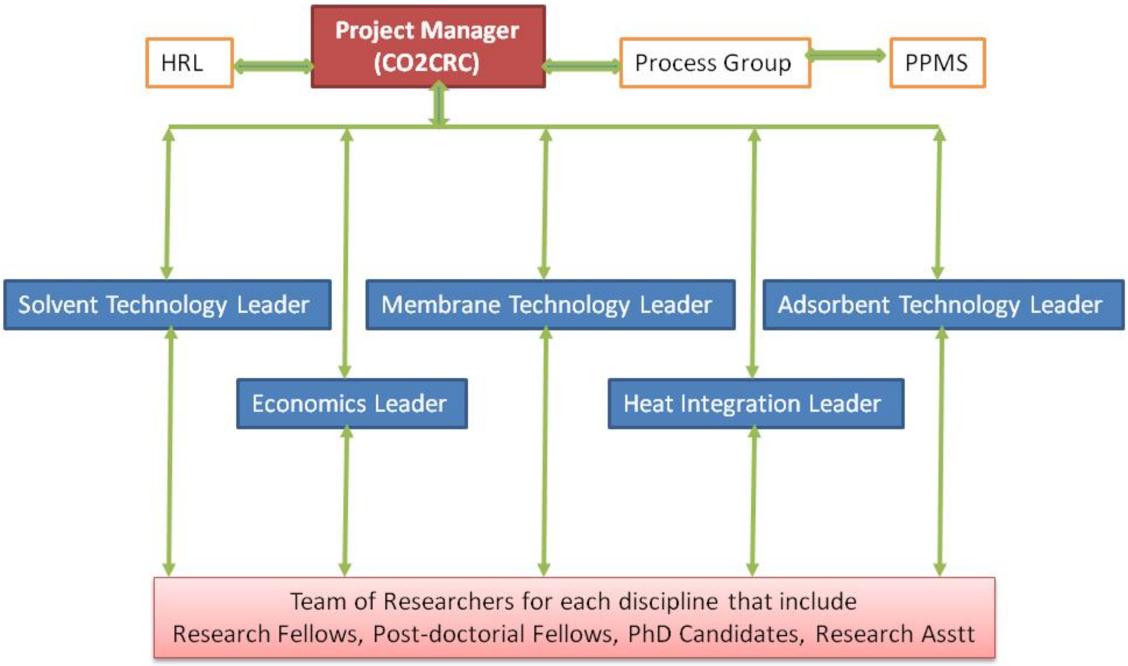


Figure 4.1 Project Management Structure

CO2CRC managed and coordinated the overall project. HRL managed the gasifier operation providing syngas to the capture plants operated by CO2CRC. The University of Melbourne was responsible for the R&D for the solvent and membrane technologies while Monash University was responsible for the adsorption technology. CO2CRC and Monash University were responsible for the heat and process integration. UNSW was responsible for the economic evaluation. CO2CRC engaged two local engineering companies, namely, Process Group and PPMS, in the design, construction and commissioning of the capture plants. Process Group was responsible for the solvent rig while PPMS was responsible for the membrane and adsorption rigs under Process Group’s direction.

4.2 Strategies, risk assessment and mitigation to meet the objectives of the Project

In such a multi-party, multi-technology and multi-objective project, a range of strategies were adopted to ensure the success of the project and to achieve:

- Quality and effectiveness of the R&D program;
- Progress of the research along the innovation chain to commercial application, keeping in mind that the three pilot plants were to be installed in real industrial setting; and
- Efficient resource utilization.

In line with adopted strategies, mitigation measures were in place to minimise associated risks. Some of those strategies and measures included,

- Mapping out a detailed research plan with strict time frame outlining the tasks for all parties involved.
- Liaising with all parties on a repeated basis to check design, construction, commissioning, process operation, equipment, and logistics to comply with project objectives. Measures involved developing a detailed schedule, inclusion of late penalties, organising regular team meetings and identifying & sourcing extra resources when needed to address delays in commissioning of the three CO2CRC rigs.
- Managing various interest groups (university researchers, government, industry, CO2CRC core participants). Tasks involved were:
  - Obtain regular updates from technology, heat integration and economics researchers as against agreed milestones and revise action plan when required
  - Monitor safety, process and equipment procedures and performance. All measures were undertaken as per expert’s advice and the respective site’s safety regulations and best practices. The day was always started with a tool box meeting
  - Resolve day-to-day site and laboratory issues
  - Maintain adequate human resources. Developed schedules and run campaign based trials to maximise staff availability
  - Coordinate and prepare progress reports

- Facilitating preparation and approval of publications and presentations for journals, seminars, workshops, conferences, public lectures, hosting visits by local and international groups to research facilities etc in order to publicise project outcomes as well as enhance CCS awareness.
- Investing extra resources and technical inputs, mainly by HRL, to ensure gasifier readiness.

5. Pilot Plant Activities

5.1 Solvents

5.1.1 Process Description

Solvent absorption is the standard industrial method for removing CO_2 from synthesis gas. Details of the solvent system studied in this trial and the equipment used are described in the following sections.

5.1.1.1 Potassium carbonate solvent system

The solvent used in the solvent absorption pilot plant was potassium carbonate, K_2CO_3, with concentrations varying from 20-30 wt%. In the third campaign boric acid was added to the potassium carbonate solvent to study its effect as a rate promoter.

Potassium carbonate has a number of advantages over the amine-based solvents with one of the most important being that improved absorption can occur at high temperatures resulting in improved power output. Potassium carbonate also has a low cost, is less toxic and is less prone to degradation effects that are commonly seen with amines at high temperatures and in the presence of oxygen and other minor gas components. The biggest challenge associated with using potassium carbonate as a solvent is that it has a low rate of reaction resulting in poor mass transfer performance. Promoters are often added to the solvent to improve the mass transfer rates. Traditionally promoters such as piperazine [1], diethanolamine [2] and arsenic trioxide [3] have been used. Other promoters such as boric acid have also been used in the past and are currently being investigated for application [4, 5].

The overall reaction for the absorption of carbon dioxide using a potassium carbonate solution is described as follows:

$$CO_2 + K_2CO_3 + H_2O \rightleftharpoons 2KHCO_3$$

Equation 1

Since potassium carbonate and bicarbonate are strong electrolytes, it can be assumed that the metal is present only in the form of K^+ ions and reaction (1) can be represented as:

$$CO_2 + CO_3{}^{2-} + H_2O \rightleftharpoons 2HCO_3{}^{-}$$

Equation 2

Reaction (2) proceeds according to the following sequence of elementary steps:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$ **Equation 3**

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$ **Equation 4**

$$H_2O \rightleftharpoons H^+ + OH^-$$ **Equation 5**

Reactions (3) and (4) are both followed by subsequent instantaneous reactions as follows:

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^-$$ **Equation 6**

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$$ **Equation 7**

The reaction sequence (3), (5) and (6) is known as the acidic mechanism [6]. The contribution of the acidic mechanism to the overall rate is negligible unless the pH of the liquid solution is very low. Almost all cases of industrial absorption are held at high pH (generally, pH>8). Hence the acidic mechanism can be neglected. Reaction (4) is the rate controlling step for absorption of CO_2 into hot potassium carbonate solution as reactions (5) and (7) are instantaneous reactions.

5.1.2 Design Basis

The design of the solvent absorption and stripping columns has been based on laboratory scale column trials and ASPEN Plus™ simulations. Equipment design and fabrication was completed by Process Group in consultation with the CO2CRC. The final design was based on considering all recommendations provided by a professional Hazard and Operability (HAZOP) study organised by CO2CRC.

5.1.2.1 Design conditions

The gas composition and conditions of the feed gas to the solvent plant (syngas exiting the Mulgrave gasifier) were supplied by HRL (refer to Table 5.1.1). Depending on the pipe routing and ambient conditions this stream may undergo further cooling before reaching the solvent pilot plant. It should also be noted that the gasifier process does not include a water-gas shift reactor which has resulted in a higher CO concentration and lower CO_2 concentration when compared to a typical commercial shifted-syngas.

Table 5.1.1 Approximate Properties of Gas Stream from Mulgrave Gasifier to Solvent Capture Plant.

Gas Flow rate	707 kg/hr 657 Sm^3/h (106 Am^3/h)
Pressure	700 kPag
Temperature	50-100°C
Composition mol % (wet basis)	
H_2	11
N_2	47
CH_4	2
CO	12
CO_2	12
H_2O	13
NH_3	<2000 ppm (dry basis)
H_2S	<500 ppm (dry basis)
Heavy hydrocarbons	Trace amounts

Equipment sizing was based on the simulated stream data obtained using ASPEN Plus^{TM}. Stream flows were specified in order that both the absorber and regenerator had a diameter of 200 mm. The packed bed heights were approximately 3.3 m in each column. The packed bed sections of the absorber and regenerator were designed as replaceable, flanged sections that could be added to or replaced so that the bed height could be altered. The columns were both filled with 16 mm SMR random packing and 30 wt% potassium carbonate (K_2CO_3) was used as the solvent. It was also intended in the design that rate promoters could also be added to the solvent to improve the absorption kinetics.

The solvent plant was designed to process 300 kg/hr (32 m^3/hr) of syngas which corresponded to a solvent flow rate of approximately 1800 kg/hr (1.5 m^3/hr). The absorber was designed to be operated at a pressure of 700 kPag and temperature of 80°C. The regenerator was designed to be operated at a pressure of 100 kPag and a temperature of approximately 120°C. The solvent plant was designed to capture up to 1000kg of CO_2 per day from the syngas.

5.1.3 Construction, Commissioning and Operation

5.1.3.1 Construction

Construction of the solvent capture pilot plant was completed by Process Group [7] . An image of the solvent capture plant on-site at HRL Mulgrave is shown in Figure 5.1.1.

Figure 5.1.1 Solvent Absorption Capture Pilot Plant onsite at HRL Mulgrave

5.1.3.2 Commissioning

Commissioning was completed on site at HRL Mulgrave during the first quarter of 2009 by Process Group and CO2CRC personnel.

5.1.3.3 Operation

The solvent capture pilot plant was run for a total of 16 days with syngas over three campaigns. Operating procedures were developed by CO2CRC.

5.1.3.4. Recommendations for future pilot and demonstration facilities

Based upon experience with operating the existing solvent pilot plant located at Mulgrave, suggestions were made for improved operability. It is recommended that these suggestions be considered for any larger scale pre-combustion capture demonstration facility being considered.

5.1.4 Large Scale Capture for the Full Scale CO2CRC Modelled Plant

Preliminary equipment sizing has also been completed for the capture of CO_2 emissions from a desktop study of a full scale (550 MW) CO2CRC Modelled Plant. Two cases have been completed for the capture facility as follows (i) pre-combustion capture of CO_2 using CO2CRC's proposed UNO process conditions with potassium carbonate upstream of the turbine and (ii) post-combustion capture of CO_2 using the CO2CRC's UNO Mk3 Process downstream of the turbine and including the emissions from the char burner.

These two cases are discussed below. The equipment sizing and basic process information for these two cases has been used as input to the heat integration and economic modelling.

5.1.4.1 Pre-combustion capture for the CO2CRC Modelled Plant UNO process

A block diagram of the air-blown coal gasification process including pre-combustion capture is presented in Figure 5.1.2. In this process, it is necessary to include a water gas shift reactor to oxidise the CO to CO_2 and allow full-capture of the CO_2 from this stream. The CO_2 emissions from the burner used in the CO2CRC Modelled Plant are emitted without capture.

The 550 MW pre-combustion full scale capture plant using 30 wt% potassium carbonate at the solvent was simulated in ASPEN Plus™. This concentration of solvent was chosen for this design study as it was the basis of the pilot test work however, more optimised designs at higher concentrations are possible. Further comment and solvent plant optimisation is provided in Section 6. The inlet feed conditions used in the simulation are provided in Table 5.1.2. The absorber and stripper were modelled with standard industrial packing (metal IMTP, Koch-Glitsch). The height of the packing in both columns was adjusted to meet a removal efficiency of 90% and the diameter of the column was set based on the gas velocity.

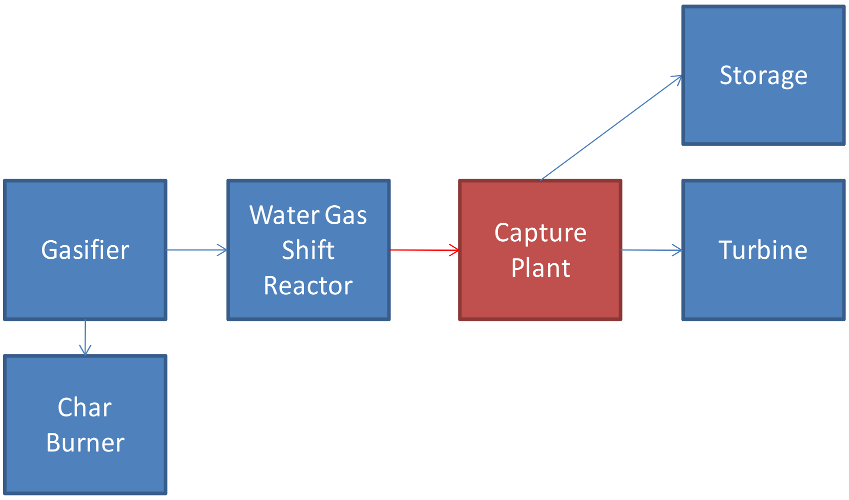


Figure 5.1.2 Block Diagram of the Coal Gasification Process Including Pre-Combustion Capture.

Table 5.1.2 Inlet Conditions of Feed Stream to the CO2CRC Modelled Plant Pre-Combustion Full Scale Capture Plant

Parameter	Units	Value
Temperature	°C	130
Pressure	kPag	2600
Gas Composition		
H_2O	Mass %	9
CO_2	Mass %	44
N_2	Mass %	39
CO	Mass %	3
CH_4	Mass %	2
H_2	Mass %	3

Given the high operating temperature and pressure of the absorber, CO_2 removal in the regenerator occurs primarily through operating the regenerator at lower pressure, say 200 kPag. Eliminating the need to heat the solvent temperature to the boiling point reduces the energy required by the reboiler per kg of CO_2 removed compared with what was achieved by the solvent pilot plant at HRL in Mulgrave.

5.1.4.2 Post-combustion capture for the CO2CRC Modelled Plant – UNO Mk3

A block diagram of a conceptual post-combustion capture process for the CO2CRC Modelled Plant is presented in Figure 5.1.3. The reason for considering this approach is to increase the overall recovery of CO_2 and to make the plant more resilient to increasing carbon cost. As capture of the CO_2 occurs after the turbine, there is no requirement for a water-gas shift reactor thus saving capital cost and complexity. Furthermore, capture of the

CO_2 emissions from the char burner is possible. Modifications to the gas turbine to incorporate exhaust gas recycling make the PCC approach more cost effective. The characteristics of potassium carbonate make this approach more flexible due to the oxygen and impurity tolerance of the solvent.

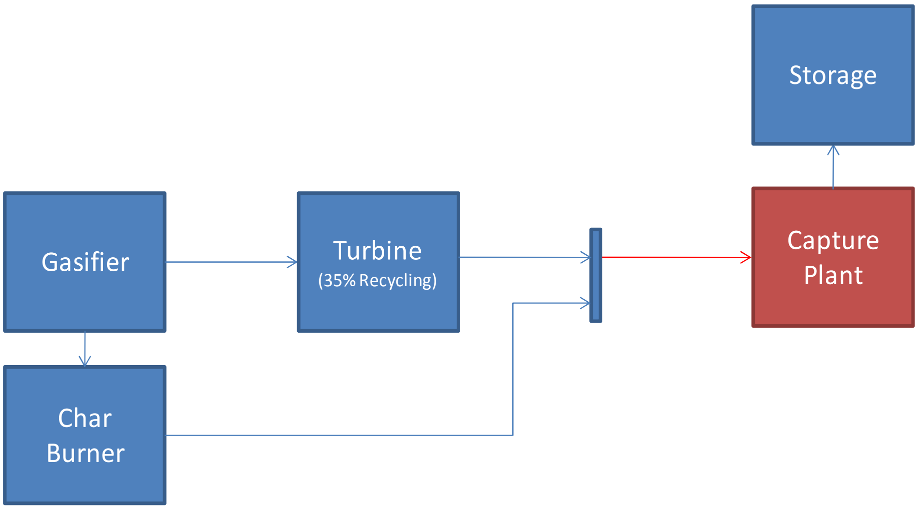


Figure 5.1.3: Block Diagram of the CO2CRC Modelled Plant Including Post-Combustion Capture.

The sizing of the 550 MW modelled post-combustion full scale plant was completed based upon the CO2CRC's patented UNO Mk3 process. This process uses a higher weight % potassium carbonate solvent, resulting in improved absorption performance and lower solvent recirculation rates. The inlet feed conditions used in the simulation are provided in Table 5.1.3 below. The height of the packing in both columns was adjusted to meet a removal efficiency of 90% and the diameter of the column was set based on the gas velocity.

Table 5.1.3 Inlet Conditions of Feed Stream to CO2CRC Modelled Full Scale Post-Combustion Capture Plant

Parameter	Units	Value
Temperature	°C	45
Pressure	kPag	2
Gas Composition		
H_2O	Mass %	5
CO_2	Mass %	17
N_2	Mass %	69
O_2	Mass %	8
Ar	Mass %	1

The sizes of the absorber and regenerator columns for the full scale post-combustion capture plant are larger than the pre-combustion counterpart. This is due to an increase in the amount of CO_2 being captured and also operation of the absorber at atmospheric pressure. Increasing the concentration of the potassium carbonate reduces the total required solvent rate to a value less than the pre-combustion case despite the higher amount of CO_2 captured. The higher amount of CO_2 captured per unit solvent flow also results in some improvement in the reboiler energy usage.

5.1.5 Other Outcomes (communications, collaborations, skills development etc)

The solvent absorption pilot plant performance has been reported at the following conferences in either presentation or poster formats:

- 17th World Hydrogen Energy Conference 2008, Brisbane, Australia
- 9th International Conference on Greenhouse Gas Technologies 2008, Washington DC, USA
- CO2CRC Symposium 2008, Queenstown, New Zealand
- CO2CRC Symposium 2009, Coolum, Australia
- CO2CRC Symposium 2010, Melbourne, Australia
- 10th International Conference on Greenhouse Gas Technologies 2010, Amsterdam, Netherlands
- Australian Institute of Energy - Melbourne Branch Postgraduate Student Energy Awards, Melbourne, Australia, 2010
- Chemeca 2010, Adelaide, Australia, 2010

The following publications (journal papers and conference presentations) have been produced as a result of this research:

Journal Papers

1. Khan, A.A., Wappel, D., Joswig, S., Smith, K.H., Kentish, S.E., Shallcross, D.C., Stevens, G.W. (2010) The Solubility of sulphur dioxide and carbon dioxide in an aqueous solution of potassium carbonate, *International Journal of Greenhouse Gas Control* (Under review)
2. Zhao, X., Smith, K.H., Simioni, M.A., Tao, W. Kentish, S.E., Fei, W. & Stevens, G.W. (2010). Comparison of several packings for CO_2 chemical absorption in a packed column, *International Journal of Greenhouse Gas Control* (Under review)
3. Zhao, X., Simioni, M.A., Smith, K.H., Kentish, S.E., Fei, W. & Stevens, G.W. (2009). Study on the interaction between NO_x and K_2CO_3 during CO_2 absorption, *Energy Fuel*, 23, 4768–4773
4. Smith, K., Ghosh, U., Khan, A., Simioni, M., Endo, K., Zhao, X., Kentish, S., Qader, A., Hooper, B., Stevens, G. (2009). Recent developments in solvent absorption technologies at the CO2CRC in Australia, *Energy Procedia,* 1, 1549–1555

Conference Presentations

1. Smith, K, Ghosh, U, Khan, A, Simioni, M, Endo, K, Zhao, X, Kentish, S, Qader, A, Hooper, B and Stevens, G, (2008). Recent developments in solvent absorption technologies at the CO2CRC in Australia. Poster presented at the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC, 16-20 November.
2. Scholes, C, Smith, K, Wilson, S, Kentish, S, Stevens, G and Webley, P, (2008). Pre-combustion carbon capture technologies pilot plant trials on coal gasification. Poster presented at the 17th World Hydrogen Energy Conference (WHEC2008), Brisbane, Australia, 15-19 June.
3. Smith, K, Zhao, X, Tao, W, Kentish, S and Stevens, G, (2008). Solvent Absorption Column Performance Trials with Potassium Carbonate Solvent. In: Program and Abstracts, CO2CRC Research Symposium 2008, Queenstown, New Zealand, 1-4 December. CO2CRC, Canberra, pp. 67. (oral presentation)
4. Khan, A, Smith, K, Kentish, S, Shallcross, D and Stevens, G, (2008). Investigation of feasibility of CO_2 removal from a gasifier flue gas stream using brown coal with an aqueous potassium carbonate solvent with Aspen Plus© . In: Program and Abstracts, CO2CRC Research Symposium 2008, Queenstown, New Zealand, 1-4 December. CO2CRC, Canberra, pp. 79. (poster presentation)
5. Anderson, C, Smith, K, Qader, A, Ghosh, U, Endo, K, Tao, W, Khan, A, Kentish, S and Stevens, G, (2009). Solvent Pilot Plant Results for Pre-Combustion Capture. In: Program

and abstracts, CO2CRC Research Symposium, Coolum, Australia, 1-3 December. CO2CRC, Canberra, pp. 49. (oral presentation)

6. Khan, A, Anderson, C, Smith, K, Tao, W, Shallcross, D, Kentish, S and Stevens, G, (2009). Modelling and analysis of CO_2 removal from a gasifier flue gas stream using brown coal with an aqueous potassium carbonate solvent in a pilot scale. In: Program and abstracts, CO2CRC Research Symposium, Coolum, Australia, 1 December - 3 November. CO2CRC, Canberra, pp. 95. (poster presentation)
7. Smith, K, Mumford, K, Anderson, C, Ghosh, U, Khan, A, Simioni, M, Endo, K, Zhao, X, Kentish, S, Qader, A, Hooper, B and Stevens, G, (2009). Commercial Technologies for Capture Research. In: Program and abstracts, CO2CRC Research Symposium, Coolum, Australia, 1-3 December. CO2CRC, Canberra, pp. 39. (oral presentation)
8. Anderson, C, Scholes, C, Lee, S, Smith, K, Kentish, S, Stevens, G, Webley, P, Qader, A and Hooper, B, 2010. Novel Pre-Combustion Capture Technologies in Action — Results of the CO2CRC/HRL Mulgrave Capture Project. Oral presentation given at the 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, The Netherlands, 19-23 September.
9. Anderson, C, Smith, K, Scholes, C, Lee, S, Kentish, S, Stevens, G, Webley, P, Qader, A and Hooper, B, 2010. Novel Pre-Combustion Capture Technologies in Action — Results of the CO2CRC/HRL Mulgrave Capture Project. *Poster presented at the 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10),*Amsterdam, The Netherlands, 19-23 September.
10. Thee, H, Smith, K, Da Silva, G, Kentish, S and Stevens, G, 2010. CO_2 Absorption by Borate-Promoted Potassium Carbonate under Pre-Combustion CO_2 Capture Conditions *.Poster presented at the Australian Institute of Energy - Melbourne Branch Postgraduate Student Energy Awards,* Melbourne, Australia, 6-7 October.
11. Anderson, C, Smith, K, Qader, A, Endo, K, Ghosh, U, Tao, W, Khan, A, Kentish, S, Stevens, G and Hooper, B, 2010. Demonstrating Pre-Combustion CO_2 Capture Using Solvent Technology. Oral presentation given at Chemeca 2010, Adelaide, Australia, 26-29 September.
12. Anderson, C, Smith, K, Mumford, K, Endo, K, Tao, W, Thee, H, Suryaputradinata, Y, Qader, A, Kentish, S and Stevens, G, 2010. Results from the Solvent Pilot Plant for Pre-Combustion Capture. Oral presentation given at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.
13. Thee, H, Smith, K, Da Silva, G, Kentish, S and Stevens, G, 2010. CO_2 Absorption by Borate-Promoted Potassium Carbonate under Pre-Combustion Capture. Poster presented at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.

14. Anderson, C, Smith, K, Mumford, K, Endo, K, Tao, W, Thee, H, Suryaputradinata, Y, Qader, A, Kentish, S and Stevens, G, 2010. Results from the Solvent Pilot Plant for Pre-Combustion Capture. Oral presentation given at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.
15. Thee, H, Smith, K, Da Silva, G, Kentish, S and Stevens, G, 2010. CO_2 Absorption by Borate-Promoted Potassium Carbonate under Pre-Combustion Capture. Poster presented at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.

Along with interactions at the numerous international and national conferences listed above, continuous collaboration occurred between the solvent capture group and the following organisations/universities:

- Process Group
- HRL
- Tsinghua University, Beijing

The skills and knowledge developed through this project have made the CO2CRC solvent research group one of the world leading experts in operating K_2CO_3 solvent based capture plants under pre-combustion conditions. This includes developing the skills of the following people in solvent pre-combustion capture:

- 2 postgraduate students
- 2 research assistants
- 4 research fellows

5.1.6 Solvent capture, conclusions:

Three separate campaigns of operating a solvent CO_2 capture pilot plant using synthesis gas feed from an air-blown gasifier have been successfully completed.

In order to avoid precipitation, the solvent pilot plant during Campaigns 1 and 2 used a lower weight% potassium carbonate solution. The performance was slightly improved in Campaign 2 due to optimisation of the absorber and condenser outlet temperatures. A boric acid promoter was added to a slightly higher weight % potassium carbonate solution used for Campaign 3. No improvement on the performance was observed despite the presence of the boric acid promoter. This can be explained by the reduction in the system pH and concentration of OH^- leading to a reduced reaction rate.

Various operational issues were encountered and overcome during the three campaigns. Campaign 1 was consumed with solvent precipitation issues, pump malfunction, and poor control of levels in the vessels. During the course of Campaign 2 one of the pressure valve failed and there were some continued problems with level control although this was eventually overcome by better water balance management. The biggest operational difficulty of Campaign 3 was the presence of black particles from the failure of a filter candle on the outlet of Mulgrave gasifier. Recommendations for the design of a larger scale demonstration capture plant based on solvent technology have been provided for improved operability. Also provided is preliminary sizing information for full scale solvent plants for capturing CO_2 from air-blown coal gasification. Two cases have been considered, namely pre-combustion capture upstream of the turbine and post-combustion capture downstream of the turbine and including the emissions from the char burner. Whilst bigger equipment is required for the post-combustion case because of the large volumes of gas being processed, the solvent flow rate and reboiler energy per kg of CO_2 capture is reduced.

5.1.7 References

[1] J. T. Cullinane and G. T. Rochelle, "Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine," *Chemical Engineering Science,* vol. 59, pp. 3619-3630, 2004.

[2] M. R. Rahimpour and A. Z. Kashkooli, "Enhanced carbon dioxide removal by promoted hot potassium carbonate in a split-flow absorber," *Chemical Engineering and Processing,* vol. 43, pp. 857-865, 2004/7 2004.

[3] M. M. Sharma and P. V. Danckwerts, "Catalysis by Broensted bases of the reaction between CO2 and water," *Trans. Faraday Soc.,* vol. 59, pp. 386-95, 1963.

[4] M. Ahmadi*, et al.*, "Advanced modelling in performance optimization for reactive separation in industrial CO2 removal," *Sep. Purif. Technol.,* vol. 63, pp. 107-115, 2008.

[5] U. K. Ghosh*, et al.*, "Absorption of carbon dioxide into aqueous potassium carbonate promoted by boric acid," *Energy Procedia,* vol. 1, pp. 1075-1081, 2009.

[6] S. Bishnoi and G. T. Rochelle, "Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility," *Chemical Engineering Science,* vol. 55, pp. 5531-5543, 2000.

[7] K. Smith*, et al.*, "Recent developments in solvent absorption technologies at the CO2CRC in Australia," *Energy Procedia,* vol. 1, pp. 1549-1555, 2009.

5.2 Membranes

5.2.1 Process Description

The purpose of the Mulgrave Capture Project Membrane Pilot Plant was to trial a range of membrane materials and membrane separation strategies to separate CO_2 from syngas, with the overall objective of identifying the most potential for successful pre-combustion carbon capture.

To achieve this objective, the Membrane Pilot Plant was designed and constructed to operate three membrane separation processes in parallel:

- Two-stage membrane module separation in series (M-101 and M-102): the retentate or permeate stream from the first membrane module was the feed stream for the second membrane module, which allowed sequential separation to occur.
- High temperature membrane separation (M-104): the membrane module was operated at high temperatures to process the syngas close to the water-gas shift temperature.
- Membrane gas-solvent absorption contactor (M-103): hybrid technology of solvent absorption and membrane separation, where CO_2 separation was achieved by absorption into a solvent, with the interaction area between the syngas and solvent rigidly controlled by a porous membrane.

The separation performance criteria reviewed to judge a membrane material, were as follows:

- Good CO_2 selectivity relative to H_2 and N_2.
- High CO_2 permeability (i.e. flux) through the membrane.
- Separation performance stability under process conditions.

Membrane materials and strategies that demonstrate these three criteria have potential for implementation in pre-combustion capture. To fully quantify membrane performance, the permeability of CO, CH_4, water, and higher hydrocarbons, along with a comparison in membrane performance under ideal conditions in the laboratory, were also studied. Unfortunately, given the restriction in operating time of the Mulgrave Capture Project, time dependent studies of membrane were limited.

5.2.2 Design basis

The Membrane Pilot Plant was designed to separate out approximately 5.6 kg of carbon dioxide per day from syngas, based on expected membrane performance. However, the main objective of the pilot plant was to trial a range of membranes and separation strategies, to measure the relative permeance of each syngas component across the membrane and to see how the membrane held up under process conditions. This helped to evaluate their effectiveness. The pressure differences across the membranes were maximized, and temperature varied where possible.

The determined performance data were then used as the basis of the simulation studies (Section 5.2.5) for large scale membrane based capture plants from syngas. The design basis for these simulations was an air-blown gasification process that provided syngas, with a composition shown in Table 5.2.1, at 27 bar and 250°C. The simulations objective was to design a membrane capture plant that recovered 90% of the CO_2 in the feed and generate a purity of 95% CO_2 for storage requirements, as per DOE requirements.

Table 5.2.1 Syngas composition (mol%) for membrane simulations.

H2	27.6
CO2	21.7
N2	30.35
CO	2.4
H2O	14.4
CH4	3.5
H2S	0.05

5.2.3 Construction, Commission and Operation

The original membrane pre-combustion pilot plant design was undertaken by the CO2CRC and Process Group Pty Ltd (PG). Further additions to the design and construction were performed by Pilot Plant Management Services Pty Ltd (PPMS) with PG’s supervision. The design was finalised after considering all the recommendations of the professional Hazard and Operability (HAZOP) study organised by CO2CRC. A photograph of the installed pilot plant is shown in Figure 5.2.1. Operations and test programs were conducted in 3 campaigns as outlined in the solvent section (5.1.2).

Figure 5.2.1 Mulgrave Capture Project Membrane Pilot Plant onsite.

To ensure the pilot plant complied with electrical zoning requirements, the cabinet roof was connected to an air extraction unit of the building which ensured continual replacement of surrounding air within the pilot plant cabinet. Emergency shutdown occurred if the LEL level and/or CO level within the cabinet or extraction unit went over the lower threshold limit or the gasifier shutdown (for any reason).

Feed gas composition was provided by the gasification operator.

5.2.4 Performance Evaluation and Results as against Simulation:

For carbon dioxide selective gas separation membranes, PDMS has the best performance in terms of high CO_2 permeability as well as good CO_2/H_2 and CO_2/N_2 selectivities under syngas conditions. Furthermore, on a dry basis, the pilot plant has shown two PDMS membranes in series were able to almost achieve the desired CO_2 purity for storage. To extend this, a PDMS membrane capture plant was simulated in Aspen HYSYS using an in-house generated membrane module (counter-current flow), based on the syngas composition, and feed rate used for the Energy Integration study. This simulation was able to achieve both 91% CO_2 recovery through the first PDMS membrane module, and produce 96% CO_2 purity in the permeate of the second PD membrane module.

5.2.5 Other Outcomes (communications, collaborations, skills development etc)

The membrane pilot plant performance has been reported at the following conferences in either presentation or poster formats:

- 17th World Hydrogen Energy Conference 2008, Brisbane, Australia
- 9th International Conference on Greenhouse Gas Technologies 2008, Washington DC, USA
- CO2CRC Symposium 2008, Queenstown, New Zealand
- 5th Conference of the Aseanian Membrane Society 2009, Nagoya, Japan
- 8th World Congress of Chemical Engineering 2009, Montreal, Canada
- CO2CRC Symposium 2009, Coolum, Australia
- CO2CRC Symposium 2010, Melbourne, Australia
- 20th Annual Meeting of the North American Membrane Society 2010, Washington DC, USA
- 10th International Conference on Greenhouse Gas Technologies 2010, Amsterdam, Netherlands
- 6th Conference of the Aseanian Membrane Society 2010, Sydney, Australia

The following peer-reviewed journal papers have been produced as a result of this research:

1. R. Hasan, C. A. Scholes, G. W. Stevens, S. E. Kentish ‘Effect of Hydrocarbons on the Separation of Carbon Dioxide from Methane through a Polyimide gas separation membrane’ Industrial & Engineering Chemical Research (2009) 48: 5415-5419
2. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘Effects of Minor Components in Carbon Dioxide capture using polymeric gas separation membranes’ Separation & Purification Reviews (2009) 38: 1-44
3. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications’ Recent Patents on Chemical Engineering (2008) 1: 52-66.
4. C. A. Scholes, K. H. Smith, S. E. Kentish, G. W. Stevens ‘CO_2 capture from Pre-combustion processes – strategies for membrane gas separation’ International Journal of Greenhouse Gas Control (2010) 4: 739-755
5. C. A. Scholes, W. X. Tao, S. E. Kentish, G. W. Stevens ‘ Sorption of Gases and Water in Matrimid 5218’ Journal of Applied Polymer Science (2010) 117: 2284-2289

6. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘The effect of hydrogen sulfide, carbon monoxide and water on the performance of a PDMS membrane in carbon dioxide/nitrogen separation’ Journal of Membrane Science (2010) 350: 189-199
7. C. A. Scholes, G. Q. Chen, G. W. Stevens, S. E. Kentish ‘Plasticization of ultra-thin polysulfone membranes by carbon dioxide’ Journal of Membrane Science (2010) 346: 208-214
8. C. A. Scholes, G. Q. Chen, S. E. Kentish, G. W. Stevens ‘Nitric oxide and carbon monoxide in glassy polymeric membranes for carbon dioxide separation’ Chemical Engineering Research and Design (2010) in review
9. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘Competitive sorption and plasticization of CO_2 selective glassy polymeric membranes by hydrogen sulfide’ AIChe Journal (2010) in review

The following book chapter has been produced as a result of this research:

C. A. Scholes, S. E. Kentish, G. W. Stevens ‘The effects of minor components on the gas separation performance of polymeric membranes for carbon capture’ Membrane Gas Separation, Eds. B. Freeman, Y. Yampolskii (2010) Wiley, Singapore, pp201-226

The following non-peer-reviewed journal papers have been produced as a result of this research:

1. C. A. Scholes, G. Q. Chen, W. X. Tao, J. Bacus, C. Anderson, S. E. Kentish, G. W. Stevens ‘The effects of minor components on the gas separation performance of membranes for carbon capture’ Energy Procedia (in press)
2. C. Anderson, C. Scholes, A. Lee, K. Smith, S. Kentish, G. Stevens, P. Webley, A. Qader, B. Hooper ‘Novel pre-combustion capture technologies in action – results of the CO2CRC/HRL Mulgrave capture project’ Energy Procedia (in press)
3. C. A. Scholes, G. Chen, W. Tao, G. W. Stevens, S. E. Kentish, A. Qader, B. N. Hooper ‘Membrane based carbon capture pilot plant trials’ 5th Conference on Aseanian Membrane Society (2009)
4. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘Minor components effects on membrane gas separation for carbon capture’ 8th World Congress of Chemical Engineering (2009
5. C. A. Scholes, S. E. Kentish, G. W. Stevens ‘The effect of condensable minor components on the gas separation performance of polymeric membranes for carbon dioxide capture’ Energy Procedia (2009) 1: 311-317

6. C. A. Scholes, K. Smith, S. Wilson, S. Kentish, G. Stevens, P. Webley ‘Pre-combustion carbon capture technologies pilot plant trials on coal gasification’ 17th World Hydrogen Energy Conference (2008)
7. C. A. Scholes ‘Capturing carbon with membranes’ Australasian Science (2010) November: 33-35
8. C. A. Scholes ‘Capturing carbon from waste gases’ Issues (2010) 92: 14-17

The following collaborations have been made:

- Pilot Plant Management and Services (PPMS) Pty Ltd
- Department of Chemical Engineering, University of Texas at Austin, USA
- Helmholtz-Zentrum Geesthacht Zentrum fur Material und Kustenforschung (GKSS)

The skills and knowledge developed through this project have made the CO2CRC Membrane research group one of the world leading experts in polymeric membranes, nanoporous carbon membranes, and membrane gas-solvent contactors for carbon capture from pre-combustion scenarios. This includes developing the skills of the following in membrane pre-combustion capture:

- 2 postgraduate students
- 3 research assistants
- 1 research fellow

5.2.6 Membrane capture, conclusions

The objectives of the Mulgrave Capture Project Membrane Pilot Plant have been achieved, with the determination of suitable membrane materials and membrane process designs that could attain the degree of CO_2 recovery and purity required for effective storage.

The Membrane Pilot Plant was successfully constructed, commissioned, and operated to achieve its design aim of being flexible to trial a wide range of membrane materials and designs. In total nine gas separation membranes and four different combinations of membrane gas-solvent contactors were trialled.

For gas separation membranes, the best performing CO_2-selective membrane was poly dimethyl siloxane (PDMS), which under the process conditions was able to achieve high CO_2 permeability while having good CO_2/H_2 and CO_2/N_2 selectivities. Pilot plant operation of a two stage process demonstrated high purity CO_2, on a dry basis, could be achieved. This was extended with an Aspen HYSYS simulation of a potential CO_2-selective membrane plant based on PDMS which demonstrated the necessary recovery and purity could be achieved by two membranes in series with recycle. The best performing H_2-selective membrane was the Nanoporous carbon membrane, which achieved adequate H_2/CO_2 and H_2/N_2 selectivities at high temperature. However, the performance of the Matrimid membranes, both flat sheet and hollow fibre, demonstrated this polymer's potential for the same application, though at a lower temperature.

For the membrane gas-solvent contactor, a porous Polytetrafluoroethylene contactor, with 30 wt% Monoethanolamine as the solvent, achieved the highest overall mass transfer coefficients. However, the corrosive nature of MEA lead to polymer degradation issues, which suggests that the more benign solvent 30 wt% K_2CO_3 at high temperature is a valid alternative option.

A major outcome of the Mulgrave Project Membrane Pilot Plant has been the training of students and researchers (6 in total) in carbon capture technologies and the communication of information and skills learnt, as well as collaborations established, with parties interested in the Carbon Capture and Storage field.

5.3 Adsorption

5.3.1 Process Description

The principle of gas separation using adsorption relies on the difference of the amount of adsorbed gas molecules under varying temperature/pressure conditions (Fig. 5.3.1). A change of temperature and/or pressure induces adsorption and desorption of gas molecules and tailored operational process can maximise separation performance based on this principle. Depending on the variable to be changed, an adsorption process can be a pressure swing adsorption (PSA), vacuum swing adsorption (VSA), pressure vacuum swing adsorption (PVSA), or temperature swing adsorption (TSA) process. Adsorption technology for gas separation requires relatively low energy consumption compared to alternate processes. The purity of the product gas can be enhanced by using more sophisticated cyclic processes. Development of novel adsorbents rapidly expands the applicability of the process in many industrial fields.

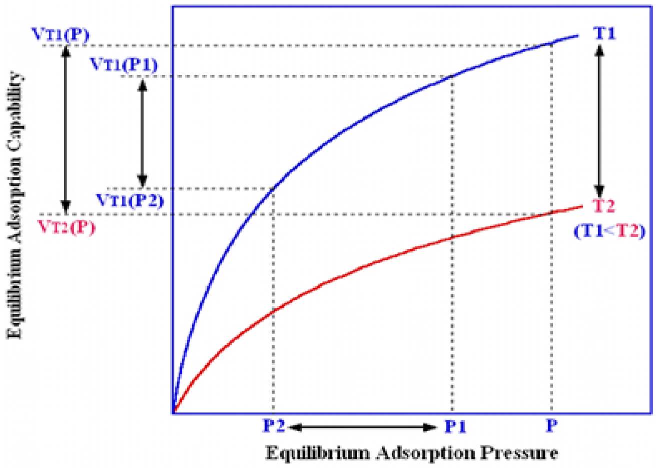


Figure 5.3.1. Concept diagram of adsorption processes

This program investigated the ability of adsorption technology to capture CO_2 from high temperature gasification process streams by performing experimental tests on syngas produced by an actual operating coal gasifier.

The program included the following phases:

- Screening of adsorbent materials in bench top units and analytical equipment to identify potential candidates and measure their properties. These properties are adsorption equilibrium isotherms and selectivity, and kinetic performance as inferred from breakthrough experiments
- Having identified appropriate adsorbents, build a fully instrumented adsorption apparatus and test the adsorbents in pressure, temperature and vacuum swing cycles

Supplementary analyses were also performed such as:

- Surface analysis – to examine the impact of impurities while using synthesis gas
- Impact of water injection

These test results provided input computer simulation tools to design cyclic processes for pre-combustion capture using adsorption technology as explained in subsequent sections.

5.3.2 Design Basis:

The adsorption apparatus (also known as Gas Separation Rig 2 or in short, GSR2) was designed to have two adsorption columns enabling the continuous separation of a multi component mixture gas. The GSR2 was designed to operate both in an industrial zone such as that at the gasifier site at Mulgrave and in a non-hazardous area such as that prevailing at a University laboratory. The key design operating conditions are as follows (Table 5.3.1):

Table 5.3.1 Design Operating Conditions

Parameter	Value
Operating Pressure, bar	Up to 30 bar.
Temperature, ºC	Up to 400°C.
Flow rate of gas (Syngas from HRL or mixture of pure gases from gas bottles in the laboratory), std litres/min	0-5 lpm.
Maximum Vacuum, kPa absolute	1 kPa, abs.
Surrounding area conditions	Must be well vented, ideal temperature of the area is 21ºC and should not exceed the boundary of 7 - 32ºC. Relative humidity should be 45% nominal.

The GSR2 is capable of evacuating both the columns under vacuum, purging with nitrogen or both, to regenerate the adsorbent. The maximum depth of vacuum is 1 kPa absolute The GSR2 can be operated in three different modes, namely breakthrough mode, manual mode and cyclic mode depending on the type of experiments to be conducted.

5.3.3 Construction, Commission and Operation

The original GSR2 pilot plant design was undertaken by the CO2CRC. Further additions to the design and construction were performed by Pilot Plant Management Services Pty Ltd (PPMS). The design was finalised after considering all the recommendations of the Hazard and Operability (HAZOP) study organised by the CO2CRC. The plant was commissioned by PPMS. Photographs of the installed pilot plant are shown in Figure 5.3.4. The dimensions of the GSR2 are; Width: 800 mm, Height: 1860 mm, Depth: 1500 mm (excluding back and front auxiliaries).

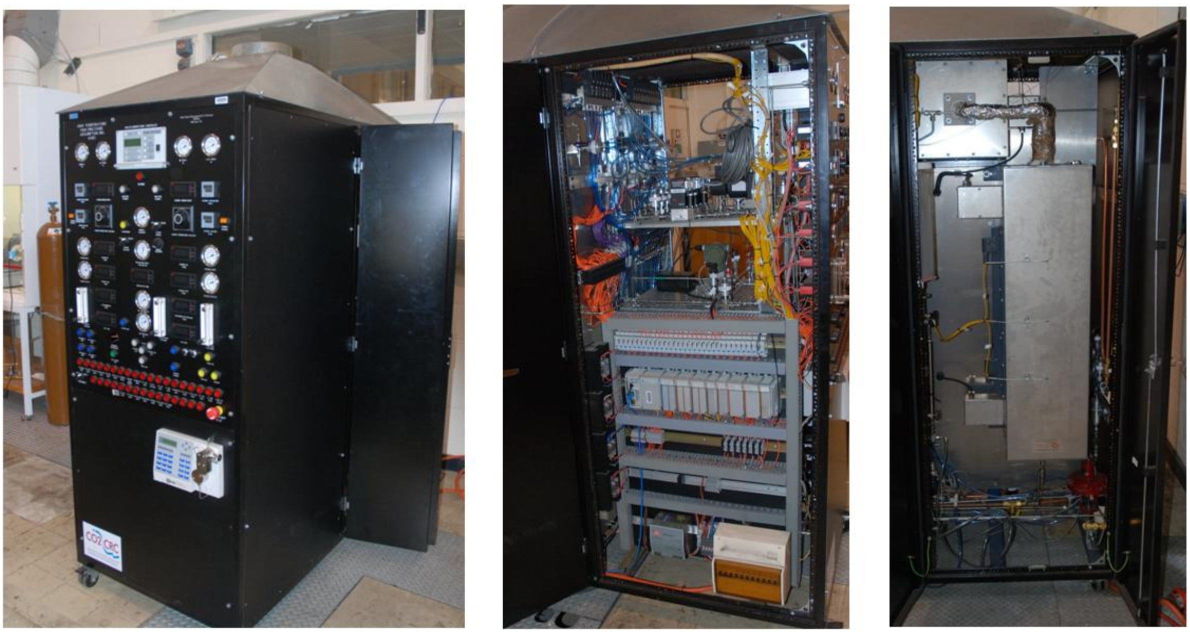


Figure 5.3.4 Exterior and interior of GSR2

This rig required;

- 3-phase power supply
- Compressed air (700 kPa) for pneumatics
- Water supply for cooling water requirements
- An ethernet cable running from the PLC to the computer

During operation, the ventilation panel on top of instrument was kept open during or after installation. GC or other gas analysers were connected as required. In some cases, gas samples were collected in a DuPont™ Tedlar bag and analysed using an independent off-line analyser.

To prepare the columns for operation, CO_2 adsorbents such as zeolites were packed into the middle of a stainless steel column (21 mm in diameter, 1.1 m in length) and both ends of the adsorbents section were packed with zeolite 3A to protect the adsorbents from contaminants including moisture. In some experiments, glass beads (~1 mm in diameter) were filled on the both side of CO_2 adsorbents to prevent complex adsorption phenomena. The adsorbents were calcined before use.

5.3.4 Performance evaluation and results against simulation

In this project, an in-house process simulator MINSA (Monash Integrated Numerical Simulation of Adsorption) has been used. MINSA has been developed for over a decade at Monash. It is a powerful tool for evaluating PSA/PVSA/TSA cycle design and investigating the influences of a large number of variables on CO_2 capture performance.

The numerical model in this simulator is built based on differential mass transfer and energy transfer for gas components in adsorption columns. Ergun's equation is used to calculate pressure drop in the packed bed, and a valve equation used to describe the changes of gas flow-rate between beds or a bed to a tank linked by the valve. In this model, all beds can repeat the same processing, so any one bed can be used to simulate a multi-bed cycle. PID (proportional integral derivative) control loops are used for adjusting the flow-rate to achieve the designed pressures in different processing steps under CSS (Cyclic steady state).

The Isotherms of pure gases such as CO_2 and N_2 for adsorbents which were measured at different temperatures were used to calculate adsorption parameters according to the dual-site Langmuir equation. An example of simulation and experimental results is shown in Figure 5.3.5.

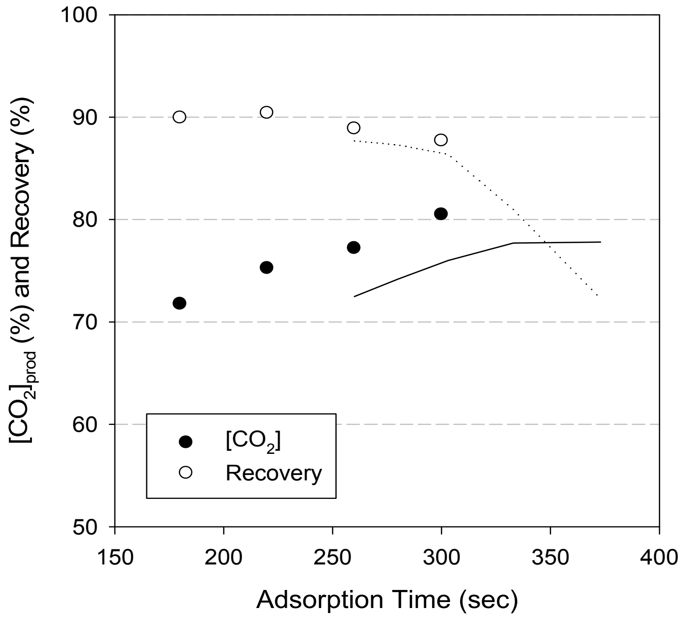


Figure 5.3.5 Example of simulation results (dots) experimental data (lines) simulation data

Simulation results were used to:

- Design novel PVSA cycles – a large scale design was completed and used for the heat integration and economic studies (see sections 6 and 7).
- Find optimum process parameters under the given condition (temperature/pressure/flow rate) such as adsorption step time, pressure equalisation pressure, etc.
- Anticipate the process results at larger scale by extrapolating experimental results.

5.3.5 Other Outcomes (communications, collaborations, skill development, etc)

The adsorption PSA pilot plant performance has been reported at the following conferences in either presentation or poster formats:

- 10th International Conference on Greenhouse Gas Technologies 2010, Amsterdam, Netherlands
- 10th International *Conference* on Fundamentals of Adsorption 2010, Awaji Island, Japan
- 5th Pacific Basin conference on adsorption science and technology 2008, Singapore
- 17th World Hydrogen Energy Conference 2008, Brisbane, Australia
- 9th International Conference on Greenhouse Gas Technologies 2008, Washington DC, USA
- CO2CRC Symposium 2010, Melbourne, Australia
- CO2CRC Symposium 2009, Coolum, Australia
- CO2CRC Symposium 2008, Queenstown, New Zealand

The following peer-reviewed journal papers have been produced as a result of this research:

1. Lee, S., Xiao, G., Xiao, P., Josh, K. V., Singh, R. K., Webley, P. A., 2010, High Temperature adsorption materials and their performance for pre-combustion capture of carbon dioxide, Energy proceedia, pp 1-8, 2010
2. Xiao, P., Wilson, S., Xiao, G., Singh, R., Webley, P. "Novel adsorption processes for CO_2 capture within IGCC process." Energy proceedia, 1, 631-638, 2009.
3. Gongkui Xiao, Ranjeet Singh, Alan L. Chaffee and Paul A. Webley. Advanced Adsorbents based on MgO and K_2CO_3 for capture of CO_2 at elevated temperatures. International journal of greenhouse gas control, submitted 2010.

The following non-peer-reviewed journal papers have been produced as a result of this research:

1. Penny Xiao, Andrew Lee, Gongkui Xiao, Ranjeet Singh, Kaustubh Joshi and Paul A. Webley, 'CO_2 Capture from Pre-combustion Gases (high temperature) by Pressure Swing Adsorption', 10th International conference on fundamentals of adsorption. May,23-28 2010. Awaji, Hyogo, Japan
2. Gongkui Xiao, Penny Xiao, Simon Wilson, Ranjeet Singh, Kaustubh Joshi, Alan Chaffee, and Paul Webley. Capture of CO_2 in pre-combustion processes by pressure swing adsorption. 5th Pacific Basin conference on adsorption science and technology, Singapore, 25-27 May, 2009.
3. Gongkui Xiao, Ranjeet Singh, Alan L. Chaffee and Paul A. Webley. Development of Adsorbents for High Temperature CO_2 Separation from Real Coal Gasification Syngas. 10th International conference on fundamentals of adsorption. May,23-28 2010. Awaji, Hyogo, Japan.
4. C. A. Scholes, K. Smith, S. Wilson, S. Kentish, G. Stevens, P. Webley 'Pre-combustion carbon capture technologies pilot plant trials on coal gasification' 17th World Hydrogen Energy Conference (2008).

The following collaborations have been made:

- Sasol Germany
- UOP

The skills and knowledge developed through this project have made the CO2CRC Adsorption research group one of the world leading experts in pressure swing adsorption for carbon capture from pre-combustion processes. This includes developing the skills of the following in membrane pre-combustion capture:

- 1 postgraduate student.
- 0.5 research assistants.
- 1 research fellow.

5.3.6 Adsorption capture, conclusions

In this research project, various carbon dioxide adsorbents were prepared and their applicability for capture at high temperature was evaluated. Zeolite 13X and calcium chabazite showed good breakthrough results at temperatures of less than 200 °C due to their reasonably high adsorption capacity and fast kinetics. Preliminary results of novel adsorbents such as PEI and double salt materials showed optimistic results for carbon capture at high temperature. Further study is required to evaluate the feasibility of the materials in a large scale process environment.

Results of pressure vacuum swing adsorption of zeolite 13X showed that sophisticated adsorption processes could produce CO_2 concentration higher than 95 % which is the minimum requirement for effective transportation and sequestration of CO_2.

Further work is needed to understand the impact of contamination in the long term and for large scale operation. The contaminants may not only reduce the adsorption performance but also damage CO_2 adsorbents irreversibly.

6. Heat and Process Integration Studies

The heat and process integration studies for the Mulgrave Capture Project involved the prediction of CO_2 capture processes on a modelled full scale Integrated Drying and Gasification Combined Cycle (IDGCC) power station (CO2CRC Modelled Plant). The Mulgrave Capture Project trials were conducted on gases from the pilot scale gasifier that are not entirely representative of the IDGCC process conditions, The Mulgrave gasifier is fuelled by dried coal, has lower pressure (8 bar only), and does not have a water gas shift to convert CO to CO_2 which would be added to a commercial IDGCC power station if CO_2 capture was included. Therefore, results from the trials based on the Mulgrave gasifier cannot be directly transferred to the design for a full scale CO_2 capture plant for IDGCC but do so via development of process models and subsequent flow sheets for CO_2 capture using each of the three capture technologies. The trials have hence provided a platform to improve the confidence in the separation technologies for the full scale operation.

In order to determine the impact of the CO_2 capture processes on the full scale power station a base case power station without CCS was required. The base case would provide a basis for the power station with CCS to be compared against and the details of this model are provided in section 6.1. For the three technologies tested at the Mulgrave Capture Project, a full scale CO2CRC Modelled Plant has been constructed to determine the impact that these capture processes have on the net power produced from the power station. The details of the heat and process integration assessments for the three pre-combustion capture technologies which capture 90% of the syngas CO_2 are provided in sections 6.2 to 6.4. Each capture process is designed to capture at least 90% of the CO_2 in the syngas and produce CO_2 with greater than 95 % purity at 100 bar.

An additional assessment has been made on the feasibility of post-combustion capture of the CO_2 from the CO2CRC Modelled Plant using solvent based capture. The post-combustion capture route offers the potential to increase the total amount of CO_2 captured, and the details of this design are provided in section 6.5.

6.1 CO2CRC Modelled Plant without CO_2 Capture (Base Case Model)

The base case for the CO2CRC Modelled Plant process was developed from publicly available data on air blown, fluidised bed gasification (Figure 6.1).. The model constructed was used merely to estimate the impact of the capture processes on the overall CO2CRC Modelled Plant process.

The CO2CRC Modelled Plant described above would require two gasifiers to provide the gas required for a single turbine. The process is modelled using Aspen Plus® simulation software. The coal composition used in the simulation is typical of the coal found in the Latrobe Valley and the details are given in Table 6.1.

The simulation developed for the heat integration studies is used to estimate the amount of power that can be generated by the CO2CRC Modelled Plant from the available heat in the process.

Table 6.1 Coal Composition

Coal Composition	wt%
Raw Coal Moisture	60.6
Dry Coal PROXANAL	
Moisture	0
Fixed Carbon	49.9
Volatile Matter	47.8
Ash	2.4
Dry Coal ULTANAL	
Ash	2.4
Carbon	68.4
Hydrogen	4.8
Nitrogen	0.6
Chlorine	0.09
Sulphur	0.27
Oxygen	23.5

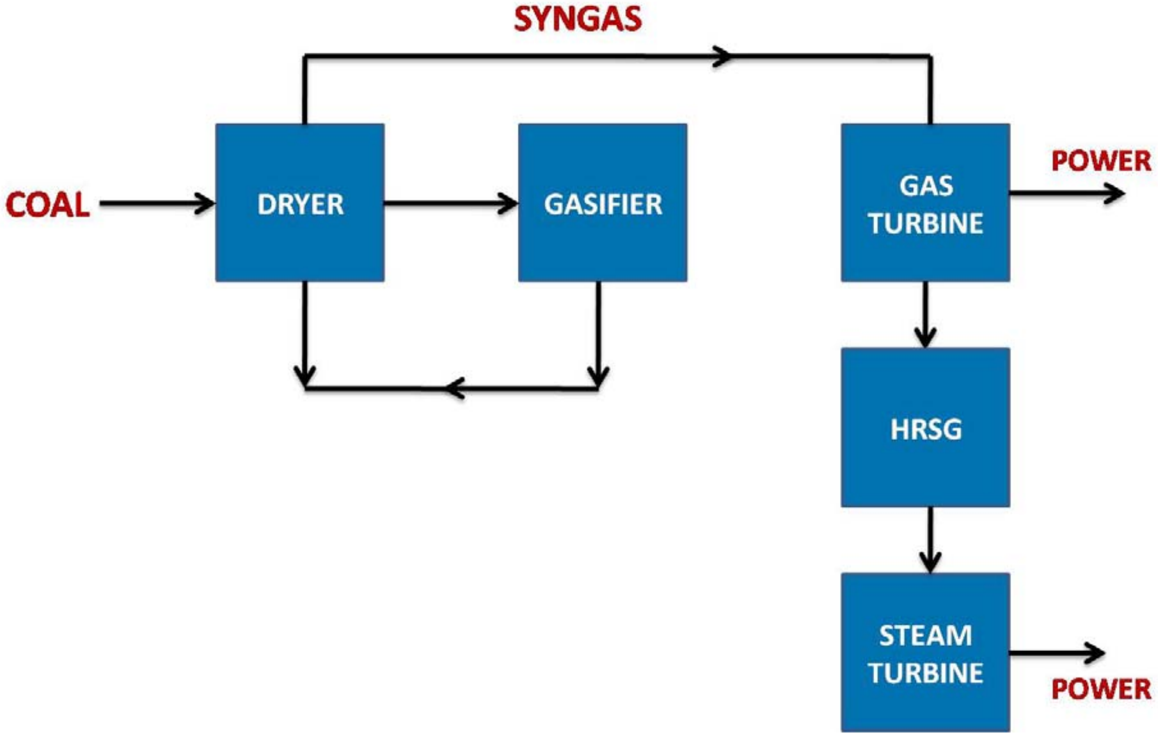


Figure 6.1 Base CO2CRC Modelled Plant Process

A linear programming optimisation method developed by the CO2CRC has been used to determine the maximum amount of power that could be produced from the steam cycle given the theoretically available heat in the CO2CRC Modelled Plant process. The method is explained in more detail in [1], which details the temperature-enthalpy data from all the streams in the process that need to be heated or cooled and combines them to form a "Grand Composite Curve" (GCC). The amount of steam generated or used at each steam level can be manipulated to create a "Steam Composite Curve" (SCC). The SCC can be used to maximise the amount of power generated by the steam turbine.

The GCC and SCC for the base case are provided in Figure 6.2; for this case steam is generated at the HP, IP and LP steam levels at rates of 111, 15.4 and 21.9 kg/s. The composite curves show a good match between the GCC and the SCC with little waste heat in the process, the majority of the cooling is for the steam condenser on the steam turbine. The exhaust gases from the HRSG and the char burner are emitted from the stacks at 140°C, there is no more useful heat in these streams for the given steam cycle.

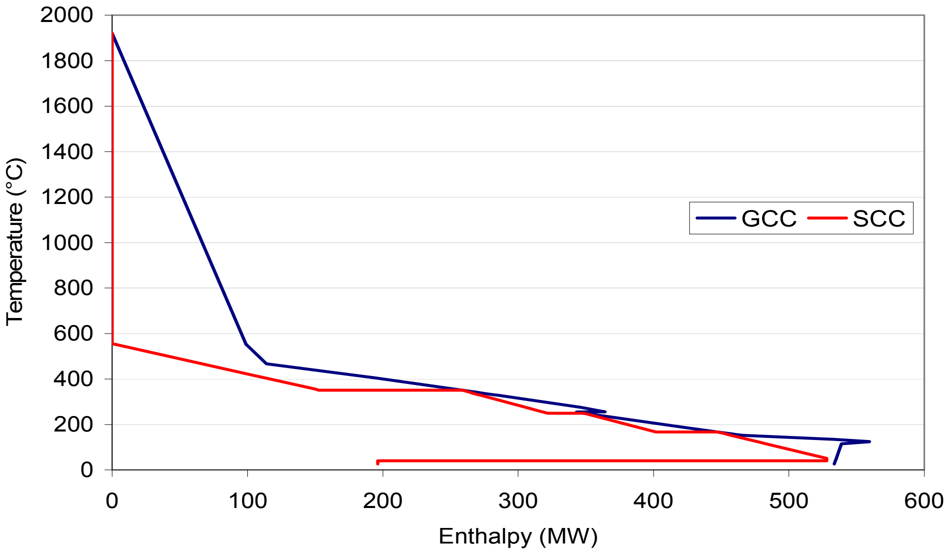


Figure 6.2 Grand Composite Curve and Steam Composite Curve for the base CO2CRC Modelled Plant process.

6.2 Solvent CO_2 Capture

6.2.1 Design modifications to the CO2CRC Modelled Plant process with Carbon Capture

When CCS is added to the CO2CRC Modelled Plant, a water gas shift reactor must be added to the process to convert the 13 vol% CO to CO_2 and H_2 so that greater levels of CO_2 can be removed. The water gas shift reaction, shown in [Eq. 1] can be done using either sour or clean shift reactors. These processes are well known in the production of hydrogen from syngas for ammonia manufacture, where the high purity hydrogen is produced in the reactor and then subsequently separated from the CO_2.

$$[\text{Eq. 1}] \quad CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.1\ \text{kJ/mol}$$

Sour shift has H_2S removal combined with CO_2 removal after the shift reactor requires a sulphur tolerant catalyst, usually Cobalt-Molybdenum, in the shift reactor that also converts the COS to H_2S. The catalyst operates at a moderate inlet temperatures of approximately 290°C, requires a small amount of sulphur to maintain activity and the H_2O/CO ratio can be adjusted to obtain the required conversion.

As the CO2CRC Modelled Plant process has inherently high levels of water in the gas stream (from the wet brown coal and integrated drying), and relatively low levels of sulphur, sour shift is proposed for the CO2CRC Modelled Plant when CCS is added to the modelled process.

6.2.2 CO_2 removal using solvent absorption

The solvent absorption process tested in the Mulgrave Capture Project was a potassium carbonate based capture process called UNO. The UNO process is similar to the Benfield process used in the gas processing industries, however the UNO process is operated at higher temperatures than the Benfield process. Operation at higher temperatures has the benefit of increased reaction kinetics, increased water content in the exhaust gas and less reboiler duty due to increased flashing from the high pressure absorption to the low pressure desorption/regeneration.

The results for the CO2CRC Modelled Plant with the solvent plant described show that the net power generation from the power station reduces from 550 MW to 470 MW, a fall of 14.5%. The total capture rate is 61.9% due to the CO_2 slip, the CO_2 generated by the CO and heavier hydrocarbons in the GT and the char burner (this is discussed further in section 6.2.4).

The GCC and SCC are provided in Figure 6.3; for this case, steam is generated at the HP and IP steam levels at rates of 94.9 and 39.9 kg/s respectively. The composite curves show that significant cooling is required in the process, where the GCC (blue line) extends beyond the SCC (red line). The process cooling starts at 110°C and therefore a significant proportion of that cooling could be conducted using air cooling.

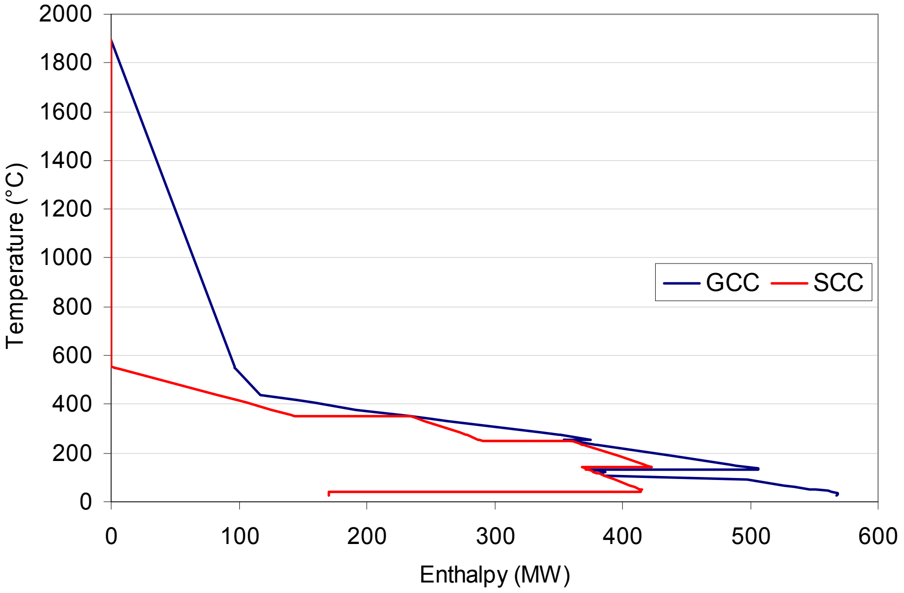


Figure 6.3 Grand Composite Curve (GCC) and Steam Composite Curve (SCC) for the CO2CRC Modelled Plant with CO_2 capture using solvent absorption

6.3 Membrane CO_2 Capture

A membrane based CO_2 capture process has been designed to capture 90% CO_2 at delivery pressure of 100 bar with a purity greater than 95%. The design of this process has been provided in section 5.2.1. The system employs a two-stage enriching cascade using PDMS membranes with CO_2 as the permeate stream.

6.3.1 Energy and CO_2 capture analysis

The results for the CO2CRC Modelled Plant with the membrane based capture process are provided in Figure 6.4. The key results are the net power generation from the CO2CRC Modelled Plant which is reduced from 550 MW to 405 MW a reduction of 26.3%. The main reduction in power generation is due to the membrane inter-compressors and recycle compressor which require 88.2 MWe, accounting for 61% of the reduction in power. The CO_2 compressor power is a further 25.2 MWe of energy (18%) and the GT loses 39 MWe (27%) due to the change in gas composition. However, the amount of power that can be generated by the steam turbine increases by 8 MWe due to the additional sources of heat in the membrane pre and inter-coolers. The losses in net power for the membrane process are different to the solvent process in that the majority are electrical loads for compression whereas the solvent process losses are for heat of regeneration; both processes lose power production from the GT by changes in gas composition.

The GCC and SCC for the CO2CRC Modelled Plant with CO_2 capture using membranes are provided in Figure 6.4. The composite curves show that there is a significant amount of excess heat in the process (150 MW) at temperatures less than 100°C. At present that heat is not used and cooling water is used to remove the heat, reductions in cooling water could be attained if air cooling is used for a portion of this cooling duty.

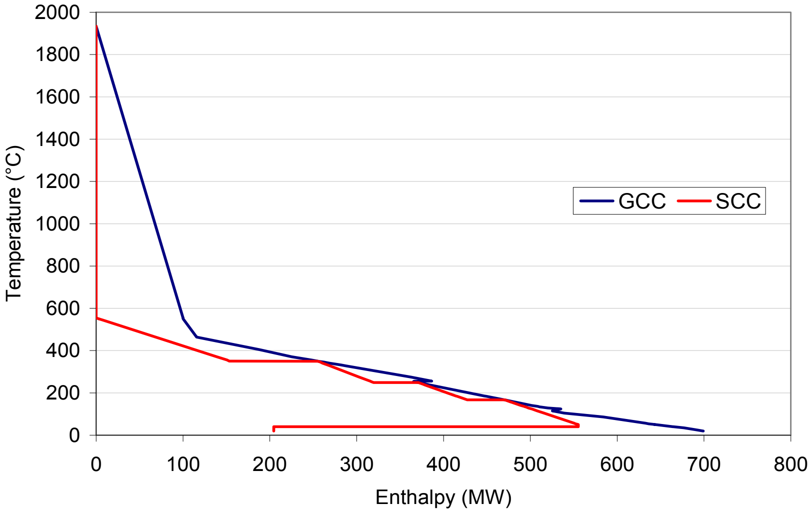


Figure 6.4 Grand Composite Curve (GCC) and Steam Composite Curve (SCC) for the CO2CRC Modelled Plant with CO_2 capture using membrane separation.

6.4 Adsorption CO_2 Capture

A method to separate the CO2 using Zeolite 13X adsorption has been designed for the CO2CRC Modelled Plant based on the results obtained in the adsorption program given in section 5.3. For the full scale CO2CRC Modelled Plant using 13X a two stage approach has been designed, the first stage removes the water and the second separates the CO2 from the remaining syngas. The process is to operate at moderate temperatures of 200°C. Due to the different feed temperature of the adsorption process compared to the solvent and membrane process, the composition of the syngas varies slightly due to the gasifier recycle gas stream which is located downstream of the syngas cooler and the increased water due to the higher gas temperature.

6.4.1 Energy and Capture analysis

The key results are the net power generation from the CO2CRC Modelled Plant which is reduced from 550 MW to 467 MW a reduction of 15.1% with a total capture rate of 64% which is lower than the solvent, as there is no methane co-captured into the CO_2 stream using the adsorption process, therefore all the methane is converted into CO_2 in the exhaust of the GT. The net water requirements for the process are also increased by 34% in total, but the water requirements are increased by 58% per unit of net power generation.

The GCC and SCC are provided in Figure 6.5. The amount of heat and quality of that heat varies throughout the adsorption cycle and therefore it would be difficult to utilise effectively in the process or back into the stream cycle. This means that there is less useful low grade heat compared to the other separation processes and therefore there is little benefit in including a third (LP) level of steam.

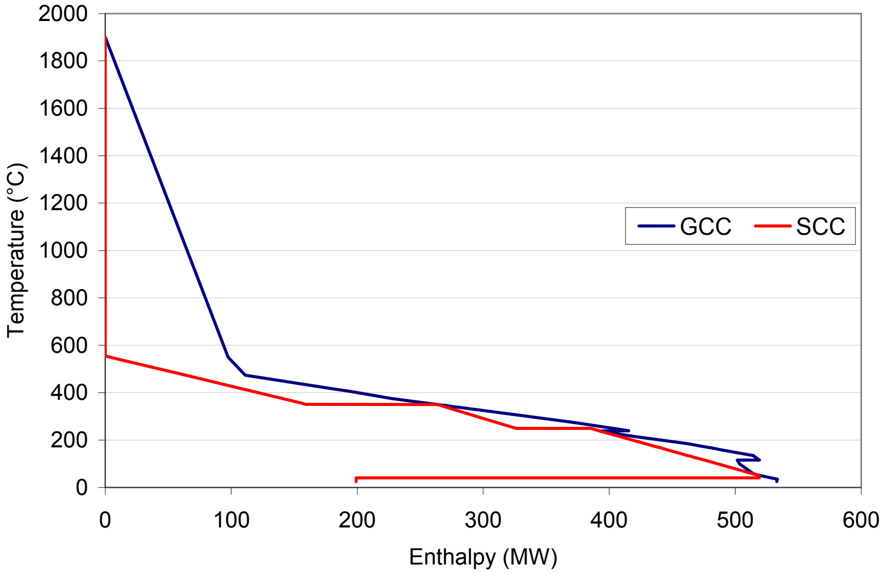


Figure 6.5 Grand Composite Curve (GCC) and Steam Composite Curve (SCC) for the CO2CRC Modelled Plant with CO_2 capture using adsorption.

The addition of CO_2 capture using adsorption separation reduces the net power generation of the CO2CRC Modelled Plant process by 83 MWe or 15.1%.

6.5 Post-Combustion CO_2 Capture of CO2CRC Modelled Plant

The pre-combustion capture modelling showed that the maximum amount of CO_2 that is captured from the CO2CRC Modelled Plant is 65% with a single stage shift reactor and CO_2 recovery of 90% in the syngas. Even using two-stage WGSR and syngas recoveries of 95% CO_2 in the syngas the CO_2 capture rate is still only 70%. When the char burner is not included in the CO2CRC Modelled Plant the CO_2 capture rate is still less than 90% (80%) and the energy penalty associated with this change is significant at 27.5%. An alternative arrangement is to capture the CO_2 on the exhaust of the gas turbine, the char burner emissions can then be added to the exhaust from the GT as they are both at atmospheric pressure and CO_2 capture rates of 90% are attainable.

The key results for the CO2CRC Modelled Plant with UNO Mk 3 based PCC is that 90% of the total CO_2 is captured from the power station at an energy penalty of 16.9%.

There is a large cooling duty for the exhaust gas recycle and the feed to the carbon capture plant as well as the cooling duty for the carbon capture plant which increases the water usage by 50% and the water usage per unit of electricity produced of 80%. However, the water usage is still lower than the existing pulverised coal power stations in the Latrobe Valley without carbon capture.

The GCC and SCC for this process are provided in Figure 6.6. Due to the HRSG and char burner exhaust gas needing to be cooled there is significant waste heat available (> 300 MWth) at temperatures below 120°C.

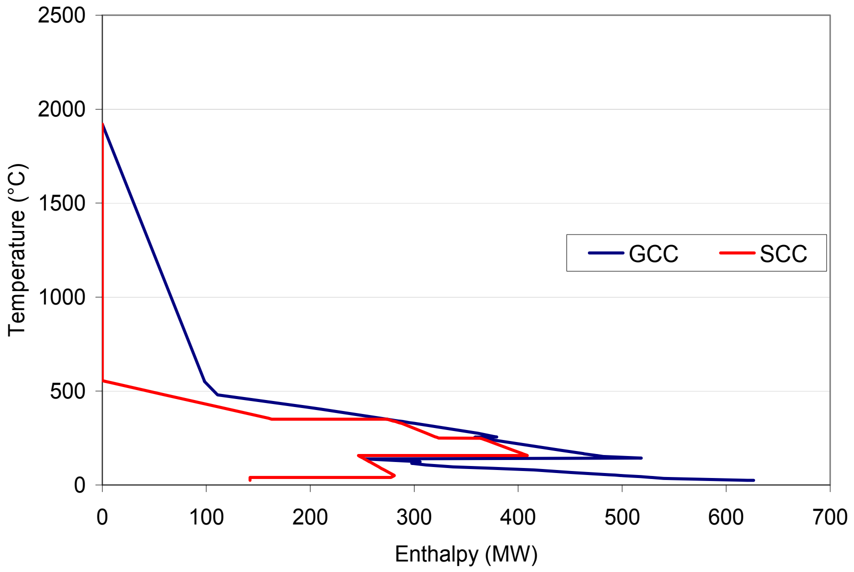


Figure 6.6 GCC and SCC for the CO2CRC Modelled Plant with PCC.

6.6 Comparative Results

Three pre-combustion capture processes based on results from the trials on the Mulgrave gasifier and a post-combustion capture process using solvent absorption have been applied to the CO2CRC Modelled Plant as detailed in sections 6.2 – 6.5. A summary of the results is shown in Table 6.2.

Each of the three pre-combustion cases capture between 62 – 64% of the total CO_2 emissions from the power station, however the CO_2 avoided ranges from 1.14 to 1.55 Mtpa due to the varying energy penalties of each process. The adsorption process with a relatively low energy penalty and relatively high capture rate, has the lowest CO_2 emissions per net power of the three pre-combustion processes. The post-combustion capture process is able to capture a greater proportion of the CO_2 and therefore the amount of CO_2 avoided and the

CO_2 emissions rate is lower than all three pre-combustion capture processes. The energy penalty for the post-combustion process is greater than the pre-combustion adsorption process but is less than the other two pre-combustion processes.

The net water consumed per unit of net power produced increases from between 58 to 107% for the four processes studied compared to the base case. However, it should be noted that the water consumption even for the membrane system, which required the largest increase, is only 5 % above the typical water consumption of the best pulverised power stations in the Latrobe Valley without CO_2 capture. It is also possible, although outside the scope of this study, to replace significant amounts of the cooling for these processes with air cooling to reduce the consumption of water. This is especially true for the post-combustion capture process where there is significant amount of cooling conducted at high temperatures (up to 120°C).

Table 6.2 Summary of CO2CRC Modelled Plant with CO_2 capture

	Units	Base	Solvent (Pre)	Membrane	Adsorption	Solvent (Post)
Net Power	MW	550	470	405	467	457
Net Efficiency (HHV)	%	44.7	38.2	32.9	37.9	37.2
CO_2 emissions	kg/MWh	771	342	394	327	93
Energy Penalty	%	-	14.5	26.3	15.1	16.9
CO_2 Capture Rate	%	-	61.9	62.3	64.0	90.0
Net Water Required	t/MWh	1.02	1.52	2.11	1.61	1.82

The results provided throughout this report provide the maximum amount of power that can be produced with the given steam cycle using all the available heat in the process.

6.7 Conclusions

This study summarises the results of the heat integration study of three pre-combustion and one post-combustion capture process with the CO2CRC Modelled Plant. The results are used to help determine costs for each capture technology as shown in Section 7 of this report.

Due to the low temperature gasification employed in the CO2CRC Modelled Plant, the amount of CO_2 captured by the pre-combustion capture processes is less than 90%. For a single WGSR with 90% capture of CO_2 from the syngas the net capture rate is less than 64% with an energy penalty of 14.5% for a solvent based capture process. The capture rate can be increased by increasing the level of CO conversion in the WGSR, by increasing the capture rate of CO_2 in the syngas and by removing the char burner from the process. The net capture rate using a solvent based capture process increases to 66, 70 and 80% for the cases described above but the energy penalty for the same cases increases to 15.3, 16.2 and 27.5% respectively. Alternatively, PCC might be applied to the CO2CRC Modelled Plant and CO_2 capture rates of 90% could be attained with an energy penalty of 16.9%.

The energy penalty for the capture processes was lowest for the pre-combustion process using solvents (14.5%), followed by the adsorption process (15.1%), the post combustion capture using solvents (16.9%), and the membrane separation (26.1%). The energy penalty of the pre-combustion solvent capture process could be decreased by the inclusion of rich solvent expanders. The multi-objective optimisation tool for CO_2 capture from power stations developed by the CO2CRC could be useful for the future optimisation of the capture processes.

6.8 Other Outcomes (communications, collaborations, skills development etc)

The heat integration work on the CO2CRC Modelled Plant has not been presented outside the CO2CRC due to restrictions on the commercial information regarding the IDGCC process. However the work done to establish heat integration strategies has been applied to other commercial gasification processes for external publication, including the following conferences;

- CO2CRC Symposium 2009, Coolum, Australia – Pre-combustion capture and pinch analysis
- 10th International conference on greenhouse gas technologies, 2010, Amsterdam, Netherlands – Optimisation of pre-combustion capture for IGCC with a focus on the water balance.

7. Economic Evaluation

7.1 Introduction

This section is a scoping-level assessment of the economics of capturing CO_2 from a gasification combined cycle process. The study assesses the economics based on the experimental results of the pilot plant trials carried out at the Mulgrave Capture Project.

The following cases were evaluated for CO_2 capture using –

- Amine solvent (Case 1)
- Potassium carbonate solvent capturing from synthesis gas – CO2CRC UNO process (Case 2)
- Potassium carbonate solvent capturing from turbine and char burner exhaust gas – CO2CRC UNO Mk3 process (Case 3)
- Gas separation membrane (Case 4)
- Vacuum swing adsorption (case 5)

7.1.1 Process Assumptions

The process data (including gas characteristic, flow rates, equipment size and energy consumption) are based on simulations of the full-scale (550 MW) CO2CRC Modelled Plant as described in Section 6. For all cases the overall recovery rate of CO_2 is at least 90% with a concentration of at least 95% in the product stream.

Cases 1, 2, 4 and 5 estimate the cost of capturing CO_2 from the synthesis gas following the water gas shift conversion. For the baseline economics, CO_2 is assumed to be captured using a commercially available chemical solvent absorption technology, a N-methyl-diethanol-amine (MDEA) solvent (Case 1). MDEA is chosen because it is used widely in industry for CO_2 recovery from natural gas and synthesis gas. Cases 2, 4 and 5 evaluate the economics of full-scale (550 MW) capture using the technologies investigated by CO2CRC at the Mulgrave Pre-combustion Pilot Plant.

Case 3 estimates the cost of capturing the flue gas after combustion in the turbine and char burner. The economic evaluation of this case assumes that a concentrated potassium carbonate solvent/slurry capture technology is used. Ancillary pre-treatment facilities such as NO_x and SO_x removal are not included for this case as they are assumed to be handled directly by this more impurity tolerant carbonate slurry system.

7.1.2 Economic assumptions

The cost estimates are generated using the techno-economic model developed by UNSW for the CO2CRC. Based on the process model outputs, the techno-economic model estimates the equipment, operating and total costs of CO_2 capture. Capture costs include costs for compression of CO_2 to 100 bar ready for transport. Costs for transport and storage are excluded unless otherwise indicated. Normal scoping level process engineering economic assumptions are used (Peters, Timmerhaus and West 2003).

The capital cost for the capture process includes all major process equipment items, plus a general facilities cost. For the capture plants, equipment items include the absorber, stripper, membrane modules, membrane housing, heat exchangers, solvent handling facilities, compressors and pumps as appropriate to each capture technology. The general facilities cost includes ancillary equipment such as storage tanks, spare pumps, valves and the control system. The capital cost for the capture process is spread over 2 years with a breakdown of 40 and 60 percent in years 1 and 2 respectively.

The operating cost for the capture process includes fixed general maintenance costs comprising labour, non-income government taxes and general insurance cost. The variable operating costs include costs for cooling water and materials (solvent, adsorbent, membrane) replacement. For the solvent absorption system, the latter incorporate costs for waste (precipitate) disposal. The annual operating cost and amount of CO_2 avoided is assumed to remain constant over the project life. Post operational (decommissioning) costs for the capture plant such as disassembly and site remediation are assumed to be offset by the salvage value of the equipment. Therefore, the decommissioning cost is assumed to be zero. A project life of 25 years is used, along with a capture plant capacity factor of 85% and a 7% real discount rate.

The cost year of the analysis is 2010. All results are presented in Australian (A$) dollars. Equipment costs are obtained from vendors and publications. For items available from the US market, the procurement cost of the item is estimated using a factor that takes into account the exchange rate for purchased equipment, freight and local labour costs. An exchange rate of 1 Australian dollar to 85 US cents is used. The costs are estimated on a pre-tax basis, thus factors such as income tax, R&D tax concessions and carbon price / tax are neglected.

7.1.3 CO_2 avoided and LCOE

The net reduction in CO_2 emissions as a result of CCS is referred to as the amount of CO_2 avoided. The amount of CO_2 avoided is different from the amount of CO_2 captured. The amount of CO_2 avoided takes into account the amount of CO_2 which is not captured from the emission source as well as a factor for CO_2 emitted due to energy use by the capture process itself, i.e.,

CO_2 avoided = CO_2 emitted to atmosphere before capture –
CO_2 emitted to atmosphere after capture –
CO_2 factor from energy consumption for capture

The cost of CO_2 avoided is calculated using standard CO2CRC methodology viz. a discounted cash flow analysis that takes into account the total project costs (capital and operating) and the net CO_2 avoided –

$$\text{Cost of CO}_2\text{avoided} = \frac{\sum_{i=1}^{n} \frac{K_i + O_i}{(1+d)^i}}{\sum_{i=1}^{n} \frac{(\text{CO}_2\ \text{avoided})_i}{(1+d)^i}} \qquad (1)$$

where K_i and O_i are the real capital and operating costs ($ million) in i^{th} year, d is the discount rate (% pa), n is the total project life and CO2 avoided is the annual amount of CO_2 avoided in million tonnes. The levelised cost of electricity (LCOE) is calculated using a similar method. More details can be found in Ho et al. (2008a, 2008b).

7.2 Capture cases

7.2.1 Case 1 – Amine solvent (MDEA)

Case 1 evaluates the cost of capturing the CO_2 from the synthesis gas from the water-shift reactor following the gasifier using MDEA solvent. The cost of the solvent is taken to be A$2/kg. The analysis does not include heat integration. Table 7.1 summarises the results.

Table 7.1 Estimate of capture and electricity cost for MDEA capture of synthesis gas

Parameter	Value
CO_2 captured (MMtpa)	1.95
CO_2 avoided (MMtpa)	1.31
Energy penalty (MJ_e/kg CO_2 captured)	1.6
Capital cost for capture plant (A$million)	300
Operating cost for capture plant (A$million/yr)	23
CO_2 avoided cost (A$/t CO_2 avoided)	60
$LCOE_{gen}$ with capture (A$/MWh) (no carbon tax)	71

7.2.2 Case 2 – UNO solvent

Case 2 evaluates the cost of capturing CO_2 from the synthesis gas from the water-shift reactor following the gasifier using potassium carbonate solvent. The cost of the solvent is taken to be A$2/kg. The analysis uses a moderate level of heat integration as outlined in Section 6. Table 7.2 summarises the results.

Table 7.2 Estimate of capture and electricity cost for UNO solvent capture of synthesis gas

Parameter	Value
CO_2 captured (MMtpa)	2.00
CO_2 avoided (MMtpa)	1.29
Energy penalty (MJ_e/kg CO_2 captured)	1.7
Capital cost for capture plant (A$million)	310
Operating cost for capture plant (A$million/yr)	24
CO_2 avoided cost (A$/t CO_2 avoided)	52
$LCOE_{gen}$ with capture (A$/MWh) (no carbon tax)	69

7.2.3 Case 3 – UNO Mk3 solvent

Case 3 evaluates the cost of capturing CO_2 from the exhaust gas from the turbine and char burner using potassium carbonate solvent/slurry system. The cost of the solvent is taken to be A$2/kg. The analysis includes an estimate of increased steam generation and a moderate level of heat integration (Section 6). Table 7.3 summarises the results.

Table 7.3 Estimate of capture and electricity cost for UNO Mk 3 solvent for post-combustion capture

Parameter	Value
CO_2 captured (MMtpa)	2.84
CO_2 avoided (MMtpa)	2.31
Energy penalty (MJ_e/kg CO_2 captured)	0.9
Capital cost for capture plant (A$million)	360
Operating cost for capture plant (A$million/yr)	45
CO_2 avoided cost (A$/t CO_2 avoided)	47
$LCOE_{gen}$ with capture (A$/MWh) (no carbon tax)	77

7.2.4 Case 4 – Membrane

Case 4 evaluates the cost of capturing CO_2 from the synthesis gas from the water-shift reactor following the gasifier using a PDMS gas separation membrane. The cost of the membrane is taken to be A$100/$m^2$ with a life expectancy of 3 years. The analysis uses a moderate level of heat integration. Table 7.4 summarises the results.

Table 7.4 Estimate of capture and electricity costs for membrane capture of synthesis gas

Parameter	Value
CO_2 captured (MMtpa)	1.96
CO_2 avoided (MMtpa)	1.11
Energy penalty (MJ_e/kg CO_2 captured)	2.0
Capital cost for capture plant (A$million)	355
Operating cost for capture plant (A$million/yr)	23
CO_2 avoided cost (A$/t CO_2 avoided)	92
$LCOE_{gen}$ with capture (A$/MWh) (no carbon tax)	80

7.2.5 Case 5 – Vacuum Swing Adsorption (VSA)

Case 5 evaluates the cost of capturing CO_2 from the synthesis gas from the water-shift reactor following the gasifier using 13X in a vacuum swing adsorption system. The cost of the adsorbent is taken to be A$6/kg with a life expectancy of 5 years. The analysis uses a moderate level of heat integration. Table 7.5 summarises the results.

Table 7.5 Estimate of capture and electricity cost for vacuum swing adsorption capture of synthesis gas

Parameter	Value
CO_2 captured (MMtpa)	2.00
CO_2 avoided (MMtpa)	1.55
Energy penalty (MJ_e/kg CO_2 captured)	1.1
Capital cost for capture plant (A$million)	445
Operating cost for capture plant (A$million/yr)	30
CO_2 avoided cost (A$/t CO_2 avoided)	62
$LCOE_{gen}$ with capture (A$/MWh) (no carbon tax)	73

7.3 Comparative Studies

7.3.1 Sensitivity analysis

In this study, the estimate of the cost for capturing CO_2 from the synthesis gas of the full-scale (550 MW) CO2CRC Modelled Plant using MDEA solvent is $60/t CO_2 avoided. MDEA solvent is selected as the base case technology for this study as it is a widely available commercial solvent used for CO_2 and sulphur removal in gasification processes (Davison and Bressan 2003).

However, there is uncertainty and variability in the parameters used to estimate the costs for CO_2 capture. Figure 7.1 shows results for a sensitivity analysis for the following key parameters:

- Discount rate (halving and doubling of the baseline value);
- Energy penalty (increased from the baseline estimate by 20%);
- Capital and operating costs (varied from the baseline estimate by 20%); and
- Electricity price (increased by 20%).

In the figure, the ratio of the upper and lower cost estimates of the novel pre-combustion capture technologies (Case 2-5) relative to MDEA are shown. For all the technologies except membrane separation, the ratio is at or below one. This indicates that all the technologies, including the membrane process under certain conditions, are cheaper capture options than using MDEA solvent.

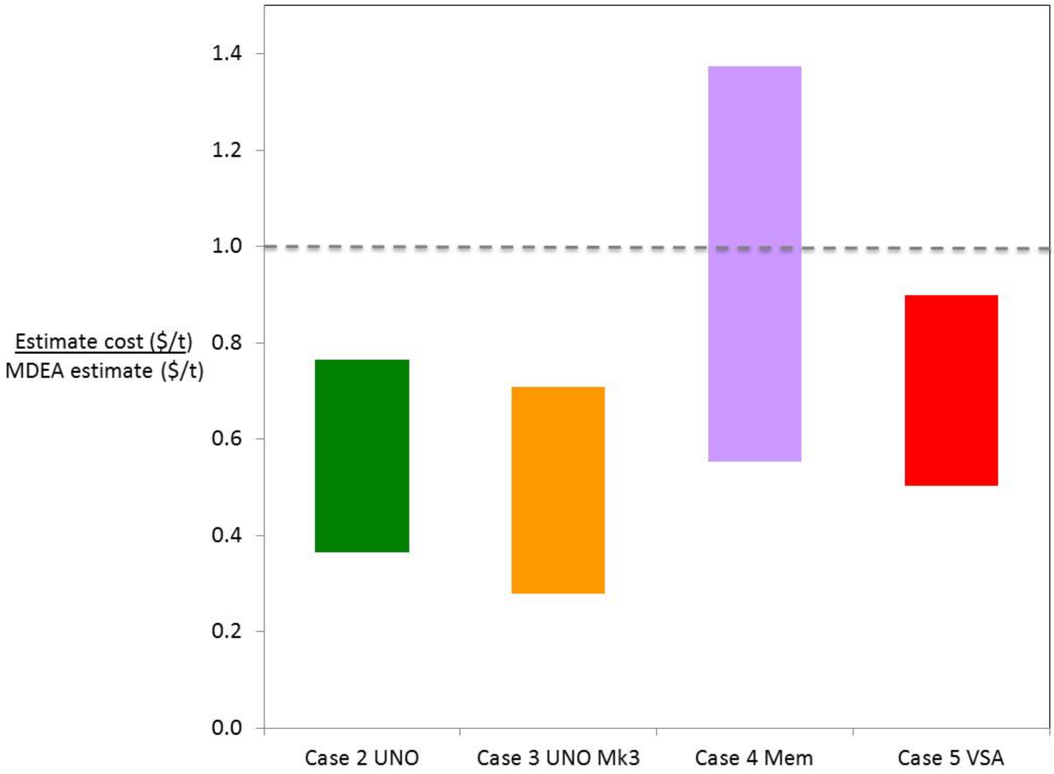


Figure 7.1 Ratio of upper and lower estimates for cost of alternative technologies compared to MDEA solvent

7.3.2 Comparison of levelised cost of electricity generation

7.3.2.1 The effect of capture

The levelised cost of electricity generation ($LCOE_{gen}$) for the full-scale (550 MW) CO2CRC Modelled Plant with capture ranges from A$67 per MWh for the UNO process (Case 2) to A$80 per MWh for gas separation membrane technology (Case 4).

The previous results in section 7 are for a carbon price of zero. Figure 7.2 shows the effect of carbon price on $LCOE_{gen}$ with capture for the different technologies.

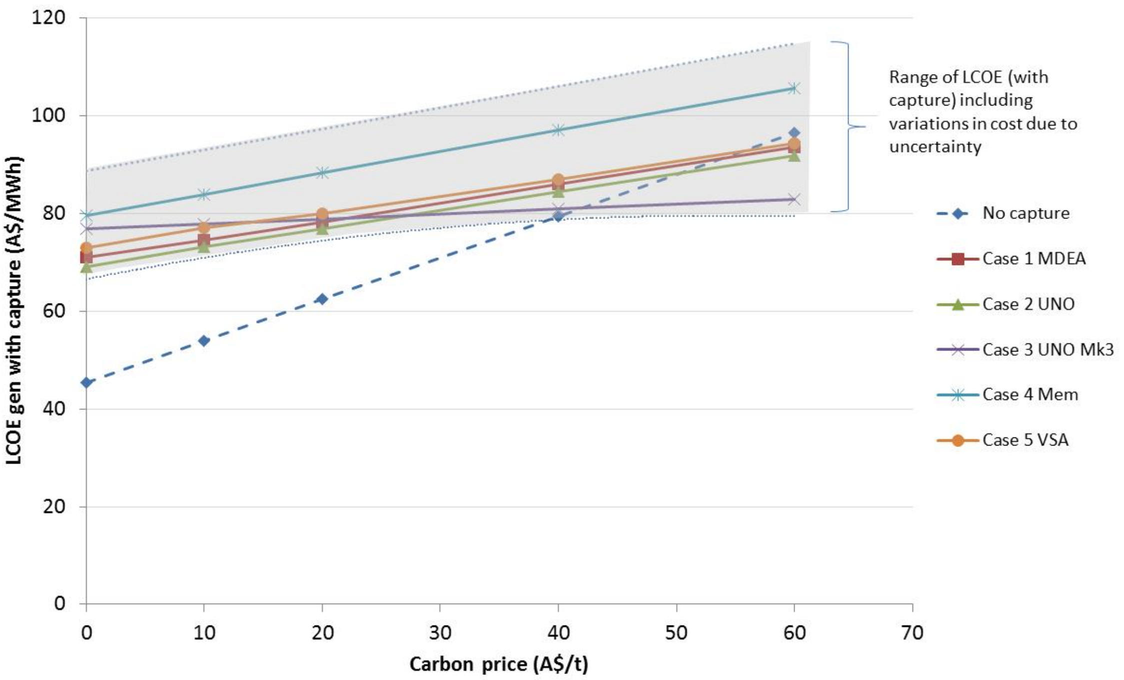


Figure 7.2 Changes in LCOE_{gen} for the full- full-scale (550 MW) CO2CRC Modelled Plant with and without capture with increasing carbon price

7.3.2.2 The additional effect of transport and storage

In the above results for the LCOE_{gen} only show the costs of CO_2 capture. However in deploying CCS, the transport and storage of CO_2 will also affect the LCOE. Capture typically represents 60% to 80% of the total CCS cost (Fimbres-Weihs and Wiley 2010). Based on this assumption, the estimated LCOE for the full-scale (550 MW) CO2CRC Modelled Plant with CCS assuming that costs for transport and storage range from A$20 to A$30 per tonne CO_2 avoided (Neal et al. 2006) is of the order of A$75 to A$100 per MWh. When no carbon price is included in the analysis, the increase in the LCOE with CCS compared to the LCOE for a power plant without CCS is 1.6 to 2.1. Figure 7.3 shows the estimated LCOE with CCS and for increasing carbon price.

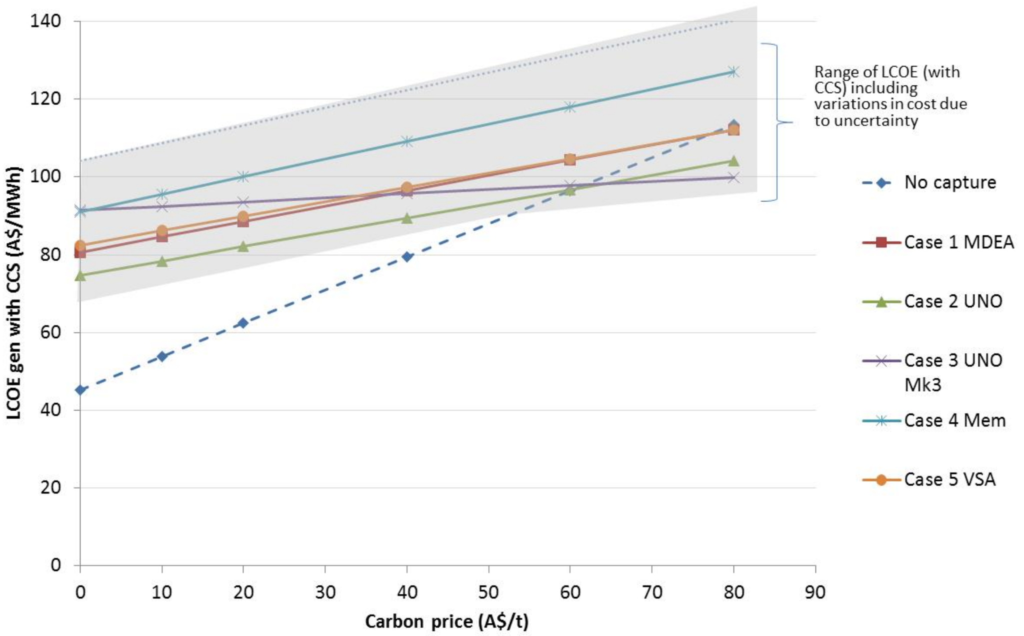


Figure 7.3 Cost of electricity generation (LCOE) with CCS (A$/MWh) with increasing carbon price

The costs of CCS projects are very case specific. This analysis does not consider the condition of the sinks or the effect of source, pipeline and storage networks. Therefore the LCOE estimates presented in this study are indicative only. Having said this it is recognised that in the case of Latrobe Valley the proximity to Gippsland offshore storage potential will offer comparatively low transport and storage opportunities.

7.4 Other Outcomes (communications, collaborations, skill development, etc)

The economic assessment carried out for this project has enabled some development of the CO2CRC techno-economic model. The professional skills of 2 research fellows have also been enhanced.

7.5 Conclusions

The capture cost estimates of CO_2 from the pre-combustion and post-combustion stream of a full-scale (550 MW) CO2CRC Modelled Plant are of the order of A$45 to over A$90 per tonne CO_2 avoided. The results show that the cost for capturing CO_2 using solvent absorption and adsorption technologies is comparable, while the cost for membrane based capture is higher. This report is a preliminary analysis based on limited process and cost data. Simplified rules of thumb and equations have been used to model the capture technologies. Detailed process simulations and process optimisation have not been used in all cases. As such, the results of this report are indicative. While some effects of a carbon price have been included, the effect of tax has been neglected.

7.6 References

1. Davison, J. and L. Bressan (2003). Coal power plants with CO_2 capture: The IGCC option. Gasification Technologies. San Francisco.
2. Fimbres-Weihs, G. A. and D. E. Wiley (2010). Steady-state optimisation of CCS pipeline networks for cases with multiple emission sources and injection sites: south-east Queensland case study. Tenth International Conference on Greenhouse Gas Technologies (GHGT-10), Amsterdam, The Netherlands.
3. Ho, M. T., G. W. Allinson and D. E. Wiley (2008a). Reducing the Cost of CO2 Capture from Flue Gases Using Membrane Technology. Ind. Eng. Chem. Res. 47(5): 1562-1568.
4. Ho, M. T., G. W. Allinson and D. E. Wiley (2008b). "Reducing the Cost of CO2 Capture from Flue Gases Using Pressure Swing Adsorption." Ind. Eng. Chem. Res. 47(8): 4883-4890.

8. Commercialisation of CO_2 Capture Technologies for IDGCC

The application of any new technology to an existing process requires considerable evaluation across a range of technical and commercial parameters. This section seeks to address a number of these factors reflecting the transition of the key findings from this study to a range of CO_2 capture technologies of varying technological maturity, as low emission additions to IDGCC technology.

The major headings consider:

- The use and relevance of the pilot plant to large scale demonstrations
- Technical maturity of the three capture separation technologies, solvents, membranes and adsorbents
- Large scale designs
- Technical and economic viability
- Project issues

8.1 Mulgrave Syngas versus Typical Commercial Syngas

Because of the fact that the Mulgrave gasifier operated at conditions somewhat different to the full-scale CO2CRC Modelled Plant (700 kPag as opposed to ~3000 kPag) and without a water gas shift reactor, the data collected did not provide useful input to larger scale design issues. The plant data however, did allow simulation models for all the capture separation techniques to be validated and compared with laboratory findings. The trials provided a degree of confidence in using the simulation and modelling tools to produce large scale designs for comparative technology and economic evaluation.

Furthermore, the methodologies developed from the trials can be applied to other gasification settings, whether air or oxygen blown.

8.2 Technical Maturity

The fact that this project compares three separate capture technologies (solvents, membranes, and absorbents) in parallel in a comprehensive technical and economic evaluation for syngas is unique to the world of CCS. This approach examines current and next generation technologies thus allowing both near term and “plant after next” options to be considered.

The characteristics of gasification processes (high pressure) mean that the scale up issues often raised for capture are not daunting. Furthermore all the technologies have been applied to some extent in syngas processing. In this light, the capture technologies trialled are quite well developed. Consequently, if they can be configured to deliver the appropriate cost performance for carbon dioxide removal future application should be forthcoming.

8.2.1 Solvent – UNO pre-combustion

Such potassium carbonate based solvents are in use and available as guaranteed process packages for bulk CO_2 removal. The CO2CRC process is modified such that guaranteed processes could be readily developed and consequently the technology is considered mature and could be applied in the near term (0-5 years).

8.2.2 Membrane - pre-combustion

Membranes are used for hydrogen separation in syngas process packages but not for bulk CO_2 removal. Some further development and review of the processes and materials issues for this application will be required. Should an economic process be demonstrated it is expected the technology will require some further refinement. However, it is expected such systems could be applied in the medium term (3-10 years).

8.2.3 Adsorbent - pre-combustion

Adsorbents are used for hydrogen separation in syngas processes but not for bulk CO_2 removal. Some further development and review of the processes and materials issues for this application will be required. Should an economic process be demonstrated it is expected the technology could be readily applied in the medium term (3-10 years).

8.2.4 Solvent – post-combustion – UNO Mk3

This process was developed as a concept to provide greater CO_2 recovery for the full-scale CO2CRC Modelled Plant. This potassium carbonate process is under review and further refinement is underway within the CO2CRC program. The technology relies on well-known solvent systems and operates in a post combustion mode on the gas turbine exhaust from the CO2CRC Modelled Plantrather than the syngas. The fact this is a PCC technology means the issues of scale are relevant and could add additional delays to implementation. Nevertheless, it is considered as a medium term (3-10 years) prospect with learning expected to come from other PCC applications under development world-wide. This should speed development.

8.3 Large Scale Designs

The laboratory, plant, and simulation data have allowed credible large scale design to be developed for all capture technologies. The heat and process integration methodologies developed in this project enabled flowsheets to be designed that target the key cost reduction areas for carbon capture. The designs presented have not been optimised, particularly in the case of membranes and adsorbents (due to time constraints) but are considered to represent feasible and conservative flowsheets. Process integration between power plant and capture facilities is often viewed with concern as it may lead to complexity and problems in control. It is considered that in this case the proposed integration opportunities do not introduce undue complexity and should not compromise large scale designs.

While credible conservative designs have been provided in this report it is recommended that further optimisation of the technologies, particularly membranes and adsorbents, be completed.

8.4 Technical and Commercial Viability

8.4.1 Technical Viability

The air blown fluidised bed nature of the IDGCC process leads to a configuration whereby the un-reacted char from the gasifier is burnt in a plant boiler providing additional energy for the process and increasing net efficiencies. The carbon dioxide produced is released to atmosphere. As this study was largely focused on pre-combustion technologies the lack of abatement of this stream results in a lower than usual CO_2 recovery. A number of alternatives were considered to improve the recovery in a pure pre-combustion configuration and are reported. Furthermore higher recoveries could be achieved by supplementing the pre-combustion capture facilities with an additional PCC component on the char burner exhaust. This was outside the scope of the project and not progressed.

However a conceptual design for a PCC approach to the CO2CRC Modelled Plantwas added as part of the BCIA extension. This concept would allow a greater resilience to future carbon price rises due to lower additional costs for unabated carbon emissions. Should the concept be successfully developed these benefits would have to be considered in the light of commercial drivers.

Water usage for all capture cases increase but are below that of the current Latrobe Valley power plants.

The overall performance from all technical parameters is best examined through the impact on LCOE which is discussed in the next section.

8.4.2 Commercial Viability

The true commercial viability of a technology can only be evaluated with a knowledge of the policy and regulatory environment in which it operates. In the current situation it is only possible to comment on the likely impact of commercially relevant performance estimates. The most relevant parameters considered here are the cost of capture and the levelised cost of electricity (LCOE).

The studies show that low emissions CO2CRC Modelled Plant configurations can provide a range of LCOE outcomes at various recovery rates. These LCOE's are at the low end of a range of studies for future Australian low emission power costs and should allow the technology to compete in whatever future regulatory regime might prevail.

It is important to note that the outcomes of this study are largely indicative and based on well thought out but un-optimised designs. Further studies and detailed review may result in revision to the current findings.

8.5 Project Issues

Finally a number of project issues must be reviewed when assessing the commercialisation of capture technologies. Issues such as safety, operability and overall risk management are but a few needing consideration.

Each of the capture technologies rely on standard chemical industry processing techniques. Given the operating conditions for gasification processes which are, in effect, chemical processing facilities the incorporation of the lower risk capture techniques is considered acceptable. There are no undue safety or operability concerns evident in any of the proposed techniques that would influence commercial implementation.

From a project management and risk assessment perspective the introduction of capture facilities is a large capital expenditure project and will require the same strict protocols and processes used for the facility without capture. Capture facilities will be subject to the same regulatory regime for the plant without capture and hence will not create additional technology related project risk.

8.6 Recommendations

The CO2CRC/HRL Mulgrave Capture Project has provided a solid base for reviewing the incorporation of carbon capture and storage to IDGCC technology. The fundamental R&D performed at the Mulgrave site has been converted into large scale designs and the techno-economic performance of a range of capture options evaluated.

As a result of this work a number of recommendations to continue various studies have been made to HRL.

8.7 Conclusions

The key objective of the CO2CRC/HRL Mulgrave Capture Project was to reduce the technical risk and cost of pre-combustion capture for Victorian coal-fired stations using new coal burning technologies.

For each of the three capture technologies (namely, solvent absorption, membrane and adsorption), the more specific objectives were to:

- Identify and quantify the impact of realistic pre-combustion gas contaminants (H_2S, CH_4, CO) and water on the performance of each capture technology;
- Identify and quantify the impact of pre-combustion gas temperature and concentration variations on the performance of the capture medium and capture process;
- Optimise process operating parameters;
- Develop engineering solutions at a scale at which confidence can be established for full scale capture plant design and assessment;
- Assess the pre-combustion capture process and energy integration options;
- Review the technical and economic viability of the commercial use of pre-combustion capture for new Victorian brown-coal power stations using the gasification process route;
- Conduct a desk-top conceptual study for post-combustion capture from CO2CRC Modelled Plant and compare the results with pre-combustion capture

In completing the research program the CO2CRC has successfully completed a multi-party, multi-technology carbon capture demonstration project in pre-combustion area unique to the CCS world. It has enabled local groups to gain confidence in construction, commissioning and operation of capture plants in a real gasifier setting.

The project has gathered valuable information to facilitate technology development for three pre-combustion capture techniques (solvent absorption, membranes and adsorption) resulting in substantial reduction in technical risk and cost for all three technologies.

Furthermore the large scale designs indicate a range of options for carbon dioxide capture on a CO2CRC Modelled Plant. Various technology cases are evaluated and result in a range of carbon capture costs and LCOE at different recovery rates.

8.7.1 Solvents

In the solvent absorption area large scale design evaluations have successfully demonstrated the CO2CRC UNO process to be a competitive pre-combustion technology for the CO2CRC Modelled Plant. A conceptual design for applying post combustion capture to the CO2CRC Modelled Plant has been developed which will increase the carbon dioxide removal rates from the CO2CRC Modelled Plant and provide greater resilience to future increases in carbon prices.

8.7.2 Membranes

Results have enabled identification of suitable membrane materials and process designs that can attain the degree of CO_2 recovery and purity required for effective storage. Further reviews of the membrane design are required.

8.7.3 Adsorbents

Zeolite 13X and calcium chabazite showed good results at temperatures of less than 200 °C due to their reasonably high adsorption capacity and fast kinetics. Preliminary tests of novel adsorbents such as PEI and double salt materials show encouraging results for CO_2 capture at high temperature.

The designs for adsorbents systems provide the lowest energy penalty and further analysis of the capital equipment is required and may lead to enhanced design outcomes.

8.7.4 Heat and Process Integration

A multi-objective optimisation tool for CO_2 capture from power stations has been developed by the CO2CRC as part of the CO2CRC's ETIS post and pre-combustion projects. The tools enable the creation of highly integrated designs that minimize energy usage and reduce costs.

Three pre-combustion and one post-combustion (solvent) capture process were evaluated for the CO2CRC Modelled Plant. While each option has positive attributes, the energy penalty is lowest for pre-combustion using solvents (14.5%) followed by the adsorption process (15.1%), post-combustion capture using solvents (16.9%), and then membrane separation (26.3%). Energy penalties could be further reduced by an optimisation procedure that maximises the net power generated from the process plant. The optimisation should include not only the capture process but also variables within the modelled PLANT process.

Pre-combustion capture cases for the CO2CRC Modelled Plant provide lower carbon capture rates of approximately 60% due to the nature of the process and the current use of the waste char from the gasifier. A number of alternatives are possible to increase the recovery rate including a post combustion concept studied by CO2CRC.

8.7.5 Economics

Using simplified methods, the cost to capture CO_2 from the pre-combustion and post-combustion stream of the CO2CRC Modelled Plant are of the order of A$47 to over A$92 per tonne CO_2 avoided. The levelised cost of electricity with capture (allowing for appropriate transportation and storage in Gippsland) for a retrofitted power plant range from A$75 to A$100 per MWh. The sensitivity results show that cost estimates are strongly affected by the discount rate and energy penalty estimates. Observations are made about uncertainty and a range of carbon prices and their impact on LCOE for all capture and non-capture cases.

8.7.6 Intellectual Property

Intellectual property has been developed / tested in the following areas:

- Knowledge in designing and operating plant & process for removing CO_2 from gas streams using;
    - Solvents
    - Gas-liquid membrane contactors
    - Gas separation membranes
    - CO_2 adsorption systems and adsorbents
- Large scale designs for these systems
- Heat & Process Integration methodologies for reduced parasitic load

8.7.7 Communications, Publications, Awards and Skills Development

One of the key features of the ETIS project was to communicate the results widely. The project has been active in this area as outlined below.

- The project has been visited by more than ten groups from Australia and overseas, raising the profile of CO_2 capture researchers and industry collaborators.
- At least 62 publications including journal articles, book chapters, media releases, news/web articles, interviews and public lectures have been produced related to this project. They have enhanced public and scientific knowledge and awareness of CO_2 capture.
- More than 18 researchers and 6 higher degree research students have been involved in the project. Their involvement with the industrial partners has assisted in developing high caliber R&D skills for the Brown Coal industry in Victoria. The capabilities of our researchers has been formally acknowledged by the awarding of a Fulbright scholarship to one of our postdoctoral fellows, Dr Colin Scholes in 2009, which provided the opportunity to collaborate with one of the leading international gas separation membrane researchers at The University of Texas at Austin, USA.

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10. Appendices

1. Appendix 1, “Large Scale Integrated Projects with Pre-combustion Capture” extracted from Global CCS Institute’s web page.