School of Engineering

Department of Chemical Engineering

CO_2 Capture by the Integrated VSA/Cryogenics method including Pipeline Transportation

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

Carbon dioxide (CO_2) emissions are one of the main sources for the increase in greenhouse gases in the Earth's atmosphere. Due to the rapidly increasing population on earth and the high energy demand, technologies for greenhouse gas mitigation particularly carbon dioxide are obligatory to prevent the negative effects associated with their release.

Carbon dioxide is conventionally separated from the flue gas emitted from a coal fired power plant via aqueous amine solution and this process is best known for its high energy consumption due to operation at high temperature and pressure. Amine solution is also caustic to the equipment, requires expensive chemical solvents and is vulnerable to thermal and contaminant degradation. At present, amine absorption process is causing an energy penalty of approximately 170-175MW to a 500MW coal fired power plant. This thesis proposes the combination of vacuum swing adsorption (VSA) and cryogenic liquefaction and aim to justify that high recovery can be achieved and the energy penalty is comparable or lower than 170-175MW. This thesis also promotes the idea of pumping liquid CO_2 through pipeline without using insulation and utilizing the ambient and ground temperature to retain its liquid phase. Pumping liquid CO_2 has been previously verified by many published literatures to be more economical than transporting supercritical CO_2 via compressors in terms of both capital and operational expenditure.

In order to validate the feasibility of cryogenic liquefaction, 6 sets of laboratory experiment were conducted for 6 different binary feed gas mixtures (60, 65, 70, 75, 80 and 85 mol% of CO_2 balanced with nitrogen) at a well-established laboratory pilot plant located at Curtin University Energy Laboratory, Technology Park. The data obtained from the experiments, i.e. experimental capture rate was compared with the theoretical capture rate obtained from Aspen HYSYS$^{®}$ simulator. Aspen HYSYS$^{®}$ was selected due to prior experience and robust thermodynamic models. The results show that more CO_2 can be captured at the same operating pressure and temperature in the experiment than in the simulation. CO_2 will also freeze at -55 ℃ therefore this has to be avoided in both the experiment and the simulation.

The development of the energy saving scheme for VSA/cryogenic hybrid was a joint project between University of Melbourne and Curtin University. Experimental data for adsorption was given by the University of Melbourne Adsorption team and the heat integration was performed using Aspen HYSYS® to achieve a satisfactory carbon dioxide recovery at the lowest possible energy penalty. The economics part of the VSA/Cryogenic hybrid was done by University of New South Wales Economics team. The model shows that CO_2 can be economically separated from the flue gas via cryogenic method at high recovery rate provided the feed is properly conditioned by adsorption. For adsorption, the recovery is inversely proportional to the CO_2 composition in the product therefore the CO_2 composition in the (VSA) product is then inversely proportional to the energy required in the cryogenic section. For cryogenic liquefaction, the optimum energy required is a balance between compression and refrigeration, i.e. the compression duty is inversely proportional to refrigeration duty. An overall CO_2 recovery of >90 mol% can be achieved by the hybrid technology and the final product is liquid CO_2 at 99mol%. In terms of capture economics, VSA/Cryogenic hybrid has the potential to offer an energy penalty comparable with the traditional amine benchmark case by implementing multistage compressors with intercoolers, air coolers and using mixed refrigerant. The footprint for VSA/Cryogenic hybrid is also smaller due to the smaller equipment size and less piping.

The modelling of liquid CO_2 pipeline was completed by using Aspen HYSYS® to continue building on existing CO_2 pipeline knowledge and to serve as a continuation of the research done for ChE491/492 Research Project. The optimized models took into account factors such as the ambient/ground temperature, buried depth, soil type, elevation and soil conductivity. The target is to investigate the potential energy savings when utilizing the ground/ambient temperature for cooling to avoid phase change, provided the pipeline is installed in areas with suitable climates. The feasibility of pumping liquid CO_2 was also verified by experiments in the laboratory pilot plant after the capture. It has been experimentally verified that liquid CO_2 can be pumped to high pressure without significant temperature change therefore its liquid phase can be retained.

DEDICATION

This PhD research program was sponsored by Cooperative Research Centre for Greenhouse Gas Technologies (CO2 CRC), one of world's leading collaborative research organization focused on carbon dioxide capture and geological sequestration. Firstly, I like to thank the program manager Professor Dianne Wiley from CO2CRC/UNSW and John Curtin Distinguished Professor Moses Tade from Curtin University for their generous offer. Next, I would like to thank my academic supervisor A/Professor Ahmed Barifcani and co-supervisor A/Professor David Pack for their constant support and patience in this endeavour. Doing PhD with them is equivalent to working with two industrial experts. I deeply appreciate their constructive commenting of my manuscripts.

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My PhD research experience was very industry relevant and practical which allows me to develop skills in the construction, maintenance and operation of laboratory pilot plant. I would like to further acknowledge my wife, Mrs Joy Koh Qian Fen, my parents and parents in law for their support. The journey of a 3 year PhD program was testing our patience and perseverance and many aspects of our life. I have a strong belief that these experiences contribute to my next role as a postdoctoral research and teaching fellow, researcher and pilot plant operator.

BIOGRAPHY AND PUBLICATIONS

ChiiJyh, Teh (Nicholas), has a ORCID: orcid.org/0000-0002-8369-2924, obtained his Bachelor of Engineering with First Class Honours in 2012 from Curtin University. Then he commenced his PhD study at the same university receiving scholarship from a research organization called CO2CRC. As a part of his PhD study, he participated in CO2CRC conferences in 2012 at Sunshine coast, Brisbane and made first presentation to other project participants regarding VSA/Cryogenic energy saving scheme. In 2013 at Hobart and in 2014 at Torquay, Melbourne, he presented a poster and provided project updates to other project participants.

From August 2013 to April 2015, he worked part time as an academic tutor for First Year Engineering unit Engineering Material. At the moment, he is working as a sales consultant/mentor for a Western Australian owned Gas Company.

His research interest includes CO_2 capture by cryogenics and membrane, regeneration and reclamation of Mono-ethylene glycol (MEG), process simulation and optimization, cascade refrigeration and mixed refrigeration, investigation of hydrate formation and dissociation and etc.

Paper in support of this thesis (refer to Appendix A)

Teh, C.J.; Barifcani, A.; Pack, D.; Tade, M. The importance of ground temperature on a liquid carbon dioxide pipeline. International Journal of Greenhouse Gas Control, Volume 39, 2015, pg 463-469. SCImago Journal Rank (SJR): 1.954, Impact Factor: 3.946, 5-Year Impact Factor: 4.727

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NOMENCLATURE

AC	Activated Carbon
CCS	Carbon Capture and Sequestration
CGTA	Clean Gas Technology Australia
CO_2	Carbon dioxide
CO2CRC	Cooperative Research Centre for Greenhouse Gas Technologies, Australia
CRA	Chemical Risk Assessment
DEA	Di-ethanol amine
ESA	Electrical Swing Adsorption
FGD	Flue Gas Desulphurization
GTL	Gas to Liquid
IGCC	Integrated Gas Combined Cycle
IEA	International Energy Agency
JT	Joule Thompson
LNG	Liquefied Natural Gas
MEA	Mono-ethanol Amine
MDEA	Methyl-diethanol amine
MR	Mixed refrigerant
MSDS	Material Safety Data Sheet
MW	Megawatt
NG	Natural Gas
PCC	Post-combustion capture
PSA	Pressure Swing Adsorption
TEA	Tri-ethanol amine
TSA	Temperature Swing Adsorption
VSA	Vacuum Swing Adsorption

CHAPTER 1 INTRODUCTION

1.1 CO_2 properties and characteristics

Carbon dioxide (CO_2) is a non-polar chemical compound which compose of two oxygen atoms covalently bonded to a single carbon atom (O=C=O). CO_2 is also inert, colourless, odourless, non-flammable, and chemically stable under recommended conditions of storage and has no heating value of combustion. The CO_2 molecule has a linear shape and zero dipole moment. CO_2 occurs naturally in the earth's atmosphere at a concentration of 0.038% by volume (DNV, 2010).

CO_2 has a molecular weight approximately 50% higher than air which means at ambient condition the density if gaseous CO_2 will be higher than air. At normal temperature and pressure, the stable CO_2 phase is vapour. The table below provides several physical properties of pure CO_2:

Table 1 Physical properties of CO2 (BOC Gases, 1996)

Property	Unit	Value
Molecular weight	g/mol	44.01
Critical pressure	bar	73.8
Critical temperature	C	31.1
Triple point temperature	C	5.18
Triple point pressure	bar	-56.6
Aqueous solubility at 25C, 1 bar	g/L	1.45
Gas density at 0C, 1 bar	Kg/m^3	1.98
Density at critical point	Kg/m^3	467
Liquid density at 0C, 70 bar	Kg/m^3	995
Sublimation temperature	C	-79
Latent heat of vaporization	kJ/kg	571
Solid density at freezing point	Kg/m^3	1562
Colour	-	none

Concentrated gaseous CO_2 can cause asphyxiation and circulatory insufficiency which lead to coma and death. It is about 1.5 times denser than air at ambient temperature. Asphyxiation is likely to occur before the effects of CO_2 overexposure. Chronic, harmful effects are not known from repeated inhalation of low concentrations. Low concentrations of CO_2 cause increased respiration and headache (BOC Gases, 1996). Effects of oxygen deficiency resulting from simple asphyxiants may include: rapid breathing, diminished mental alertness, impaired muscular coordination, and faulty judgement, depression of all sensations, emotional instability, and fatigue. As asphyxiation progresses, nausea, vomiting, prostration, and loss of consciousness may result, eventually leading to convulsions, coma, and death (BOC Gases, 1996).

CO_2 exist naturally in the atmosphere and it is essential for life. It can be stored underground in natural rock formation for millions of years. CO_2 has also been injected into reservoir to put out more oil. CO_2 will be held securely in the reservoir for millions of years by an impermeable ‘cap’ rock (Shell, 2011). CO_2 causes global warming which results in rising and acidifying of sea water.

A CO_2 pressure-temperature PT phase diagram shown in Figure 1 provides important information such as the operating temperature and operating pressure required for cryogenic liquefaction experiment and the typical envelope for normal operations of the transportation of liquid CO_2. At different temperature and pressure, CO_2 can exist in solid, liquid, vapour and supercritical phase while liquid phase is the main interest in this paper. Liquid CO_2 is produced mainly for the food industry several places in the world. The triple point of CO_2 is where the three phases of CO_2 coexist and occurs at -56.6 ℃ and at 5.1 bar. Any point on the saturation line will cause the CO_2 to exist in both liquid and vapour phase and similarly solid and liquid phase for melting line and solid and vapour phase for sublimation line. Supercritical CO_2 is where it is held at or above its critical temperature (31 ℃), a temperature at and above which CO_2 vapour cannot be liquefied at any pressure and critical pressure, a pressure required to liquefy CO_2 at its critical temperature (73 bar).

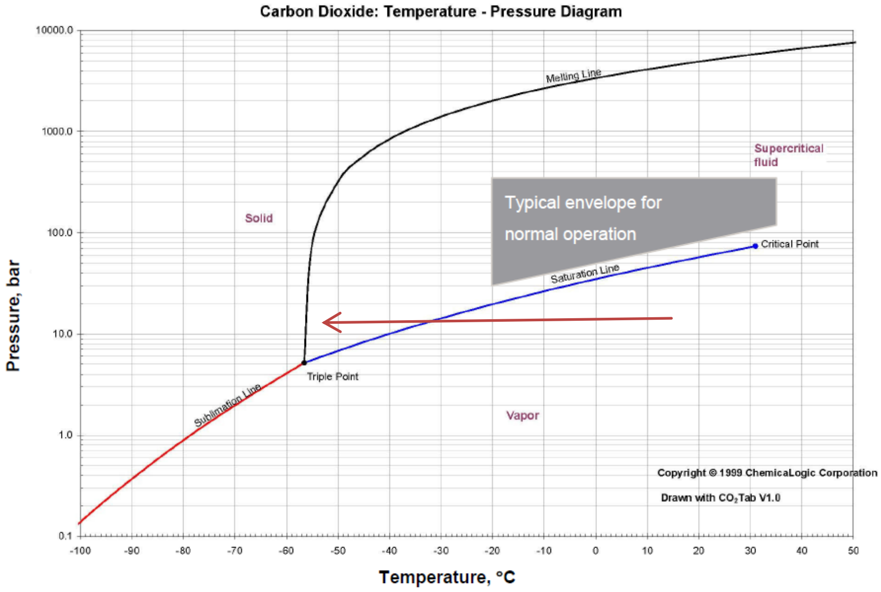

Figure 1 CO_2 Phase Diagram (DNV, 2010)

The red arrow being shown on the phase diagram above signifies the aim of this research program, i.e. by bringing CO_2 from gaseous phase to liquid phase.

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Supercritical CO_2 is also excellent for dissolving small, non-polar organic compounds but less effective in dissolving many polar or ionic compounds and large polymers. (ISCO 2012). Several applications for supercritical CO_2 are given as below:

- **Supercritical fluid extractions (SFE):** solvents such as methylene chloride were traditionally used for extracting fats from foods or pesticides from soils and foods, using an apparatus called a Soxhlet extractor. Supercritical CO_2 has the ability to mimic solvents and penetrates matrices easily and may replace Soxhlet extrations. Supercritical CO_2 can also be combined with chelating agents for the extraction of uranium from aqueous solutions produced in the processing of the ore and removal of heavy metals from soils and sludges.
- **Supercritical Fluid Chromatography (SFC):** supercritical CO_2 can replace solvents as the mobile phase in high performance liquid chromatography (HPLC).
- **Cleaning**: supercritical $CO_{2,}$ with the enhanced wetting and diffusion properties, can be used to remove oils, fats, waxes and other contaminates without damaging the matrix. It improves the cleaning of components with small openings, delicate equipment or porous materials.
- **Plastic production**: CO_2 has successfully replaced Freon as a polymer foaming agent and can be an excellent solvent for reaction involving a strong oxidizing or reducing agent due to its inertness.
- **Manufacture of electronic chip**: supercritical CO_2 along with appropriate detergents may eliminate the need for water and reduce energy consumption in the manufacturing process for electronic chip which consumes a large amount of chemicals and fossil fuels.
- **Injection moulding and extrusion**: CO_2 can be used as an expanding or foaming agent for injection moulding or extrusions by adding air pockets in plastic, reducing the amount of material used, decreasing shrinkage and warpage and improving tolerances. The presence of CO_2 in plastic melts lowers viscosities therefore lowering the injection moulding pressures required, and/or decreasing the injection times.
- **Particle formation**: supercritical CO_2 can be used to produce powders or micro-particles in pharmaceutical industry by rapid depressurizing materials dissolved in CO_2. Production of micro-particles with drugs or other component s of interest embedded in a substrate can be achieved by pumping the mixture through a capillary where the CO_2 is vaporized at the outlet and leave powers behind.
- **Catalyst/Reactant feed**: supercritical CO_2 can be used to replace solvent and increase and control the reaction kinetics by altering the pressure.

1.2 Background of CO_2 capture

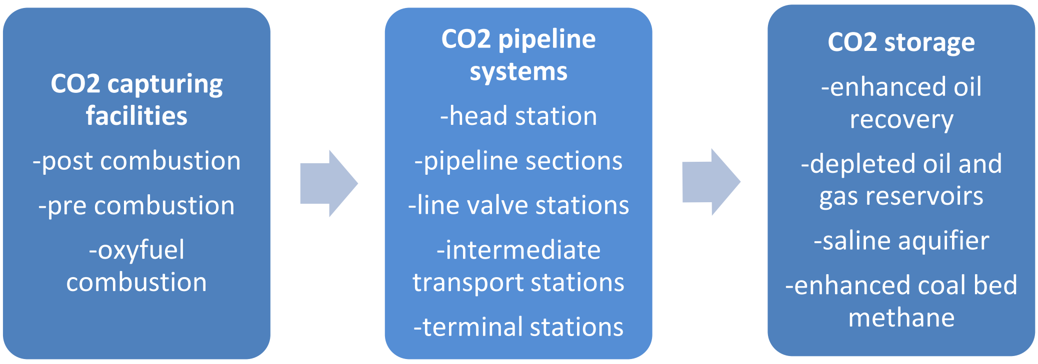


Figure 2 Basic scheme of CO_2 capture, pipeline transportation and storage options (Kaufmann, 2008)

Carbon capture and sequestration (CCS) is a methodology to capture CO_2 from large point sources such as fossil fuel (oil, gas and coal) power plant and storing it instead of releasing it into the atmosphere. As a part of a portfolio of climate change mitigation options available to policy makers and industry, it is a process which consists of several steps from capture to transport, well injection, sequestration and monitoring. CCS can also be used to capture and store CO_2 emitted from a range of industrial processes such as cement manufacturer, fertilizers, natural gas purification and gas to liquid (GTL).

Generally speaking, it is a three step process which involves a CO_2 source facility, a long term CO_2 storage site, and an intermediate mode of CO_2 transportation. A basic scheme of CCS is shown as above. Firstly the CO_2 emitted to the atmosphere would be captured and purified. This is typically an expensive process because the compression of low pressure CO_2 requires a large amount of energy. Secondly, the captured CO_2 is pumped or compressed to dense phase before entering pipelines to an underground sequestration site. Finally, CO_2 is injected into deep geological formations where it will be trapped for thousands or millions of years after injection.

CO_2 capture technology for fossil fuel fired power plants can be divided into 4 categories which are post-combustion, pre-combustion decarbonisation, oxy-combustion and chemical looping combustion (Figure 3). In this thesis, post-combustion capture (PCC) will be the main focus and each of the PCC approaches, namely chemical and physical absorption, solid physical adsorption, low temperature distillation (cryogenic separation) and membrane separation possesses their own unique advantages and disadvantages will be discussed.

- Post combustion systems

CO_2 is usually diluted with other inert such as nitrogen, argon, oxygen and water. The flue gas is normally at near atmospheric pressure with CO_2 concentration depending on carbon intensity of the fossil fuel as well as air fuel ratio in the combustor. Amines are used to absorb CO_2 and it is regenerated by reversing the reaction. The regeneration of amines usually requires a large amount of heat therefore additional power requirement on the plant. An advantage of this capturing method is that it can be utilized to any flue gas stream. The impact of flue gas impurities (SOx, NOx, particulates) must be taken into account.

- Pre-combustion decarbonisation systems

This process is more complex than post combustion systems as it consists of three steps. Firstly the fuel reacts with oxygen, air or stream and turn into a mixture of carbon monoxide (CO) and hydrogen (H_2), this is known as gasification, partial oxidation or reforming.. Secondly, the synthetic gas is converted to hydrogen and CO_2. Thirdly, the CO_2 is separated from the H_2. CO_2 is captured from predominantly H_2 at high pressure (15-40 bar) and medium CO_2-content (15-40%). More hydrogen can be produced by passing the CO/H_2 mixture through a catalytic converter and hydrogen can be used as fuel in gas turbine combined cycle plant. Other impurities include CO, H_2S and other sulphur components.

- Oxyfuel combustion systems (De-nitrogenation processes)

This process is a modified post-combustion method and is still under development which replaces combustion air with oxygen and recirculated flue gas, resulting in a flue gas that is composed mostly of CO_2 and water vapour. Nitrogen is excluded from the combustion process before or during the combustion/conversion process therefore only simple CO_2 purification is required.

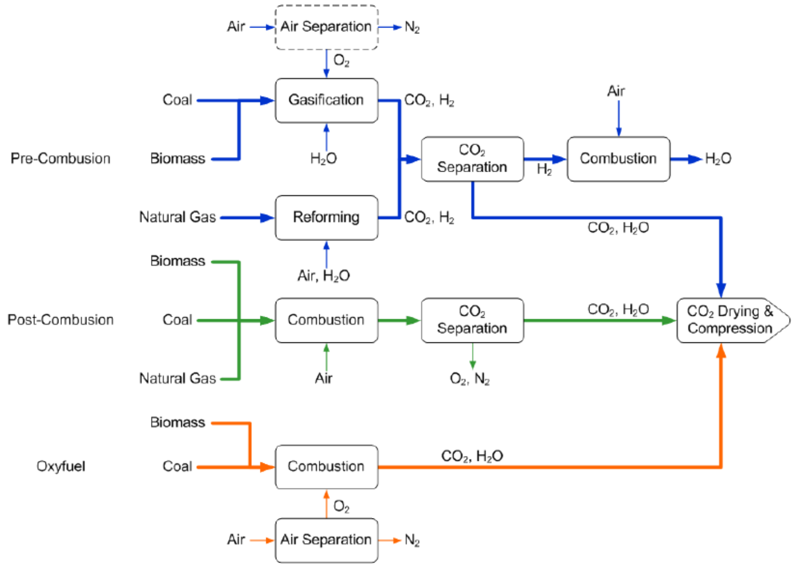


Figure 3 Major Processes of three carbons capture technologies (McCoy, 2008)

A summary of advantages and disadvantages of different capture technologies is provided below:

Table 2 Advantages and disadvantages of CO_2 capture technologies (Olajire 2010)

Capture technology	Advantages	Disadvantages
Post-combustion capture	- Existing technology - Retrofit to existing power plant designs - Extra removal of NO_x and SO_x	- Energy penalty due to solvent regeneration and loss of solvent
Pre-combustion capture	- Existing technology - Very low emissions	- The need of cooling the gas to capture CO_2 - Loss of efficiency in water-gas shift reaction
Oxyfuel combustion capture	- Existing technology - Absence of nitrogen therefore eliminates the need of removing NOx - Absence of nitrogen therefore lower volume of gases to be compressed and reduce the size of entire process	- High energy required for air separation to produce pure oxygen - Combustion in pure oxygen is challenging

1.3 Motivation of research

One of the key environmental issue happening in Australia and the world is to decrease greenhouse gas emission to the atmosphere. According to CO2CRC, the International Energy Agency (IEA) predicts a 40% increase in CO_2 emissions from energy between 2006 and 2030 and 80% of the energy demand will be met by fossil fuels. Australia has the highest emissions per capital even though it only represents 1.5% of global greenhouse gas emissions (Herald Sun, 2011). Studies have shown that approximately 60% of the global CO_2 emissions are attributed to large stationary sources such as power plants. Electricity generation is Australia's largest source of greenhouse gas emissions. 80% of the total electricity generation is contributed by existing coal fired power generation in Australia. However, post-combustion capture has never been applied at full-scale and integrated in a coal fired power plant. A 30% efficiency loss will be caused by using a standard liquid absorbent process to capture 90% of CO_2 present in flue gases from a coal-fired power plant. Therefore many businesses and individuals are concerned about climate change and want to make their own contribution to reducing greenhouse gas emissions.

Carbon capture and sequestration (CCS) is believed to serve as an effective method and the only technology available to make a deep cut in preventing CO_2 from entering the atmosphere. CCS technology also serves as a potential 'bridging technology' which allows fossil fuel to be utilized until alternative energy sources become more popular (McCoy et al, 2007). CCS is also regarded as the 'critical enabling technology' for allowing the use of coal and other fossil fuels to meet energy needs. However, CCS still suffers from economic and technical issues such as high capital cost and a high energy requirement will ultimately push up the price of electricity. The energy penalty due to capture and compression is believed to cause an immediate loss in revenue for energy companies without even considering the capital cost for the capture plant. (Wang and Oko 2015) identified the common difficulties experienced by pilot CCS plants are cost, scalability and flexibility and proposed that process modelling, simulation and optimization would provide solutions to these difficulties by filling the knowledge gaps previously identified by pilot work, and supporting decision-making for CCS design and operation. Since CCS is capital intensive, process modelling and simulation can be used to assess different heat integration options to determine their impact on plant flexibility.

This PhD program is motivated as there is still a lack of knowledge, attention and confidence in capturing CO_2 via cryogenic method due to its energy penalty, economic viability and technical challenges and transporting liquid CO_2 through pipelines using pumps. The author want to discover new knowledge and establish the confidence that energy optimized cryogenic method can be partnered with other capturing technologies to capture CO_2 with energy penalty that is comparable with the traditional amine process. This thesis also promotes an alternative option that is to transport liquid CO_2 via pipelines and fully utilizing the ground temperature for cooling to maintain its phase and ultimately result in energy savings for both capital expenditure and operating expenditure.

1.4 Thesis objectives

Several major objectives were defined for this PhD study:

- Literature review for different capturing technologies and comparing their advantages and disadvantages.

- Re-simulating CO_2 capture processes available in open literature using Aspen HYSYS® to identify its feasibility.

- Complete the data required for simulation and optimization of the overall integrated VSA/Cryogenic scheme by conducting further experiments at an existing laboratory pilot plant located in CGTA laboratory, Technology Park for capturing CO_2 by cryogenic method and pumping liquid $CO_{2.}$

- Using Aspen HYSYS® simulation software to develop and optimize an integrated design scheme for the VSA/Cryogenic for CO_2 capture from flue gases including the drier package to be located after the VSA section in full coordination with University of Melbourne Adsorption team.

- Performing more in-depth optimization studies on pipeline operational and design studies include changes in pipeline elevation and ambient temperature, continuation of research project done in 2012.

- Evaluating the economics side of energy optimized VSA/Cryogenic energy saving scheme after attending a meeting with a project participant from University of New South Wales (UNSW) to discuss energy figures for economic evaluation.

1.5 Thesis chapter outline

The structure of the thesis is summarized in the attached diagram (Figure 4). **Chapter 1** provides introductory material for this thesis. Firstly, it introduces the properties of $CO_{2,}$ the sponsor of this PhD research program CO2CRC and the environmental effect of CO_2. Then it addresses the objectives and motivations for this PhD research program.

Chapter 2 covers literature review on post-combustion capture (PCC) of CO_2 and the design of high pressure CO_2 transmission pipeline. This chapter evaluates the design considerations, technical advantages and disadvantages of each capturing technologies for PCC such as amine absorption, adsorption, membrane gas separation and cryogenic condensation. Hybrid technology such as membrane-cryogenic hybrid was also discussed. Specifically for the energy saving scheme for cryogenic condensation, this chapter evaluates different low temperature separation processes developed in various published journal articles. These include a novel CO_2 cryogenic liquefaction and separation system, open CO_2 liquefaction cycle, low temperature syngas separation, condensed rotational separation (CRS), and four liquefaction systems for ship based CO_2 capture, three processes are open cycle (The Linde Hampson systems, the Linde dual-pressure system and the precooled Linde Hampson system), one closed process. Most of these processes were re-simulated using Aspen HYSYS software and advantages and disadvantages of each process were briefly discussed.

Chapter 3 describes the operation of laboratory pilot plant for capturing CO_2 by cryogenic method. It is a legal requirement under the Western Australian Occupational Safety and Health Regulations 1996 and under Curtin University's Health, Safety and Emergency Management that Chemical Risk Assessments (CRA) and Plant Risk Assessment must be conducted. These assessments can be found in appendix. The main objective of this chapter is to demonstrate laboratory experiments for capturing CO_2 by cryogenic method using the existing laboratory pilot plant facilities and proves that the experimental CO_2 capture rate (recovery) matches (or even better than) theoretical CO_2 capture rate calculated by Aspen HYSYS® software V7.2, using the Peng Robinson property package. Aspen HYSYS® was selected due to prior experience and robust thermodynamic models. CO_2 is physically separated from N_2 based on the dew and sublimation points. The main product is refrigerated and liquefied CO_2. 6 different binary feed gas mixtures (60, 65, 70, 75, 80 and 85 mol% CO_2 balanced with nitrogen N_2) were experimented at a liquefaction temperature of around -55 ℃ but different pressure. The freezing temperature of CO_2 was verified by both Aspen HYSYS® software and experiment to lie between -56 ℃ and-58 ℃. The experimental capture rate was obtained by physically analysing the composition and the flow rate of depleted gas from the gas liquid separator. This chapter will describe step by step experimental procedures and equipment needed for capturing CO_2 by cryogenic method, its engineering issues and the optimization of the process.

Chapter 4 describes the development of an energy saving scheme for CO_2 capture using vacuum swing adsorption/ cryogenic hybrid. The main objective is to develop a novel energy saving scheme for the cryogenics liquefaction process using Aspen HYSYS® software, addressing the energy requirement and evaluating potential ways to reduce the energy penalty while partnering with vacuum swing adsorption which different feed specifications were provided by CO2CRC Adsorption group from University of Melbourne in year 2012. Then, evaluate the capital expenditure and operational expenditure calculation provided by University of New South Wales for the energy saving capture scheme to show that the energy penalty is comparable with the mono-ethanol-amine (MEA) benchmark case. A plot plan was sketched based on equipment sizing of major equipment to evaluate the footprint and retrofitting potential of this hybrid scheme. The development of refrigeration package, i.e. the comparison between cascade refrigeration and mixed refrigeration was briefly discussed.

Chapter 5 focuses on the transportation of liquid CO_2 via pipeline and highlights the importance of ground and ambient temperature on a realistic pipeline design. The high-pressure CO_2 pipeline will be buried for the majority of the pipeline route therefore the optimization of CO_2 transport via pipeline must account for the impact of ground temperature together with seasonal and diurnal ambient temperature conditions because of heat exchange along the pipeline between the CO_2 fluid and the surroundings. In reality, the pipeline system will also inevitably face variations in topography such as hills and valleys, variations in soil conditions and the requirement to meet special pipeline code conditions where the pipeline route goes under major load bearing zones, such as railway lines, roads and river crossings, or through or near residential or industrial areas. In this chapter, a liquid CO_2 pipeline is modelled by using Aspen HYSYS®, using the Peng Robinson property package and taking into account the heat transfer aspect of a pipe. In a steady state operation, the fluid temperature can decrease or increase as it flows along the pipeline due to the heat transfer between the pipe wall and the surrounding environment. Provided the pipe segment is long enough, the temperature of the CO_2 will eventually reach near equilibrium with the soil temperature. The model will incorporate parameters such as the ambient temperature, ground material, buried depth and elevation. Insulation and coating of pipeline will also be briefly discussed.

Chapter 6 describes the extension of the laboratory pilot plant demonstrated in Chapter 3 to incorporate a flow loop for pumping liquid CO_2. Liquid CO_2 has many applications such as in nuclear power generation, recirculation in commercial refrigeration plant, use as a blowing agent in foam-making processes and the extraction of essential oil from plant materials. All these applications demand a pump which has the ability to cope with high pressure at the pump inlet, poor lubricity and low temperature. However there is a notable shortage of published literatures relating to pumping liquid CO_2. In this chapter, a packed plunger metering pump (20 to 682 GPH; up to 7200 PSI) is used to pump liquid CO_2 collected at the bottom of gas liquid separator through a close loop back to the feed line of the gas liquid separator. The pump has an accuracy of ±0.5% at steady state and capacity can be manually adjusted. The discharge pressure of the pump can be controlled by an integral bonnet needle valve located on the pump discharge line. One major benefit of using this type of plunger pump is that it provides heavy duty positive displacement for continuous, accurate metering and fast response at higher flow rates and/or pressures can be provided by standard single ball check valve located on both suction and discharge side of the pump.

Chapter 7 provides results and discussions for chapter 3, 4, 5 and 6. For chapter 3, the results for capturing CO_2 at high pressure and low temperature were verified experimentally and were compared against the simulation results. The comparison shows that the vent gas composition for experiment is lower than the one given by Aspen HYSYS® for the same capturing temperature, pressure and gas composition. It means that more CO_2 can be liquefied in reality and consequently provide more energy savings for the refrigeration package. For chapter 4, the final results strengthen the potential of cryogenic condensation to be partnered with other capturing technology to achieve a high overall recovery. While developing and optimized the model, a key finding was discovered that is the optimum energy for a cryogenic process is the trade-off between compression and refrigeration for a given feed CO_2 composition and desired amount of recovery. Higher feed pressure and/or higher feed CO_2 composition will favour the liquefaction process.

Chapter 8 gives recommendations and conclusions for **Chapter 3, 4, 5 and 6**.

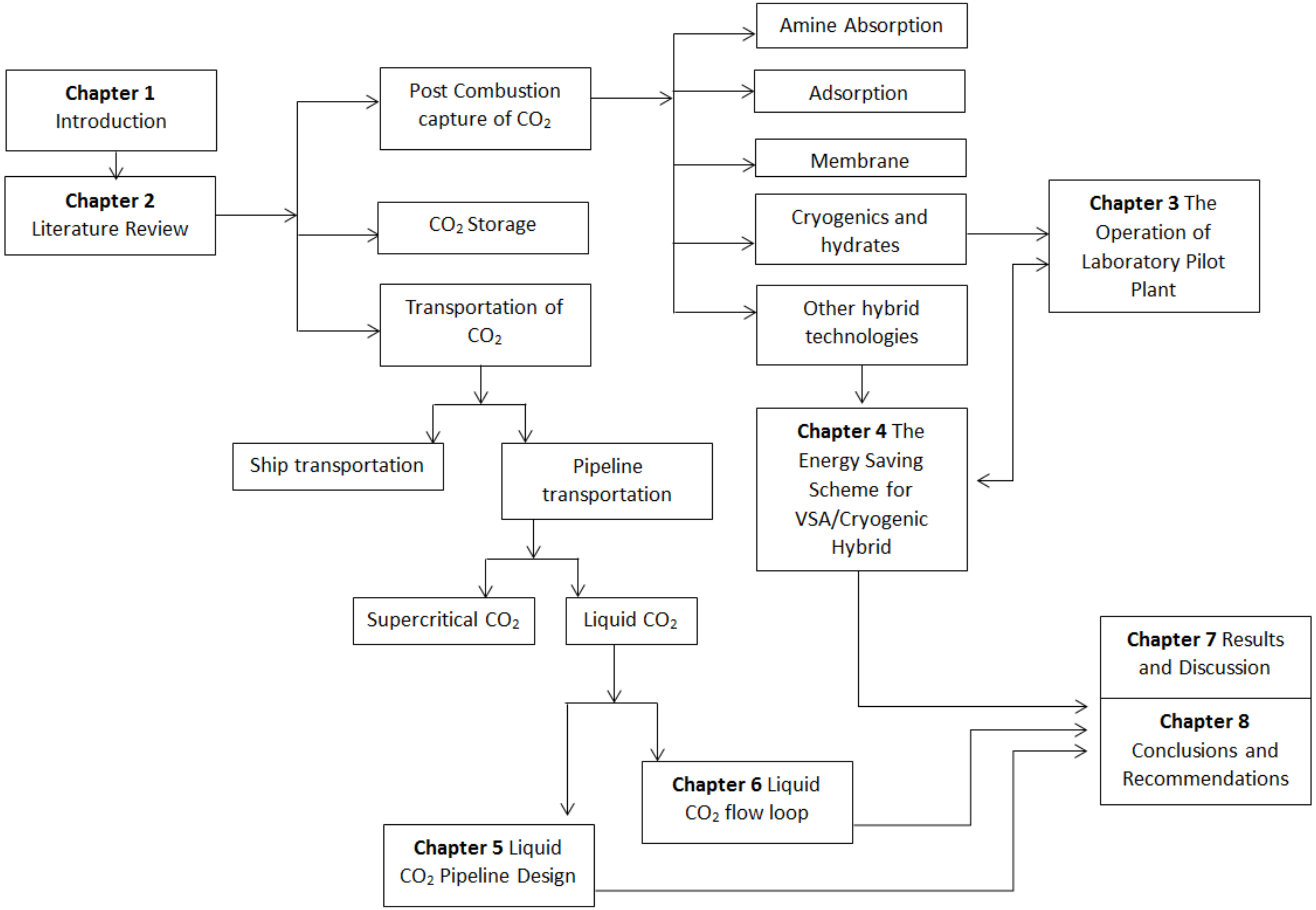


Figure 4 Outline of the thesis

CHAPTER 2 LITERATURE REVIEW

2.1 Post combustion capture of CO_2

2.1.1 Solvent absorption

Solvent absorption involves the use of absorbent such as mono-ethanol amine (MEA) to absorb CO_2 from a gas stream. Generally speaking, there are two types of absorbents: potassium carbonate and amine based absorbents (such as mono-ethanolamine (MEA)). Potassium carbonate will cause stress corrosion and erosion to the units and react with some corrosion inhibitors therefore amine based solvent is more common (Niu and Rangaiah 2014). Smith et al (2009) defended that potassium carbonate has a lower cost, less toxic and less prone to degradation effects that are commonly observed with MEA at high temperatures and in the presence of oxygen and other flue gas impurities. Potassium carbonate also has the capacity to absorb SO_x and NO_x. The biggest challenge related to using potassium carbonate as solvent is its low rate of reaction therefore poor mass transfer performance. This problem can be solved by adding promoters/activators/catalysts however traditional promoters such as piperazine, di-ethanolamine and arsenic trioxide are recognized as toxic and dangerous to environment.

MEA has been the traditional solvent of choice for CO_2 absorption and acid gas removal because it is the least expensive of the alkanolamines, has the lowest molecular weight and possesses the highest theoretical absorption capacity for CO_2. MEA also has the highest vapour pressure of any of the alkanolamines and high solvent carryover can occur during CO_2 removal from the gas stream and in the regeneration step. MEA solution with 30wt% concentration is commonly used due to its high reactivity with CO_2 and can absorb about 80-95% of CO_2 in the flue gas. However, MEA also has serious limitations such as corrosion resulting in the need of expensive equipment, irreversibly reacting with NO_x and SO_x and form heat stable corrosive salts which also leads to solvent degradation and forming problem (Smith et al. 2009). Some other solvents such as Di-ethanol amine (DEA), Tri-ethanol amine (TEA), and Methy-diethanol amine (MDEA) can also be explored and each of them has different selectivity to CO_2 and H_2S and tendency of degradation. Different amines vary in their equilibrium absorption characteristics for the various acid gases and have different sensitivities with respect to solvent stability and corrosion factors.

CO_2 is removed by a two steps process, firstly the gas dissolves in the liquid and secondly the dissolved gas reacts with the weakly basic amine. The process of absorption from the gas phase is governed by the partial pressure of the CO_2 while the reactions in the liquid phases are controlled by the reactivity of the dissolved species. Fig 3 below shows a process flow diagram for MEA absorption and its typical operating conditions (1 ℃ is 33.8F, 1psig is 6.89kPa):

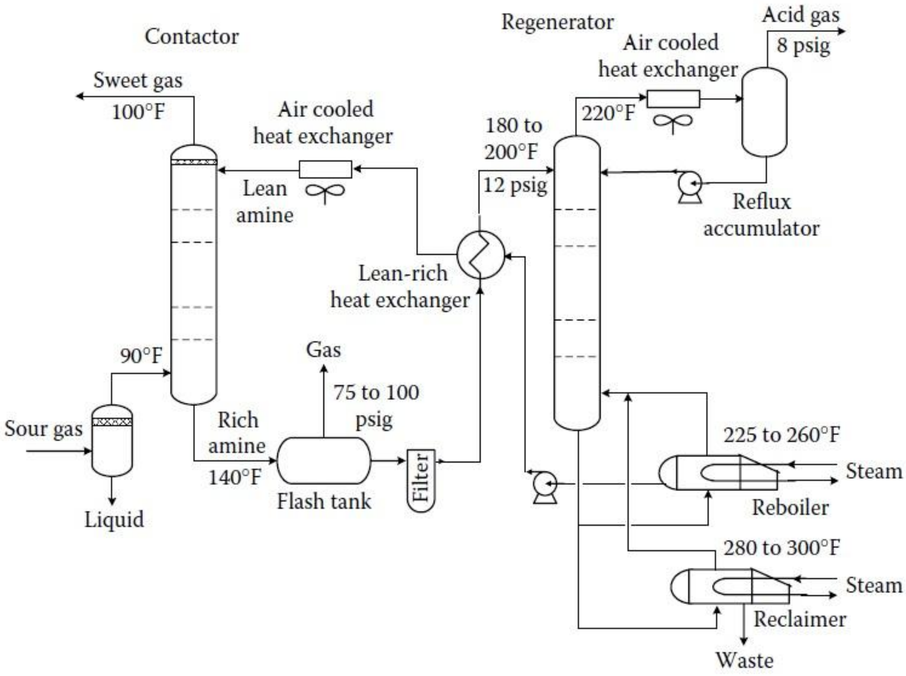


Figure 5 Process flow diagram for MEA absorption (J.Kidnay and R.Parrish 2006)

Firstly the gas with CO_2 (sour gas) at a high pressure (70 bar) and temperature (32 ℃) enters the bottom contactor (absorber) and come in contact with lean amine solution counter-currently. The contactor tower consists of trays of packing to promote the intimate contact between the gas and the solvent. Most of the absorption and reactions occur at the bottom of the contactor and the temperature can reached up to 80 ℃ due to exothermic reaction. The treated gas leaves the contactor around 38 ℃ and the temperature is controlled by the lean amine after being cooled by an air cooled heat exchanger. A regenerator column (stripper or desorption tower) is used to regenerate the solvent. Reboiler(s) generates vapour by low pressure steam and the vapour flow upwards through either tray or packing to strip the acid gases from the rich amine that flows down. Finally, the lean amine generated from the regenerator is pumped to the pressure of the top of the contactor and exchanges heat with the rich amine stream at the lean-rich heat exchanger to reduce the reboilers heat load. According to CO2CRC, a 500MW regenerator would need approximately 6ML of solvent, half in the absorber column and half in the regenerator column.

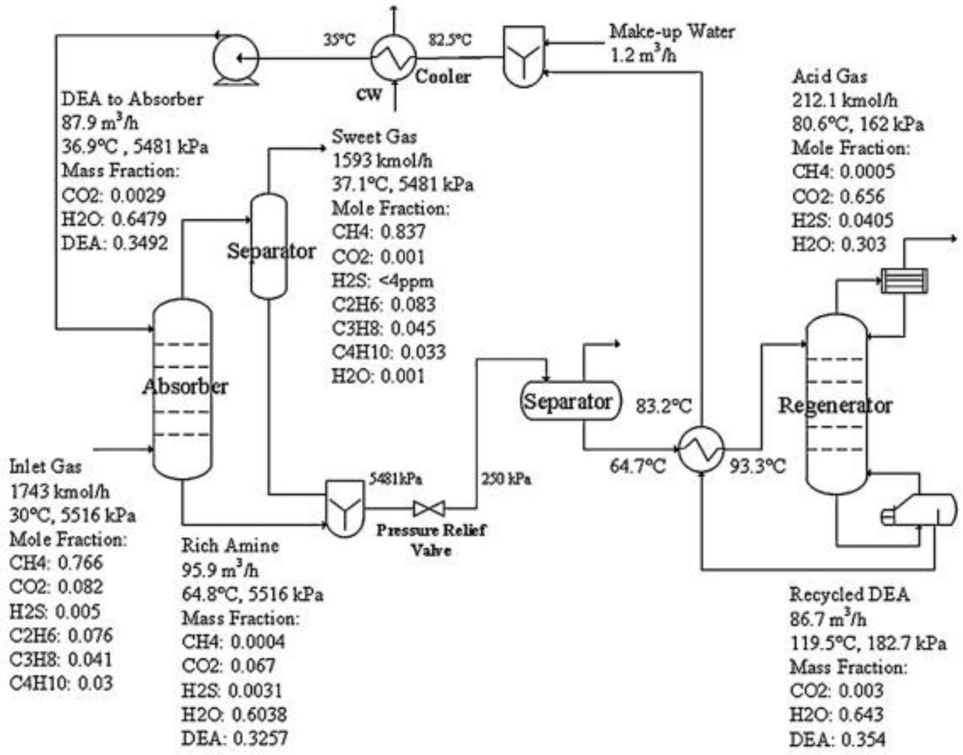


Figure 6 Process flow diagram for DEA absorption (Niu and Rangaiah 2014)

In figure 7 above, amine absorption process (DEA) is modelled and simulated using Aspen Plus 7.2 with amine package as the fluid package. Several highlights have been given:

- The initial guess for amine circulation rate is estimated using equations from design of *Gas-Handling Systems and Facilities Volume 2* written by Ken Arnold and Maurice Stewart.

- Solvent temperature at absorber inlet is set at 5-7 ℃ higher than inlet gas to ensure occurrence of absorption.

- For absorber: 35kPa pressure drop, 20 stages. For regenerator, 20.7kPa, 18 stages

- Normal operating range for bottom temperature of regenerator is 110-121 ℃ for DEA

CO2CRC/H3 post-combustion project (Qader et al. 2011)

The CO2CRC/H2 Capture Project was commissioned in 2009 on a lignite fired power plant in the Latrobe Valley, Victoria, Australia. This demonstration project is associated with a 25 tonnes per day CO_2 capture plant at International Power's Hazelwood power plant in Victoria. Process Group under contract to International Power designed and supplied this plant to the CO2CRC under the H3 Capture Project. A process flow diagram of the solvent pilot plant for post-combustion capture is shown in figure below:

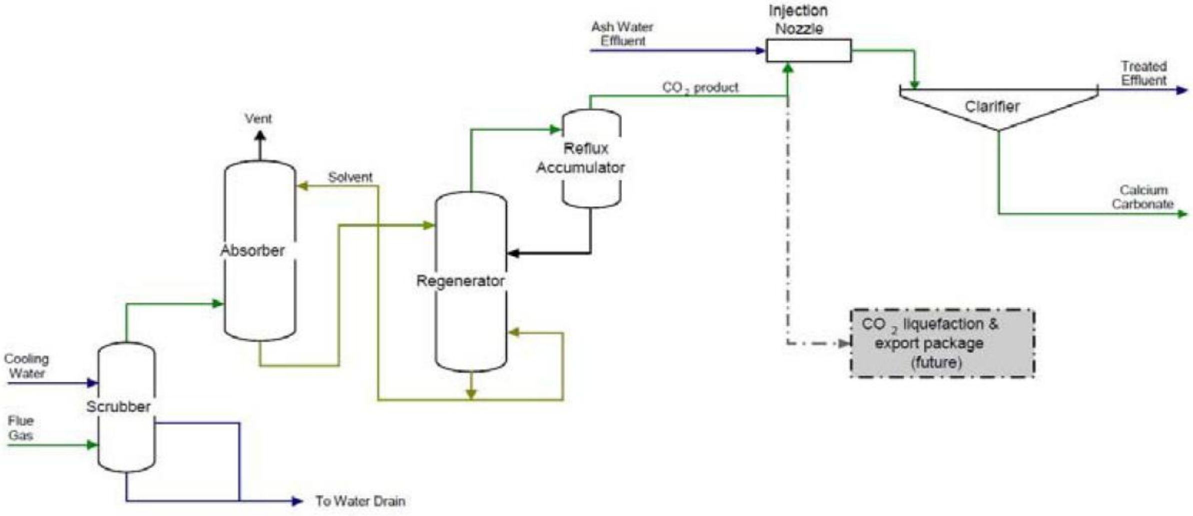


Figure 7 CO2CRC/H3 post-combustion project

Before entering the absorber, the feed gas will enter the scrubber/direct contact cooler (DCC) which cools the gas from around 200C to 40C. The DCC is equipped with a spray section which removes the entrained particles within the flue gas. The flue gas will be compressed to 10kPag by the flue gas blower after exiting from DCC. In the absorber, the gas will rise through two sections of Nutter rings and come in contact with lean solvent. Before entering the regenerator, rich solvent will be pumped by a rich solvent pump and will be preheated to 117C. The regenerator which contains Nutter rings random packing is equipped with a steam heated reboiler to provide the heat for regeneration. The lean solvent from the reboiler will be cooled to 40C by a lean solvent cooler before returning to absorber. An antifoam chemical reagent Potassium hydroxide (KOH) will be added to maintain solvent efficiency from a separate automated dosage tanks. A promoted potassium carbonate based solvent is being investigated since May 2010 in a separate trial which is known as the CO2CRC/IPT H3 project. This solvent capture plant has been operated in steady state mode for more than 1800 hours between July 2009 and April 2010. 20-25 tonnes per day of CO_2 have been captured with a recovery of 80-90%.

2.1.2 Adsorption

Adsorption process involves the use of the adsorbent solid, typically commercial mineral zeolite 13X or activated carbon (AC) to remove CO_2. The adsorption capacity of adsorbent depends on the pore structure and the surface chemistry between the adsorbent and CO_2. An ideal adsorbent would have these following characteristics:

- High adsorption capacity, High CO_2 selectivity
- Low cost, Easy to regenerate
- Lifetime of adsorbents
- Tolerance to other impurities such as H_2O, SO_x, NO_x, and O_2. This tolerance has direct impact on the economics of the capture process

Adsorption operates in 3 steps: adsorb CO_2 (adsorbate), purge (remove impure gases) and desorb CO_2. According to CO2CRC, there are also different types of adsorbents such as metal organic frameworks (MOFs), other organic-inorganic hybrids, mesoporous carbons, silica gels, aluminas and etc. (Li et al. 2013) stated that a number of patents have been published on soda-lime, active carbon, zeolites, molecular sieve, alkali metal oxides, silver oxide, lithium oxide, lithium silicate, carbonates, silica gel, alumina, amine solid sorbents, metal organize frameworks and others. Generally speaking, there are two types of adsorption:

- Physical sorption

CO_2 is weakly bound onto the adsorbent by a combination of Val der Waals forces and electrostatic forces. No covalent bonds are formed and the adsorption process is exothermic.

- Chemical sorption

CO_2 is bound onto the adsorbent by covalent bond and it offers larger adsorption capacity.

For desorption (the removal of CO_2 from the adsorbent), vacuum swing adsorption is the main focus of this thesis:

- Vacuum swing adsorption (VSA)

The desorption of CO_2 is triggered by creating a near-vacuum. This system will operate at near ambient temperature therefore it requires less energy. To ensure a stable and flexible operation of VSA, the adsorbent chosen has to show hydrophobic (tendency to repel water) characteristic and high adsorption capacity of CO_2. Depending on the sources of material and method of preparation, activated carbon is a common and useful adsorbent which offers both hydrophilic and hydrophobic sites to varying extents. CO_2 is able to adsorb on both hydrophilic and hydrophobic sites because of its acidic characteristic (Dong et al. 2013). A schematic diagram and details of adsorption column from Monash University is shown below:

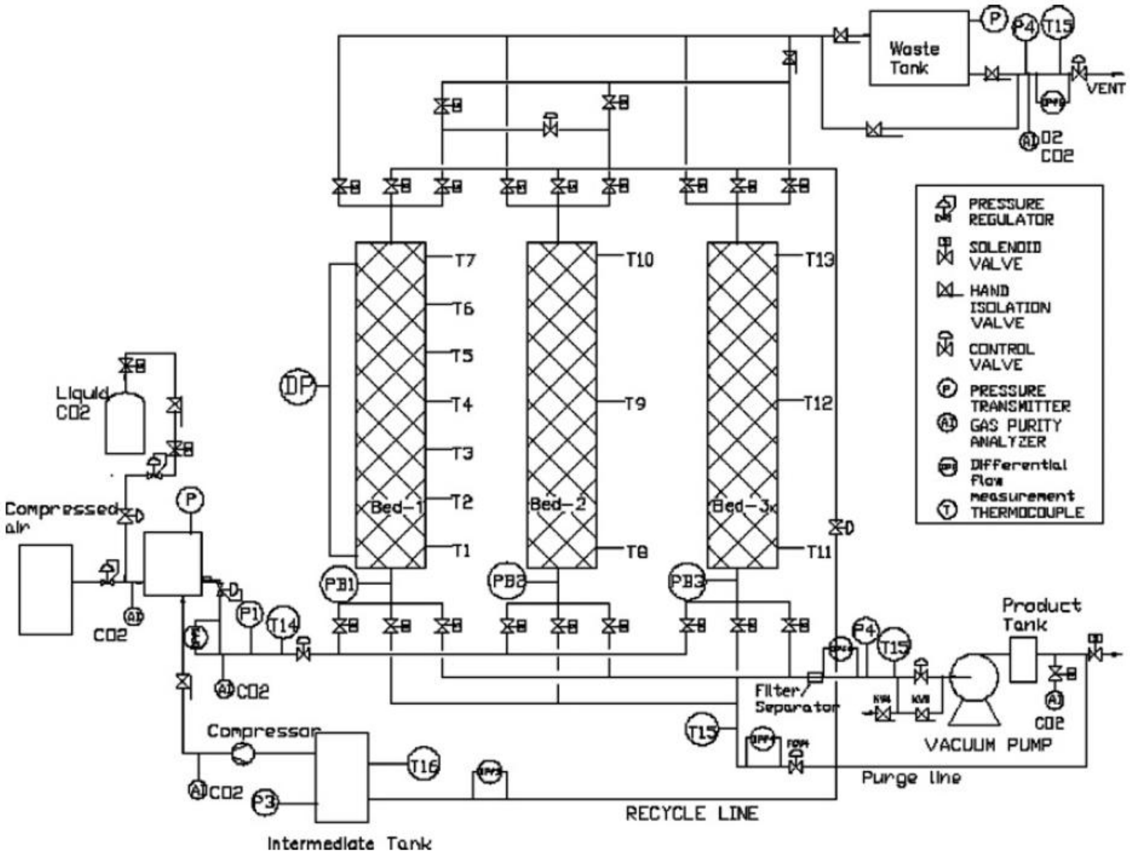


Figure 8 CO2VSA schematic diagram and details of adsorption column (Zhang, Webley, and Xiao 2007)

Previous studies have claimed that vacuum pump contributes more that 70% of the power consumed by VSA and the most determining parameter for energy performance is the evacuation pressure (Zhang, Webley, and Xiao 2007). The relationship between feed concentration and process temperature on VSA performance has also been evaluated as such: the purity and recovery of the process increases with feed concentration at constant feed temperature and evacuation pressure; the operating cost therefore decreases. Increasing the feed temperature will increase the capture cost as the adsorbent working capacity starts decreasing.

The same study has concluded that adsorbent 13X zeolite has the capability to produce >90% CO_2 purity with a recovery of >60% from a stream of 12% CO_2 operating between 40 ℃ -50 ℃. A quick comparison between 13X zeolite and activated carbon is provided as below:

Table 3 Comparison between 13X zeolite and activated carbon(Zhang, Webley, and Xiao 2007)

Type of adsorbent	13X zeolite	Activated carbon
Advantage	- Stronger capacity in CO_2 adsorption for low pressure applications	- Strong capacity in CO_2 adsorption
Disadvantage	- Hydrophilic to water molecule - CO_2 isotherms are nonlinear due to its relatively high adsorption energy therefore result in high regeneration energy	- Offers both hydrophilic and hydrophobic sites

There are also other several desorption methods which can be investigated (CO2CRC 2011):

- Pressure swing adsorption (PSA)

The desorption of CO_2 is triggered by a decrease in pressure, usually from an elevated level to near atmospheric pressure. PSA process was first invented by Esso Research to separate oxygen and nitrogen from air. A patent was published in 1960 describing the technology as two parallel beds with two cycles known as Skarstrorm cycle where the feed air is first compressed, dried, filtered and sent for adsorption. PSA is usually a repeating process which can be described as follows:

- Feed compression
- Adsorption at feed pressure
- Co-current depressurization to a set pressure
- Counter-current depressurization to pressure less than 1 bar starting at 10% to 70% of feed pressure
- Counter-current purge with product gas at atmospheric pressure
- Counter-current, sometimes co-current pressure equalization
- Co-current pressurization with feed

- Temperature swing adsorption (TSA)

The desorption of CO_2 is triggered by an increase in temperature. This is energy intensive and slow since the entire mass of adsorbent must be heated. TSA technology is similar to PSA and VSA and is still currently used for drying gases and gas sweetening. In a TSA capture system, the increase in temperature is usually controlled to avoid degradation of the adsorbents and loss in adsorption capacity. The main disadvantage of TSA is that it requires a long period of time to heat the adsorbent bed and cool down for next cycle therefore results in needing a larger adsorption bed for a given throughput rate and higher capital cost. The temperature requirement for TSA depends on the target species for example in the removal of carbon monoxide from hydrogen (hydrogen purification), 40 ℃ is required for adsorption cycle and 120 ℃ is required for desorption. Another example is capturing CO_2 by calcium oxide where carbonation reactions (adsorption) requires a temperature range between 600-800 ℃ while the calcination reaction (desorption) requires >900 ℃.

TSA is more favourable comparing with PSA for several reasons:

- Lower operating pressure
- Higher purity product can be achieved than the one from PSA
- The benefit of recycling the waste heat to provide heating for desorption cycle if integrated with other processes

- Electrical swing adsorption (ESA)

ESA is similar to TSA but the desorption of CO_2 is triggered by an applied voltage. This method has the advantage of faster heating of adsorbent bed. However the requirement of electricity will escalate the operating cost and carbon footprint of this process.

2.1.3 Membrane gas absorption (membrane contactor system)

CO_2 can be captured by membranes which made of polymers or ceramics with a solvent. The flue gas stream is fed along one side of the membrane while the absorption liquid is fed along another side of membrane. CO_2 diffuses between the pores in the membrane and is absorbed by the solvent. Surface area between gas and liquid phases has to be maintained. Membrane gas absorption method is used when the CO_2 has low partial pressure because the driving force for gas separation is small. Only CO_2 is absorbed by the solvent due its selectivity and the membrane itself does not separate CO_2 from other gases however it maintains a barrier between the liquid and gas with permeability through the pores. It is crucial that the gas and liquid phase do no mix therefore the membrane has to be hydrophobic (Spigarelli and Kawatra 2013).

Advantages of this method include:

- The gas the liquid flows are not dependent on one another.
- Possible size reduction of the absorption unit due to a reduced volume of gas
- Easy to scale up, high gas-liquid interfacial area and increased mass transfer rates

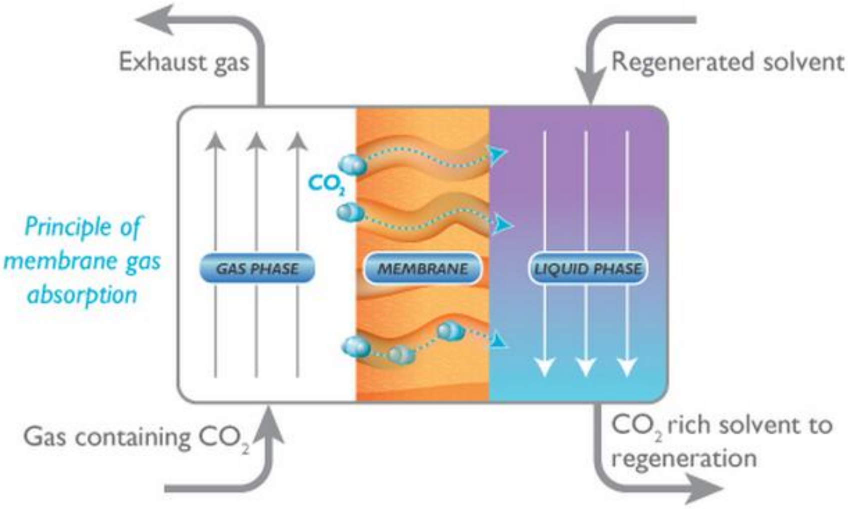


Figure 9 Membrane gas absorption(CO2CRC 2011)

2.1.4 Membrane gas separation (MGS)

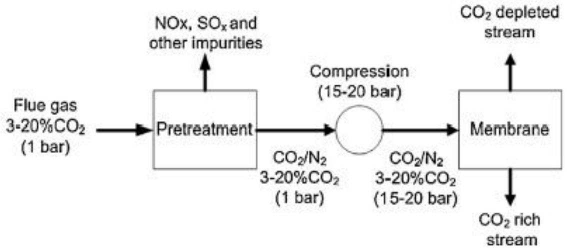


Figure 10 Process flow diagram for membrane gas separation (Spigarelli and Kawatra 2013)

Membrane separation processes are commercially used for CO_2 removal from natural gas. In figure 12, the membrane acts as a filter to remove CO_2 from a mixture and generate a CO_2 component rich permeate. The main driving force for separation is the pressure differential between the feed side and permeate side of the membrane which can be provided either by compressing the feed gas or creating a vacuum on the permeate (Merkel et al. 2010) . This driving force can be observed by Fick's Law in equation below:

$$J_i = \frac{P_{i*}}{\delta} A_m \Delta p$$

Where J_i is the flux of component i across the membrane (cm^3/s), P_i^* is the permeability of the membrane in terms of component i, δ is the membrane thickness (cm), A_m is the membrane area (cm^2), ΔP is the pressure difference (mmHg) across the membrane. Despite of the fact the membrane system offer the potential to reduce cost through better energy utilization, minimize equipment size and waste, one major limitation is the inverse relationship between permeate concentration and component recovery. This limitation can be overcome by using multi-stage membrane units to gradually increase the recovery and permeate concentration while controlling the flow with recycling streams.

Types of membrane

Membrane can be natural or manufactured from synthetic material based on the type of application. Generally speaking there are three types on membranes:

- Organic membranes

These includes polyamides (PA), polycarbonates, polyacrylonitrile (PAN), polyethylene oxides (PEO), polyacetylenes, polyanilines, polyvinylidedefluoride (PVDF), poly(arylene ether), polyarylates, polyphenylene ethers, cellulose acetate (CA), regenerated cellulose, polyethersulfone (PES), and polysulfones (PS).

- Inorganic membranes (porous and non-porous)

These include α-alumina, γ-alumina, borosilicate glass, pyrolyzed carbon, silica, zirconia carbon, zirconia/stainless steel and zeolites. Non porous membranes are used for highly selective separation of small molecule gas. Porous membranes are cheaper than non-porous membranes and are less selective with respect to CO_2.

- Mixed matrix membranes

These consist of micro or nano sized inorganic particles incorporated into a polymeric matrix. Mixed matrix membranes offer enhanced physical, thermal and mechanical properties but induce high cost, brittleness and difficulty in commercial scale manufacture. Mixed matrix membranes are the most applicable for gas separation processes due to the embedded fillers resulting in high selectivity and permeation rate.

Feed compression or vacuum on permeate

A comparison between feed gas compression and vacuum on permeate to create the pressure differential for separation have also been investigated. Assuming the vacuum pumps, compressors, blowers and expanders have same efficiency, despite of the fact that energy can be partially recovered by using turbo-expander, feed compression requires a smaller membrane area compared with permeate vacuum but induces higher energy consumption due to compressing large amount of gas (Merkel et al. 2010).

Cross-flow module or counter-flow module

The same literature has also evaluated the differences between cross flow and counter flow module as shown in Figure 12. The result shows that counter-flow module requires a smaller membrane area, provides a higher permeate concentration and induces lower power consumption. Counter-flow module also offers the potential to accommodate permeate-side sweep process which further reduces the membrane area required by introducing a small portion of the CO_2-stripped residue gas to the permeate side at the residue end of the module (Merkel et al. 2010).

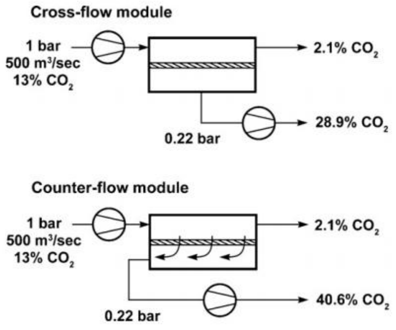


Figure 11 Cross-flow module versus counter-flow module (Merkel et al. 2010)

There are several mechanisms for membrane gas separation and the most common are molecular sieving and solution diffusion (CO2CRC 2011):

- Molecular sieving

Gas components are separated based on size exclusion, the size being the kinetic diameter of the gas molecules.

- Solution diffusion

Gas components are separated based on their solubility within the membrane and their diffusions through the dense membrane matrix. The solution diffusion model describes three step mechanisms in which the component is firstly adsorbed into the membrane material, and then diffuses through the membrane before finally desorbing out from the other side.

- Surface diffusion

Gas molecules with higher polarity are selectively absorbed onto the surface of the membrane and pass through the membrane by moving from one adsorption site to another.

- Knudsen diffusion

Gas components are separated based on the difference in the mean path of the gas molecules.

The efficiency of a membrane separation for any gas mixture depends on these factors:

- The composition of gas mixture
- The feed flow rate
- The pressure difference between permeate and feed
- The area of membrane
- The operating temperature

Membrane configurations

There are two types of configurations for membranes which are the spiral wound membranes and hollow fibre membranes. The spiral wound membranes consist of a number of membrane envelopes which wrapped around the perforated tube with a net like spacer sheet. The spacer sheet not only keeps adjacent membranes apart from the feed channel but also promotes turbulence for the feed mixture. The feed gas enters the modules, flows axially along the feed spacers and membrane and exit from the other axis side as residue gas (retentate) while the permeate gas pass through the membrane spiral path into perforated tube and exit from the other side as permeate. On the other hand, hollow fibre membranes are very similar to a shell and tube heat exchanger design. Thousands of hollow fibres are packaged in bundle (tube side) and enclosed in a high pressure vessel (shell side). The optimization of both membrane configurations can be achieved by varying the physical layout of membranes and dimensions (length and diameter) therefore optimizing pressure drop across the membrane and membrane area per unit volume.

2.1.5 Low temperature separation (Cryogenics and hydrates)

Cryogenic technique was first used in the late 18th century for air separation and is currently one of five CO_2 capture/separation technologies (solvent absorption, membranes, adsorption, and chemical looping) which utilizes low temperature to cool, condense and purify CO_2 from gas streams. This technique can be vapour liquid separation (CO_2 rich liquid phase) namely cryogenic condensation, vapour solid separation namely the hydrate precipitation and a combination of both such as CO_2 slurry separation. For cryogenic condensation, flue gas under high pressure is cooled to sub-zero temperatures which allow only CO_2 to condense. The process of liquefying CO_2 can provide two types of conditions, one is liquid CO_2 for pipeline transport, and another one is liquid CO_2 for ship transport. Seo et al. (2005) has claimed that there are two types of liquefaction system, one is open which the working fluid is compressed and expanded while another one is closed which utilizes refrigerants.

For hydrate precipitation, clathrate hydrates are crystalline solid compounds which gaseous CO_2 molecules (guest) are trapped in water cavities (host) by hydrogen-bond under appropriate thermodynamic conditions (such as high pressure and/or low temperature). Hydrate based CO_2 capture (HBCC) has been receiving attention due to its moderate operating temperature range, the ease of recycling or aqueous solution containing additives, the capability for continuous operation which allows large scale treatment and its unique separation mechanism. According to (Dashti, Yew, and Lou 2015), CO_2 forms structure I (S_I) while N_2 form structure II (S_{II}) hydrates. HBCC has several advantages such as high volume of CO_2 storage and the whole process does not release any pollutant because water is the raw material. A flow diagram for HBCC processing unit is shown as Figure 12 below.

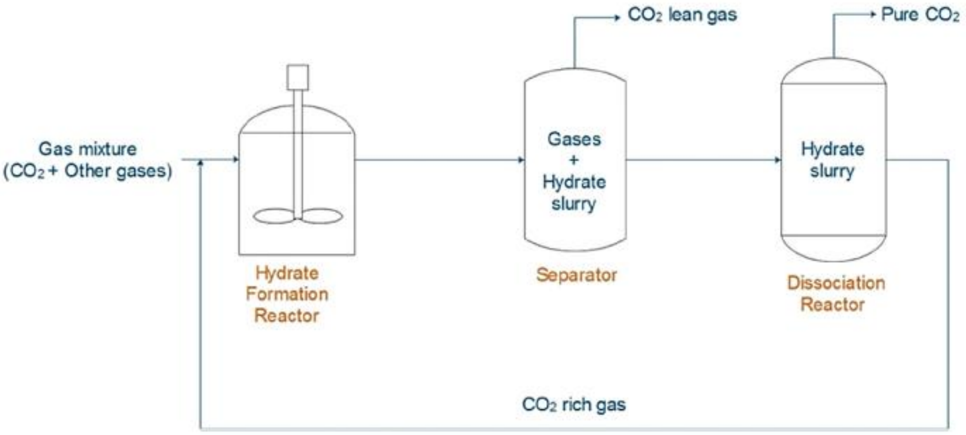


Figure 12 Flow Diagram of a HBCC processing unit (Dashti, Yew, and Lou 2015)

HBCC is still a novel, immature technology and requires a high pressure operating condition and large footprint. Consequently, chemical additives acting as hydrate promoters can be used to reduce equilibrium hydrate formation pressure, shorten the induction time, increase the hydration rate, enhance gas uptake and improve the selectivity of CO_2 in hydrate cages. These chemical additives can be categorized into two types:

- **Kinetic promoters**: mostly surfactants that increase the rate of hydrate formation without taking part in the hydrate formation itself. Commonly used surfactants in hydrate forming systems include sodium dodecyl sulphate (SDS), Tween-80 (T-80) and dodecyl-trimethyl-ammonium chloride (DTAC).

- **Thermodynamic promoters (surfactants)**: small molecules that take part in hydrate formation by competing with gas molecules for hydrate cages which include tetrahydrofuran (THF), cyclopentane (CP), propane (C3H8) and tetra-n-butyl ammonium bromide (TBAB). Other low concentration quaternary ammonium salts such as tetrabutyl-ammonium floride (TBAF) tetrabutyl ammonium chloride (TBAC) tetra-iso-amyl ammonium bromide (TiAAB), tetra-n-butylphosphonium bromide (TBPB) and tetra-n-butylammonium nitrate ($TBANO_3$) can also be uesed to decrease the hydrate equilibrium pressures of CO_2 hydrates especially TBAF and TiAAB. (Wang, Lang, and Fan 2013),

Apart from additives, hydrate reactor is another key factor which determines the industrialization of HBCC. Several factors which affect the energy efficiency for HBCC are hydrate formation temperature and pressure, hydrate induction time, CO_2 recovery or split fraction (S.Fr.), separation factor (S.F.), gas hourly space velocity (GHSV, i.e. gas volume of hydration in unit time per unit reactor volume), energy consumption, and etc. Short induction time, high gas consumption and high separation factor are desirable in HBCC. In order to reduce the induction time and improve the gas consumption, mechanical methods can also be investigated to improve contact area and mass transfer between gas and water. Three mechanical methods have been summarized by (Dashti, Yew, and Lou 2015) as below:

Table 4 Mechanical methods for HBCC

Mechanical methods	Description
Fixed bed crystallizer with porous silica gel	Porous silica gel used in the fixed bed can significantly enhance the contact area between gas and water, allowing more gas to be enclathrated in a shorter time and consequently improve gas consumption and induction.
Bubble method	It requires a large bubbling column and makes it limited for further investigation.
Temperature fluctuation method	The solubility of CO_2 decreases in the hydrate forming region while increasing in the non-hydrate forming region as the temperature decreases

Pilot plant for integrated cryogenic and hydrate CO_2 capture (Surovtseva and Barifcani 2010)

A pilot plant has been constructed by Clean Gas Technology Australia for an integrated cryogenic and hydrate CO_2 capture is provided as below:

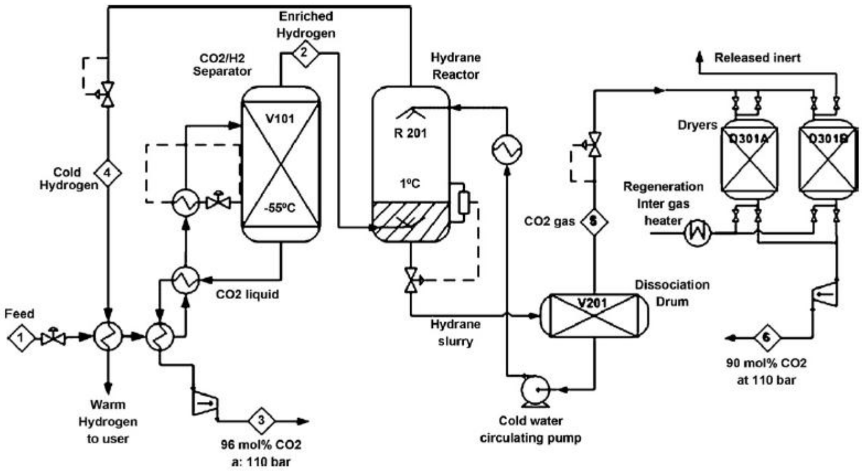


Figure 13 Process flow diagram for integrated cryogenic and hydrate CO_2 capture(Surovtseva and Barifcani 2010)

Part I: Cryogenic condensation

In the first stage, feed consisting CO_2 and H_2 at elevated pressure is cooled to -55 ℃ to ensure that only CO_2 gets condensed at the bottom of the CO_2/H_2 separator. The liquefied CO_2 can be reused as refrigerant to chill its feed and can be pumped to 110 bar high pressure for transportation(Surovtseva and Barifcani 2010).

It has been observed from the CO_2 phase diagram that the liquefaction temperature is predominantly determined by its pressure and the increase in pressure improves the liquefaction temperature which provides energy saving in refrigeration. Apart from pressure, a study has also claimed that increasing CO_2 concentration can also improve the liquefaction temperature and therefore separation (Xu et al. 2012).

Part II: Hydrate precipitation

The uncondensed CO_2 and non-condensable H_2 from the top of CO_2/H_2 separator are fed into a hydrate reactor where the gas comes in contact counter-currently with cold water-promoter solution and forms hydrate-in-water slurry. Hydrate promoter such as hydrogen sulphide to facilitate the hydrate formation. The solid hydrate crystals will deposit in the lower part of reactor and can be dissociated to release CO_2 at high concentration at between 20 to 40 bar in dissociation drum (Surovtseva and Barifcani 2010).

CANMET's pilot scale CO_2 capture and compression unit (CO_2CCU) (Zanganeh, Shafeen, and Salvador 2009)

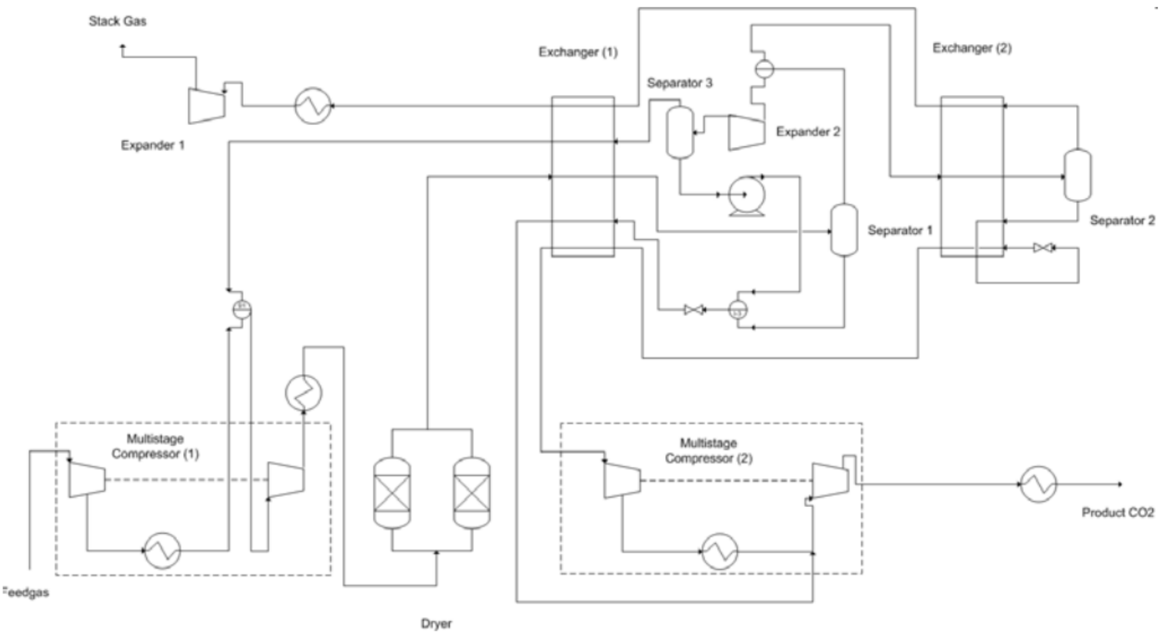


Figure 14 CANMET's pilot scale CO2 capture and compression unit

This CO_2CCU was designed for integration with the CANMET's $0.3MW_{th}$ oxy-fuel combustion facility and there were several system requirements for the unit:

- The ability to handle flue gas stream with different concentrations of CO_2 and impurities such as Ar, N_2, O_2, NO_x, SO_2, H_2
- The unit must be housed in a container mounted on a mobile trailer chassis for the consideration of transportation and relocation
- The unit must be able to run continuously and intermittently
- The ability to control all of the CO_2CCU functions though an independent control system, including requirements to control from a different location
- The venting of any non-condensable gases to atmosphere and the noise level must be consistent with standard compressed gas venting practices
- Sample points are available at preferred point of interest

Novel CO_2 cryogenic liquefaction and separation system (Xu et al. 2012)

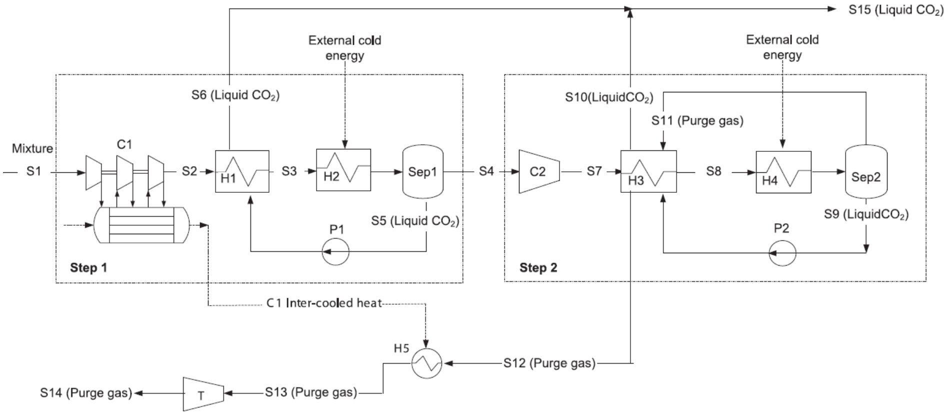
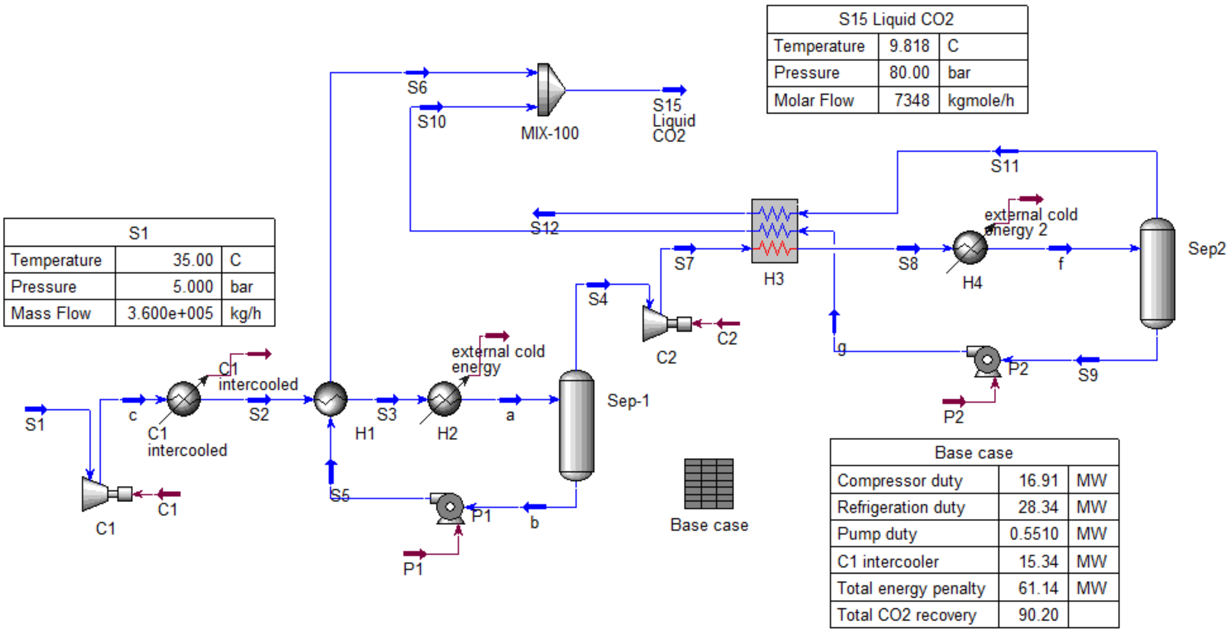


Figure 15 Novel CO_2 cryogenic liquefaction and separation system

Using a mass flow rate of 100kg/s of 80mol% CO_2 and 20mol% H_2, a novel cryogenic liquefaction and separation system which consists of two stage compressions, two stage refrigeration and two stage separations was developed by Xu et al. (2012). Using Aspen PLUS software and Peng Robinson property package, this study has claimed that two stage refrigeration and two stage separations can reduce energy demand for refrigeration and compression. It was given that the liquid CO_2 (stream S5) has a temperature of -31.7 ℃ and a pressure of 21 bar for first stage (Sep1) while -30.6 ℃ and 50 bar for stream S9 from second stage (Sep2). The final results claimed that for a CO_2 recovery ratio of 90%, the energy penalty for compression is **16.9 MW**, 19.85 MW for refrigeration, 0.52MW for pumping and the total energy penalty is 35.81 MW after recovering 1.57 MW from expansion. The final liquid CO_2 has a pressure of 80 bar and a temperature of 12.7 ℃, and a purity of 99.33 mol%.



S15 Liquid CO2		
Temperature	9.818	C
Pressure	80.00	bar
Molar Flow	7348	kgmole/h

S1		
Temperature	35.00	C
Pressure	5.000	bar
Mass Flow	3.600e+005	kg/h

Base case		
Compressor duty	16.91	MW
Refrigeration duty	28.34	MW
Pump duty	0.5510	MW
C1 intercooler	15.34	MW
Total energy penalty	61.14	MW
Total CO2 recovery	90.20	

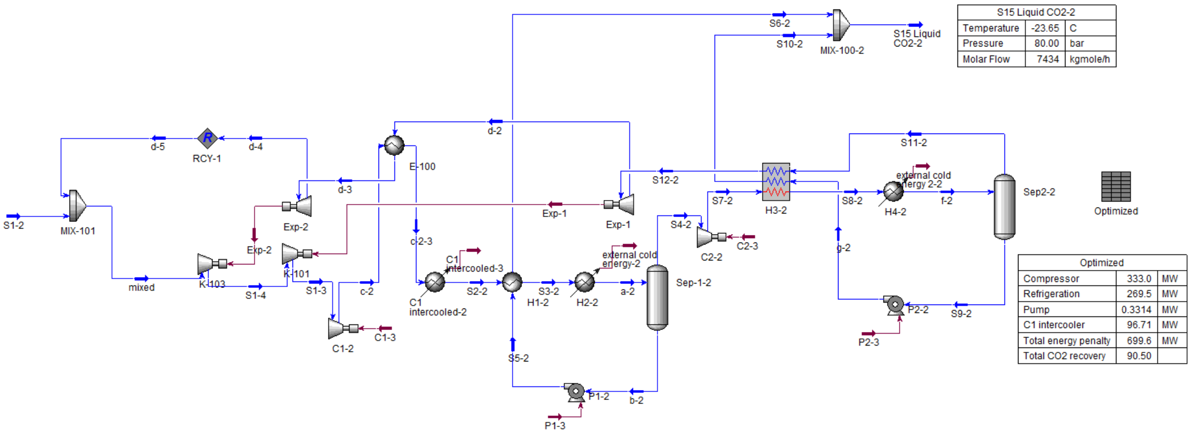
Figure 16 Novel CO2 cryogenic liquefaction and separation system (Aspen HYSYS)

The same process has been simulated using Aspen HYSYS® following the same feed condition, amount of equipment, configuration and property package. It is then observed that the novel system developed by Xu et al. (2012) has not considered the pressure drop across heat exchangers and more importantly the duty of intercooler for compressor C1 (15.34MW) has not been included in the total energy penalty. Xu et al (2012) also assumed 85% efficiency for compressors. Despite the reported CO_2 recovery ratio of 90%, an amount of 10kg/s purge gas was still depleted into atmosphere (Stream 12). Two stages compression/refrigeration/separation will be described further in Chapter 4.

Stream data

Table 5 Stream data for novel CO_2 cryogenic liquefaction and separation system

Stream	Temperature (℃)	Pressure (bar)	Molar flow rate (kgmole/hour)	CO_2 mol%	H_2 mol%
S1	35	5	10109.24	0.8	0.2
S2	35	21	10109.24	0.8	0.2
S3	-25	21	10109.24	0.8	0.2
S4	-35.60	21	4933.17	0.5943	0.4057
S5	-31.95	80	5176.07	0.9961	0.0039
S6	14.2	80	5176.07	0.9961	0.0039
S7	33.72	50	4933.17	0.5943	0.4057
S8	-13.5	50	4933.17	0.5943	0.4057
S9	-36	50	2172.17	0.9846	0.0154
S10	-1.758	80	2172.17	0.9846	0.0154
S11	-36	50	2760.99	0.2872	0.7128
S12	27	50	2760.99	0.2872	0.7128
S15	-23.65	80	7433.64	0.9927	0.0073



S15 Liquid CO2-2		
Temperature	-23.65	C
Pressure	80.00	bar
Molar Flow	7434	kgmole/h

Optimized		
Compressor	333.0	MW
Refrigeration	269.5	MW
Pump	0.3314	MW
C1 intercooler	96.71	MW
Total energy penalty	699.6	MW
Total CO2 recovery	90.50	

Figure 17 Modified novel CO_2 cryogenic liquefaction and separation system

S12 was left un-recycled by Xu et al.

Open CO_2 liquefaction cycle patented by (Aspelund, MØlnvik, and Koeijer 2006)

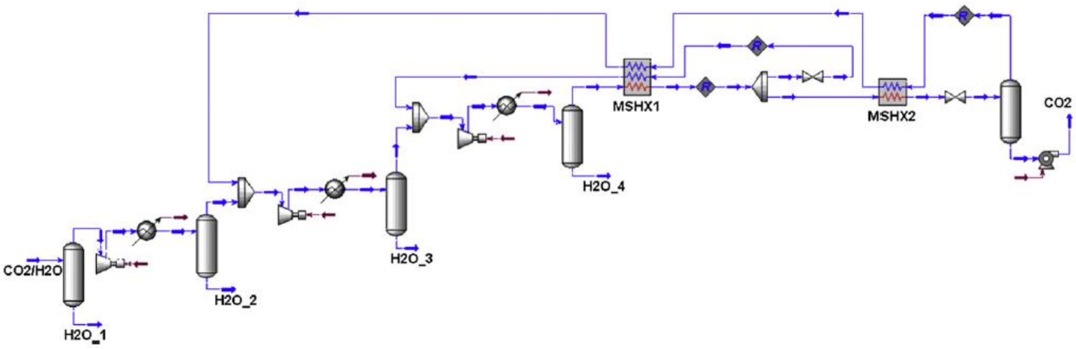


Figure 18 Open CO_2 liquefaction cycle

Aspelund et al. (2006) has patented an open CO_2 liquefaction cycle for liquefying CO_2 from a stationary source and has claimed that an open cycle which partially or fully uses CO_2 feed as refrigerant is the best method for large scale liquefaction of CO_2. Using the captured CO2 is liquefy itself is the working principle of this open cycle. Therefore Alabdulkarem et al (2011) modelled the open CO_2 liquefaction cycle using Aspen HYSYS as shown in figure above.

The open cycle consists of three compression stages, three intercoolers and two multi-stream heat exchangers. A portion of the compressed CO_2 is recycled and expanded through and expansion valve. Temperature of recycled CO_2 will be reduced due to the effect of expansion therefore it can be used to cool the incoming CO_2 feed stream. Then the recycled CO_2 in vapour state will be sent back to the feed of third stage intermediate compressor. Finally a final expansion valve is used to expand the compressed and cooled CO_2 to a low pressure at a saturation stage where the vapour and liquid are separated in the fifth gas liquid separator. Again the vapour CO_2 can be used for cooling before recycling it back to the feed of second stage intermediate compressor. Parameters such as seawater temperatures, the mass recirculation ratio and pressure values such as the discharge pressure of each compressor and the two pressure values for expansion will determine the power consumption of this open CO_2 liquefaction cycle. Alabdulkarem et al (2011) also found that the power consumption is not very sensitive to the mass recirculation ratio.

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, arrangement. The observation is that the final liquid CO_2 produced by this open cycle is at low pressure and low temperature which may be suitable for ship transport but not for high pressure transmission pipeline, unless it can be proven that pumping liquid CO_2 does not increase the temperature significantly which would cause the re-vaporization of liquid CO_2. The process conditions such as pressure and temperature must ensure complete removal of H_2O after the forth gas liquid separator to prevent freezing issues. Plus, the convergence of this model was not easy. Realistically speaking, the performance of this model is heavily dependent on the availability of low temperature sea water and/or air coolers therefore the site location because there is no requirement of refrigerant other than CO_2.

Low temperature syngas separation (Berstad, Anantharaman, and Neksa 2013)

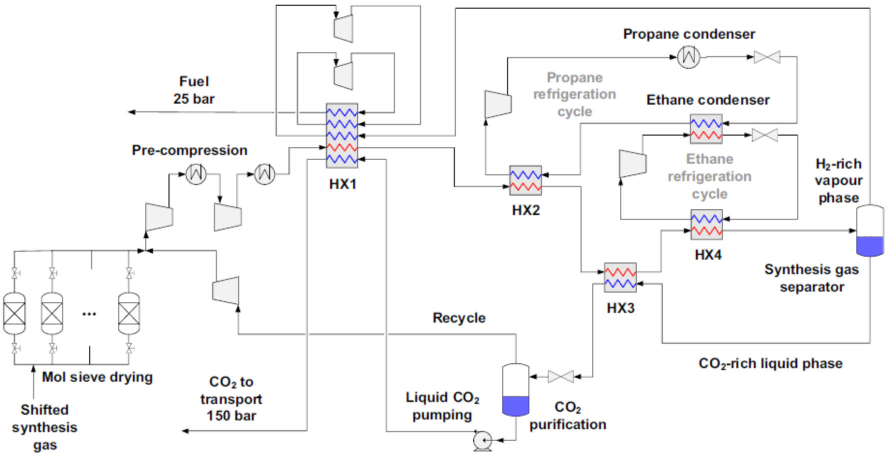


Figure 19 Low temperature syngas separation

Berstad et al. (2013) investigated the application of CO_2 capture for an integrated gasification combined cycle (IGCC) and developed two configurations, one for pipeline transport and one for ship transport. The shifted synthesis gas contains approximately 54 mol% H_2, 38mol% CO_2, 5 mol% N_2 and small fractions of CO and Ar and is firstly compressed to 110 bar from 35 bar feed pressure in order to increase the separation pressure level. A combination of auxiliary refrigeration and heat integration of process streams yields a liquefaction temperature of -56 ℃ at the synthesis gas separator and an overall CO_2 capture ratio (CCR) of 85%. The incondensable H_2 stream from the synthesis gas separator can be reused for cooling and expanded for more cooling before it is reused as fuel at 25 bar.

For a capture rate of 85%, Berstad et al. (2013) reported a specific power requirement for 8 bar ship transport of 321 kJ_e/kg CO_2 while 275 kJ_e/kg CO_2 for 150 bar pipeline transport. Therefore, Berstad et al. (2013) concluded that due to a higher requirement for auxiliary refrigeration, lower degree of process to process recuperation in the liquid CO_2 case, the specific power requirement is higher for producing liquid CO_2 for ship transport than for high pressure pipeline transport.

Process flow diagrams (PFDs) for two separation concepts, one for high pressure CO_2 pipeline and another one for ship transport, are given as below:

Figure 20 PFD for the case of high pressure CO_2 pipeline

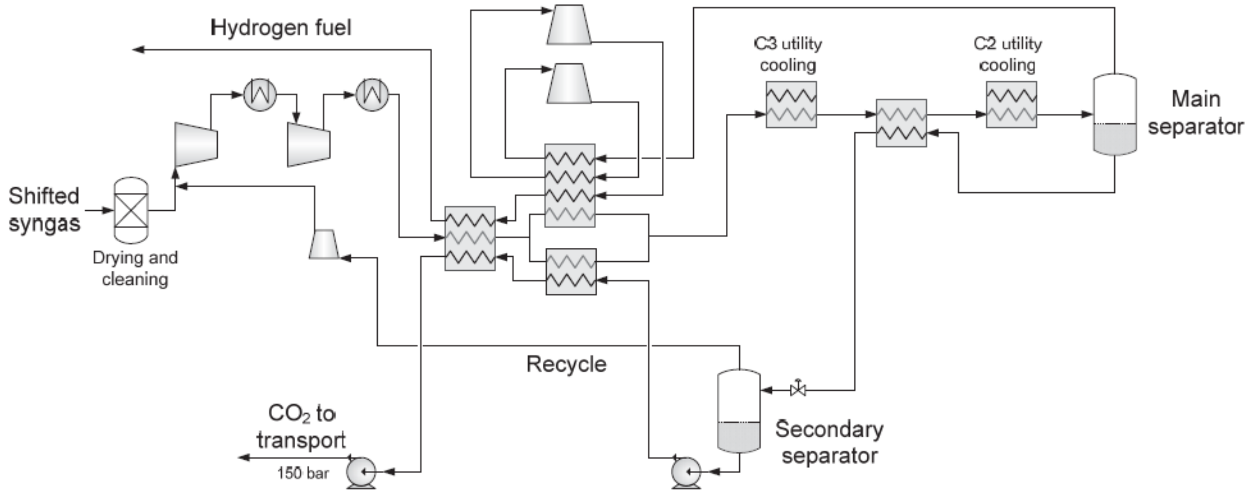
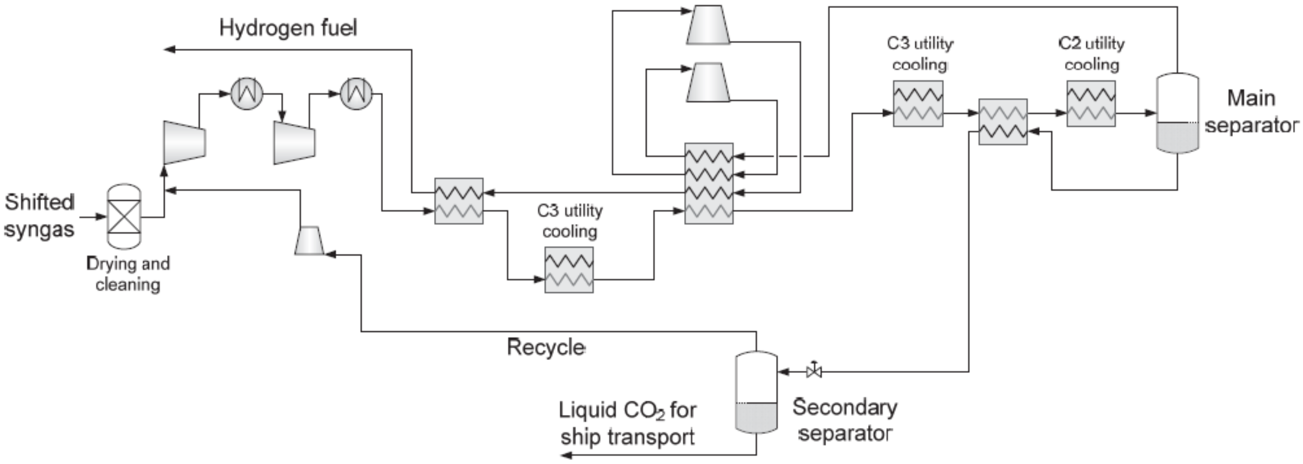


Figure 21 PFD for the case of liquid CO_2 for ship transport



Condensed rotational separation (CRS) (Benthum et al. 2011)

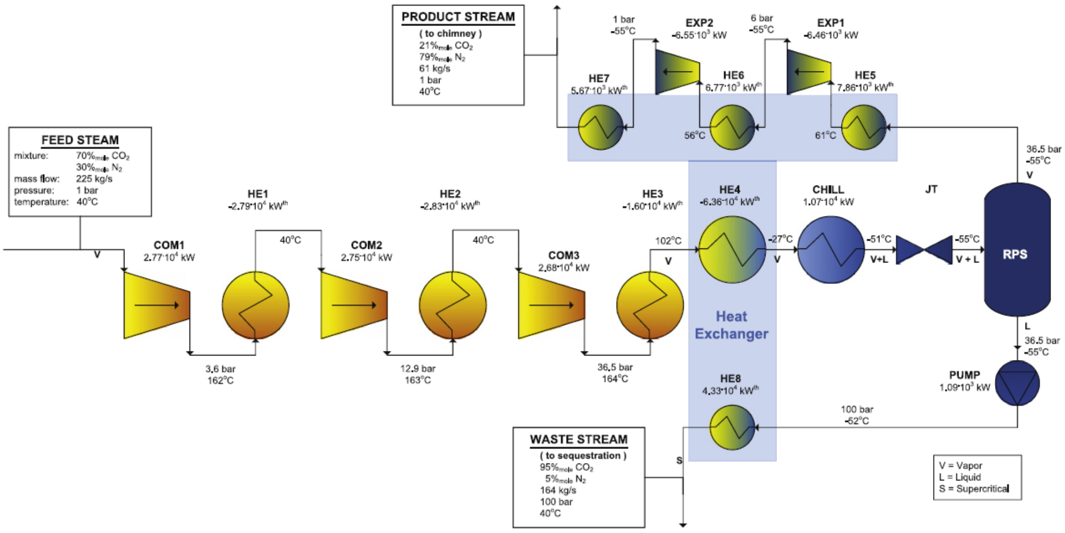


Figure 22 Condensed rotational separation (CRS)

Condensed Rotational Separation (CRS), as explained by Benthum et al. (2012), is a technique which requires partial purification of CO_2 to concentration above 50% prior to mechanical centrifugal separation using a rotational particle separator (RPS). Benthum et al. (2012) claimed that the feed must contain at least 70% CO_2 for the separation conditions of -55 ℃ and 36.5 bar to achieve 90% capture rate. A separation temperature of -55 ℃ can be used for any binary CO_2/N_2 mixture since the boundary line of the solids area is hardly affected by the CO_2 concentration. Separation pressure and the CO_2 concentration in the feed streams are two parameters which determine the separation performance and this statement is also supported by Xu et al. (2012). The CRS process developed in figure X above applies to a $500MW_e$ coal-fired power plant.

The rotational particle separator (RPS) is an axial flow cyclone containing a rotating element and is designed to separate large amount of liquid CO_2/H_2S droplets, down to 1 micrometre from a gas stream. The rotating element consist a very large number of axial channels of a few millimeters in diameters and micron-sized droplets are collected at the wall due to the centrifugal force in a channel. Benthum et al. (2012) explained that many RPS devices were designed for areas of application such as ask removal from flue gas, air cleaning in domestic appliances, product recovery in pharmaceutical and food industry and oil/water separation. Factors such as the size of separation element (length, radius, channel, height and etc), angular speed, flow rate, particulate matter shall be assessed for determining the separation efficiency.

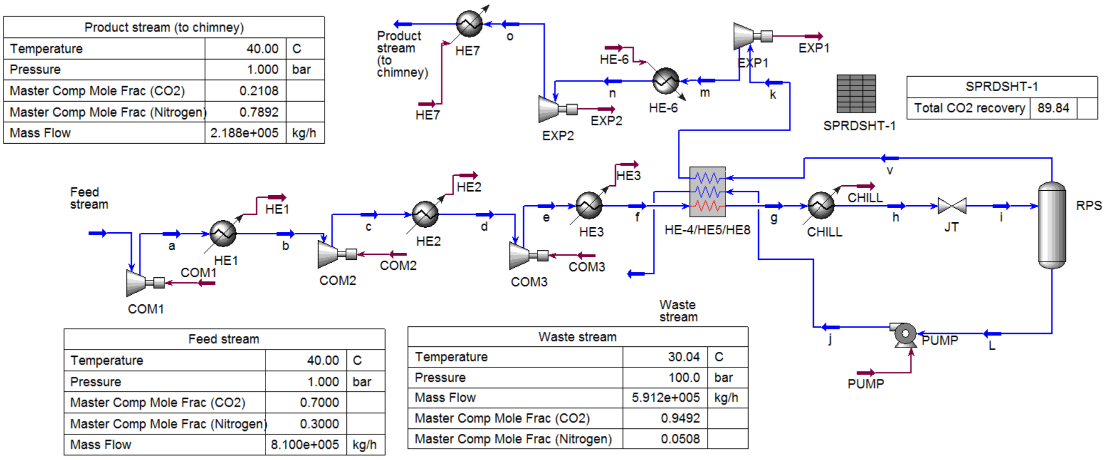
The same process has been simulated using Aspen HYSYS® using the same amount of equipment; arrangement except for rotational particle separator (RPS) was simulated using a 2 phase separator. There are several issues noticed:

- No pressure drop across the JT valve by comparing the discharge pressure of compressor (COM3) and product pressures of RPS. Therefore temperature reduction from -51 ℃ to -55 ℃ unexplained.

- Compressors (COM1, COM2, and COM3) have different adiabatic efficiencies due to specified discharge pressure and temperature.

- Pressure drop across each heat exchanger has not been specified therefore assuming 0 pressure drop.

- Temperature cross issue in multiple stream heat exchanger is not reported.



Product stream (to chimney)		
Temperature	40.00	C
Pressure	1.000	bar
Master Comp Mole Frac (CO2)	0.2108	
Master Comp Mole Frac (Nitrogen)	0.7892	
Mass Flow	2.188e+005	kg/h

SPRDSHT-1		
Total CO2 recovery	89.84	

Feed stream		
Temperature	40.00	C
Pressure	1.000	bar
Master Comp Mole Frac (CO2)	0.7000	
Master Comp Mole Frac (Nitrogen)	0.3000	
Mass Flow	8.100e+005	kg/h

Waste stream		
Temperature	30.04	C
Pressure	100.0	bar
Mass Flow	5.912e+005	kg/h
Master Comp Mole Frac (CO2)	0.9492	
Master Comp Mole Frac (Nitrogen)	0.0508	

Figure 23 Condensed rotational separation (CRS) (Aspen HYSYS)

A comparison for results is given as below:

Table 6 Comparison between results given by Benthum et al (2011) and Aspen HYSYS

Parameters	(Benthum et al. 2011)	Aspen HYSYS
Feed mass flow (kg/s)	225	225
Waste mass flow (kg/s)	164	164.22
Waste stream CO_2 mol%	95	95
Product mass flow (kg/s)	61	60.78
Product stream CO_2 mol%	21	21
COM1 duty (MW)	27.7	25.94
COM2 duty (MW)	27.5	25.79
COM3 duty (MW)	26.8	25.56
CHILL duty (MW)	10.7	**44.04**
HE1 duty (MW)	27.9	26.34
HE2 duty (MW)	28.3	27.25
HE3 duty (MW)	16	14.62
HE4 duty (MW)	63.6	**42.37**
HE5 duty (MW)	7.86	Integrated with HE4
HE6 duty (MW)	6.77	6.75
HE7 duty (MW)	5.67	5.67
HE8 duty (MW)	43.3	Integrated with HE4
PUMP duty (MW)	1.09	1.237
EXP1 (MW)	6.46	6.474
EXP2 (MW)	6.55	6.537

The mass flow rates for feed, waste and product stream given by Aspen HYSYS are very close to the results reported by Benthum et al. (2012). The energy consumption of this process is heavily dependent on the ability to recycle thermal energy from HE5, HE6, HE7 and HE8 back into HE4 and consequently save energy for ‘CHILL’. In Aspen HYSYS, only HE5 and HE8 have been recycled due to temperature cross issues. Potential energy savings can be achieved by reusing energy from EXP1 and EXP2 for feed compression.

Integration of Molten Carbonate Fuel Cell (MCFC) in a combined cycle with cryogenic CO_2 separation (Chiesa et al. 2010)

Chiesa et al. (2010) claimed that a carbon capture ratio of 80% can be achieved by integrating the Molten Carbonate Fuel Cell (MCFC), where CO_2 is moved from the cathode to anode side, cooled in the heat recovery steam generator and sent to cryogenic section. The layout of the cryogenic section is shown below:

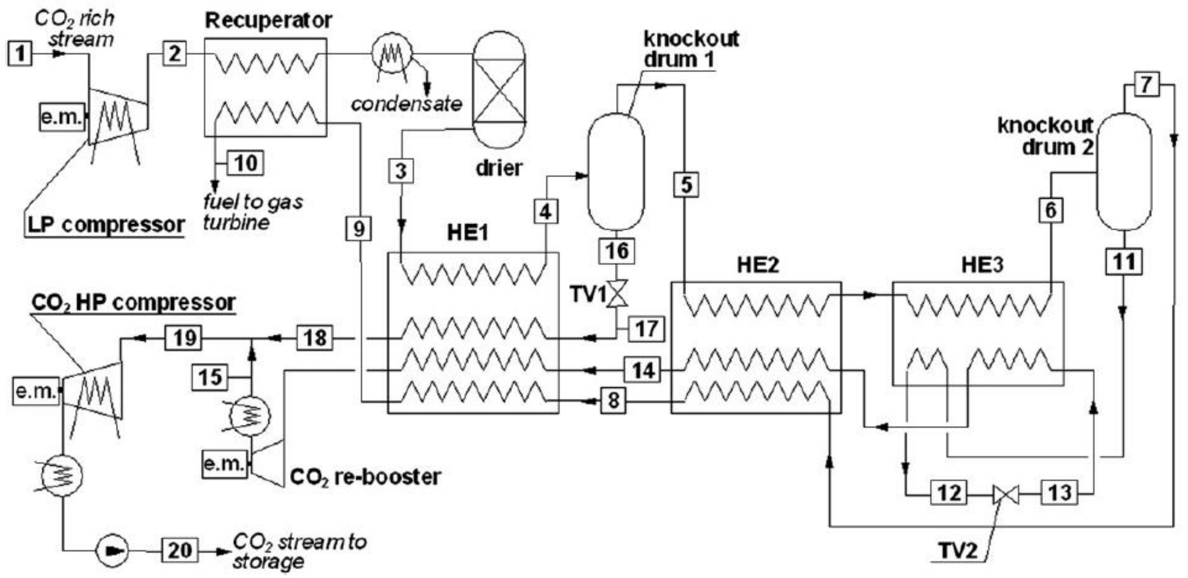


Figure 24 Integration of Molten Carbonate Fuel Cell (MCFC) in a combined cycle with cryogenic CO_2 separation

The cryogenic section is based on a two-step flash separation which reduces the compression power required to overcome the pressure losses imposed by the process. CO_2 rich stream (Stream 1), at 1 bar and 30 ℃, is compressed to 27 bar and cooled down to 121.4 ℃ by a 4 stages intercooled compressor. After passing through the drier (by circulation of triethylene glycol dessicant and/or molecular sieve), HE1 cools the partially condenses stream 3 and the temperature of stream 4 is set at -33 ℃ to minimize the overall compression power. Chiesa et al. (2010) claimed that the temperature of stream 4 is a determining parameter in this process because lowering its temperature is a trade-off between the duty of heat exchanger HE1 and the mass flow rate of the second stage condensate (stream 11) circulated to the CO_2 re-booster and the associated power. The liquid from first knockout drum (stream 16) is throttled though valve TV1 and is heated and evaporated in HE1. A 3 ℃ minimum approach in HE1 is ensured by the pressure drop in TV1 (11.7 bar). The final CO_2 product (stream 20) is pumped to 150 bar for transportation and has a purity of 98.8 mol%.

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, arrangement. The first observation is that the reported temperatures for feed stream 6 (-36.1 ℃) and product stream 7 (-53 ℃) are different. This is technically incorrect unless there was external refrigeration being applied to knockout drum 2 (the energy stream 2.894MW shown in HYSYS).

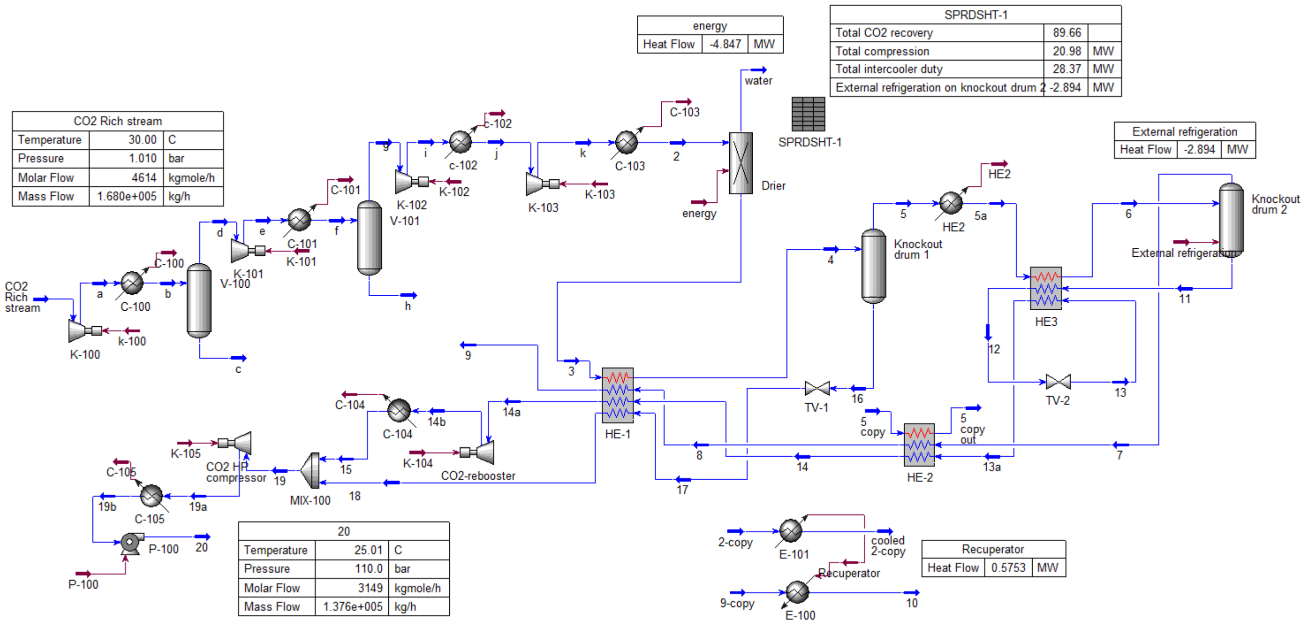


Figure 25 Integration of Molten Carbonate Fuel Cell (MCFC) in a combined cycle with cryogenic CO_2 separation (Aspen HYSYS)

A detailed comparison between the reported results given by Chiesa et al. (2010) and Aspen HYSYS is given in table below:

Table 7 Comparison between the reported results given by Chiesa et al. (2010) and Aspen HYSYS

	Chiesa et al. (2010)					Aspen HYSYS				
Stream	T ℃	P, bar	Vapour fraction	Kg/s	Kmol/s	T ℃	P, bar	Vapour fraction	Kg/s	Kmol/s
1	30	1.01	1	46.66	1.282	30	1.01	1	46.66	1.282
2	121.4	27	1	45.82	1.235	121.4	27	1	45.81	1.234
3	30	26.2	1	45.9	1.234	30	26.2	1	45.69	1.23
4	-33	25.7	0.476	45.9	1.234	-33	25.7	0.468	45.69	1.23
5	-33	25.7	1	17.62	0.5876	-33	25.7	1	17.15	0.575
6	-36.1	24.7	0.923	17.62	0.5876	-36.1	24.7	0.924	17.15	0.575
7	-53	24.7	1	7.664	0.3597	-53	24.7	1	7.48	0.354
8	-44.6	24.2	1	7.664	0.3597	-44.6	24.2	1	7.48	0.354
9	26.9	23.7	1	7.664	0.3597	26.9	23.7	1	7.48	0.354
10	76.4	23.2	1	7.664	0.3597	76.4	23.2	1	7.48	0.354
11	-53	24.7	0	9.957	0.2279	-53	24.7	0	9.675	0.2216
12	-42.9	24.7	0.001	9.957	0.2279	-42.9	24.7	0.0009	9.675	0.2216
13	-56	6.3	0.086	9.957	0.2279	-55.83	6.3	0.0883	9.675	0.2216
14	-44.6	6.1	1	9.957	0.2279	-44.6	6.1	1	9.675	0.2216
15	30	13.9	1	9.957	0.2279	30	13.9	1	9.675	0.2216
16	-33	25.7	0	28.27	0.6464	-33	25.7	0	28.55	0.653
17	-37.7	13.9	0.039	28.27	0.6464	-37.7	13.9	0.0411	28.55	0.653
18	17.6	13.6	1	28.27	0.6464	17.6	13.6	1	28.55	0.653
19	20.8	13.6	1	38.23	0.8743	20.66	13.6	1	38.22	0.8747
20	25	110	0	38.23	0.8743	25	110	0	38.22	0.8747

Several issues have also been noticed:

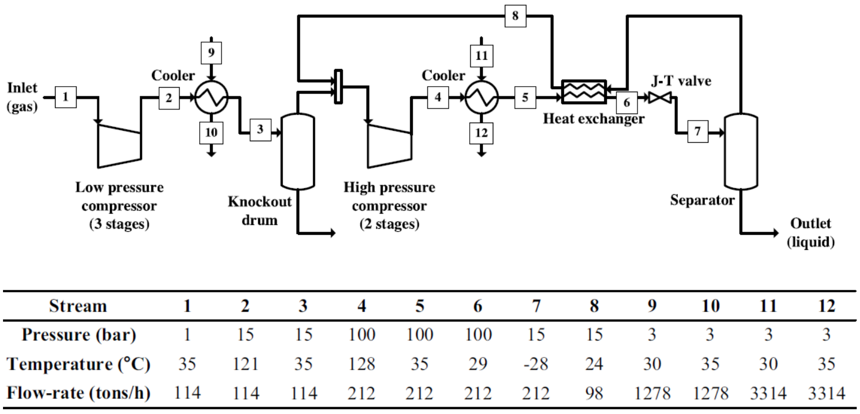
- 75% adiabatic efficiency, zero pressure drops has been assumed for all compressors and coolers.

Stream 9 has a temperature of 26.9 ℃ and is used to cool stream 2 with a temperature of 121.4 ℃. This is not economically feasible because only 0.5753 MW were recovered by ‘Recuperator’ (shown in HYSYS). This stream could have been used to cool the feed gas before entering a compressor, condense the water and save energy in downstream compressors and coolers.

- A total CO_2 recovery of 89.66% can be achieved however there is some issue in HE2 (shown in HYSYS). Despite of specifying the same pressure and temperature for stream 8 and stream 14, the outlet temperature of steam 5 from HE2 drops to -47.8 ℃.

Seo et al. (2005) compared four liquefaction systems for pure CO_2, three processes are open cycle and one process is closed. For open cycle, the working fluid is compressed and expanded and there is Linde Hampson system and the Linde dual-pressure system. On the other hand, the precooled Linde Hampson system and the closed system use refrigerant. The main purpose is to determine the optimal CO_2 liquefaction system for ship-based carbon capture and storage (CCS).

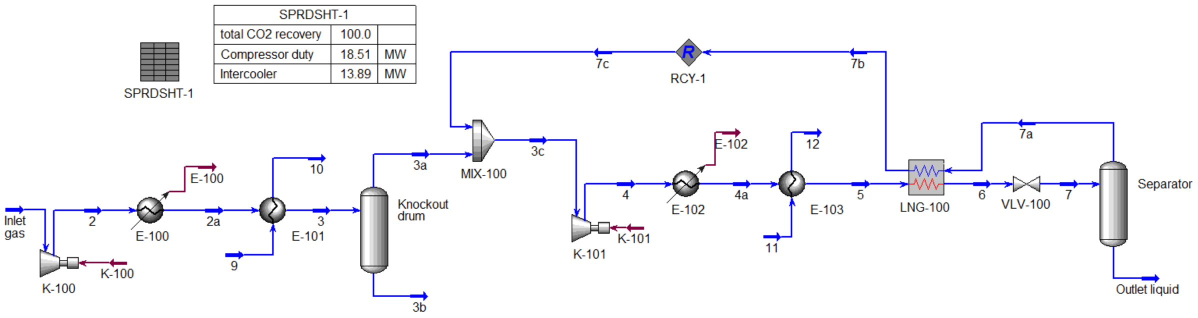
Linde-Hampson system (Seo et al. 2015)



Stream	1	2	3	4	5	6	7	8	9	10	11	12
Pressure (bar)	1	15	15	100	100	100	15	15	3	3	3	3
Temperature (°C)	35	121	35	128	35	29	-28	24	30	35	30	35
Flow-rate (tons/h)	114	114	114	212	212	212	212	98	1278	1278	3314	3314

Figure 26 Linde-Hampson system

This system utilizes a Joule Thompson valve to produce a cold gas stream to cool an incoming compressed stream which is similar to the open CO_2 liquefaction cycle patented by Aspelund et al. (2006) and modelled by Alabdulkarem et al (2011). A portion of gas is liquefied while the remaining cold gas is recycled to the heat exchanger. Seo et al. (2005) experimented different pressures from 75 to 200 bars after the compression and claimed that the performance of the system varies with the pressure after the compression. The final results show that the required energy decreases sharply from 75 to 100 bars then increase gradually up to 200 bars. As the pressure after compression increases, the recycled gas from the separator decreases therefore the required power of the compressor increases. The decreased flow rate of the recycled gas reduces compressor power.

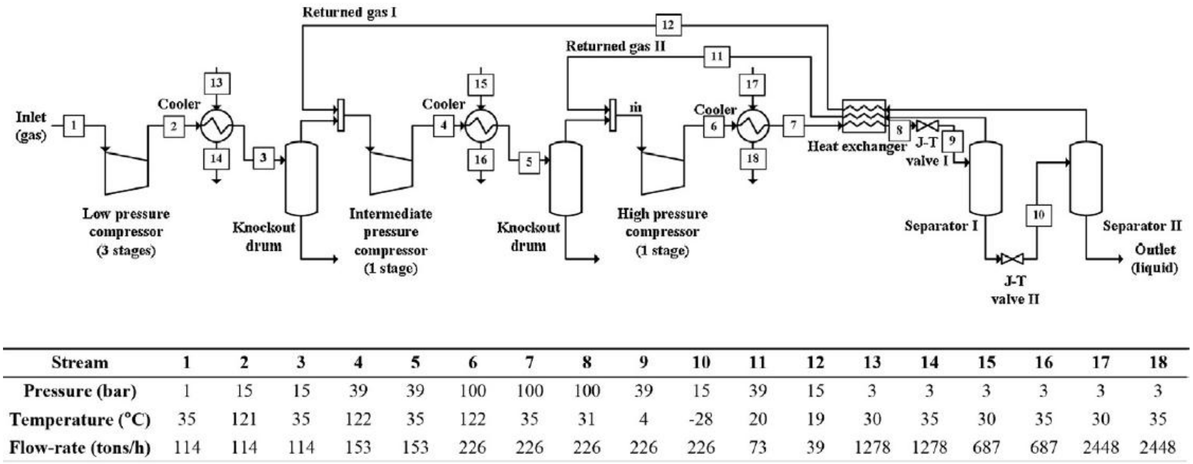


SPRDSHT-1		
total CO2 recovery	100.0	
Compressor duty	18.51	MW
Intercooler	13.89	MW

Figure 27 Linde-Hampson system (Aspen HYSYS)

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, operating conditions and arrangement. The observation is that intercoolers consume significant amount of energy 13.89MW. The pumping energy required to pump sea water at atmospheric pressure to 3 bar should also be addressed for both E-101 and E-103 coolers.

The Linde dual-pressure system (Seo et al. 2015)



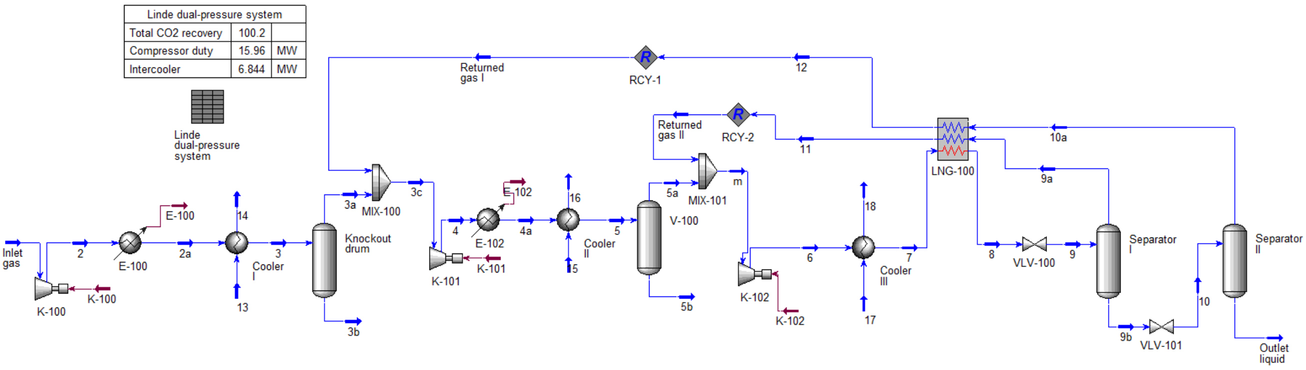
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Pressure (bar)	1	15	15	39	39	100	100	100	39	15	39	15	3	3	3	3	3	3
Temperature (°C)	35	121	35	122	35	122	35	31	4	-28	20	19	30	35	30	35	30	35
Flow-rate (tons/h)	114	114	114	153	153	226	226	226	226	226	73	39	1278	1278	687	687	2448	2448

Figure 28 The Linde dual-pressure system

This dual pressure system is the modification of the Linde- Hampson system and its performance is determined by the flow rate of intermediate pressure stream (the feed to high pressure compressor 1 stage) which varies with the flow rate of returned gas II. The flow rate of returned gas II is determined by the pressure of intermediate stream.

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, operating conditions and arrangement. The results agrees with Seo et al. (2005) that both intercoolers and compressors consume less energy compared to the Linde-Hampson system in figure 28. However, one drawback is that the duty of sea water (i.e. the amount of sea water) is higher than the one consumed by the Linde-Hampson system.

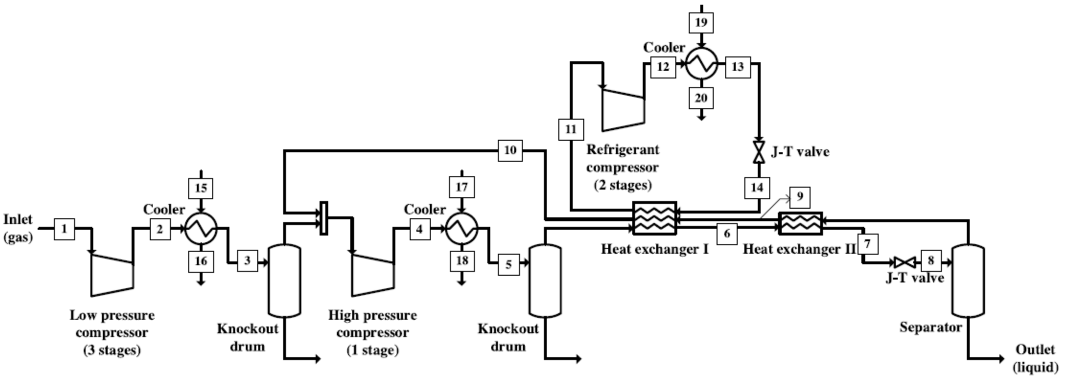
Seo et al. (2005) claimed that the compressor efficiency for multistage compression system increases due to smaller compression ratio of each stage. Again the pumping energy required to pump sea water at atmospheric pressure to 3 bar should also be addressed for Cooler I, II and III.



Linde dual-pressure system		
Total CO2 recovery	100.2	
Compressor duty	15.96	MW
Intercooler	6.844	MW

Figure 29 The Linde dual-pressure system (Aspen HYSYS)

The precooled Linde Hampson system (Seo et al. 2015)

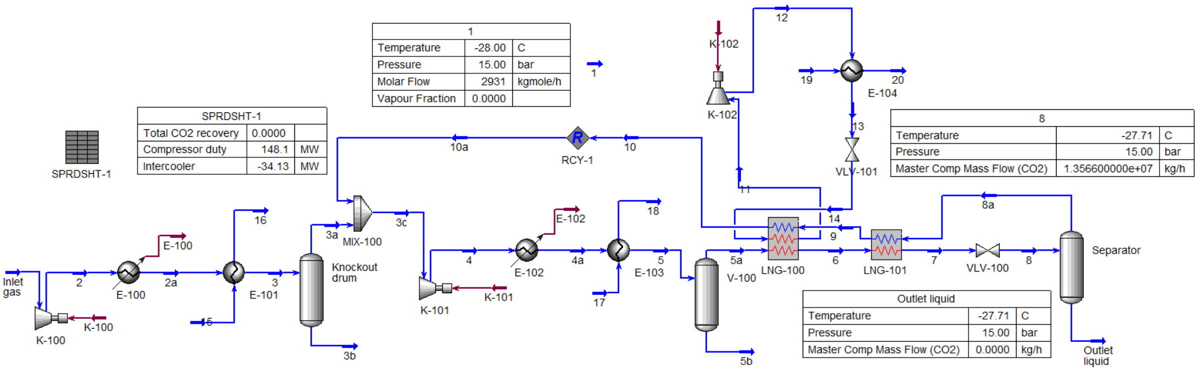


Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Pressure (bar)	1	15	15	25	25	25	25	15	15	15	2	14	14	2	3	3	3	3	3	3
Temperature (°C)	35	121	35	82	35	-11.4	-12	-28	-16	25	-14	125	35	30	30	35	30	35	30	35
Flow-rate (tons/h)	114	114	114	129	129	129	129	129	15	15	37	37	37	37	1278	1278	286	286	2475	2475

Figure 30 The precooled Linde Hampson system

The precooled Linde Hampson system uses a refrigeration system for decreasing the temperature of compressed gas. The performance of this precooled system depends on the pressure after compression and the load of refrigeration system. Seo et al. (2005) claimed that the best performance is when the pressure after compression is 25 bars and the load of refrigeration system is 3350 (US) RT.

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, operating conditions and arrangement. There is no liquid formation at -27.71 ℃ and 15 bar (stream 8). Using another stream (stream 1) for checking, CO_2 is completely in liquid phase at -28 ℃ and 15 bar. This makes the results given for the precooled Linde Hampson system questionable.



1		
Temperature	-28.00	C
Pressure	15.00	bar
Molar Flow	2931	kgmole/h
Vapour Fraction	0.0000	

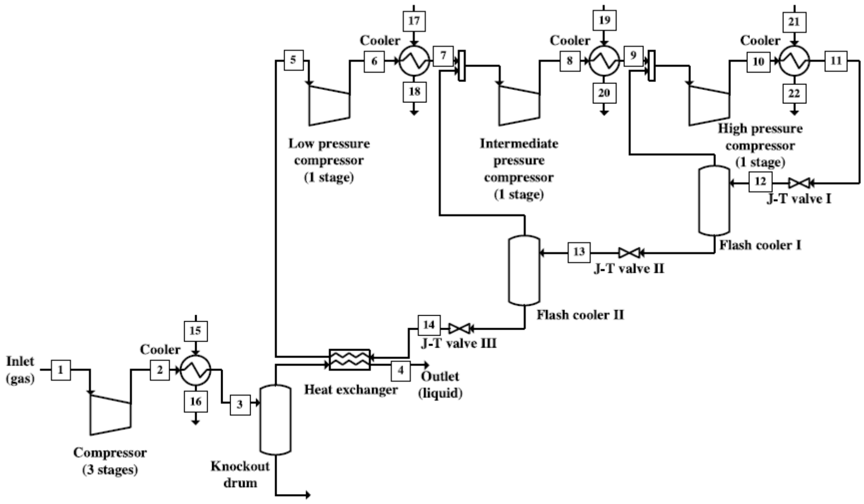
SPRDSHT-1		
Total CO2 recovery	0.0000	
Compressor duty	148.1	MW
Intercooler	-34.13	MW

8		
Temperature	-27.71	C
Pressure	15.00	bar
Master Comp Mass Flow (CO2)	1.356600000e+07	kg/h

Outlet liquid		
Temperature	-27.71	C
Pressure	15.00	bar
Master Comp Mass Flow (CO2)	0.0000	kg/h

Figure 31 The precooled Linde Hampson system (Aspen HYSYS)

The closed system (Seo et al. 2015)



Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Pressure (bar)	1	15	15	1	1	2.5	2.5	6	6	14	14	6	2.5	1	3	3	3	3	3	3	3	3
Temperature (°C)	35	121	35	-28	-31	42	35	117	35	118	35	9	-13	-32	30	35	30	35	30	35	30	35
Flow-rate (tons/h)	114	114	114	114	32	32	34	34	34	38	38	38	34	32	1278	1278	46	46	293	293	2427	2427

Figure 32 The closed system

The closed system shown above utilizes three stage refrigeration systems (i.e. a three-stage vapour compression system). A multistage vapour compression system consists of more than a single stage and has several compressors connected in series. Despite several disadvantages of multistage system such as high initial cost and more complicated system, Seo et al. (2005) explained the benefits of using multistage vapour compression stages instead of single stage and there are:

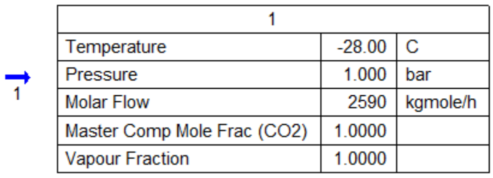
- Increased compressor efficiency due to smaller compression ratio of each stage

- Lower discharge temperature of the high compressor because the gas is superheated by the cold gas of the flash cooler at the intermediate stage

- Liquid refrigerant enters the evaporators at a lower enthalpy

The same process has been simulated using Aspen HYSYS® using the same amount of equipment, operating conditions and arrangement. Several issues have been noticed as follows:

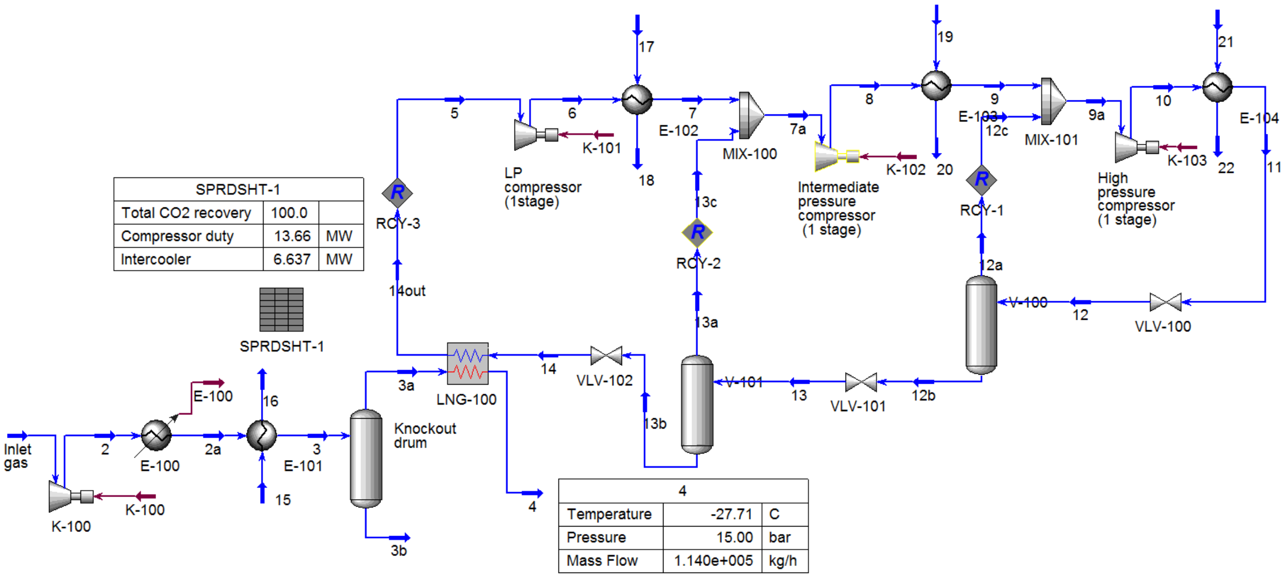
- The results show that CO_2 outlet is liquid at 1 bar and -28 ℃ (stream 4), referring to CO_2 phase diagram, the state is not liquid.



1		
Temperature	-28.00	C
Pressure	1.000	bar
Molar Flow	2590	kgmole/h
Master Comp Mole Frac (CO2)	1.0000	
Vapour Fraction	1.0000	

- Pressure reduction from 15 bar (stream 3) to 1 bar (stream 4) will result cause the CO_2 to freeze

- When mixing the recycled ammonia back to the feed of intermediate pressure compressor (1 stage), ammonia will be partially liquefied and cause issues in compressor.



SPRDSHT-1		
Total CO2 recovery	100.0	
Compressor duty	13.66	MW
Intercooler	6.637	MW

4		
Temperature	-27.71	C
Pressure	15.00	bar
Mass Flow	1.140e+005	kg/h

Figure 33 The closed system (Aspen HYSYS)

The performance of liquefaction systems proposed by Seo et al. 2015 may provide 100% recovery of CO_2. However, the energy required to pump sea waters for cooling has to be considered. These systems are also limited to 100% pure CO_2 and for ship based CO_2 capture. If there are other impurities such as nitrogen, hydrogen or water, the HYSYS simulation will not converge easily. Realistically speaking, these processes also have the constraint that is to build the liquefaction plant near the sea side due to heavily relying on sea water for cooling.

2.1.6 Other hybrid methods

A hybrid process offers a higher degree of freedom compared with a standard process and combines two or more ‘standard’ systems to compliment the advantages and disadvantages of each technology (Fong et al. 2013).

Two step vacuum membrane cryogenic hybrid (Merkel et al. 2010)

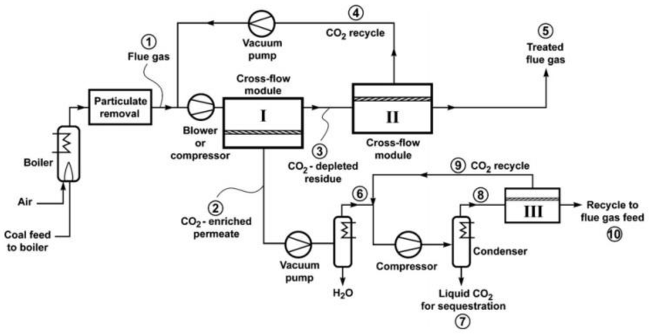
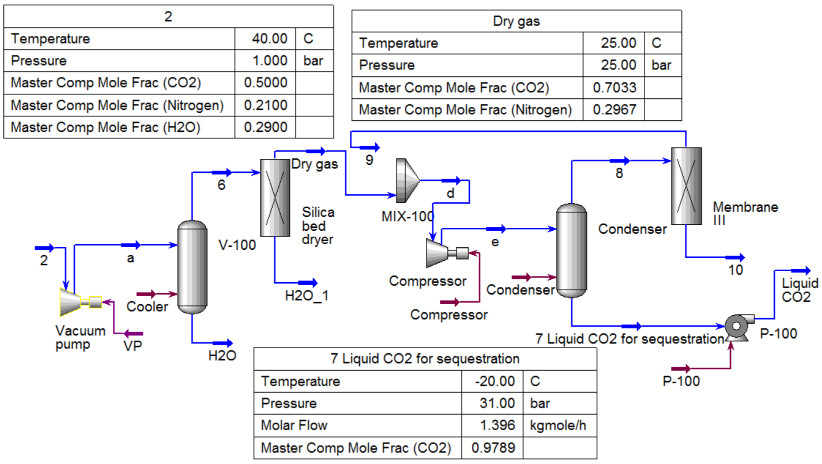


Figure 34 Process flow diagram for two step vacuum membrane process with cryogenics (Merkel et al. 2010)

A membrane and cryogenic hybrid process for achieving 90% CO_2 capture and producing 95%+ supercritical CO_2 for sequestration has been investigated as shown in Figure 35. This process consists of two membrane stages which are used to reduce the CO_2 composition from 11.6% (stream 1) to 1.8% CO_2 (stream 5). The wet permeate gas composition (stream 2) contains 50% CO_2, 29% H_2O and the rest should be N_2 based on material balance. Stream 2 is further compressed to 25 bar and cooled to room temperature. After removing all the traceable water, the captured CO_2 is compressed and liquefied at -20 ℃, the liquid CO_2 is pumped to 140 bar for sequestration and the uncondensed CO_2 (stream 8) is recycled to the feed of compressor. Stream 10 is recycled to feed flue gas of membrane stage 1. The permeate from the membrane stage 2 (stream 4) which contains 24% CO_2 is considered as too dilute to be combined with the permeate (stream 2). Therefore it is compressed and recycled to the feed of membrane stage 1. The permeate from membrane stage 3 is recycled to its own feed. There is a silica bed dryer (not shown) used to remove final traceable water. This study has claimed that this hybrid process achieves 90% CO_2 capture for a flue gas flow rate of using 131 MW of total compression and pumping power and 14MW for refrigeration.

Starting from stream 2, the same process has been simulated using Aspen HYSYS$^{®}$ using information available, amount of equipment, and configuration. Aspen HYSYS$^{®}$ is not able to simulate membrane and drying unit therefore a component splitter is used to represent the membrane and silica bed dryer. The component splitter does not take into account membrane properties such as permeance and selectivity which primary govern component separation. Due to insufficient information given for membrane stage 3, the recycle loop is left open. The observation is that vacuum pump needs to be able handle wet flue gas. At a liquefaction temperature of -20 ℃, 31 bar is the minimum pressure required for condensing CO_2. However to achieve sufficient liquefaction, higher pressure is needed so that more CO_2 can be liquefied. This would contribute to higher compressor duty and condenser duty.

The amount of energy required for cooling stream 2 to room temperature can be significant as well. Merkel et al.(2010) did not perform any energy optimization for cryogenic section.



2		
Temperature	40.00	C
Pressure	1.000	bar
Master Comp Mole Frac (CO2)	0.5000	
Master Comp Mole Frac (Nitrogen)	0.2100	
Master Comp Mole Frac (H2O)	0.2900	

Dry gas		
Temperature	25.00	C
Pressure	25.00	bar
Master Comp Mole Frac (CO2)	0.7033	
Master Comp Mole Frac (Nitrogen)	0.2967	

7 Liquid CO2 for sequestration		
Temperature	-20.00	C
Pressure	31.00	bar
Molar Flow	1.396	kgmole/h
Master Comp Mole Frac (CO2)	0.9789	

Figure 35 Two step vacuum membrane process with cryogenics (Aspen HYSYS)

Membrane cryogenic hybrid (Belaissaoui et al. 2012)

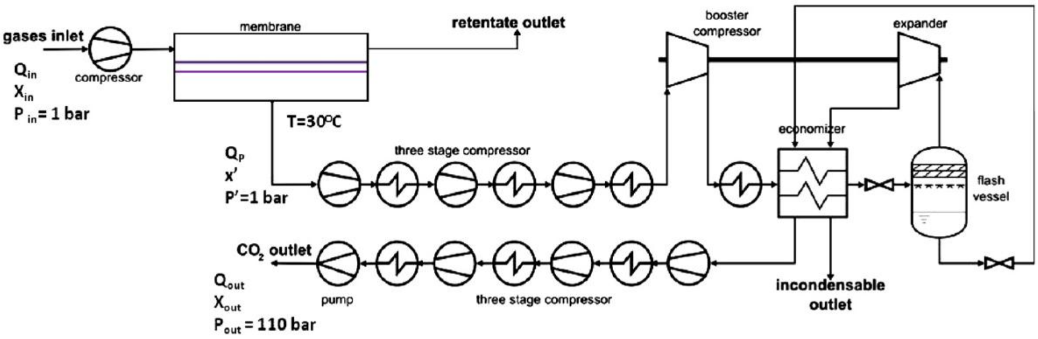


Figure 36 Membrane cryogenic hybrid

Another membrane cryogenic hybrid process has been modelled by Belaissaoui et al. (2012). Belaissaoui et al. (2012) stated that this hybrid process offers a reduced energy requirement compared to the reference technology, monoethanolamine (MEA) absorption for a feed concentration between 15-30%. After pre-concentrating the CO_2 using a one stage membrane module, the CO_2 gas is compressed by three intercooled stages and the process of heat integration is simplified by using an economizer. The liquid CO_2 captured is heated in the economizer, is further compressed to 90 bar by another three intercooled stages and is then pumped to the delivery pressure 110 bar. Simulation results given by Belaissaoui, et al. (2012) claimed that CO_2 product has a purity of > 92% and >94% CO_2 recovery can be achieved for a range of inlet CO_2 %. However, Belaissaoui et al. (2012) did not report the temperature cross issues in heat recovery exchangers and the handling of the incondensable outlet from the flash vessel and the waste (retentate) stream from the membrane module. More importantly, the reported outlet economizer temperatures (-73 ℃ to -125 ℃) and corresponding flash pressures (6 bar to 54 bar) has also entered the solid region of the CO_2 phase diagram. Belaissaoui et al. (2012) did not refer to the phase diagram while developing this hybrid system consequently these results is not reliable.

Table 8 Summary of liquefaction systems reported by different journal articles

Liquefaction systems	Feed specification	Liquefaction Pressure And Temperature	Total CO_2 recovery (mol%)	Compressors duty (MW)	Intercoolers (for compressor) duty (MW)	External Refrigeration Duty (MW)	Seawater coolers Duty (MW)
Linde Hampson system (Seo et al. 2015)	100 mol%, 31.67 kg/s CO_2 at 1 bar, 35 ℃	15 bar, -28 ℃	100	18.51	13.89	N/A	16.71
The Linde dual-pressure system (Seo et al. 2015)	100 mol%, 31.67 kg/s CO_2 at 1 bar, 35 ℃	15 bar, -28 ℃	100	15.96	6.844	N/A	21.21
The precooled Linde Hampson system (Seo et al. 2015)	100 mol%, 31.67 kg/s CO_2 at 1 bar, 35 ℃	15 bar, -28 ℃	Unknown due to either no liquid or vapour formation	Unknown due to either no liquid or vapour formation	Unknown due to either no liquid or vapour formation	Unknown due to either no liquid or vapour formation	Unknown due to either no liquid or vapour formation
The closed system (Seo et al. 2015)	100 mol%, 31.67 kg/s CO_2 at 1 bar, 35 ℃	1 bar, -28 ℃ (the phase is not liquid based on CO_2 phase diagram)	100	13.66	6.64	TBC	18.02
Two stage compression/ Refrigeration system (Xu et.al 2012)	80 mol% 100kg/s CO_2, at 5 bar, 35 ℃	1st stage: 21 bar, -31.7 ℃ 2nd stage: 50 bar, -30.6 ℃	90	16.9	15.34	28.34	N/A
Two step vacuum membrane with cryogenics (Merkel et al. 2010)	70 mol% CO_2, room temperature (exact temperature not reported)	25 bar, -20 ℃. -45 ℃ reported by Scholes et al. (2013) for the design without Membrane Stage III	90	Depending on the discharge pressure of vacuum pump	N/A	14	N/A
Open CO_2 liquefaction cycle (Alabdulkarem et al. 2012)	90 mol% CO_2, 80.47 ton/hr,	TBC by HYSYS	--	--	--	--	--
Membrane cryogenic hybrid (Belaissaoui et al. 2012)	1 bar, 30 ℃	6 bar to 54 bar, -73 ℃ to -125 ℃	--	--	--	--	--
Condensed rotational separation (Benthum et al. 2012)	70mol% CO_2, 225kg/s at 1 bar, 40 ℃	36.5 bar, -55 ℃	89.84	55.12 (after recycling energy from expanders)	68.21 (HE1+HE2+HE3)	32.62 (after recycling energy from HE6 and HE7)	N/A
Integration of Molten Carbonate Fuel Cell (MCFC) in a combined cycle with cryogenic CO_2 separation (Chiesa et al. 2010)	75mol% CO_2, 46.66kg/s at 1 bar, 30 ℃	24.7 bar, -53 ℃	89.66	20.98	28.37	2.894	N/A

N/A stands for ‘Not Available’, MW stands for ‘Megawatts’, TBC stands for ‘to be confirmed’

2.1.7 Summary for post combustion capture of CO_2

Capturing technology	Design Considerations	Advantages	Disadvantages
Amine absorption (MEA)	- The solubility of the CO_2 in the solvent - The reactive properties of CO_2 and the solvent - Operating pressure - Amine circulation rate	- High chemical potential (or driving force) can be provided for selective capture from streams with low CO_2 partial pressure - Wet scrubbing allows good heat integration and ease of heat management - The process technology is mature	- Low CO_2 loading capacity of solvent - Solvent cannot be fully regenerated (solvent loss by evaporation) - Amine concentration (higher concentrations favour corrosion) - Amines are in a water solution therefore the treated gas leaves saturated with water - Operational issues such as foaming, flooding, entrainment and channelling - Amine degradation due to O_2 rich environment, SO_x and NO_x and particulate matter - High energy consumption during solvent regeneration - Huge plant footprint
Adsorption	- For adsorbent: its lifetime, CO_2 selectivity, CO_2 adsorption capacity, BET (Brunauer-Emmett-Teller) surface area, micro pore volume, nominal pore size, particle density, tolerance to impurities and water, cost of adsorbent - Feed gas temperature, pressure, concentration and water concentration - For the bed: effective working length, internal diameter, wall thickness, adsorbent loaded, bed bulk density, sample loading - Evacuation pressure and time - Adsorption time, desorption time, re-pressurization time - Vacuum pressure for VSA	- Chemical sites provide large capacities and fast kinetics enabling capture from streams with low CO_2 partial pressure - High capacities on a per mass or volume basis than similar wet-scrubbing chemicals - Low heating requirements than wet-scrubbing in many cases (CO_2 and heat capacity dependent) - High adsorption capacity can be achieved at mild conditions (0-100 ℃, 0.1-1 bar) therefore suitable for post combustion gas streams	- Presence of SO_x and NO_x, and water can significantly impact the adsorbent's performance - The desorption process is energy and time intensive process - The need of cooling and drying the flue gas for pressure swing adsorption and vacuum swing adsorption
Gas separation membrane	- Pressure drop across the membrane therefore the mechanical strength of the membrane - Permeability, selectivity, thickness and cost of membrane - Membrane skid cost - Flow rate of feed gas per unit area - Operating temperature - Operating pressure - Vacuum pressure - Compressor, turbo expander, vacuum pump efficiency - Flow arrangement (counter current, parallel, radial cross flow, etc)	- Simplicity of the process, no moving parts for single stage units, process can be run unattended - Low capital investment compared with solvent systems - Compact design, ease of installation, units are usually skid mounted, good weight and space efficiency (especially for offshore application) - No chemicals needed therefore no waste disposal by-products are generated - Higher separation energy efficiency relative to equilibrium based processes - Mature application to other industrial processes such as air separation and hydrogen recovery	- Feed to membrane must be clean - Poor balance between permeability and selectivity - The inverse relationship between permeate concentration and component recovery - Gas stream must be compressed to high pressure for efficient separation (the need of huge and energy consuming compression equipment) - High temperature of flue gas will degrade the organic membranes - Issues with polymeric membrane such as penetrant induced plasticization (hardening), compaction, physical aging, competitive sorption, fouling - Single stage membrane system is usually incapable of high CO_2 recovery, therefore multistage is required
Cryogenic condensation	- CO_2 concentration of feed gas - Liquefaction temperature - Operating pressure - Freezing temperature of CO_2	- No chemical reagents are required - CO_2 can be liquefied at high concentration - Liquid CO_2 is produced at relatively low pressure, avoiding huge compression energy required to compress the pressure for transportation and sequestration - Liquid CO_2 can be transported easily using pipeline and be re-used as refrigerant before entering the pipeline	- Water content of the feed stream must be removed to prevent equipment plugging from the formation of ice - High capital cost of equipment - Substantial energy consumption required for refrigeration and compression - Freezing of CO_2 (solidification) must be avoided to prevent blockage of pipes

Table 9 Summary for post combustion capture of CO2

2.2 Transportation of CO_2

CO_2 can be commercially transported as a gas and liquid by pipes, tankers, cargo vessels, barges, trucks or railroad cars. Many studies have stated that large scale implementation of carbon capture and sequestration (CCS) would require a transmission system to efficiently and economically transport CO_2 from the capture site to the permanent storage site. It is then recognized that one of the practical ways to transfer dense phase CO_2 (either supercritical fluid or sub-cooled liquid) in large quantity would be a dedicated pipeline network. This is based on the experience that several millions of tonnes of CO_2 have been transported by pipelines mostly for (EOR) enhanced oil recovery fields in United States, Canada and Norway (Lauer 2008).

CO_2 has to be transported in high density if it is in a large amount. The dense phase of CO_2 exist in the phase diagram for pressure and temperature combinations above the vapour (gas)- liquid line and under the solid-liquid line. Solid CO_2 (dry ice) has a theoretical density of 1500kg/m^3 however it seems uneconomical due to complex handling procedures. Zhang et al. (2005) has proposed that transporting gaseous CO_2 is disadvantages due to its low density and results in higher pressure drop and larger pipe diameter. However, Knoope et al. (2013) defended that gaseous CO_2 transport may be cost effective if the mass flow rates are relatively small; pressure requirement is less than 80 bar and for short distance. Another attractive way of transportation is by semi-pressurized ship which is similar to the one for transporting liquefied petroleum gas (LPG) and ethylene. However ship transportation will consume space and extra cost for constructing an intermediate storage before the ship docks, loading and unloading system. Therefore, this thesis is written in the context of transporting a large amount of CO_2 from single source to an onshore injection site using a buried pipeline, for example the CO_2 captured from a 500MW coal fired power plant, and at high pressure for the requirement of storage / sequestration site.

Neele et al. (2014) has summarized the advantages and disadvantages for two transportation method:

Table 10 The advantages and disadvantages for two transportation method

Transportation method	Advantages	Disadvantages
Pipeline	- Low operating expenditure - The need for onshore compression - Can be built both onshore and offshore	- High capital cost - Relatively low flexibility - Low potential for re-use - Large sunk cost
Ship	- Low capital expenditure - Large flexibility (volume and route) - Re-use potential - Lower sunk cost - Short delivery time	- High operating expenditure - The need for onshore intermediate storage and liquefaction plants

2.2.1 Pipeline transportation

CO_2 pipeline are usually operated at ambient temperature and high pressure and the pipelines consist of primary compressor stations located at the injection points and booster compressors located as needed further along the pipeline. CO_2 is a difficult gas to compress because it behaves like liquid at its supercritical compression (Saxena et al, 2006). The construction of CO_2 pipelines is similar to natural gas pipelines (Parformak et al, 2009). The former Soviet Union has built a total of 54000km of 58inch natural gas pipelines which equals to 1.4 times the distance around the equator (Skovholt, 1993). Therefore it is highly expected that same attention to design, monitoring for leaks, and protection against overpressure.

Zhang et al. (2006) studied both pipeline transportation schemes for supercritical state transport and sub-cooled liquid transport and concluded that transporting sub-cooled liquid states has the advantages such as lower compressibility; higher density for the considered pressure range therefore offers smaller pipe sizes and lower pressure losses. Zhang et al. (2006) also concluded that pipeline transportation of sub-cooled liquid CO_2 can be ideal for areas of cold climate by burying and insulating the pipeline.

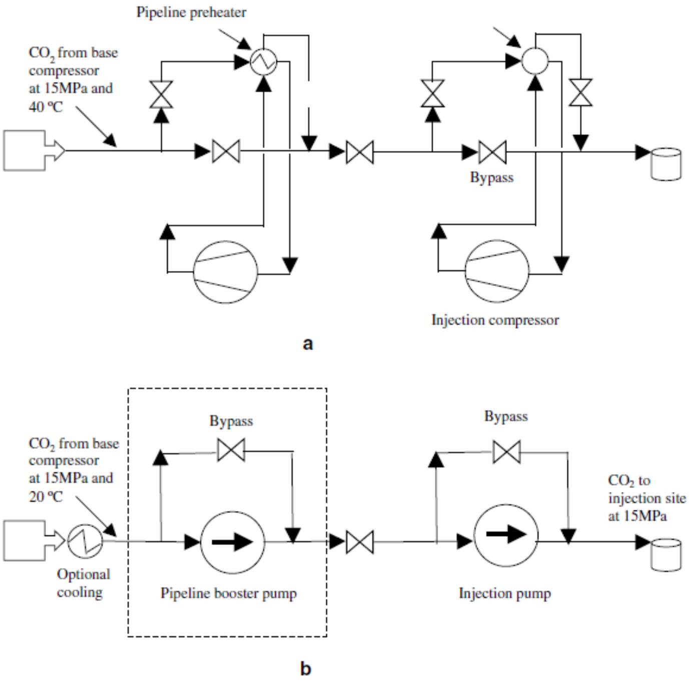


Figure 37 CO_2 transport: (a) supercritical transport of CO_2 using compressor (b) liquid transport of CO_2 (Zhang et al. 2006)

On the other hand, Wang et al. (2013) analysed the economics of using oversized and parallel pipelines for different typical pipeline length and CO_2 flow rates combinations. Wang et al. (2013) highlighted the benefits of using oversized CO_2 pipelines under several simplified CCS development scenarios.

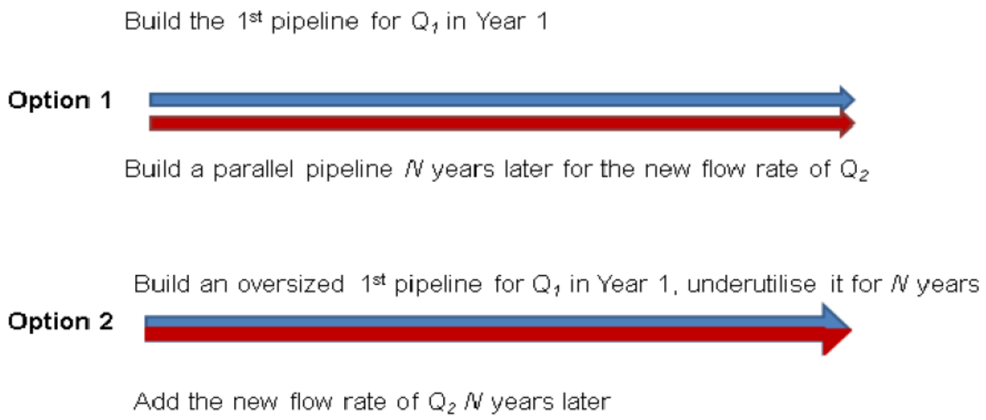


Figure 38 Oversized CO_2 pipelines under several simplified CCS development scenarios

CO_2 pipelines do have an excellent safety record which proven by a report issued in 2004 that no injuries or fatalities associated with CO_2 pipelines found in the United States during the previous 13 years. A CRS report has claimed that the oldest long distance CO_2 pipeline is in Texas, United States which has 225km. This Canyon Reef Carriers Pipeline began its service in 1972 for Enhanced Oil Recovery (EOR) in regional oil fields. Approximately 5800 km of CO_2 pipelines are operating today in United States (Parfomak et al, 2009) therefore we can conclude that pipeline transportation of CO_2 is accessible.

CO_2 pipeline shall be designed according to industry recognized standard and applicable regulatory requirements. The pipeline layout usually consists of various valves as well as intermediate pump/compressor stations and instrumentation within the battery limits. Various codes and standards are available and applicable to pipeline design and operation including the US Federal Code of Regulations, ASME standards B31.4 and B31.8 (B31.8s), IP6, BS EN 14161, BS PD 8010, ISO13623 and DNV OS-F101. ASME pipeline design code (ASME B31.4) and Federal Regulations (49CFR195) are recommended for CO_2 pipeline practice. The construction technique shall also be in accordance with the requirements of AS2885 and the Australian Pipeline Industry Association Code of Environmental Practice.

The optimized design of a CO_2 pipeline system requires the determination of the optimum pipeline diameter (Kaufmann, 2008). Piping design is governed by 'design factor' which defined as the ratio of hoop stress to the specified minimum yield stress (SMYS) of the pipe material. A design factor of 0.72 is suggested by ASME for liquid hydrocarbons and other liquids and this value is widely used around the world (ElementEnergyLimited, 2010).

The optimization of the pipeline cost model requires the determination of the optimum pipeline diameter and to obtain that, it involves the development of pipeline performance model. The pipeline performance model developed by (McCoy 2008) consists of several basic design parameters such as the fluid density, fluid viscosity, Reynolds number (RE), friction factor, pipe diameter and length. Knoope et al. (2013) identified several types of cost models exist in literature such as the linear models, models based on the weight of the pipeline, quadratic equations and CMU model but these models have their own limitations. These models are shown in figure below.

CO_2 Pumps

The centrifugal pump technology used for pumping liquefied gases may be applied to liquid CO_2 because of their similarities in viscosity, density and compressibility. (Bergamini, Vescovo, and Milone 2011) has claimed that currently available centrifugal technology can provide a discharge pressure of 25MPa. Similar to the case of centrifugal compressors, the high compressibility of supercritical CO_2 must be taken into account during the selection of pump. Specifically for CO_2 pump, the optimization of the intermediate pressures between the last compression stage and pump inlet is necessary for the overall train consisting compressor and pump. Constraints to be considered include the available cooling power, the total footprint, the cooling temperature when heat recovery is possible, the operating range and the different duty points that may be applicable in future.

A plunger pump has a piston which moves in and out of a cylinder, only moves the fluid and does not develop pressure. Unlike a centrifugal pump, the downstream pressure has to be determined by the downstream piping system. According to (Pumps 2014), a plunger pump utilizes spring-loaded closed and hydraulically opened inlet and discharge valves to direct flow though the pump manifold. The plunger displaces the liquid in the manifold chamber and forces the discharge valve to open at the beginning of the stroke. The discharge valve will close when the plunger reaches the end of the stroke.

In this research program, a Jaeco Hi-Flo^{TM} packed plunger metering pump shown in figure X below has been used to pump liquid $CO_{2.}$

Figure 39 Jaeco Hi-Flo packed plunger metering pump

Pump stations

AS2885 has notified that the pump station shall be designed, constructed and maintained so that equipment is protected from damage due to accident, third party damage and other random causes. The pumping station should also comply with requirements of the engineering design for safety of operating personnel and the public and for performance and operation.

Firstly ventilation should be provided for a pump station to ensure normal operating conditions and keeping the accumulation of dangerous concentration of carbon dioxide gas to the minimum. More than one emergency exit should also be available for emergency evacuation from the inside of pump station. AS 2885 has specified a distance of less than 25m from any point of the building to the nearest exit, it is measured along the centrelines of walkways and stairways. The emergency exit door shall open from inside without the use of a key and shall open in the direction of egress.

Overpressure protection shall also be provided if a pump produces excessive pressure against a closed outlet, or change in ambient temperature in closed section of piping. Overpressure protection would shut down the source of the overpressure and relieve the system at a rate sufficient to prevent unsafe pressure.

An emergency shutdown system is also needed to totally or partially shut down the station in an unsafe event such as fire, control system failure, excessive temperature or pressure, leakage of carbon dioxide or any flammable chemicals. The power supply to the pump station shall be independent so that it can be shut down in an emergency.

For the fence around the pump station, AS2885 has specified that the fence should be at least 2meter to restrict unauthorized entry and appropriate warning and prohibition sign is carried on each side.

Safety issues

Previous study has identified that one of the major hindrances in getting approval for the construction of a CO_2 transmission pipeline would be the concern of potential leakage or rupture from landholders and community residents close to the proposed pipeline route. A comprehensive supervisory control and data acquisition (SCADA) system and leak detection system is required for monitoring the pipeline operational parameters and isolating the proposed pipeline in the event of any leakage or rupture.

Subcooled liquid transport may receive the operational benefits in areas with cold climates however if the pipeline has to go through areas with warm climates like summer, periodic cooling will be required. The location for intermediate cooling station is subject to the availability of underground well water, electricity and/or fuel (for onsite generation of electricity if there is no power grid nearby). Otherwise, cooling water and fuel has to be provided by domestic tanker or via another pipeline and this will contribute extra cost. For areas with extremely hot weather such as countries with tropical climate, intermediate refrigeration has to be considered for reliquefying CO_2 and this will cause the whole transmission process extremely uneconomical.

2.2.2 Design consideration for CO_2 pipeline

Three main factors influencing the flow process of CO_2 along the pipeline have been identified as:

- Friction force, which is a function of CO_2 viscosity and flow velocity - this will hinder the CO_2 fluid.
- Heat conduction between CO_2 and environment (mostly soil since long distance pipeline are usually buried).
- Elevation change (Zhang et al. 2011).

A flow of 9684 kgmole/hour (equivalent to 3.7 million tonnes per annum MTPA) of CO_2 at 31.12 ℃ and 110 bar, mass density of 709.5 kg/m^3, viscosity of 4.82x10^{-5} Pa s, has been applied in the modelling process. This mass flow rate value is similar to one 500MW power plant with an annual mass flow of 3.98 MTPA (Chandel, Pratson, and Williams 2010) and the Gorgon Project led by *Chevron* which will be designed to capture 3.5 MTPA of CO_2 from Greater Gorgon gas fields. This feed to the pipeline is the liquid product from a cryogenic hybrid and has a molar percentage as below:

Component	Mole percentage (%)
CO_2	98.6
N_2	1.4
Total	100

There are some basic requirements for transporting CO_2 in a pipeline such as high pressure, high density, low viscosity and single phase. A phase diagram (Fig.1) with identified typical envelope for operation of liquid CO_2 pipeline has been given by DNV standards (DNV 2010). It is clear that when the fluid temperature decreases along the pipeline due to heat exchange with the surrounding soil and fluid pressure decreases along the pipeline due pipe friction affects, saturation line has to be avoided for maintaining the CO_2 at liquid state.

Pipe material

Several aspects have to be evaluated when choosing the piping materials for example (Peter et al, 2004):

- possible exposure to fire with respect to the loss in strength or combustibility of pipe and support
- susceptibility of the pipe to brittle failure or thermal shock failure when exposed to fire
- ability of thermal insulation to protect pipe from fire
- susceptibility of the pipe and joints to corrosion or adverse electrolytic effect
- susceptibility of packing, seals, gaskets and lubricants used on joints and connections
- refrigeration effect during sudden loss of pressure with volatile fluids
- compatibility with fluid handled

Aspen HYSYS is able to take into account the heat transfer aspect of a pipeline by offering different pipe materials. Carbon steel is the most attractive alternative for long distance pipelines whereas 13% Cr steel can be considered for shorter distance CO_2 transport (Patchigolla and Oakey 2013). Mild steel with default pipe roughness value of $4.572\text{x}10^{-5}$m has been selected for modelling (McCoy and Rubin 2007) and this roughness height is also cited by Perry's handbook (Perry, Green, and Maloney 1987). X70 steel with a roughness of $4.57\text{x}10^{-5}$m, conductivity of 25 (W/mk) has also been used (Zhang et al. 2011).

Table 11 Available pipe material and corresponding pipe wall conductivity

Pipe material	Default roughness (m)	Default pipe wall conductivity (W/mK)
Mild steel	$4.572\text{x}10^{-5}$	45
Asphalted iron	$1.22\text{x}10^{-4}$	45
Galvanized iron	$1.52\text{x}10^{-4}$	45
Cast iron	$2.59\ \text{x}10^{-4}$	48
Smooth riveted steel	$9.14\text{x}10^{-4}$	45
Rough riveted steel	$9.14\text{x}10^{-3}$	45

Pipe size

Several technical features of the pipeline must be provided in order to estimate the diameter, length and allowable pressure drop for a given mass flowrate of CO_2. Two equations available for estimating the diameter of CO_2 pipeline are given as below:

MIT formula

$$(P2 - P1) = 32\frac{Lfm^2}{\pi^2 \rho D^5}$$

Where
P1 and P2 are the pressures in Pascals at the beginning and end of the pipe; L is the length of the pipe in metres; f is the Fanning friction factor; m is the mass flow rate in kg/s; ρ is the density in kg/m^3; D is the diameter in metres
This formula does not take into account for change in altitude.

Carnegie Institute of Technology formula

$$D = \left(-\frac{64ZRTfm^2L}{\pi^2 M(P2^2 - P1^2)}\right)^2$$

Where
Z is the compressibility defined as P M/ρ R T; P = 2/3(P2+P1-P2P1/ [P2+P1]); M= Molecular weight ρ is the density in kg/m^3; R=8.3145; T= Temperature in Kelvin
This formula takes into account for change in altitude

(Zhang et al. 2005) uses:

$$D_{opt} = 0.363\left(\frac{Q_m}{\rho}\right)^{0.45} \rho^{0.13} \mu^{0.025} \qquad (1)$$

With D_{opt} the optimum inner diameter (m), Q_m the mass flow rate (kg/s), ρ the density (kg/m^3) and μ the viscosity (Pa s).

In terms of the selection of a particular pipe size, Aspen HYSYS offers a range of sizes based on two non-dimensional numbers: nominal pipe size (NPS) for diameter and schedule number for wall thickness. The selection of a pipe size has to ensure the velocity of fluid is maintained around 2m/s suggested (Vandeginste and Piessens 2008). Outlet fluid velocity has been calculated manually by dividing the outlet volumetric flow rate by cross sectional area of pipe. By comparing with existing CO_2 pipeline experience in table 16, it can be preliminarily anticipated that the pipe diameter required for delivered 3.7 MTPA to lie between 0.3~ 0.4 meter. A formula (1) for determining the optimum inner diameter proposed in a published journal also agrees with this figure (Zhang et al. 2005).

Table 12 Available nominal diameter (mm) in HYSYS

25.40	152.4	406.4
38.10	203.2	457.2
50.80	254.0	508.0
76.20	304.8	609.6
101.6	355.6	

Existing CO_2 pipeline experience

Table 13 Existing CO_2 pipeline(Chandel, Pratson, and Williams 2010) (Patchigolla and Oakey 2013) (Vandeginste and Piessens 2008)

Name	Location	Mass flow rate (MTPA)	Pipe diameter (m)	Pipe length (km)
Weyburn	North Dakota, USA, and Saskatchewan, Canada	1.8	0.3	330
Val verde	Texas, USA	2.5	0.3	130
Tranpetco	Texas and Oklahoma, USA	3.4	0.3	193
Our case	Australia	3.7	x	y
Canyon reef carriers	Texas, USA	4.4	0.41	225
Sheep Mountain-1	Texas, USA	6.4	0.51	296
Bravo	New Mexico/Texas, USA	7.4	0.51	351
Sheep Mountain-2	Texas, USA	9.3	0.51	360

MIT pipeline diameter and the CO_2 flow rate range

Table 14 MIT pipeline diameter and the CO_2 flow rate range("Carbon Management Gis: Co2 Pipeline Transport Cost Estimation " 2009)

Pipeline diameter (mm)	CO_2 flow rate (Mt/yr)	
	Lower bound	Upper bound
4		0.19
6	0.19	0.54
8	0.54	1.13
12	1.13	3.25
16	3.25	6.86
20	6.86	12.26
24	12.26	19.69
30	19.69	35.16
36	35.16	56.46

Operating temperature

In order to transport supercritical CO_2, the pressure has to be kept above 7.38MPa and temperature above 31.1 ℃. However temperature limit for transportation CO_2 as liquid is not so strict as long as the pressure is high enough to overcome a phase change due to topographic variations (Golomb 1997) . The optimization of CO_2 transport must take into account the impact of ambient temperature and the reason is because of heat exchange along the pipeline between the CO_2 in the pipe and the surrounding. A study (Fig 41) predicting the flowing gas temperature profiles in buried pipelines proves that the flowing stream will eventually reach a relatively steady temperature after a certain distance (Zhou and Adewumi 1997). Since the liquid has a much better convective heat transfer coefficient than gas, a better performance can be anticipated for liquid CO_2 pipeline.

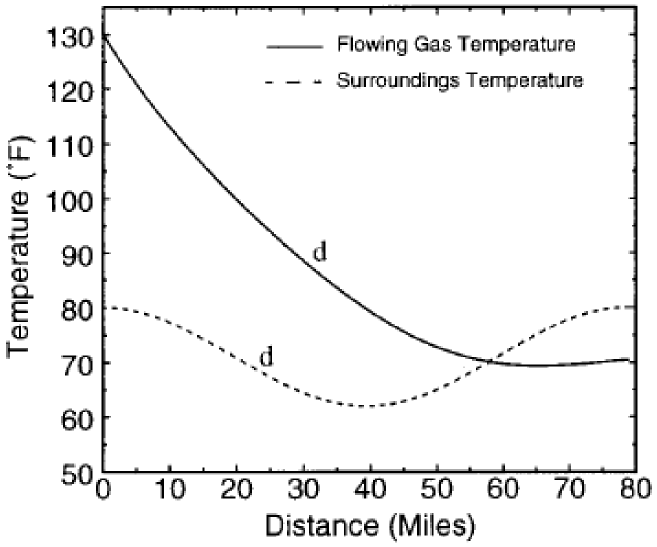


Figure 40 Predicted temperature profile with variable surroundings temperature distribution

The transmission process usually occurs between adiabatic and isothermal condition (Zhang et al. 2005). In this paper, pipelines have been simulated under isothermal conditions to allow sufficient heat exchange to the ground even though there is no much difference between adiabatic and isothermal conditions due to the fact that the liquid is relatively incompressible than gas.

Operating temperature of CO_2 pipelines are generally dictated by the temperature of the surrounding soil (McCoy and Rubin 2007). The heat ingress from the surroundings for a pipeline is determined by the difference between the ground (ambient) temperature and the temperature of the CO_2 inside the pipeline, combined with the insulation properties and burial depth of the pipeline (DNV 2010).

Operating pressure

The pressure will reduced along the pipeline due to friction and temperature is reduced due to heat exchange with the ambient (Eldevik et al. 2009). 7.38 MPa as the lowest operating pressure has been suggested to transport CO_2 in liquid phase (Golomb 1997). The maximum allowable pressure drop per unit length can be determined by the difference between the pipeline inlet and outlet pressures divided by the pipeline length. A pressure drop of 25kPa/km has been suggested for determining the CO_2 pipeline diameter (Vandeginste and Piessens 2008)

Ground material

The pipe will be placed on a bed of sand compacted around it to protect it from rocks and other hard material. Thus, wet and dry sand will be the main concern. In order to compute heat loss through buried pipelines transporting CO_2, an important parameter such as thermal conductivity of soils is required (Rawat et al. 1979). The soil thermal conductivity has been identified to be a function of dry density, saturation, moisture content, mineralogy, particle size/shape/arrangement and the volumetric proportions of solid, liquid and air phases. An average ground temperature of 15 ℃ has been applied.

An increase in soil density will result in an increase in conductivity at constant moisture content. On the other hand, an increase of moisture content will result in an increase in conductivity at a constant density (Rawat et al. 1979). A ground conductivity value of 1.2 W/mK has been assumed in an open literature (Zhang et al. 2005) and this value agrees with the average value between dry sand and wet sand conductivity. The soil stiffness and the quality of installation would determine the pipe performance.

Table 15 Available ground materials in HYSYS and corresponding conductivity

Ground material	Default ground conductivity given by HYSYS (W/mK)
Dry sand	**0.5**
Dry clay	0.48
Wet sand	**2.2**
Wet clay	1.4
Limestone	1.3
Sand gravel	2.5

Buried depth

CO_2 pipeline will have similar design features to natural gas or water pipelines and will usually be buried due to environmental, security and safety reasons. There are several advantages for burying the pipeline such as to avoid the hot weather in some regions and to significantly protect the pipeline from external interference (Zhang et al. 2005). 1.2 meter buried depth has been used in simulation as suggested by CSBP however 2 meter depth is required for under a railway (Chopra and Thakur 2012). Pipe support components consist of bedding, haunch, side support, overlay and backfill. A foundation is required only when the native trench bottom is not able to act as a working platform for pipe bedding materials. Initial backfill zone is the critical zone of embedment soil surrounding the pipe from the foundation to at least 6 inches over the pipe. The quality of embedment material and the quality of its placement determines the pipe's ability to support loads and resist deflection. Initial backfill zone consist of bedding, hauching, primary and secondary zones.

The bedding levels out any irregularities and ensures uniform support along the length of the pipe while haunching is the backfill under the lower half of the pipe distributes the superimposed loadings. Primary initial backfills is the zone of backfill which provides the primary supports against pipe deformation and in order to ensure the availability, this zone would be extended from trench grade up to at least 75% of the pipe diameter. Secondary initial backfill is the zone which distributes overhead loads and to isolate the pipe from any adverse effects of the placement of the final backfill. Final backfill is used to promote a load reduction on the pipe and it should be free of large rocks, organic material and debris. The material and compaction requirements for the final backfill should reflect sound construction practices and satisfy local ordinances and sidewalk, road building or other application regulations.

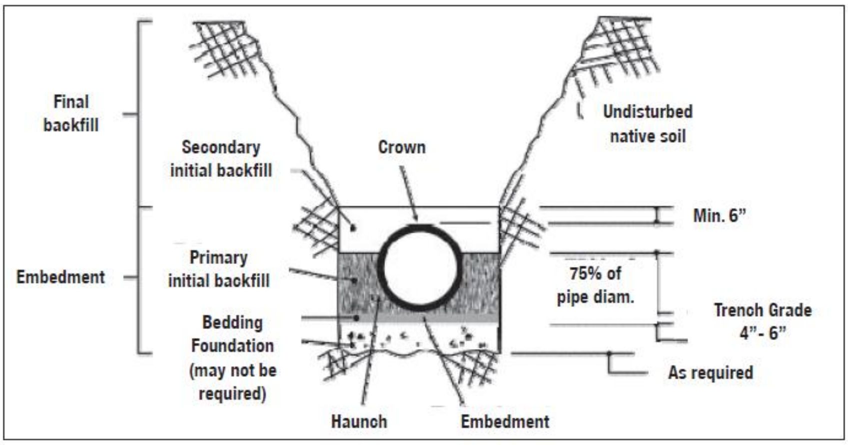


Figure 41 Pipe trench

Protective coating

Coatings are known as the first line of deference against corrosion. All buried steel pipes and components, including stainless steel, shall have a protective coating to maximise the life of the piping systems by preventing serious and irrecoverable damage by surface corrosion attack (Chopra and Thakur 2012). Several requirements have to be considered such as adhesion (how well the coating sticks to the pipe steel), soil stress and installation cost when selecting a particular type of coating. The coating usually consists of one or two layers or polyethylene (PE) or polyvinyl chloride (PVC) which comes in a thickness range between 500 to 1500 µm) (Richard 1999). The minimum thickness shall be as specified in Australian Standards AS 1518 (Chopra and Thakur 2012) .

In this liquid CO_2 pipeline system, despite the negligible thickness of coating, the thermal conductivity of the coating shall also be considered so that it does not significantly hinder the heat transfer activity between the fluid and surrounding soil.

Thermal insulation of pipeline

Insulation shall be considered and installed in locations where there is a potential for heat gain, for example above ground facilities like an intermediate pumping/cooling station. In the event of planned or unplanned shut down for maintenance, insulation is also required to maintain the fluid temperature (Guan and Shaw 2012). A 5cm cellular glass type of insulation with a thermal conductivity of 0.058 W/mK has been used in the modelling (Zhang et al. 2005). However for the main trunkline, it will not be considered due to the consideration of capital cost and more importantly to allow the heat transfer between the fluid and the surrounding soil.

Reinforced cement concrete (RCC), pre-stressed concrete (PSC) casing shall be used for locations where there is a potential for pipe movement such as river crossings, major roads, railway track and etc.

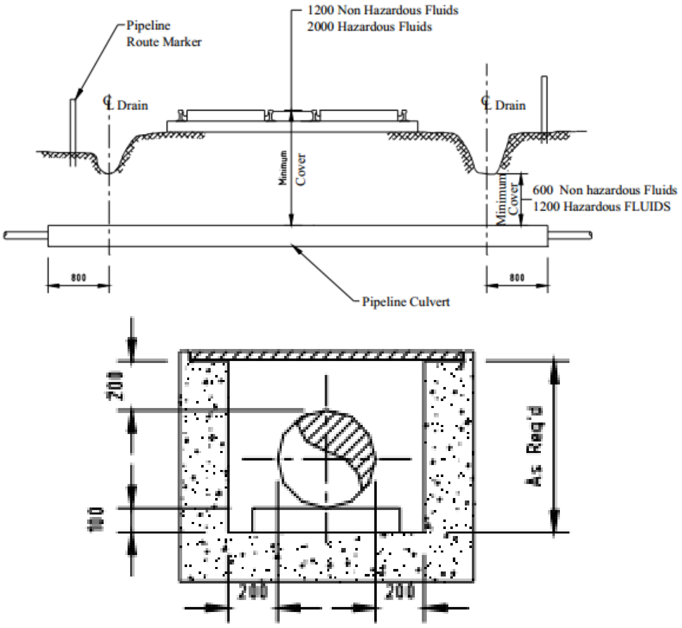


Figure 42 Typical cover over the pipeline crossing under a railway (left) Cross sectional view (Right)

Table 16 Available insulation materials in HYSYS and corresponding conductivity

Insulation material	Default ground conductivity given by HYSYS (W/mK)
Urethane foam	$1.8\text{x}10^{-2}$
Fiber blanket	$7\ \text{x}10^{-2}$
PVC	$4\ \text{x}10^{-2}$
Fiberglass block	$3.5\ \text{x}10^{-2}$
Concrete	$1\ \text{x}10^{-2}$

Air temperature across Australia

Australian Government Bureau of Meteorology website provides credible information for the air temperatures across Australia. Figure 44 and 45 show the maximum and minimum temperature from 1st June 2013 to 31st May 2014. It can be predicted that South Australia, Victoria, New South Wales, Tasmania, southern part of Western Australia and eastern part of Queensland had a maximum temperature of 27~30℃ (AustralianGovernmentBureauofMeteorology 2014). These areas can be considered for liquid CO_2 pipelines however abnormal weather might still occur and it should be carefully accounted for.

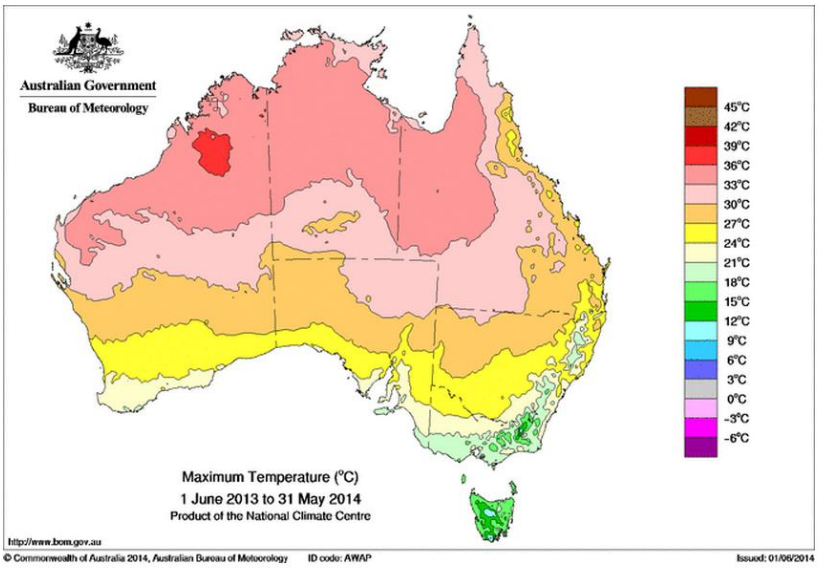


Figure 43 Twelve-monthly mean maximum temperature for Australia(AustralianGovernmentBureauofMeteorology 2014)

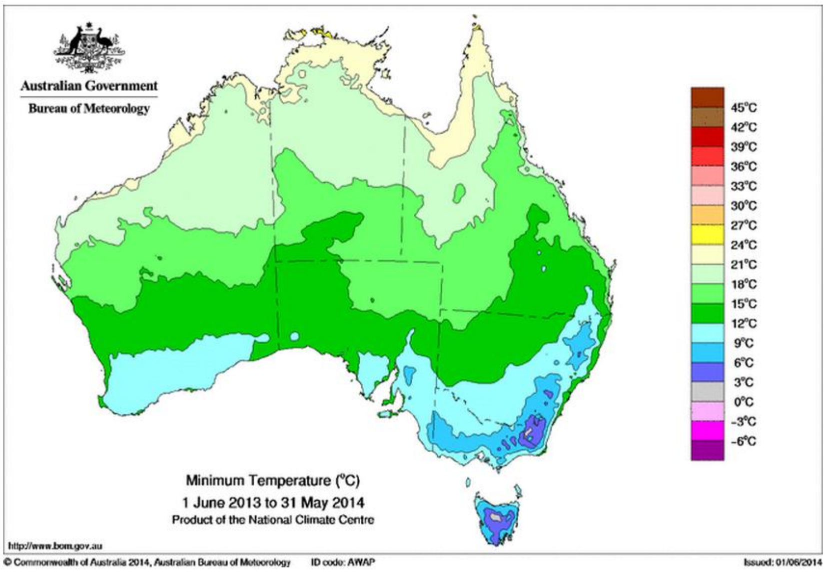
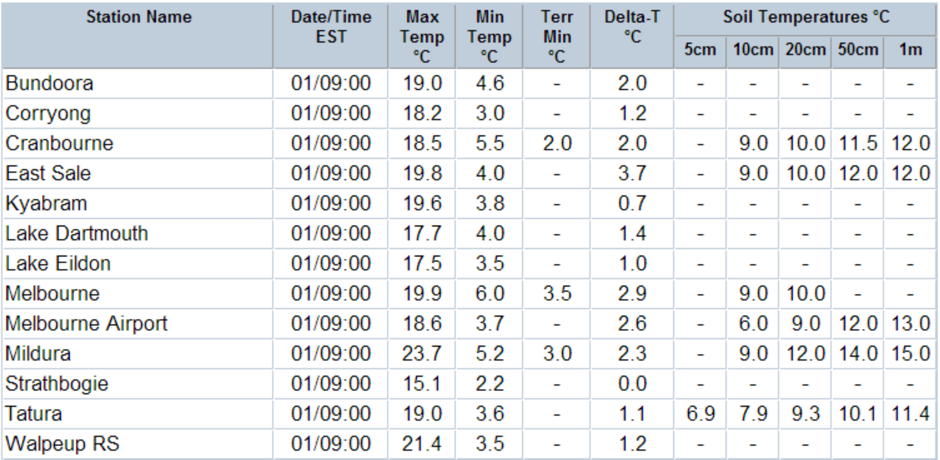


Figure 44 Twelve-monthly mean minimum temperature for Australia(AustralianGovernmentBureauofMeteorology 2014)

Soil temperature across Australia

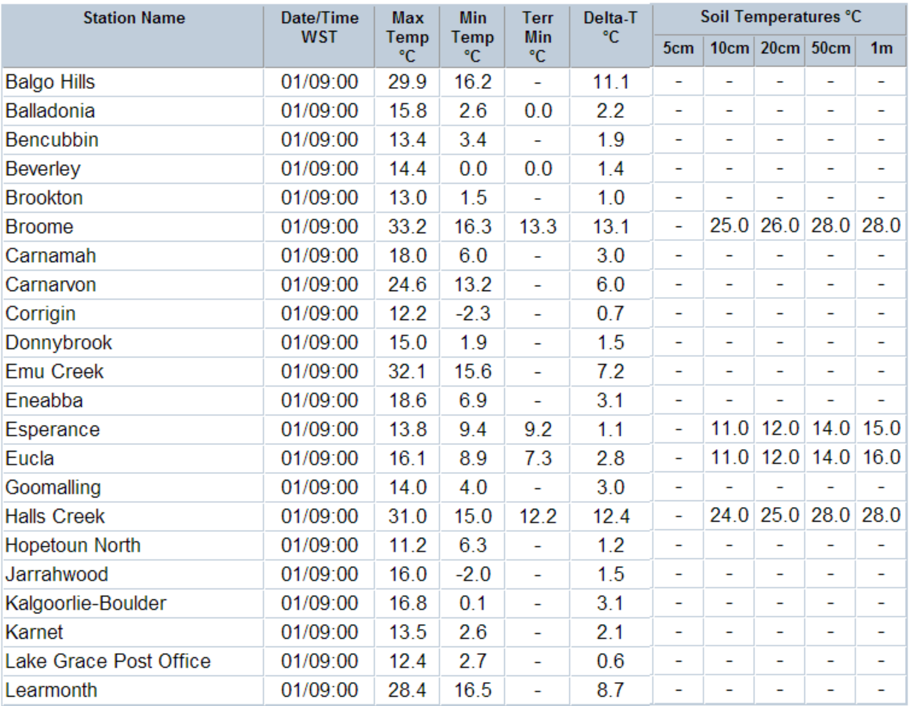
Australian Government Bureau of Meteorology website also provides information for the soil temperature at several buried depths and stations. It is important to keep in mind that the ambient temperature is not necessary the same as the ground temperature under a certain buried depth (AustralianGovernmentBureauofMeteorology 2014). Comparing the available soil temperature data for Victoria and Western Australia, it can be predicted that Victoria provides a much better soil temperature for liquid CO_2 pipeline. In Western Australia, regions like Broome and Halls Creek having a soil temperature of 28 ℃ at 1 meter buried depth will not be suitable.

Table 17 Agricultural observations bulletin for Victoria (AustralianGovernmentBureauofMeteorology 2014)



Station Name	Date/Time EST	Max Temp °C	Min Temp °C	Terr Min °C	Delta-T °C	Soil Temperatures °C				
						5cm	10cm	20cm	50cm	1m
Bundoora	01/09:00	19.0	4.6	-	2.0	-	-	-	-	-
Corryong	01/09:00	18.2	3.0	-	1.2	-	-	-	-	-
Cranbourne	01/09:00	18.5	5.5	2.0	2.0	-	9.0	10.0	11.5	12.0
East Sale	01/09:00	19.8	4.0	-	3.7	-	9.0	10.0	12.0	12.0
Kyabram	01/09:00	19.6	3.8	-	0.7	-	-	-	-	-
Lake Dartmouth	01/09:00	17.7	4.0	-	1.4	-	-	-	-	-
Lake Eildon	01/09:00	17.5	3.5	-	1.0	-	-	-	-	-
Melbourne	01/09:00	19.9	6.0	3.5	2.9	-	9.0	10.0	-	-
Melbourne Airport	01/09:00	18.6	3.7	-	2.6	-	6.0	9.0	12.0	13.0
Mildura	01/09:00	23.7	5.2	3.0	2.3	-	9.0	12.0	14.0	15.0
Strathbogie	01/09:00	15.1	2.2	-	0.0	-	-	-	-	-
Tatura	01/09:00	19.0	3.6	-	1.1	6.9	7.9	9.3	10.1	11.4
Walpeup RS	01/09:00	21.4	3.5	-	1.2	-	-	-	-	-

Table 18 Agricultural observation bulletin for Western Australia(AustralianGovernmentBureauofMeteorology 2014)



Station Name	Date/Time WST	Max Temp °C	Min Temp °C	Terr Min °C	Delta-T °C	Soil Temperatures °C				
						5cm	10cm	20cm	50cm	1m
Balgo Hills	01/09:00	29.9	16.2	-	11.1	-	-	-	-	-
Balladonia	01/09:00	15.8	2.6	0.0	2.2	-	-	-	-	-
Bencubbin	01/09:00	13.4	3.4	-	1.9	-	-	-	-	-
Beverley	01/09:00	14.4	0.0	0.0	1.4	-	-	-	-	-
Brookton	01/09:00	13.0	1.5	-	1.0	-	-	-	-	-
Broome	01/09:00	33.2	16.3	13.3	13.1	-	25.0	26.0	28.0	28.0
Carnamah	01/09:00	18.0	6.0	-	3.0	-	-	-	-	-
Carnarvon	01/09:00	24.6	13.2	-	6.0	-	-	-	-	-
Corrigin	01/09:00	12.2	-2.3	-	0.7	-	-	-	-	-
Donnybrook	01/09:00	15.0	1.9	-	1.5	-	-	-	-	-
Emu Creek	01/09:00	32.1	15.6	-	7.2	-	-	-	-	-
Eneabba	01/09:00	18.6	6.9	-	3.1	-	-	-	-	-
Esperance	01/09:00	13.8	9.4	9.2	1.1	-	11.0	12.0	14.0	15.0
Eucla	01/09:00	16.1	8.9	7.3	2.8	-	11.0	12.0	14.0	16.0
Goomalling	01/09:00	14.0	4.0	-	3.0	-	-	-	-	-
Halls Creek	01/09:00	31.0	15.0	12.2	12.4	-	24.0	25.0	28.0	28.0
Hopetoun North	01/09:00	11.2	6.3	-	1.2	-	-	-	-	-
Jarrahwood	01/09:00	16.0	-2.0	-	1.5	-	-	-	-	-
Kalgoorlie-Boulder	01/09:00	16.8	0.1	-	3.1	-	-	-	-	-
Karnet	01/09:00	13.5	2.6	-	2.1	-	-	-	-	-
Lake Grace Post Office	01/09:00	12.4	2.7	-	0.6	-	-	-	-	-
Learmonth	01/09:00	28.4	16.5	-	8.7	-	-	-	-	-

Codes and standards

For CO_2 service, pipelines are generally constructed with materials meeting American Petroleum Institute (API) specification (McCoy et al, 2007). Australian Standard AS1210 has also given several reference standards for standard components: flanges, nozzles, pipe fittings, bolting and valves. There materials are required for design calculations which based on total thickness including cladding. Refer to the table below:

Table 19 Codes and Standards for piping components

Piping components	Standards
Pipe fittings	ASME B16.9, ASME B16.11, AS/NZS 4331
Pipe flanges	AS 2129, AS/NZS 4331, BS 3293, EN 1092, ASME B16.47, ASME B16.5
Bolting	AS1110(series), AS1111(series), AS1112(series), ASTM A193, AS2528, BS4882, BS4439
Pipe threads	AS1722.2, ASME B1.20.1, ASME B1.20.3, API Std 5B
Valves	AS1271, ASME B16.34
Integrally clad plate	ASTM A263, ASTM A264, ASTM A265, ASTM B898

In specific, ASME B31.4 is a liquid pipeline code intended for CO_2 while ASME B31.8 excludes CO_2 transportation piping systems.

2.3 CO_2 pipeline economics

According to MIT, the amount of cost data on CO_2 pipeline in the open literature is very limited. Due to the similarity between CO_2 and natural gas pipeline, the cost data for natural gas pipelines were used to estimate the construction cost for CO_2 pipelines ("Carbon Management Gis: CO_2 Pipeline Transport Cost Estimation " 2009).

The pipeline transport cost can be divided into two components: the land construction cost (LCC) and the Operating& Maintenance (O&M) cost. The equation below estimates the annualized cost over the operating life of the pipeline:

$$Annualized\ Cost = Land\ Construction\ Cost * Capital\ Charge\ Factor + O\&M\ Cost$$

The MIT correlation and CMU correlation shown as below have been incorporated into this package to estimate the LCC.

<u>MIT correlation</u>

$$LCC = a * D * L * Index$$

Where a= $33’853, D=pipeline diameter in inches (function of CO_2 flow rate), L=least cost pipeline route length in miles, Index=2.92 in year 2007

Developed by the Carbon Capture and Sequestration Technologies Program (CCSTP) at MIT, this correlation assumes that the CO_2 pipeline LCC has a linear correlation with pipeline diameter and length. It is important to note that the ‘a’ value can be replaced by self-defined values. The presence of an index is to take into account the increased cost and inflation.

<u>Carnegie Mellon University correlation</u>

$$LCC = \beta * D^x * L^y * z * Index$$

Where β=$42’404, x=1.035, y=0.853, z= weights for different regions in US (1.000 for central, 1.248 for Southwest, 1.341 for West, 1.516 for Midwest, 1.687 for Southeast, 1.783 for Northeast), Index=2.07 for year 2007

This CMU correlation relaxes the linearity restriction in the MIT correlation and allows a double-log (nonlinear) relationship between pipeline land construction cost and pipeline diameter and length. This correlation also takes into account regional differences in CO_2 pipeline land construction costs by considering weight for different regions.

Operation and maintenance cost

O&M for a given year is generally expressed as a percentage of the installed capital costs. That cost is assumed to be about 3 to 5%.

Tolls

A rough estimate of a pipeline toll can be found by taking the capital cost and multiplying by a capital recovery factor plus 5% for O&M and dividing these costs by the volume of CO_2 moved in a given year.

This performance model uses input engineering design parameters for examples pipeline length, design CO_2 mass flow to calculate required pipe diameter. A series of inputs defining the design of the pipeline are taken into the pipeline performance model in order to calculate required pipe diameter which is also the input to the cost model (McCoy, 2008).These models are shown in figure below.

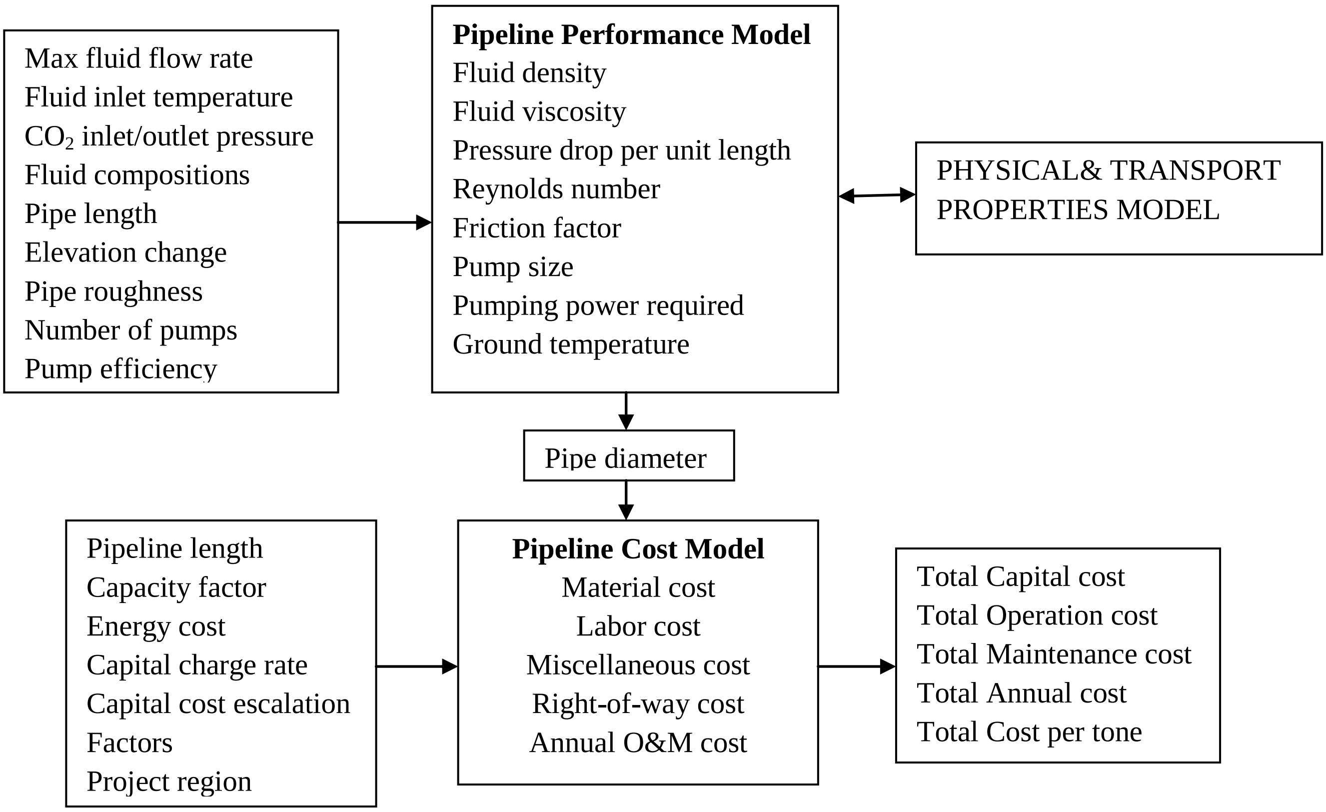


Figure 45 The pipeline performance model

2.4 Ship transportation

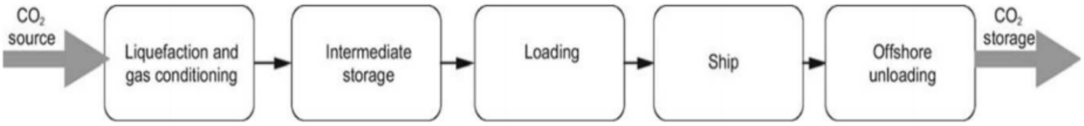


Figure 46 Main processes in the ship transport system (Aspelund, MØlnvik, and Koeijer 2006)

Large scale ship based transport of CO_2 is relatively new. Ship transport offers flexibility compared to regional constraints of pipelines. A few key engineering parameters for ship transport is the optimal pressure- temperature conditions for CO_2 and taking into account the re-liquefaction process, boil-off rate in the tank, hydrate and dry ice formation. These conditions shall be investigated in the aspect of manufacturability of pressure tank, cost of tanks and carrier vessels and total energy efficiency of CO_2 flow. For cost parameters, (Weihs, Kumar, and Wiley 2014) claimed that the largest shipping cost components are electricity and fuel. Detailed economic study also includes parameters such as ship speed, ship loading and unloading time, ship size, load factor, project life, offshore pipeline depth, pipeline steel grade and etc. Aspelund et al. (2006) has identified the concept of transporting by ships which consists of five main processes as shown in figure above: liquefaction and gas conditioning, intermediate storage, loading, ship and offshore unloading.

Intermediate storage

Before the ship dock at quay, the CO_2 is stored at the bubble point in semi-pressurized storage tanks which are similar to the one for liquefied petroleum gas (LPG) and ethylene. Kokubun et al. (2013) has stated that the design methodology for LPG cargo tanks is regulated by international standards such as the 'International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk' which is also known as IGC code. The intermediate storage is necessary because of continuous capture of CO_2 on shore. The shape of tank can be sphere, cylindrical or underground storage in caverns. The pressure vessels can be installed above ground on racks or on the ground where they are fully or partially covered. The size, location and ground conditions of the storage facilities must be flexible enough to accommodate the variation of storage volume and geographical location. The total storage capacity is set to $30000m^3$ which is 1.5 times the ship capacity.

Loading system

Liquid CO_2 will be loaded from the storage tanks to the ship by loading system. The loading system consists of pumps, marine loading arm, export building and all necessary piping between tanks and ship. Two parallel product pipes between tanks and loading arm for export of CO_2 and a return line for CO_2 vapour generated at the ship are recommended solutions for the loading system. Operational issues such as formation of dry ice and problems with thermal cycling have to be prevented when developing the loading procedures.

Ship

LPG ships maybe rebuilt for CO_2 transport and the issue is that CO_2 needed to be transported at higher pressures, higher densities and lower temperatures than LPG. The ship is semi pressurized for a working pressure of 5-7 bara and operate at low temperatures for example -48C for LPG and -104C for ethylene. The design pressure of the cargo tank should include operating and safety margins to allow for pressure increase during cruise. (Neele, Haugen, and Skagestad 2014) claimed a rise in pressure of 0.1-0.2 bar/day on board due to thermal leakage which is subject to temperature and amount of CO_2. The ship will be kept in the position at one point during the injection operation offshore using a Dynamic Positioning System (DPS), consisting of one azimuth propeller (ship aft) and two side thrusters (ship fore). During cruising of ship, the azimuth propeller is powered by electricity generated by diesel engines and acts as the main propulsion device. Re-condensation facilities on board which consists of heat exchangers and pumps may be necessary depending on the distance for CO_2 transport.

Offshore unloading system

The CO_2 conditions should be at 6.5 bar and -52 ℃ when arriving at the oil field. The liquid pressure will be increased to 200-300 bar and temperature will be increased to 15-20 ℃ to avoid wax and hydrate formation. The offshore unloading system will be connected to the platform via a riser and a seabed pipeline for the transfer of CO_2. The offshore unloading system should include the followings:

- a submerged turret loading (STL) system;
- a submerged cargo pump in the cargo tank and a booster pump on the ship deck;
- a CO_2 heating system on the ship and/or a waste heat recovery heating system at the platform;
- a flexible riser from the ship to the seabed;
- a pipeline at seabed;
- a pipeline from seabed to platform deck;
- a pumping system on the platform for pressure increase up to injection pressure;
- An expansion system on the platform to avoid pressure build-up in the transfer lines between transmission

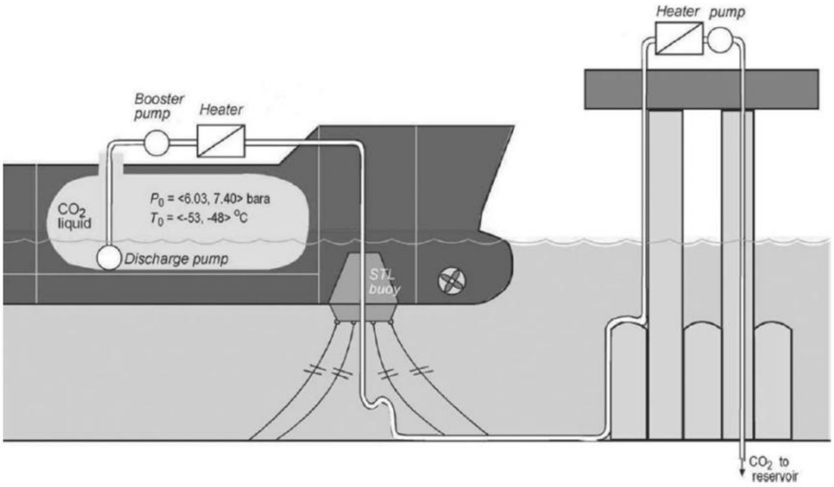


Figure 47 Offshore unloading system

(Kokubun, Ko, and Ozaki 2013) stated that the pressurized and heated CO_2 is sent thought the CO_2 injection flexible riser pipe to the wellhead equipment installed on the seabed at the injection point. At the scheduled injection rate set for individual wells which is controlled by electrically controlled flow control valves, the CO_2 is injected into the underground geological formation as shown in figure below. (Neele, Haugen, and Skagestad 2014) stated that the injection rates are constrained by thermal gradient (cooling and heating of tubing, casing and cement), erosion limit and vibration limit. The injection control system on the CO_2 tanker will receive the data signals on the flow rate from the wellhead.

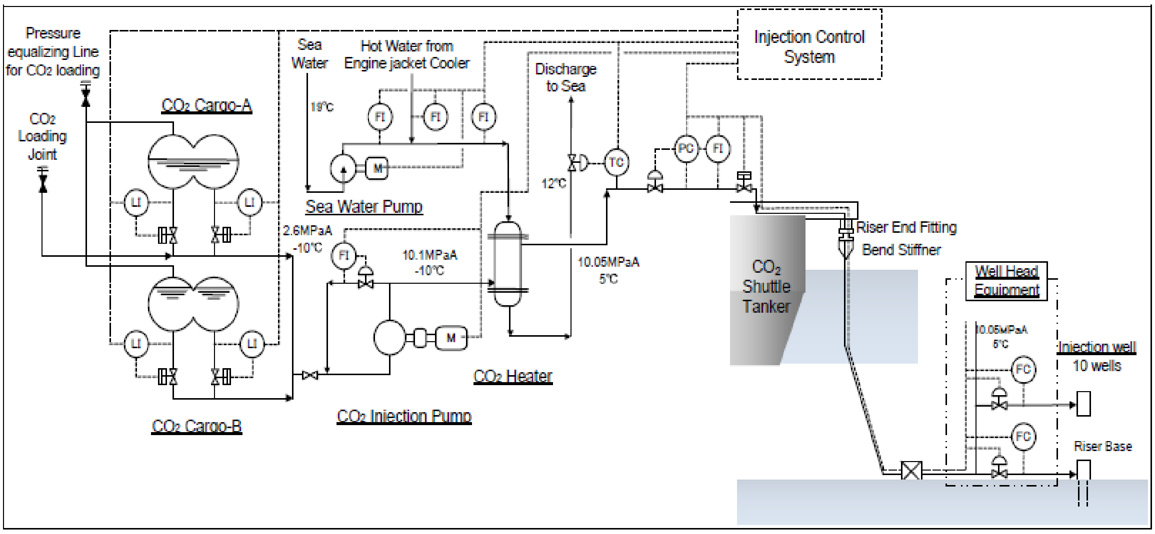


Figure 48 CO_2 injection flow (Kokubun, Ko, and Ozaki 2013)

Boil-off gas (BOG) re-liquefaction process (Lee et al. 2012)

Lee et al. (2012) clarified that the boil off rate is determined by many variables such as insulation, thickness, surface area, and the number and size assumed in tank design as an economic trade off. Impurities such as Nitrogen which is non-condensable in re-liquefaction process, changes the vapour-liquid equilibrium is considered as one major factor in boil-off gas. Therefore, Lee et al (2012) developed an Aspen HYSYS® simulation, using Soave- Redlich-Kwong (SRK) equation of state, in order to study the BOG liquefaction for CO_2 transport. Lee et al. (2012) assumed the sphere tank volume and liquid volume flowrate are 10’000 m^3 and 10’000 m^3/hour, overall heat transfer area is 2245 m^2. Heat ingress to storage tank is calculated as 64656 kJ/hour with the overall heat transfer coefficient of 0.72 kJ/m^2hr ℃. Boil-off gas mass flow rate is 117.4kg/hr containing 12mol% N_2 and 88mol% CO_2 contained in boil-off gas in the tank. The re-liquefaction process is similar to liquefaction process in such a way that using CO_2 as refrigerant by itself and two stage compression-intercooling-expansion loop. Lee et al. (2012) reported a recovery rate is only 43%.

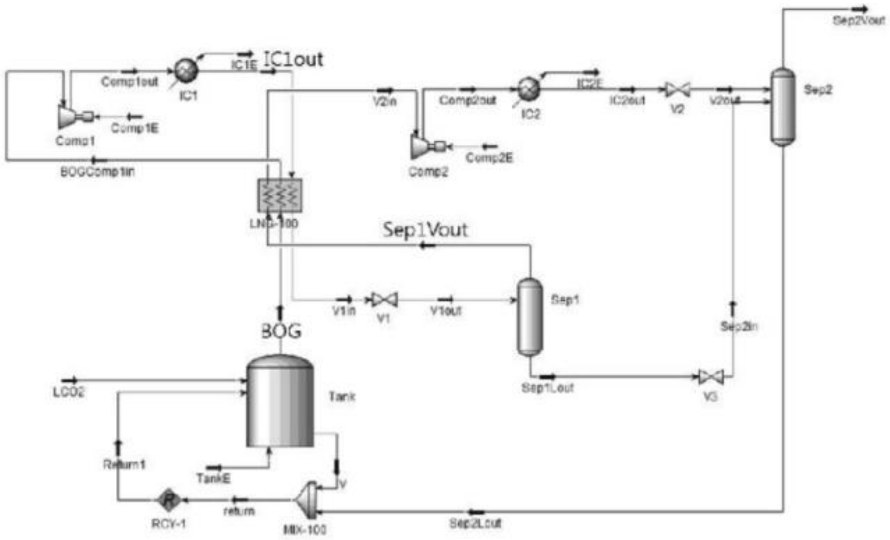
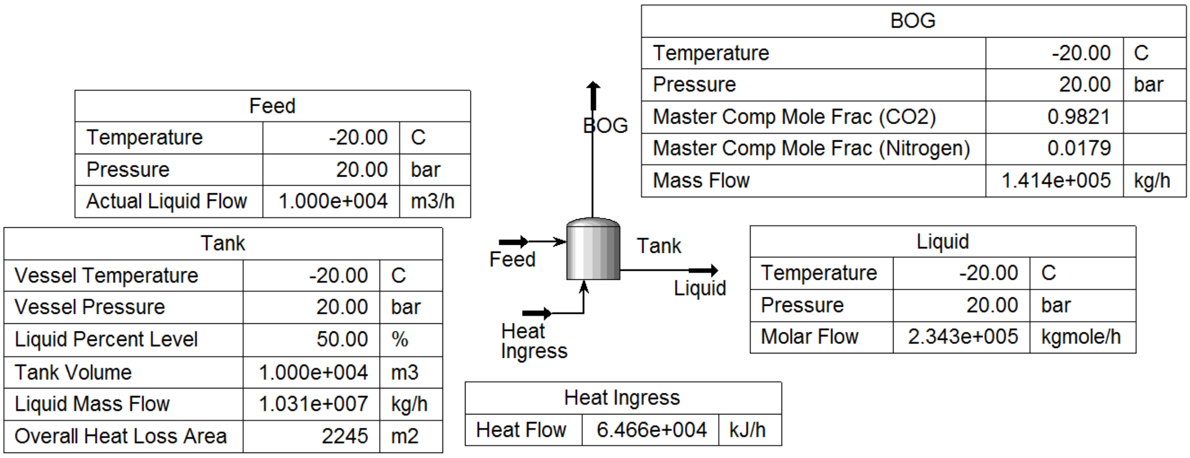


Figure 49 Boil-off gas (BOG) re-liquefaction process



Feed		
Temperature	-20.00	C
Pressure	20.00	bar
Actual Liquid Flow	1.000e+004	m3/h

BOG		
Temperature	-20.00	C
Pressure	20.00	bar
Master Comp Mole Frac (CO2)	0.9821	
Master Comp Mole Frac (Nitrogen)	0.0179	
Mass Flow	1.414e+005	kg/h

Tank		
Vessel Temperature	-20.00	C
Vessel Pressure	20.00	bar
Liquid Percent Level	50.00	%
Tank Volume	1.000e+004	m3
Liquid Mass Flow	1.031e+007	kg/h
Overall Heat Loss Area	2245	m2

Liquid		
Temperature	-20.00	C
Pressure	20.00	bar
Molar Flow	2.343e+005	kgmole/h

Heat Ingress		
Heat Flow	6.466e+004	kJ/h

Figure 50 Boil-off gas (BOG) re-liquefaction process (Aspen HYSYS)

The same process has been simulated using Aspen HYSYS® shown in Figure 50. It is then observed that the boil-off gas mass flow rate is 141400 kg/hour not 117.4 kg/hour, the boil-off gas composition is 98.21mol% CO_2 and 1.79mol% N_2, not 88mol% CO_2 and 12mol% N_2, despite of following the same heat ingress value, overall heat loss area value, overall heat transfer coefficient value, sphere tank volume and liquid volume flow rate.

Table 20 Summary of liquid CO_2 conditions for ship transport suggested by different journal articles

Reference	Liquid CO_2 conditions for ship transport
Kokubun et al. 2013	-10 ℃, 28 bar
Lee et al. 2012	-20 ℃, 20 bar
Aspelund et al. 2006	-52 ℃, 6.5 bar
Seo et al. 2015	-28 ℃, 15 bar
Neele et al. 2014	-50 ℃, 7-8 bar
Ozaki et al. 2014	-10 ℃, 26.5 bar
Kjarstad et al. 2014	-50 ℃, 7 bar

Table 21 Quick comparison between pipeline transport and ship transport

Design consideration	Pipeline transportation	Ship transportation
Transport condition of CO_2	Either sub-cooled liquid or supercritical at high pressure	Sub-cooled liquid at low pressure, very close to triple point of CO_2
Requirement of re-liquefaction facilities as safety precaution	In cold climate if above/below ground, no In warm climate if above ground, yes	On board liquefaction facilities for boil up
The location of injection site preferred	Both on-shore and offshore	Offshore Onshore unless crossing countries
Maturity of technology	Mature and the pipeline design is very similar to the one for natural gas (Parfomak, Folger, and Vann 2009)	Not yet mature therefore using the similar technology for LPG and ethylene(Aspelund, MØlnvik, and Koeijer 2006)
Codes and standards	ASME standards B31.4 and B31.8 (B31.8s), IP6, BS EN 14161, BS PD 8010, ISO13623 and DNV OS-F101	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk, also known as IGC Code (Kokubun, Ko, and Ozaki 2013)

2.5 CO_2 storage

According to CSIRO, Australia has a gigantic potential resource for geological storage of CO_2 and the cheapest locations identified are Latrobe Valley in the Gippsland basin (A$7 per tonne of CO_2 avoided), the Southern Queensland in the Surat basin (A$12 per tonne) and the Perth region in the Bunbury Trough of the Perth Basin (A$10 per tonne) (Feron and Paterson 2011). In Australia, the Gorgon Carbon Dioxide Injection Project is in the execution stage. (H.Socolow 2005) claimed that the best location for storage will be underground formations of sedimentary rock loaded with brine and addressed two classes of risk, one is gradual leakage and another one is sudden leakage.

There are three storage options categorized by IPCC (2005) which are: geological storage, ocean storage or mineralization.

Geological storage

Geological storage options are: depleted oil and gas reservoir or in combination with enhanced oil recovery or enhanced gas recovery, saline aquifiers, and unminable coal seams or in combination with enhanced coal bed methane recovery. Several factors of the reservoir must be taken into account such as: storage capacity (adequate porosity and thickness) and permeability (injectivity), a satisfactory sealing caprock and a stable geological environment to prevent compromising the integrity of storage site. General speaking, several requirements for storing CO_2 underground given by (Pires et al. 2011):

- Safe, verifiable storage, Minimal environmental impact, the storage liability is indefinite

Ocean storage

Ocean storage consists of injecting CO_2 to great depth where it dissolves or forms hydrates or heavier than water plumes that sinks at the bottom of the ocean. Several techniques have been tested to transfer CO_2 to the ocean such as vertical injection, inclined pipe, pipe towed by ship and dry ice. The main disadvantage of ocean storage is that marine life will be affected by ocean acidification due to increase of CO_2 concentration.

Mineralization

This process involves the conversation of CO_2 to solid inorganic carbonates using chemical reactions similar to natural weathering.

Biological/terrestrial sequestration

Enhancement of biological systems (e.g. soil tiling practices, reforestation, new forest development

Existing CO_2 storage experience, six largest CO2-EOR projects

Table 22 Six largest CO_2-EOR projects (Heddle, Herzog, and Klett 2003)

Operator	Field	Basin/region	Injection Strategy	Area (km^2)	Production wells	Injection wells	EOR production (bbl/day)	EOR production (bbl/day/well)	Est. CO_2 effectiveness (scm/bbl)
Altura	Wasson (Denver)	Permian	WAG	113	735	385	29000	40	136
Amerada Hess	Seminole (Main)	Permian	Continuous	64	408	160	25900	64	
Chevron	Rangely Weber Sand	Rocky Mountain	WAG	61	341	209	11208	33	127
Exxonmobil	Salt Creek	Permian	WAG	49	137	100	9300	68	--
Devon Energy	SACROC	Permian	Continous	202	325	57	9000	28	153
Altura	Wasson (ODC)	Permian	WAG	32	293	290	9000	31	--

Depending on the reservoir pressure and crude oil composition, miscible displacement involves the injected CO_2 mixing thoroughly with the oil in the reservoir, while immiscible displacement means that the CO_2 remains physically distinct from the oil (Heddle, Herzog, and Klett 2003). The six largest CO_2-EOR projects listed above are all miscible CO_2 floods. Water-Alternating-Gas (WAG) is a process which CO_2 is to be alternated with water injection to help overcoming the problem of high CO_2 mobility which significantly reduced the effectiveness of CO_2 flooding (known as the phenomena of gravity tongue and viscous fingering). The block flow diagram below shows the overall flow and distribution of CO_2 from the IGCC power plant to the EOR field. After the transportation pipeline, CO_2 is mixed with the recycled CO_2 and injected into the EOR CO_2 injection wells. On the production site, the oil produced at the EOR wells is separated from water and CO_2 at the surface. The CO_2 is dehydrated, compressed, and mixed with fresh incoming CO_2.

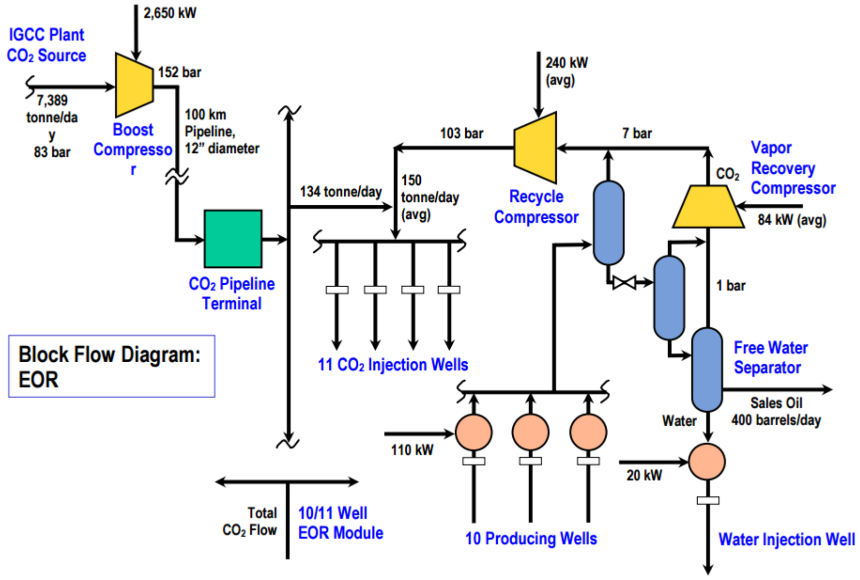


Figure 513 Enhanced Oil Recovery block flow diagram

2.6 CO_2 storage economics

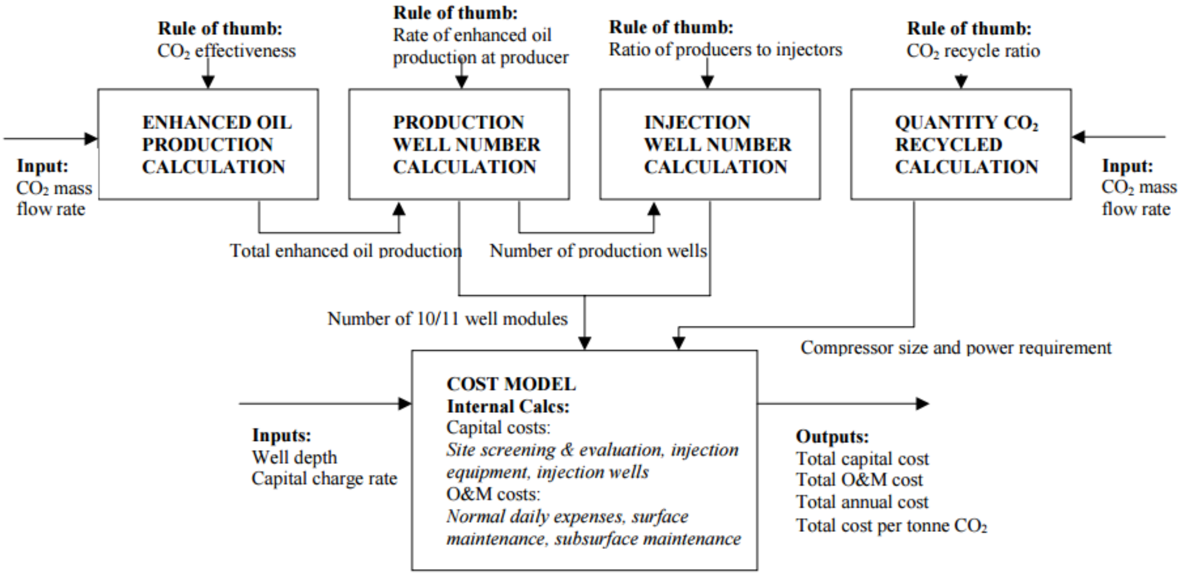


Figure 525 Enhanced oil recovery cost overview diagram

The storage costs consist of transaction, transportation, sequestration and monitoring costs. The total capital cost comprises the injection (e.g. recycle& vapour compressors, plant, distribution lines, header and electrical service) and production equipment costs (e.g. tubing replacement, rods & pumps, equipment, makeover of existing wells), and the cost of refurbishing the existing wells. The O&M costs include normal daily expenses (e.g. supervision & overhead, labour, consumables, operative supplies, pumping & field power, recycle compressor power) and surface (e.g. labour, supplies & services, equipment usage) and subsurface maintenance costs (e.g. workover rig services, remedial services, equipment repair).

CHAPTER 3 THE OPERATION OF LABORATORY PILOT PLANT

The Clean Gas Technology Australia (CGTA) laboratory pilot plant is situated at building 614 Technology Park, in between Fuels and Energy Technology Institute (FETI) and Corrosion Centre for Education, Research and Technology (Corr-CERT). Address is 5, De Laeter Way, Bentley. This laboratory pilot plant is designed for high pressure gas and hazardous substance operations and consists of a PVT Sapphire Cell and a comprehensive flow loop for capturing CO_2 via cryogenic method (liquefaction and/or hydrate) and pumping liquid CO_2. Office and general amenities are situated next to the laboratories.

3.1 The PVT Sapphire Cell

Figure 53 The PVT Sapphire Cell

The PVT Sapphire Cell (Figure 53) can be used for the determination of hydrate formation and dissociation conditions and evaluation of hydrate inhibitors. The PVT cell is equipped with 2 Sony digital Hyper HAD colour video camera (5x magnifying lens) for visual confirmation of gas behaviour and can be easily transported by truck, ship or air.

It consists of a 500cc piston bottle and has a working pressure up to 7250 psia (500 bara), working temperature down to -256 ℉ (-160 ℃) which R22 refrigerant is used as the coolant. The cell itself is protected by thick glass (allowing it to experience high pressures) and is separated from the outside environment by a reinforced and insulated glass door. A magnetic stirrer is available for promoting sufficient mixing and is controlled manually by a switch and a dial for changing rotational velocity. Six clamps attached to the door allow for a tight seal, minimizing heat transfer through the housing of the PVT cell.

To establish the operating conditions for gas hydrate testing,

Temperature control

The PVT Cell is connected to a R2G2 Series Cooler-Serial number: 2773 manufactured by *AQUA* for cooling and an electrical heater for heating. The model number for cooler is R1330A3-P4 and has a max pressure of 2800 kPa. The cooling and heating is boosted by a fan which circulates the heated/cooled air throughout the air bath around the piston bottle.

Pressure control

The design pressure of canister is 120 bar. The pressure can be controlled by one compressed air operated pump manufactured by Haskel Inc, serial number: 807-72, spec number: 2477515 and one piston pump. The pressure is monitored by pressure transmitters and controlled via a Baldor motion PID controller which is connected to Mint Workbench v5 ABB Motion Control for inputting required pressures.

Gas composition

Gas sample can be prepared at desired composition on weight basis by the following procedures:

1) Empty the any residual gas and air from sample bottles (canisters) by using a vacuum pump serial number: SV130310 manufactured by *Dynapumps*

2) Weight each sample bottle by using an electronic balance manufactured by Shimadzu Corporation Japan N595, type UW6200H, number D447811063 (readability 0.01g, capacity 6200g) and record the empty weight (W1)

3) Fill up the sample bottles with desired gas

4) Weight each sample bottle filled with gas and record the filled weight (W2)

5) Subtract W2 by W1 to get the weight of gas in the sample bottle, divide it by the molecular weight of the gas to convert weight to moles

Prior to transferring the sample into the PVT Sapphire cell, the gases will be mixed in a manifold and the total pressure is monitored via a pressure indicator. The mixture will then be transferred via the piston pump, and the pressure is monitored by the pressure indicator. The sample is then transferred into the cell and the pressure observed via the pressure indicator. Total CO_2 composition can be verified by sampling prior to each experiment and using a Gas Alarm Systems' CO_2 analyser. Gas and liquid phases are sampled and the CO_2 content are determined directly. A process flow diagram for the PVT cell is given in Figure 57. Detailed start up, shut down and emergency procedures for the operation of pilot plant can be found in Appendix B.

Process flow diagram for PVT Sapphire Cell

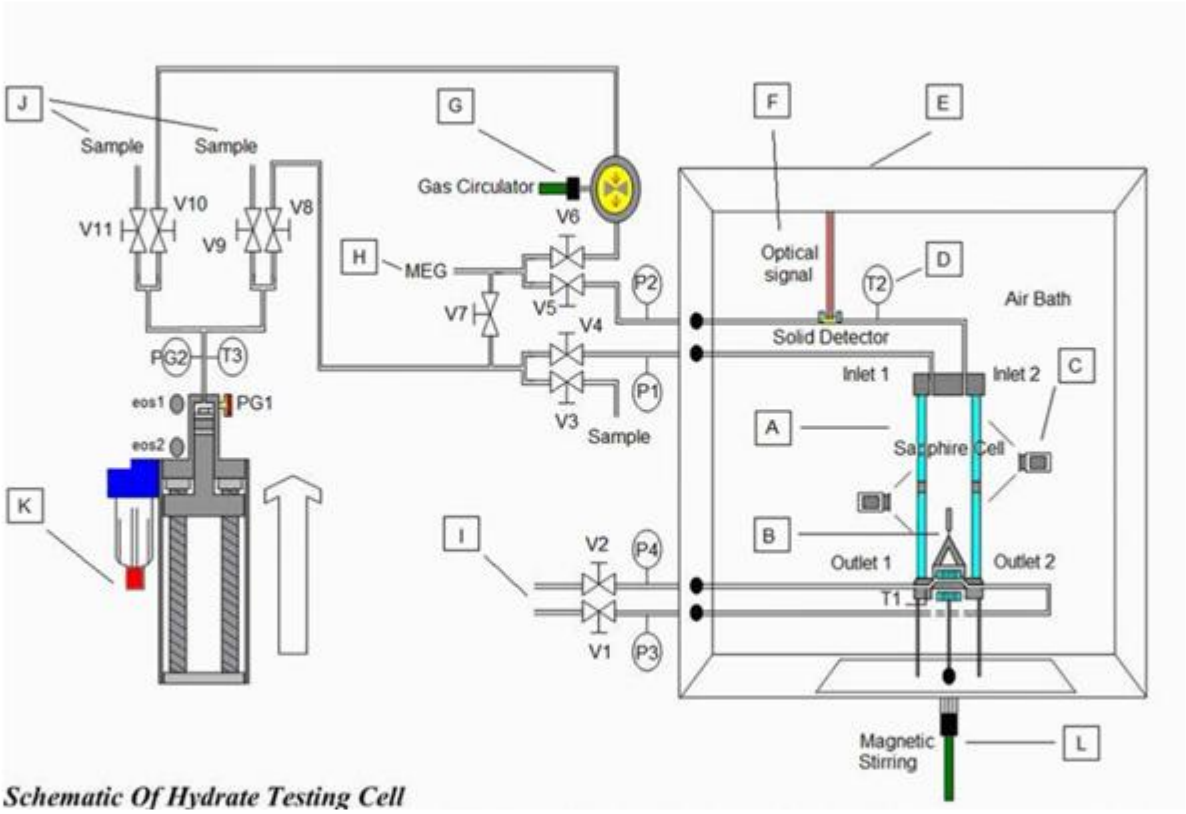


Figure 54 Process flow diagram for PVT Sapphire Cell

A - High-pressure variable-volume optical cell;

B - Magnetic Stirrer;

C - Visualization video camera x2;

D - Temperature measurement;

E - Climatic Air Bath;

F - Optical Solid Detection System;

G - Gas Circulation System;

H – Liquid Sample transfer systems;

I - Liquid phase sampling system;

J - Feed Sampling systems;

K - Positive Displacement Pump for Gas Pressure Control;

L - Motor drive for the magnetic stirrer.

3.2 Comprehensive flow loop for capturing CO_2 via cryogenic method

3.2.1 Process flow diagram (PFD) and Piping& Instrumentation diagram (P&ID)

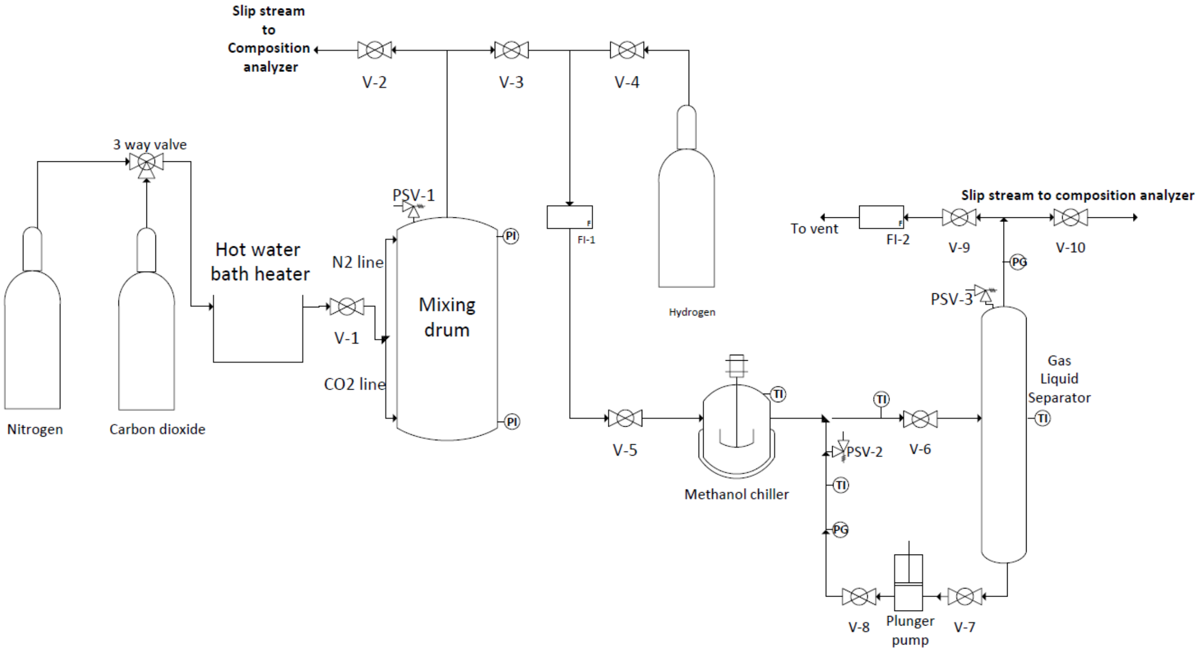


Figure 55 Flow scheme for cryogenic section

Figure 58, 59 and 60 show the process instrumentation diagram for the cryogenic flow loop which can be divided into the feed preparation section and the cryogenic section.

V-1: Ball valve for isolation

V-2 and V-10: Needle valve which acts as sampling point

V-3: Needle valve which isolates the flowing of imitation gas (H_2) from the feed gas in the feed drum

V-4: Pressure regulator which regulates the flow of imitation gas (H_2)

V-5: Pressure regulator which regulates the feed pressure for capture

V-6: Needle valve for isolation

V-7: Needle valve for isolation

V-8: Needle valve for controlling the discharge pressure of plunger pump

V-9: Pressure regulator for controlling the flow/pressure of vent gas

FI 1: Flow meter 1 for reading the flow rate of feed gas

FL2: Flow meter 2 for reading the flow rate of depleted gas

AI: Sampling points for analysing the CO_2 composition

PI: Pressure indicator

TI: Temperature indicator/gauge

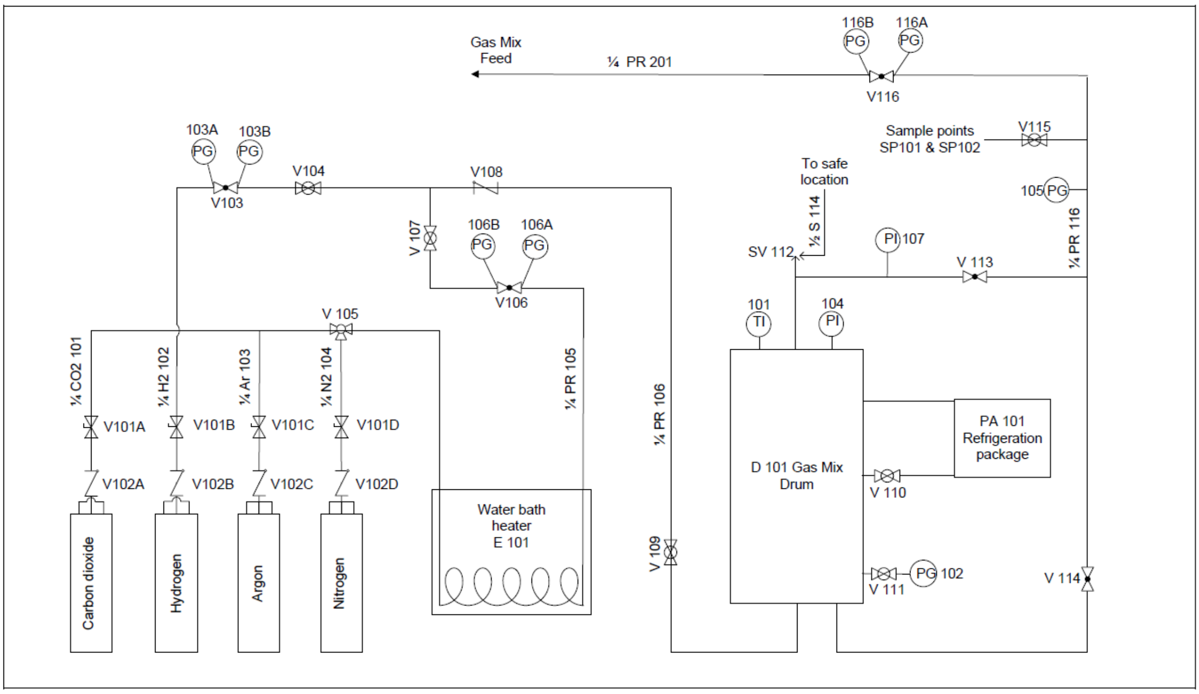


Figure 56 Feed preparation section

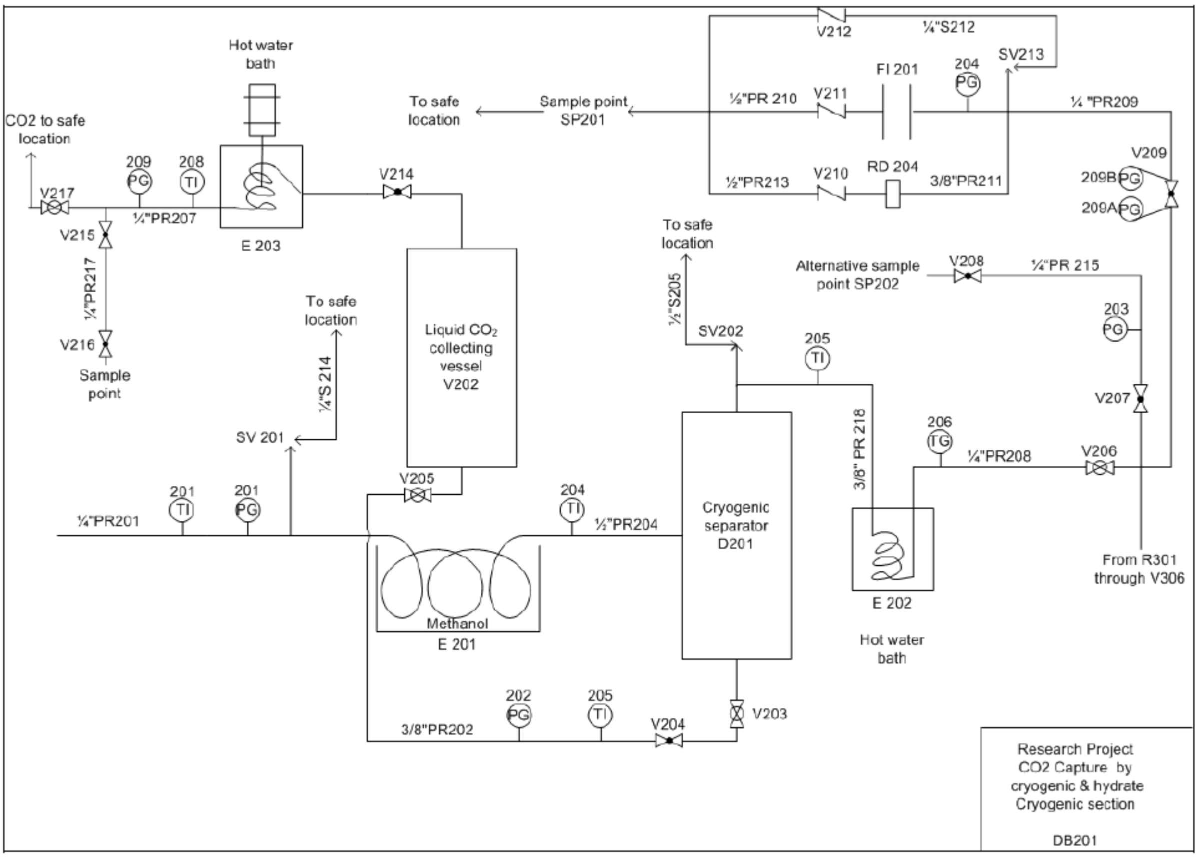


Figure 57 Cryogenic section

3.2.2 CO_2 capture by cryogenic experiment

Before conducting any experiments, it is essential to conduct Chemical Risk Assessments (CRA) to determine the possible hazards of the chemicals and gases involved and the control measures required for their safe use. It is under Curtin University's Health and Safety Policy that all personnel working in the lab must review the Safety Data Sheets and labels to further identify the risks, the use of the product including the concentration and duration, the existing procedures for safe handling according to the hierarchy of controls and the use of personal protective equipment. It is also a legal requirement under the Western Australia Occupational Safety and Health Regulations 1996 that all personnel working in the lab must conduct Plant Risk Assessments at the site where the plant or equipment is located. Chemical risk and Plant Risk Assessment forms can be found in appendix. A general lab safety rules manual for CGTA (in appendix) was also given by the previous lab manager.

One major concern is that the feed gas and flow loop must be completely dry to avoid the formation of solid CO_2 clathrates and ice. It is therefore recommended to purge the whole flow loop using an inert gas. Low cost nitrogen (N_2) gas is preferred while other inert gases such as Argon can also be used. The purpose is to blow out any water vapour or impurities within the flow loop. Next, fill up the chiller with methanol (at least half full) and reduce its temperature to a range of -50 ℃ to -55 ℃ by adding dry ice. The bottom of the separator is also blanketed by dry ice with the purpose to prevent the re-vaporisation of liquid CO_2 when the CO_2 starts condensing at the bottom of the separator.

The industrial grade CO_2 from the commercially supplied gas cylinder is highly pressurized and it is in liquid form. Therefore, the gas flow can be promoted by passing the CO_2 through a heater filled with hot water. The CO_2 (molar mass 44.01gmol^{-1}), which is heavier than N_2 (molar mass 14 gmol^{-1}), is fed from the top of the mixing drum so that it gradually settles down. Feeding the N_2 gas from the bottom can also avoid the re-condensation of CO_2 due to the cushioning effect of N_2. Sufficient time has to be allowed for the gas mixture to mix and reach equilibrium, preferably at least 2-3 hours. Then, analyse and record the initial gas composition from the top and bottom of the drum by passing a small amount of gas (slip stream) to the composition analyser.

The hydrogen (H_2) gas will be used as a dummy gas for achieving the process conditions required for liquefying CO_2. Once the desired temperature and pressure is reached, the imitation gas will be switched to the gas mixture prepared beforehand in the mixing drum. Start chilling the separator by pouring liquid nitrogen on the outside of the separator until the temperature reaches -55 ℃ and at the same time maintaining this temperature by adding dry ice into the methanol chiller. Valve at the suction and discharge of the pump (V-7 and V-8) shall be closed at this time. The composition and the flow rates of depleted gas from the separator shall be analysed by using a composition analyser and a flow meter (FI-2) while the readings are relatively consistent. When the desired operating pressure cannot be maintained, the cryogenic condensation experiment ends.

3.2.3 Pilot plant capabilities

The existing laboratory pilot plant has been mainly constructed using Swagelok® ¼, 3/8, ½ inch tubing and fittings. Ball, check, needle, 3 way valves are used for regulation, direction and isolation purposes. It is essential for lab operators to complete the *Swagelok Total Support Installation Training* in order to ensure, leak-free, reliable connections.

The current pilot plant has several following capabilities:

- Preparing the feed gas at required composition

According to *Dalton's law of partial pressure,* the total pressure exerted in a mixture of non-reacting gases is equal to the sum of the partial pressures of the individual gases. Thus a desired feed gas composition can be established on the pressure basis by analysing the pressure of the gas being fed from the top and bottom of mixing drum. The total pressure of the feed gas has to be as high as possible to prolong the duration of experiment.

- Establishing sub-zero temperatures

-55 ℃ can be achieved by two stage refrigeration using a methanol chiller filled with dry ice and pouring liquid nitrogen directly onto the insulated gas liquid separator. Insulation has also been installed onto the feed and product line of separator.

- Establishing high pressure

High pressure is readily available from the industrial grade *BOC Gas* cylinders so additional external compression is not needed.

- Estimating the capture rate

The composition of the depleted gas will be monitored by using a CO_2 MSR composition analyser while the CO_2 is being liquefied. The liquefied CO_2 will have a composition of 98~99mol%, the experimental capture rate can be calculated by material balance using the composition and flow rate of the vent gas as shown in Appendix A.

- Venting of non-condensable gases

This pilot plant has appropriate venting system which releases any non-condensable gases to atmosphere. Gas detectors and alarms were also installed in this pilot plant.

- Sampling points

Two sampling points are currently implemented, one is for analysing the composition of feed gas and one is for analysing the composition of depleted gas.

- Pumping of liquid CO_2

Refer to Chapter 6.

3.2.4 Process parameters

Operating pressure

The liquefaction temperature of CO_2 is determined predominantly by its pressure and it can be enhanced by increasing the CO_2 pressure (Xu et al. 2012). The operating pressure required for the experiment has to be obtained from the phase diagram, by reading from the liquid CO_2 region and will be controlled by a pressure regulator.

Operating temperature

-57 ℃ has been experimentally verified and identified as freezing temperature of CO_2 therefore -55 ℃ has been used to maximize the liquefaction. This temperature will be controlled by the frequency of pouring liquid nitrogen and dry ice methanol chiller.

Freezing temperature of CO_2 estimated by Aspen HYSYS®

Pure CO_2 at atmospheric pressure has a freezing temperature of -78 ℃ (Fig 61). However the feed gas to cryogenic section does not always contain 100mol% CO_2 and the operating pressure is not atmospheric. One of the Aspen HYSYS®'s utilities called 'CO_2 Freeze Out-1' is capable of estimating the freezing point of CO_2 based on the pressure and molar composition. It has been predicted by Aspen HYSYS® that the freezing temperature lies between -56 ℃ to -58 ℃ for a range of operating pressures and is independent of composition (except 100 mol%). This CO_2 solids prediction is restricted to the Peng Robinson (PR) and Soave Redlich Kwong (SRK) equation of state. Table 1 and Figure 2 agree with the actual freezing temperature at-57 ℃ obtained from experiment.

Table 23 Freezing temperatures estimated by Aspen HYSYS

Feed gas CO_2 composition balanced with N_2	Pressure (bar)	Freezing temperature (℃) By Aspen HYSYS®
85 mol%	15	-57.17
80 mol%	18	-57.38
75 mol%	20	-57.51
70 mol%	28	-58.04
65 mol%	30	-58.17
60 mol%	30	-58.17

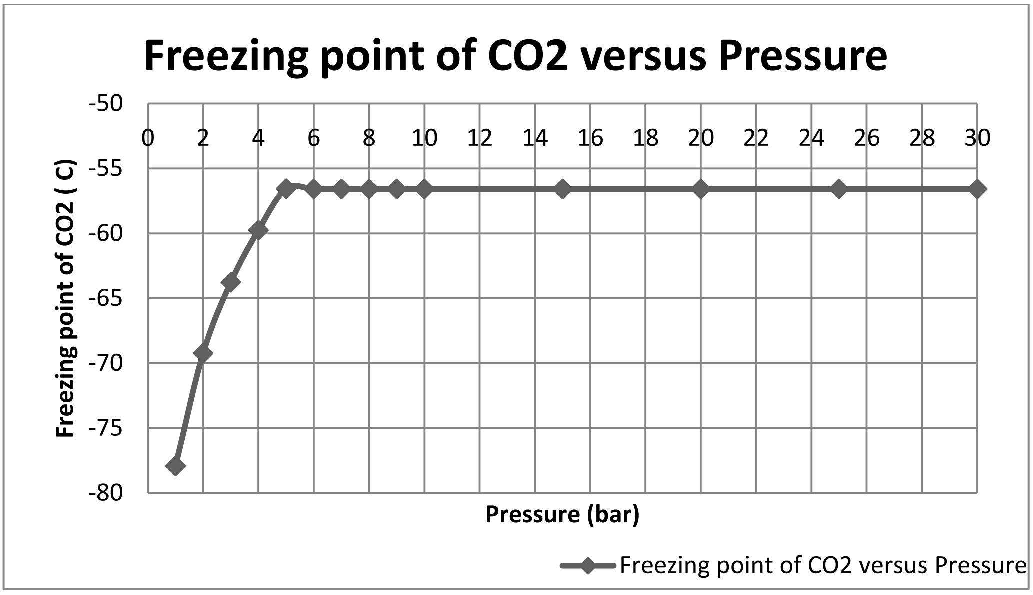


Figure 58 Freezing temperature of pure CO_2 versus pressure

Product specification

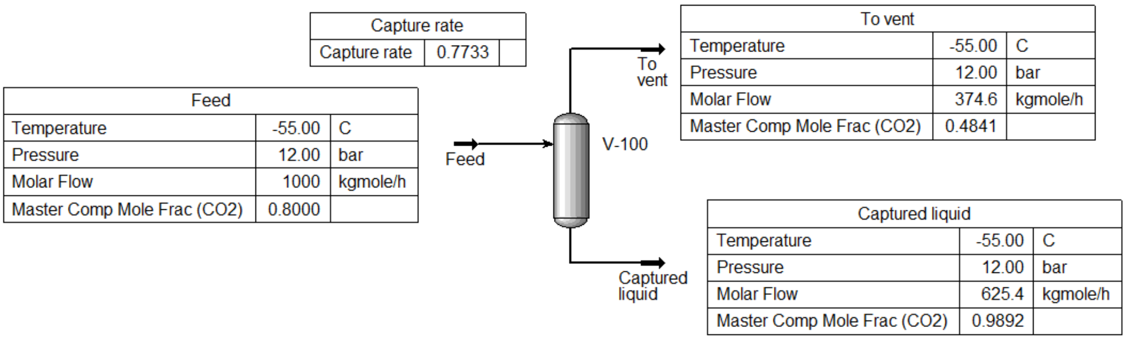
The main product for cryogenic condensation is concentrated CO_2 liquid with 95-97 mol% purity at high pressure (Surovtseva and Barifcani 2010). For a flue gas containing CO_2 between 60-90 mol%, 99mol% CO_2 product purity has been achieved in simulation results (Belaissaoui et al. 2012) . As a result, the liquid CO_2 of 99 mol% was assumed for calculating experimental capture rate in this paper.

Theoretical capture rate

Aspen HYSYS® is used to estimate the theoretical capture rate, i.e. how much liquid CO_2 can be liquefied under a certain composition and operating conditions. Peng Robinson is able to take into account the phase equilibria of mixture system especially non-polar gases like CO_2 and N_2 (Xu et al. 2012). This package is also reliable for three phase systems over a wide range of temperatures and pressures (Scholes et al. 2013). Several assumptions have also been made:

- Negligible pressure drop across the separator
- Negligible heat exchange with the surrounding
- Steady state operation

The results for capturing CO_2 at different composition and pressure have been plotted in a graph (Fig. 63). It is evident that higher pressure will be required to provide higher capture rate at a constant temperature. At a constant pressure, lowering the CO_2 concentration in feed gas will require a lower liquefaction temperature (Tuinier, Annaland, and Kuipers 2010). At a constant pressure, higher CO_2 concentration and lower temperature will enhance CO_2 separation rate (Xu et al. 2012).



Capture rate	
Capture rate	0.7733

Feed		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	1000	kgmole/h
Master Comp Mole Frac (CO2)	0.8000	

To vent		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	374.6	kgmole/h
Master Comp Mole Frac (CO2)	0.4841	

Captured liquid		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	625.4	kgmole/h
Master Comp Mole Frac (CO2)	0.9892	

Figure 59 Estimating capture rate using HYSYS at different operating conditions

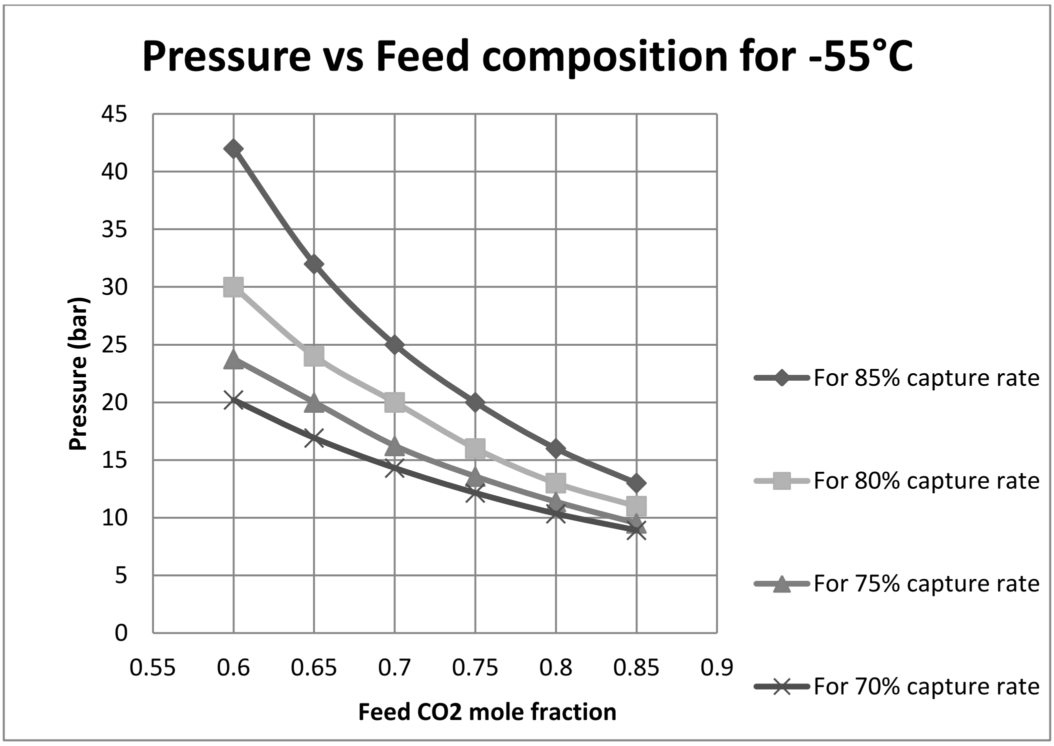


Figure 60 Pressure versus feed composition at constant temperature by Aspen HYSYS

Experimental capture rate

At a temperature of -55 ℃ and the adequate pressure, CO_2 will be liquefied and stays at the bottom of the gas liquid separator while nitrogen which does not freeze will move to the vent along with remained CO_2. The composition of the vent is then analysed and can be used to compute the experimental capture rate as follows:

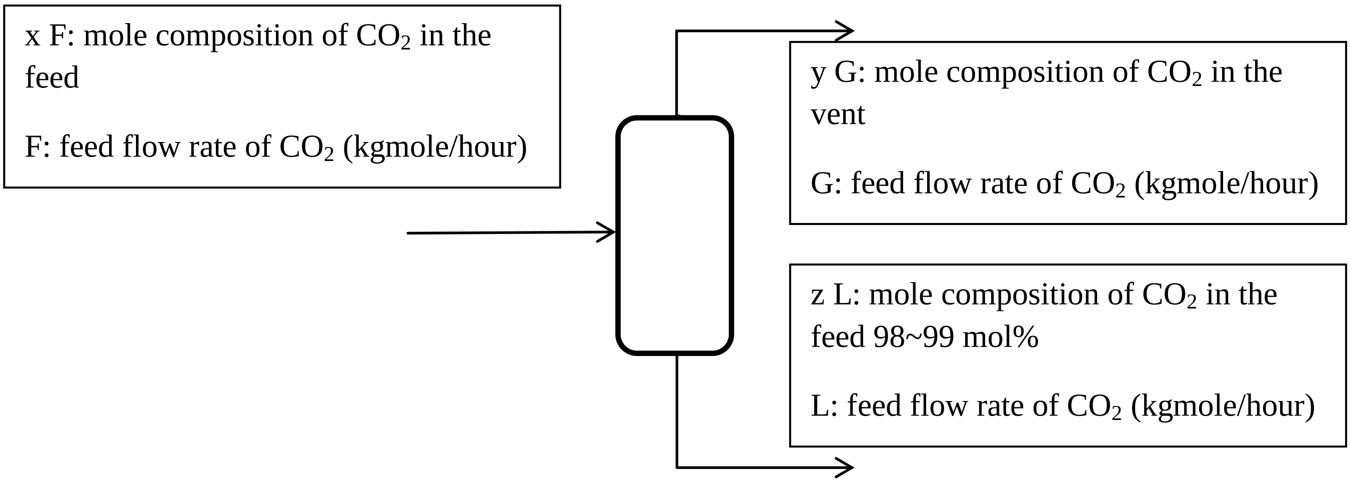


Figure 61 Material balance around gas liquid separator

Overall material balance:

$$F = G + L$$

CO_2 component material balance:

$$xF * F = yG * G + zL * L$$

Calculating capture rate:

$$Capture\ rate\ (\%) = \frac{yL *\ L}{xF *\ F}\ x\ 100\%$$

3.3 Equipment and chemical used

3.3.1 Gases and chemicals used

ICEBITZZZ^{TM} Dry ice pellets by the kg (gas code 088)

Dry ice appears as a translucent white solid and it changes from a solid to gas at normal temperatures without going through a liquid state (sublimation). The dry ice is supplied by *BOC Scientific* and has a temperature of -78.5 ℃ therefore it acts as a very effective cold blanket to the gas liquid separator. Other applications may include fabrication shrink fitting, freeze-branding and etc.

Liquid nitrogen (gas code 713)

Liquid nitrogen is supplied by *BOC Scientific* by cryogenic tankers into small, cryogenic containers available in the laboratory. It is an odourless, colourless liquid and has a purity of >99.5% vol, a boiling point of -195.8 ℃. Liquid density at absolute pressure of 1 atm is 807 (kg/m^3)

Compressed nitrogen (gas code 032)

G size industrial grade nitrogen is supplied by *BOC Gas* and has a content of >99.9% vol, a gauge pressure of 163-200 bar. The outlet connection for this cylinder is AS2473 Type 50. It's applications in this lab include:

- Purging vessels and pipelines
- Purging applications to dilute the feed gas to desired mole composition

Other applications may include:

- Blanketing and purging applications to displace or dilute all unwanted gas or vapour
- Inerting reactors and storage tanks
- Shielding or assist gas for plasma cutting aluminium and stainless steel, and as an assist gas for laser cutting
- Pressurizing accumulators for batch-testing applications

Compressed carbon dioxide (gas code 081)

G size industrial grade CO_2 is supplied by *BOC Gas* at a pressure of 6300 kPa (at 25C) when full. It has a content of 99.9% vol. The outlet connection for this cylinder is AS2473 Type 30.

Compressed Hydrogen (gas code 135)

G size industrial grade hydrogen is supplied by *BOC Gas* at a gauge pressure of 13700 kPa. The hydrogen composition is >99.5% and is odourless, colourless and tasteless. Hydrogen burns with a clean carbon-free and soot-free flame and will ignite easily therefore the cylinders must not be snifted. The flame is invisible and is lighter than air there it will collect at ceiling level. When used with oxygen, a flame of approximately 2834 ℃ can be produced. Common applications include:

- Heat transfer applications

- An important addition to argon in a range of argon-hydrogen shielding gases for plasma welding

- As an alternative power source when used with a fuel cell to generate electricity

The outlet connection for this cylinder is AS2473 Type 20.

Compressed Oxygen (gas code 020)

G size industrial grade oxygen is supplied by *BOC Gas* at a gauge pressure of 163000kPa-20000kPa. The oxygen composition is >99.5% and it is colourless, odourless and does not burn but supports and accelerates combustion. Common applications include:

- Used with a fuel gas for cutting, welding, brazing and soldering. The use of oxygen gives higher flame temperatures than if air is used.
- In plasma and laser cutting steel, an arc or a laser beam is used to heat the steel to its ignition temperature. Oxygen is then used in the same way as with oxygen cutting to create an exothermic reaction and to blow away any metal oxide or slag
- Thermal lancing oxygen is used in conjunction with the steel lance to create a high temperature melting process capable of drilling or cutting through materials such as concrete, brick, stone and most metals
- Used as an assist gas in lasers for cutting mild steel

The outlet connection for this cylinder is AS2473 Type 10.

Methanol

Methanol is supplied by *Sigma Chemicals* and it has a freezing point of -98 ℃. It is a colourless, light and flammable liquid therefore it has to be stored in the flammable cabinet after use.

3.3.2 Equipment used

Mixing drum

The mixing drums V-002 and V-003, manufactured by *Westralia Engineering Services* in year 2000 according to code AS1210-1997 class 2B, are used for preparing the gas at the required concenration and has the following specifications: design review number WAP18572, inner diameter of 6.8 inches, height of 104cm, design pressure of 150 bar, shell/head nominal wall thickness of 18.26 mm, corrosion allowance is 0.5mm, maximum design temperature (shell/tube) is 100 ℃, minimum design temperature (shell/tube) is -25 ℃, and made of carbon steel. The shell material is ASTM A333 Gr6 while the tube material is ASTM A350 LF2. Design code is AS/NZS 1210/2B 1997. This mixing drum is being protected by a pressure relief valve rated at 150 bar. In accordance with AS3788 2006, statutory internal/external inspection should be carried out every two years. Each mixing drum consists of a GD lock closure door for inspection purposes. Detail installation and dismantling procedure for these closure door is given in section 3.5. The vent valve (circled in red) is located on the top of mixing drum and the valve which isolate two drums is circled in purple.

Figure 62 Mixing drum

Figure 63 Gas liquid separator

Gas liquid separator

The gas liquid separator manufactured by *Lightning Fabrications* has a design pressure of 70 bar and a design temperature of 50 ℃, -75 ℃. It has an inner diameter of 4 inches and height of 80cm. This gas liquid separator is being protected by a pressure relief valve rated at 70 bar.

Figure 64 Methanol chiller

Methanol chiller

This chiller consists of spiral tubings for process fluid to flow through and a mechanical stirrer manufactured by *John Morris Scientific Pty Ltd*, type RZR1, serial number: 070636614 which promotes the chilling effect by inducing more turbulence. This chiller also has a drain plug which prevents the methanol from getting overfilled.

3.3.3 Valves and fittings list

Parts	Swagelok part no	Function	Schematic
SS 1-piece 40 series ball valve	SS-43GS4	Open and close, isolation purpose	
SS Poppet 6000 psig(413bar) check valve	SS-CHS4-1	Prevent backflow	
SS integral bonnet needle valve, 0.37Cv, ¼ in regulating stem	1RS-4	For regulating purpose	
SS Low pressure proportional relief valve, 1/4’’ Swagelok tube fitting	RL3S4	Prevent overpressure the vessel and to be connected to the vent line	
SS 1-piece 40 series 3 way ball valve	SS-42GXS4	For switching flow pattern	
Union Tee, 1/4 inch	SS-400-3	For combining two streams into one or splitting one stream into two	
Stainless Steel Pipe Fitting, Pipe Cap, 1/4 in. Female NPT	SS-4-CP	For plugging extra end connections	
Union cross, ¼ inch	N/A	For combining or splitting of streams	
SAF 2507 Super Duplex Swagelok Tube Fitting, Union Elbow, 1/4 in. Tube OD	2507-400-9	For connecting two tubing with an angle of 90 degrees	
Alloy 400 Swagelok Tube Fitting, Female Branch Tee, 1/4 in. Tube OD x 1/4 in. Tube OD x 1/4 in. Female NPT	M-400-3-4TTF	For installation of pressure gauges with male thread	
SAF 2507 Super Duplex Swagelok Tube Fitting, Union, 1/4 in	2507-400-6	For connection of two tubing	
316/316L SS Seamless Tubing, 1/4 in.	SS-T4-S-035-20	Tubing	
316 SS Nut and Ferrule Set (1 Nut/1 Front Ferrule/1 Back Ferrule) for 1/4 in.	SS-400-NFSET	For connection of tubing, fittings, parts	

3.3.4 Calibration of pressure relief valve

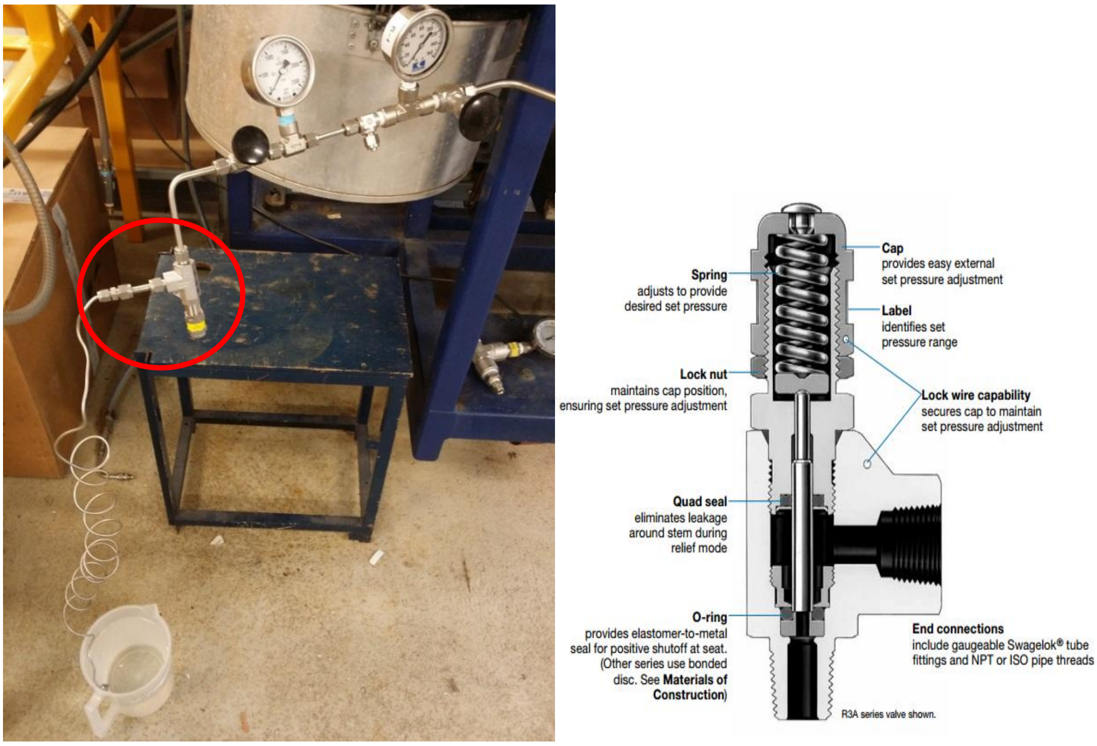


Figure 65 Calibration of pressure relief valve (left) and key components of the pressure relief valve (right)

The proportional relief valve circled in red above is a Swagelok® R series relief valve (in this scenario the ordering number is SS-RL3S4 for ¼ inch connection) which open when system pressure reaches the set pressure and close when system pressure falls below the set pressure. This valve is used as a safety device to prevent overpressure of line and vessel. It consists of several key components such as a cap, lock nut, spring, spring support, bonnet, stem, and main body. The lubricant used is Molybdenum disulphide-based dry film and paste. It is important to note that this relief valve will open gradually as the pressure increases therefore it does not have a capacity rating at a given pressure rise (accumulation) and is not certified to ASME or any other codes. The set pressure can be set by the configuration shown in Figure 65 above by using 2 regulating valves, 2 pressure gauges, a flexible coil and a bucket filled with water. Assuming the set pressure required is at 2 bar, a few steps for setting the set pressure are given as below:

- keep all the regulating valves close, fully loosen the lock nut and tighten the cap to over-set the set pressure

- slowly open the first regulating valve to provide a pressure of say 5 bar, then slowly open the second regulating valve to provide a pressure of 2 bar (the set pressure)

- Slowly loosen the cap and stop loosening when the gas release from the end connections which can be observed by gas bubbling into the water

- tighten the locking nut to ensure that the set pressure is left untouched. The set pressure can be verified by introducing a higher pressure and observe the gas bubbling into the water.

3.3.5 Instrumentation used

Figure 66 6 channel Shimaden controller

Temperature sensor

A 6 channel Shimaden controller with an accuracy of ±0.1 ℃ will be used to monitor the temperature of the inlet line to the gas liquid separator and the temperature of the gas liquid separator. (Note: a temperature of -43C is being shown in Figure above)

Thermometer

A Deluxe Dual Input Thermometer with an accuracy of ±0.1 ℃ will be used to monitor the temperature of the cold methanol-ice bath.

Flow meter

An ELSTER RVG G16 rotary gas meter is used to measure the flow rate of vent gas coming out from the gas liquid separator which its flow rate is controlled by the pressure control valve at 0.1~0.2 kg/hour. This meter has a maximum pressure rating of 20 bar, measures flow range between 0.8 m^3 per hour to 25 m^3 per hour and a flange rating of ANSI 150.

CO_2 Composition Analyser

MSR CO_2 composition analyser is used for measuring the CO_2 composition on mole basis. Its accuracy can be tested by feeding in 100 mol% CO_2. This composition analyser is connected to PolyGard® Cellar Alarm Controller, mGC-03-02-02-9-110005011, serial number: 03-31/08 made in Germany.

3.3.6 Regulators used

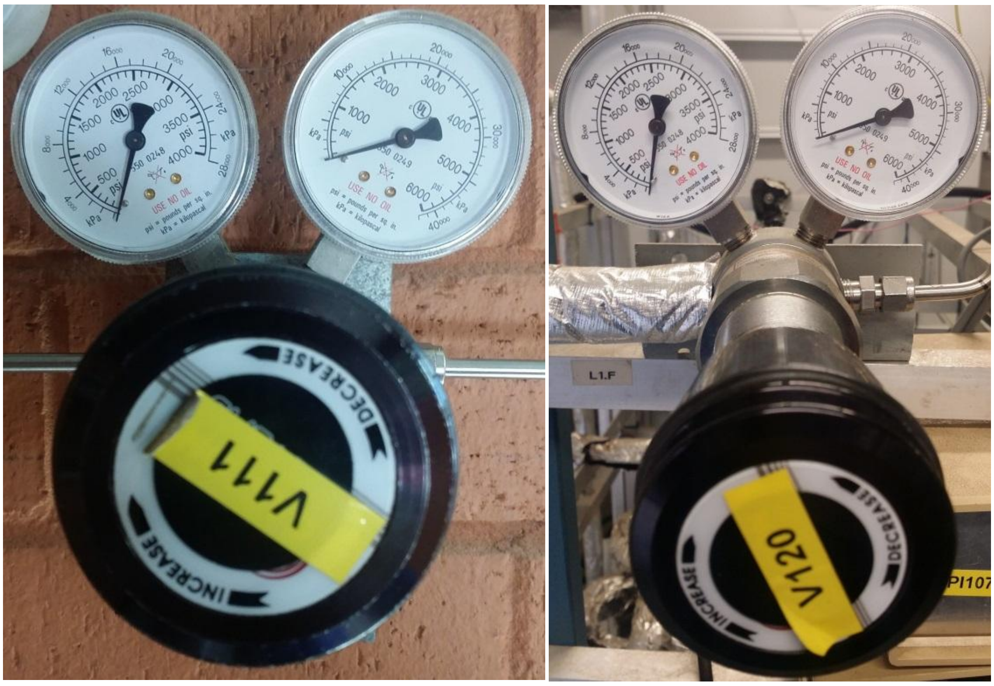


Figure 67 Pressure regulators used

Having a maximum inlet pressure of 379 bar, these two pressure regulators were manufactured by *Controls Corporation of America (CONCOA)* in Virginia Beach in United States of America. The regulator on the left acts as a manifold for reducing the high pressure from the BOC gas cylinders. It has a serial number of 05A036R7. On the other hand, the regulator on the right is used to control the operating pressure for experiments. It has a serial number of 078088HK. Specific procedures for the safe use of these regulators are given below:

- Never subject the regulator to inlet pressure greater than its rated inlet pressure, as shown on regulator body.

- Never use the regulator for gases other than those for which it is intended.

- Before attaching regulator, remove any dirt or foreign matter that may be in the cylinder valve outlet by wiping with a clean, lint-free cloth.

- Never pressurize a regulator that has loose or damaged parts or is in questionable condition. Never loosen a connection or attempt to remove a part until gas pressure has been relieved. Under pressure, gas can dangerously propel a loose part.

- Check regulator and all connections for leaks after installation, periodically thereafter, and after any service in which parts or connections were loosened. Brush with an approved leak detection solution. Bubble indicates leak.

3.4 Vessel inspection

The vessel inspection was carried out in accordance with the guidelines and statutory requirements of:

- AS/NZS 3788 2006 Pressure Equipment In Service Inspection,
- Western Australia, Occupational Health and Safety Regulations,
- ApplusRTD technical procedure TP-05-07-19, *In Service Inspection of Pressure Equipment*.

The inspection scope consisted of a visual internal/external inspection where accessible. Visual examination of the exterior of the vessel shells was limited by the presence of insulation. The top and bottom insulation from the vessels was removed with both surfaces in generally good condition. There was no evidence of indications warranting further review.

Internally; the inspections were carried out from the lower end and the vessels were found to be in a stable condition with no advanced concerns since the last inspection report. The minor surface scouring identified in the previous report for V-002 has not propagated any further nor raised concerns for further investigation. The internal of the vessel presented in a fair condition with only light surface oxide present.

The due date for calibration/renewal of the vessels' pressure relief valves, numbers PSVV-1 and PSVV-2 remains unknown. Testing and calibration was recommended during the previous inspection but still appears to have been missed. To comply with statutory regulations and ensure the future safety of these vessels while in operation, the PSV's need to be recertified.

Consideration to remove the insulation should be discussed during normal maintenance period to perform a full external shell review. The operating parameters of these vessels place these vessels in the range susceptible to Corrosion Under Insulation (CUI). Being that a full external inspection has not been performed nor recorded for 2 years, removal for the next interval is necessary.

The band lock closure at the lower end is of the quick release type. The condition of the end plates and mechanics are in good condition with one plate showing minor surface oxide. The gasket faces were in acceptable condition for both plates.

Detailed procedure for installing and dismantling the closure doors for vessels can be found in Appendix.

CHAPTER 4 THE ENERGY SAVING SCHEME FOR VSA/CRYOGENIC HYBRID

4.1 Development of cryogenic hybrid method

This chapter focuses on the development of a novel cryogenic process and the heat integration to achieve the lowest possible energy penalty and the CO_2 recovery has to be satisfactory. The biggest motivation is that cryogenic processes are very often regarded as overly energy intensive and there is a limited amount of published literatures addressing energy saving strategies for cryogenic process. The cryogenic process can be illustrated by using a block flow diagram shown in Figure 75.

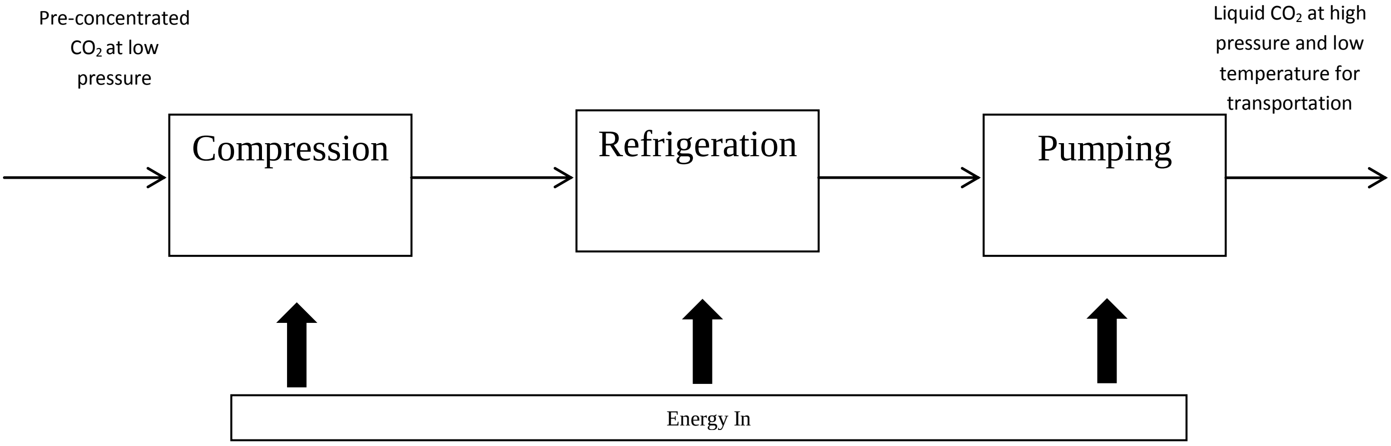


Figure 68 Block Flow Diagram for CO_2 capture by cryogenic method

In order to reduce the cost for compression and transportation, (Belaissaoui et al. 2012) proposes that a target of 90% CO_2 capture ratio (CCR) and 90% CO_2 purity has to be met. These two major concerns have been taken into account in the modelling. The model was developed based on the assumption that CO_2 from the power plant flue gas will be pre-concentrated by other capturing technology, in this scenario VSA, to at least 60-70mol% $CO_{2,}$ before entering the cryogenic section. For the steady state modelling of this VSA/Cryogenics hybrid process, Aspen HYSYS® software package, version 7.2 was used and Peng Robinson (PR) thermodynamic model was selected for cryogenic gas processing. The modelling of VSA is beyond the scope of this thesis.

The pre-concentrated CO_2 has been compressed and cooled to the required operating conditions which only CO_2 gets condensed, then using liquid CO_2 as refrigerant to chill its feed streams and result in energy savings for both compressors and refrigeration package and the removal of sea water coolers. The development of actual refrigeration loop will be briefly explained in later section of this chapter.

One major highlight for the energy saving scheme is that air coolers are used after discharge of compressors to reduce the overall energy penalty. CO_2 remains as liquid phase after the heat integration and is readily pumped to the required pressure for geological storage. Not only that pumps are less energy intensive than compressors but also liquid CO_2 requires a smaller pipe sizes and equipment compared with CO_2 in supercritical phase. The depleted gas stream from the gas liquid separator was also recycled back to the upstream for improving recovery instead of purging it into atmosphere.

Different feed and product gas composition has been provided by CO2CRC adsorption group from University of Melbourne. By plotting the VSA recovery (%) and CO_2 composition (%) in product stream, it can be noted that when the VSA recovery is high, the CO_2 composition in product stream is low (inverse relationship) and the CO_2 composition in VSA product stream has a strong impact on the energy consumption for cryogenic. Assuming a 100% recovery for cryogenic section by recycling the vent stream from cryogenic to VSA feed, the VSA recovery represents the recovery for VSA/Cryogenic hybrid. Therefore it can be concluded that VSA recovery is inversely proportional to the energy consumption in cryogenic.

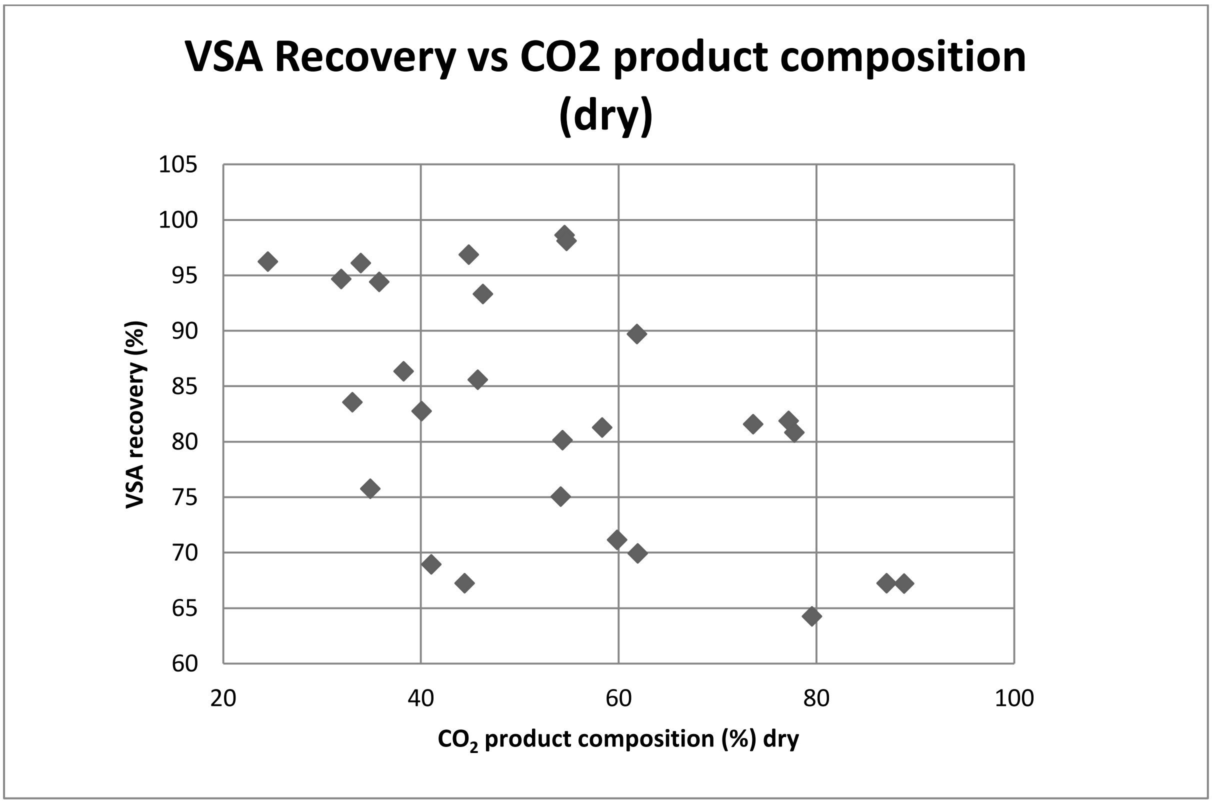


Figure 69 VSA recovery vs CO_2 product composition (dry)

The feed gas composition given used in the model is very similar to the flue gas compositions for PCC of a 500-600 MW power plant given in other published literatures are shown in table 26.

Table 24 Comparison between flue gas specifications

Flue gas specifications	(Dong et al. 2011)[1]	(Merkel et al. 2010)[2]	(Scholes et al. 2013)[3]	(Zhang, Webley, and Xiao 2007)[4]	Feed gas composition used in this model
Pressure (bar)	--	1	1.16	1.016	1.5
Temperature (℃)	--	--	30	93.1	50
Flow rate (kg/s)	--	945.8	899.44	606.25	741.11
Power plant size (MW)	--	600	500	500	500
N_2 (mol%)	68-75	73	73.4	71	77.97
CO_2 (mol%)	10-15	11.6	13	12.6	12.26
H_2O (mol%)	5-10	11	4.6	11.1	4.22
O_2 (mol%)	2-5	4.4	9	4.4	5.55
Argon (mol%)	--	--	--	0.8	--
NOx (ppm)	Trace	--	170	--	--
SOx (ppm)	Trace	--	350	--	--

Before optimizing the energy, seawater coolers were used for cooling. Alabdulkarem, Hwang et al (2011) studied the liquefaction/compression/pumping of CO_2 and proposed that seawater at the sea surface has a temperature of 35 ℃ while the deep sea water has a temperature of 4 ℃. Deep sea water may provide more cooling due to its low temperature however extracting deep sea water would elevate the cost. Therefore 35 ℃ was specified for seawater coolers before any heat optimization to help achieving the liquefaction temperature of CO_2 (not shown after optimization). The heat integration of the cryogenic liquefaction process developed in this paper is very similar to an open CO_2 liquefaction cycle cited by Alabdulkarem, Hwang et al (2011) and developed by Aspelund et al (2006) which consists of three compression stages, three intercooler and two multi-stream heat exchangers. However, Aspelund et al (2006) has only reused a portion of compressed CO_2 for heat integration by expansion and the cold temperature available in liquid CO_2 has not been fully utilized for cooling. One common point is that the compression of feed gas in that paper is also achieved in multistages and the optimum combination of operating pressure and liquefaction tempeature is the key to optimum energy required for this energy saving scheme. It means that the refrigeration duty will increase as the compresion duty decreases to meet the CO_2 recovery target and vice versa.

Several assumptions have also been made in the simulation as follows:

- NO_x and SO_x have been pre-treated and not being regarded in this process
- Feed and product of VSA have the same temperature and pressure for the purpose of simulation

- The dryer has a pressure drop of 35kPa and assuming 910 kgmole/hour of air required for regenerating the solid adsorbent for the purpose of simulation
- 15kPa pressure drop for heat recovery exchangers, air coolers
- Negligible pressure drop across separators, valves, splitters and mixers
- 85% efficiency for compressors and pumps

In Aspen HYSYS® simulation, five types of unit operation models are available for performing separations. The actual process for both pre-concentration of CO_2 and dryer package was simulated by using 'Sep2' while the cryogenic gas liquid separator was simulated using "Flash2'.

Table 25 Unit Operation Models for component separations in HYSYS

Model	Description	Purpose	Use for
Flash2	Two-outlet flash	Separates feed into two outlet streams, using rigorous vapor-liquid or vapor-liquid equilibrium	Flash drums, evaporators, knock-out drums, single stage separators
Sep2	Two-outlet component separator	Separates inlet steam components into two outlet streams, based on specified flows, split fractions or purities	Component separation operations, such as distillation and absorption, when the details of the separation are unknown or unimportant

Components such as water, nitrogen and oxygen CO_2 have been removed. Two knockout drums V-100 and V-102 were used to knockout the excess water from the gas to provide more energy savings in compression. The dryer package uses physical adsorbent which in reality, it should consist of two bed adsorber columns (A-100 and A-101). One bed, A-100 dries the gas while the other bed, A-101 goes through a regeneration cycle. The compressor K-103 and furnace H-100 were used to generate hot air for regenerating the adsorbent. The temperature required to regenerate the adsorbent was assumed to be 250 ℃. The feed gas should enter from the top of the dryer to prevent fluidization. For the basis of simulation, 85% adiabatic efficiency was assumed for compressors, pumps and expanders. 15kPa pressure drop is assumed for heat recovery exchangers and air coolers. The air coolers were assumed to have the ability to cool the compressors discharge stream to 55 ℃.

The dried feed (stream 27) to cryogenic section contains 77.12 mol% CO_2 and 22.88 mol% N_2. After going through a three stage compressors (K-100, K-101 and K-102), air coolers (AC-100, AC-101 and AC-102) and heat recovery exchangers (E-100, E-102 and E-103), a refrigeration package (R-

100) was assumed to have the capability of chilling the gas to -55 ℃ using mixed refrigerant or cascade refrigeration method. The cryogenic condensation and separation occurs at 13.95 bar and at -55 ℃. Before entering the refrigeration package, the process stream (stream 3) is also split into a ratio of 70:30 (by iteration) to maximize the efficiency of cooling. The discharge pressure of each compressor was iterated to ensure the overall compression duty is minimum and taking into account the overall CO_2 recovery, pressure ratios, and the limitation of discharge temperature for compressor.

Gas liquid separator V-101 separates the liquid and incondensable CO_2. The gaseous CO_2 was used to chill its feed at E-103, expanded by turbine (Exp-101) to 165 kPa for more cooling at E-101 and recycled back to upstream at a pressure same as upstream feed pressure to enhance the recovery of CO_2. The heat recovery exchanger E-101 condenses excess water out of the wet feed gas to save compression energy in K-104. On the other hand, the cryogenic energy available in liquid CO_2 was recycled to chill the feed streams at E-100 and E-102 and eliminates the previous use of sea water coolers in this simulation (not shown). The energy from turbine was recovered to provide compression in one of the process streams (stream 8). The final liquid product was pumped to 110 bar by pump P-102.

Figure 77 shows the block flow diagram for the VSA/Cryogenic energy saving scheme and figure 78 shows the optimization of VSA/Cryogenic energy saving scheme considering the water removal and figure 79 is for the optimized scheme without considering water removal.

Vacuum swing adsorption (VSA)

The vacuum pump for VSA has been identified as the biggest contributor for both the energy penalty and capital cost (Fong et al. 2013). However detail investigation is beyond the scope of this thesis. Therefore the VSA was modelled using ‘Sep2’ in HYSYS because the details of separation are not known. ‘Sep2’ also offers a wide variety of specifications, e.g. the purity (mole fraction) specification of a component can be specified and has no dynamic features. VSA has to vent most of the nitrogen and all oxygen, therefore the product (stream 17) has only CO_2, N_2 and H_2O. The ‘split fractions’ has undergone an iterative process to ensure the vent gas composition is satisfied and result in split fractions as shown below:

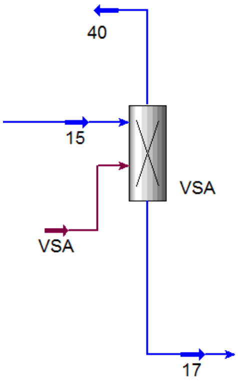
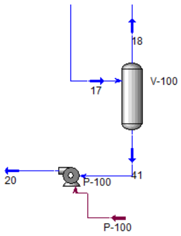


Table 26 Vacuum Swing Adsorption stream specification

Stream	40	17
CO_2	0.0451	0.9549
N_2	0.947	0.053
O_2	1	0
H_2O	0	1

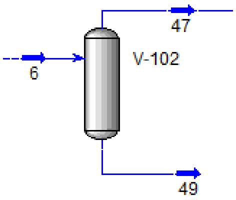
Water separator V-100 and V-102

There is a significant amount of water in the VSA product, water knockout drum has been used. The main purpose is to flash out as much water as possible under the existing conditions (pressure and temperature) before going into the dryer section. As a result, it saves energy for drying (i.e. compressor, air for adsorbent regeneration).

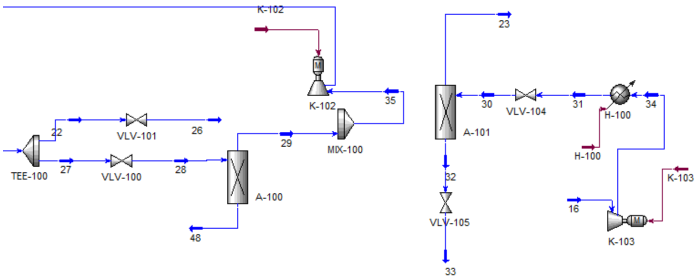


Stream 41 and Stream 49 contains 99 mol% water and 0.03 mol% CO_2. When CO_2 dissolves in water it exists in chemical equilibrium producing carbonic acid, a weak acid. These streams can be treated and reused.

In this scenario, ‘Flash2’, a two instantaneous flash with no dynamic effect (e.g. pressure drop across separator is not being considered) has been used because this dynamic model assumes perfect mixing and that all phases are always in equilibrium.



Drying



The drying process has been simulated using ‘Sep2’ component splitter due to the fact that most of the design parameters (type of adsorbent, size of particle, average pore diameter, and etc) are not specifiable in HYSYS. Assuming A-100 reach a dew point of -80 ℃ (LNG specification) while A-101 is in regeneration mode using hot air. (J.Kidnay and R.Parrish 2006) has stated that the pressure drop across the molecular sieve dehydration units shall not exceed 69kPa, ideally 35kPa. Therefore 35kPa pressure drop has been assumed for both A-100 and A-10. For regeneration of adsorbent, (J.Kidnay and R.Parrish 2006) also claimed that 200-315 ℃ is required. Therefore 250 ℃ has been assumed. Due to insufficient information available for simulating the dryer, the duty for drying considers only the compression and heating of air and the compression of process stream to overcome the pressure drop across the column.

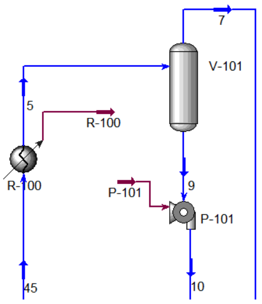
Table 27 Adsorber column specification

Feed rate	$2.08 \times 10^{-4} – 2.91 \times 10^{-3}$ m^3/min
Superficial velocity	9-11 m/min
Pressure drop	35kPa, not to exceed 69kPa
Cycle time	240 -1440 min
Adsorption temperature, pressure	10-45°C, ≈10342kPa
Desorption temperature, pressure	200-315 ℃, same as adsorption pressure or lower

Table 28 Properties of molecular sieves 4A

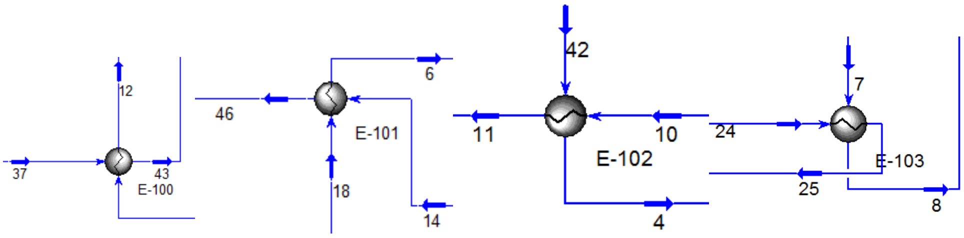
Shape	Pellets (extruded cylinders) and beads
Regeneration temperature (℃)	200-315
Packed bed % voids	35
Particle size (mm)	1.6, 3.2, 6
Bulk density (kg/m^3)	640-720
Specific heat (kJ/kg-K)	1
Pore volume (cm^3/g)	0.28
Surface area (m^2/g)	600-800

Cryogenic liquid separator



'Flash2' has been used for simulating the cryogenic separator V-101. Both previous laboratory experiment and HYSYS simulation have showed that CO_2 will freeze at -57℃ and previous modelling has also showed that pressure has more impact on the capture rate compared to temperature. Therefore for stream 5; the capturing temperature has been set at -55℃, the lowest possible temperature for liquefying CO_2. The liquid CO2 (stream 9) has to be pumped to a high pressure (in this case ≈90 bar) to prevent CO_2 from vaporising again. The pumping action does not increase the temperature of chilled CO_2 very significantly therefore it can be used to reduce refrigeration energy.

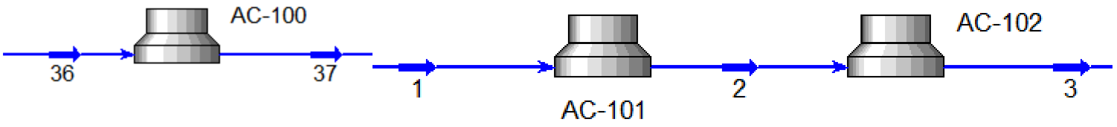
Heat recovery exchangers E-100/E-101/E-102/E-103



Shell and tube heat exchangers are used to recover heat i.e. using cold stream to chill hot stream in order to reduce the refrigeration duty. The outlet temperature of cold stream has been undergone an iterative process in order to obtain the highest possible (to maximize the heat recovery) without violating several constraints such as temperature cross error, vaporisation of CO_2 liquid and etc. 15kPa pressure drop has been assumed for both shell and tube side for the purpose of simulation (obtained from Tubular Exchanger Manufacturers Association TEMA) [9]. From the Heat Exchanger Model drop down list, 'Exchanger Design (Weighted)' has been selected because it is an excellent model to deal with non-linear heat curve problems such as the phase change of pure components in one or both heat exchanger sides. No heat loss has also been assumed for simulation purpose. Heat recovery exchangers have been placed at their ideal location by observing several factors:

- Is the temperature cold enough to chill the hot stream?
- Is the flow rate of cold stream sufficient to chill the hot stream?

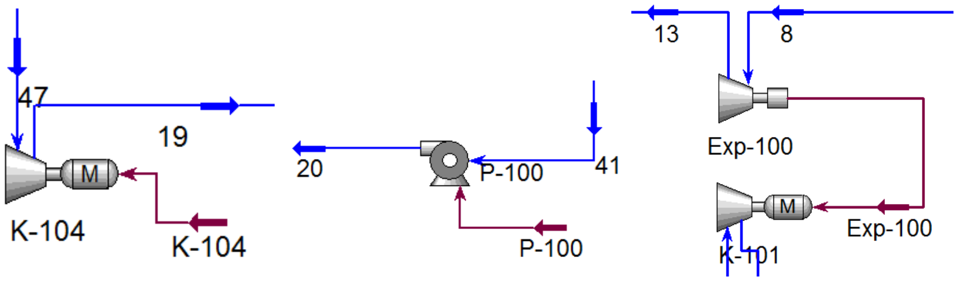
Air Coolers AC-100/AC-101/AC-102



An idea of using an air cooler after a compressor has been introduced due to the fact that temperature of the stream will increase significantly due to compression. Assuming the air intake condition is at ambient 25 ℃ and 1.013 bar.

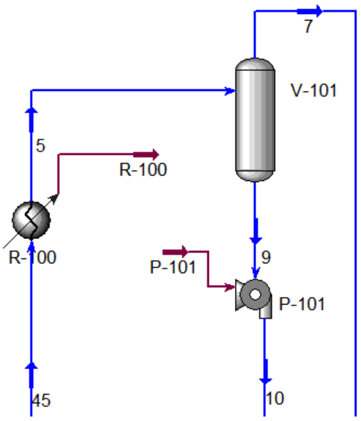
1) Assuming the pressure drop 15kPa for simulation purpose
2) Assuming the air cooler has the ability to cool the process stream down to 55 ℃. Cheremisinoff, N (2000) has suggested the approach temperature differences between the outlet process fluid temperature and the ambient air temperature are generally in the range of 10 to 15 ℃.

Compressors K-100/K102/K-104, Pumps P-100/P-101/P-102 and Expander Exp-100



Assume compressors, pumps and expander has 85% adiabatic efficiency. For compressing CO_2 to the capturing pressure of 13.95bar and to overcome pressure drop across heat recovery exchangers and air coolers, compressors have been used in multistage mode. Each discharge pressure has been subjected to an iterative process whilst focusing on the overall power requirements and discharge temperature. 110 bar has been assumed for the pump discharge pressure [3] The expander has been used to recycle the available energy for compression while recycling the process stream back to VSA to boost its recovery.

Refrigeration package R-100



The refrigeration package has been simplified by using a ‘cooler’ in HYSYS for simulation purpose. ‘Cooler’ is a one sided heat exchanger and the inlet stream 45 is cooled to the required outlet (stream 5) conditions, i.e. -55℃. 15kPa pressure drop has been assumed for this cooler for simulation purpose. This refrigeration package is essentially a refrigeration loop (e.g. cascade refrigeration, mixed refrigerant, etc) which consists of compressor, air cooler, sea water cooler, and a Joule Thomson valve. As a result, the duty given by this ‘cooler’ is divided by an assume efficiency of 85% (same as compressors and pumps).

4.2 Block flow diagram for VSA/Cryogenic hybrid process

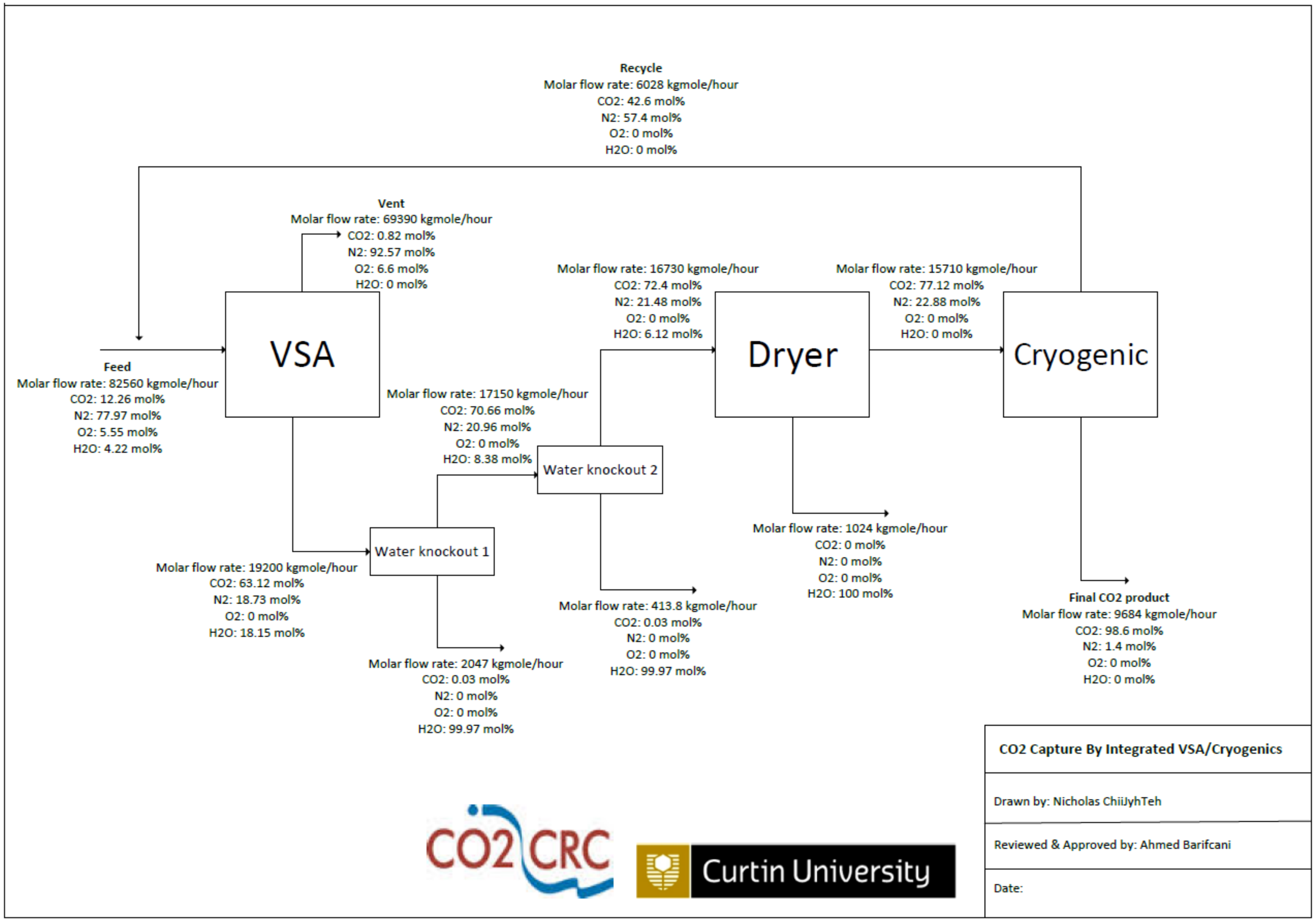
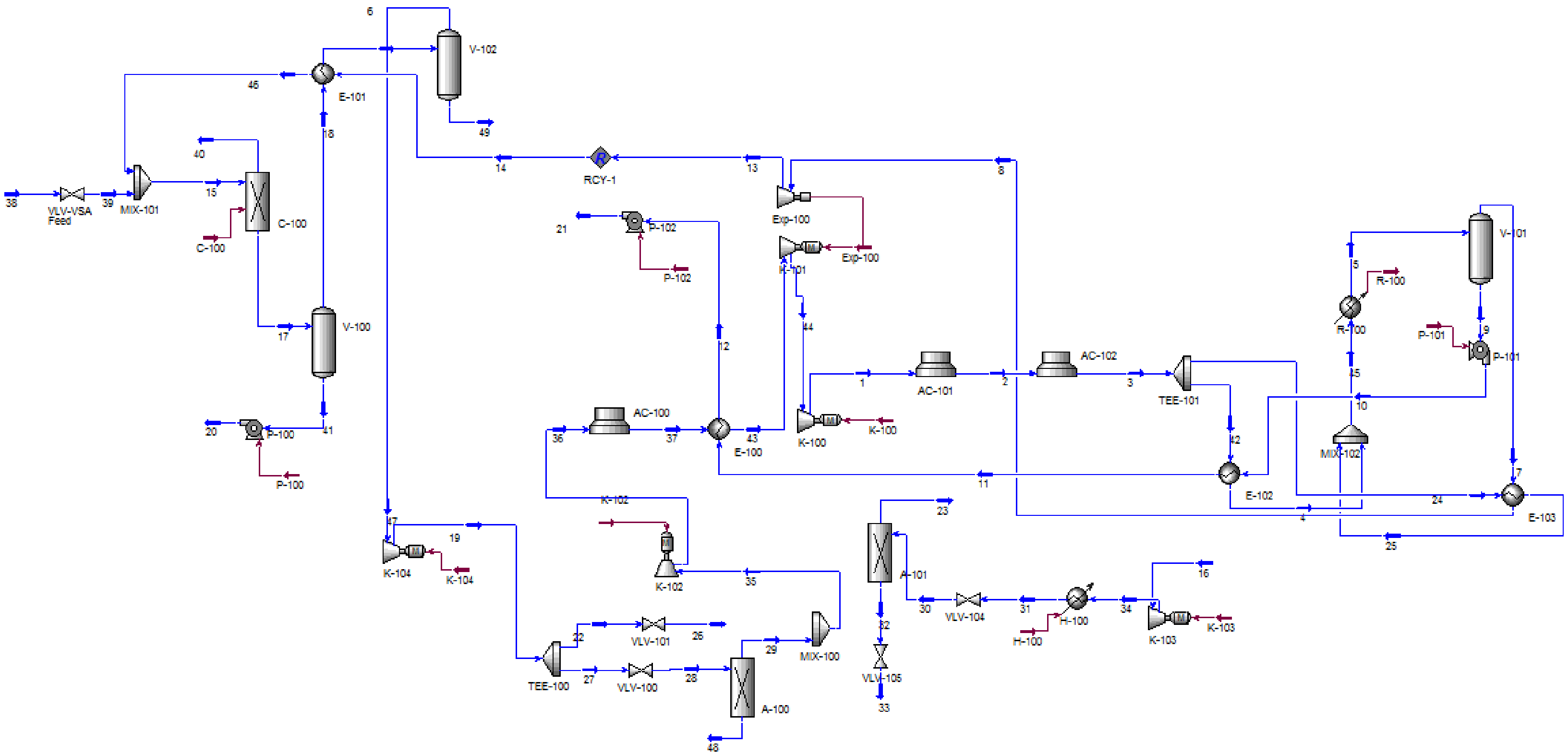


Figure 70 Block flow diagram for VSA/Cryogenic hybrid process

4.3 Aspen HYSYS simulation for VSA/Cryogenic hybrid process



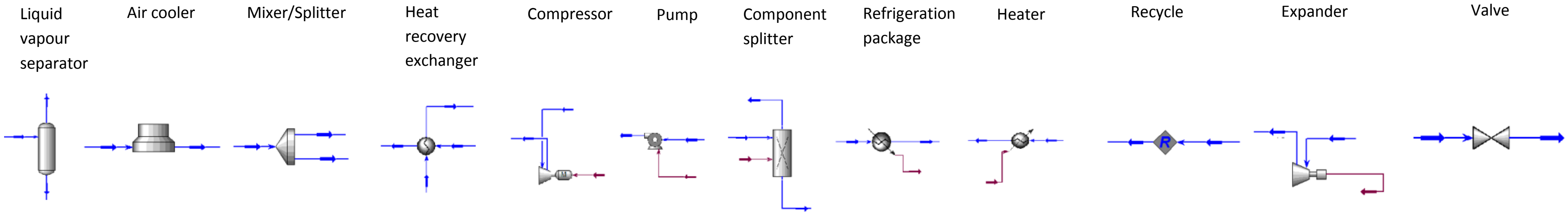
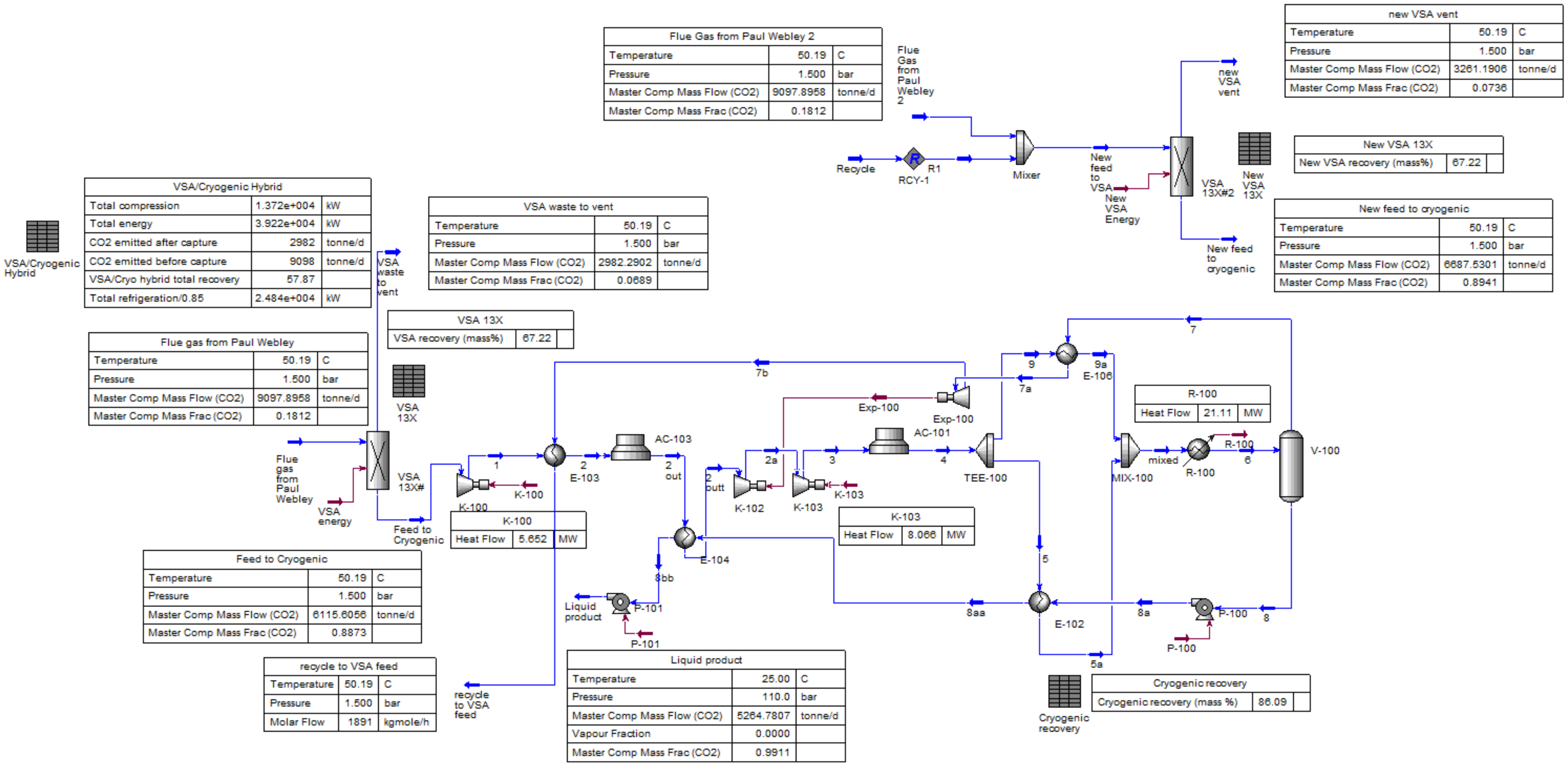


Figure 71 Aspen HYSYS® simulation for the optimization of cryogenic hybrid with other capturing process



Flue Gas from Paul Webley 2		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	9097.8958	tonne/d
Master Comp Mass Frac (CO2)	0.1812	

new VSA vent		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	3261.1906	tonne/d
Master Comp Mass Frac (CO2)	0.0736	

New VSA 13X		
New VSA recovery (mass%)	67.22	

New feed to cryogenic		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	6687.5301	tonne/d
Master Comp Mass Frac (CO2)	0.8941	

VSA/Cryogenic Hybrid		
Total compression	1.372e+004	kW
Total energy	3.922e+004	kW
CO2 emitted after capture	2982	tonne/d
CO2 emitted before capture	9098	tonne/d
VSA/Cryo hybrid total recovery	57.87	
Total refrigeration/0.85	2.484e+004	kW

VSA waste to vent		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	2982.2902	tonne/d
Master Comp Mass Frac (CO2)	0.0689	

VSA 13X		
VSA recovery (mass%)	67.22	

Flue gas from Paul Webley		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	9097.8958	tonne/d
Master Comp Mass Frac (CO2)	0.1812	

R-100		
Heat Flow	21.11	MW

K-100		
Heat Flow	5.652	MW

K-103		
Heat Flow	8.066	MW

Feed to Cryogenic		
Temperature	50.19	C
Pressure	1.500	bar
Master Comp Mass Flow (CO2)	6115.6056	tonne/d
Master Comp Mass Frac (CO2)	0.8873	

recycle to VSA feed		
Temperature	50.19	C
Pressure	1.500	bar
Molar Flow	1891	kgmole/h

Liquid product		
Temperature	25.00	C
Pressure	110.0	bar
Master Comp Mass Flow (CO2)	5264.7807	tonne/d
Vapour Fraction	0.0000	
Master Comp Mass Frac (CO2)	0.9911	

Cryogenic recovery		
Cryogenic recovery (mass %)	86.09	

Figure 72 Aspen HYSYS simulation for VSA/Cryogenic hybrid process (without considering the water removal)

4.4 Feed gas conditions for VSA given by University of Melbourne

Feed gas conditions: (aspen plus results according to cryogenic file flue gas conditions)

Temperature (°C)	40	40	40
Pressure (bar)	1.1	1.3	1.5
CO_2 mol%	12.06%	12.18%	12.26%
H_2O mol%	5.73%	4.86%	4.22%
N_2 mol%	76.74%	77.45%	77.97%
O_2 mol%	5.46%	5.51%	5.55%

Product Gas

Relationships of compositions of components in product stream (from the vacuum pump to the cryogenic), the product gases were at 1.01 bar and 40 °C.

x: waste CO_2 concentration (%); y: feed pressure (kPa); z: vacuum pressure (kPa)

CO_2 purity: $purity= 0.1004x+0.0109y-0.0672z-0.00776x^2-0.000041y^2-0.000171z^2+0.000234xy-0.00007yz-0.00314zx$

CO_2 recovery: $recovery= -0.0486x+0.0151y+0.0050z-0.0012x^2-0.000054y^2-0.000026z^2+0.000206xy-0.000051yz-0.00080zx$

H_2O purity: $purity= 0.068097x+0.004356y-0.025382z-0.0034x^2-0.000018y^2+0.000505z^2-0.000101xy+0.000056yz-0.001196zx$

H_2O recovery: 100%

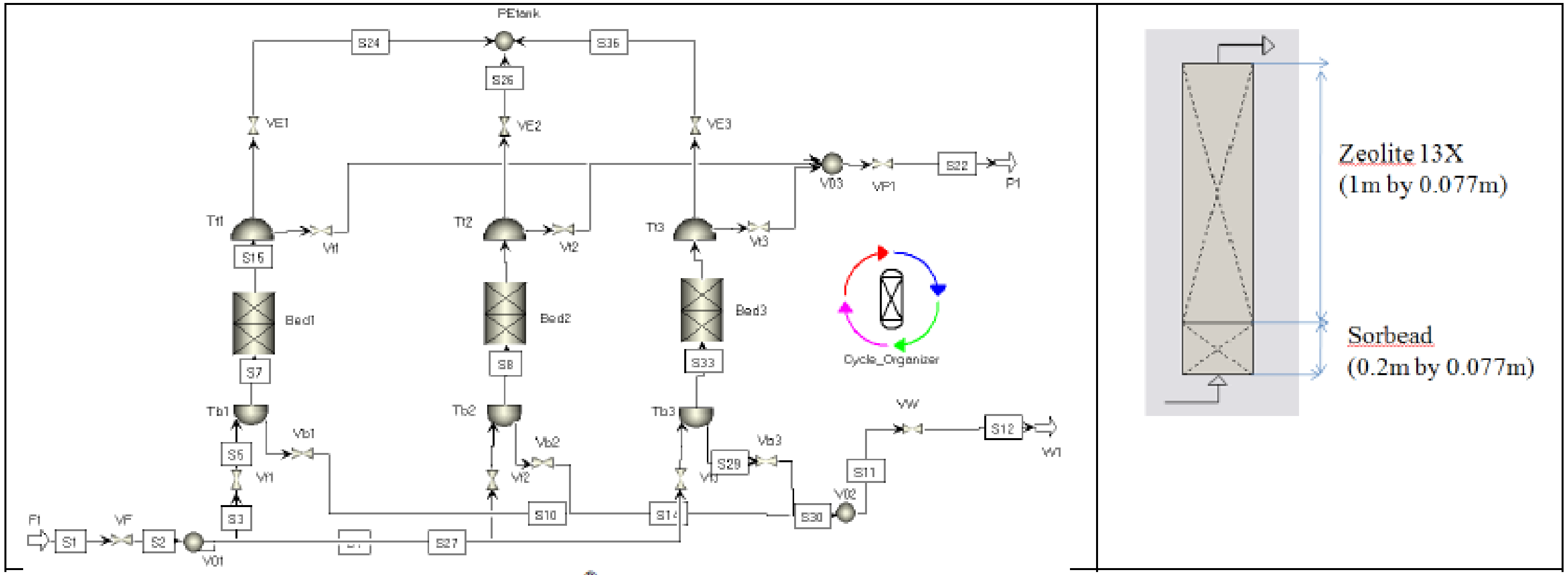
N_2 purity: $purity= -0.10036x+0.002881y+0.061505z+0.008542x^2-0.000010y^2-0.001273z^2-0.000131xy-0.000109yz+0.002057zx$

N_2 recovery; $recovery= -0.129335x+0.001261y+0.051863z+0.009904x^2-0.000006y^2-0.000240z^2+0.000450xy-0.000214yz-0.001981zx$

O_2 purity: $purity= -0.007206x+0.000207y+0.004417z+0.000614x^2-0.000001y^2-0.000091z^2-0.000009xy-0.000008yz+0.000148zx$

O_2 recovery: $recovery= -0.111441x+0.001086y+0.044708z+0.008537x^2-0.000005y^2-0.000207z^2+0.000387xy-0.000185yz-0.001708zx$

Simulation flowsheet:



Aspen Adsorption® simulation flowsheet & Adsorption bed configuration

Cycle

	I	II	III	IV	V	VI	VII	VIII	IX
A	RP	AD	PE ↑	PE ↑	EV	EV	PE ↓	IDLE	PE ↓
B	PE ↓	IDLE	PE ↓	RP	AD	PE ↑	PE ↑	EV	EV
C	PE ↑	EV	EV	PE ↓	IDLE	PE ↓	RP	AD	PE ↑

Results

	waste	Vac (kPa)	CO_2 % Waste (wet)	CO_2 (%) Product (dry)	Rec (%)	Specific power (MJ/kg CO_2)	Productivity (mole CO_2/hr/kg ads)	Productivity (kg CO_2/hr/kg ads)
110 kPa	1%	5	0.68%	54.53%	98.64%	0.787	2.84	0.125
		10	0.76%	33.92%	96.12%	0.789	3.05	0.134
		20	0.98%	24.52%	96.25%	0.856	3.37	0.148
	3%	5	3%	73.60%	81.59%	0.666	2.23	0.098
		10	2.5%	45.75%	85.60%	0.633	2.39	0.105
		20	3%	33.07%	83.57%	0.584	2.30	0.101
	5%	5	5.1%	79.55%	64.26%	0.623	1.71	0.075
		10	3.8%	54.14%	75.06%	0.608	1.83	0.081
		20	4.1%	34.88%	75.77%	0.569	2.04	0.090
130 kPa	1%	5	1.8%	61.85%	89.72%	0.478	7.24	0.32
		10	1.0%	46.27%	93.33%	0.676	7.20	0.316
		20	1.1%	31.94%	94.68%	0.654	6.37	0.28
	3%	5	2.92%	77.77%	80.84%	0.653	6.71	0.295
		10	3.07%	54.32%	80.15%	0.606	6.17	0.27
		20	2.60%	38.25%	86.36%	0.573	5.98	0.26
	5%	5	4.57%	87.10%	67.25%	0.610	5.57	0.245
		10	4.49%	59.84%	71.16%	0.578	5.52	0.242
		20	5.11%	41.05%	68.95%	0.523	4.74	0.21
150 kPa	1%	5	0.8%	54.73%	98.12%	0.756	11.97	0.53
		10	1.1%	44.84%	96.88%	0.667	11.21	0.49
		20	1.07%	35.78%	94.42%	0.630	9.09	0.40
	3%	5	2.91%	77.19%	81.89%	0.653	10.94	0.48
		10	2.94%	58.33%	81.29%	0.574	10	0.44
		20	2.94%	40.07%	82.77%	0.547	8.25	0.36
	5%	5	4.68%	88.87%	67.22%	0.575	9.25	0.41
		10	4.46%	61.93%	69.94%	0.581	8.61	0.38
		20	4.89%	44.42%	67.25%	0.48	7.22	0.32

Table 29 VSA energy results

4.5 Table of results based on the different condition of VSA (Provided by Prof. Paul Webley) (for 12.26% CO_2 VSA Feed)

Table 30 Combined result for VSA, dryer, Cryogenic and PSA

Pressure	waste	Vac (kPa)	CO_2 Product dry (mol %)	VSA (MW)	**Dryer (MW)	Compressors (MW)	Refrigeration (MW)	****Corrected Refrigeration (MW)	Total Cryogenics (MW)	Total VSA+ Dryer+ Cryogenics (MW)	Overall Recovery (%)	***Corrected Depleted Gas CO_2 composition (mol %)	Depleted gas temperature(℃)	Depleted Gas Pressure (bar)
110kPa	**1%**	5	54.53	63.72	6	17.75	21.06	16.26	39.22	104.14	41.19	34.21	-2.734	14.8
*		10	33.92	63.88										
*		20	24.52	69.31										
	3%	5	73.6 (69.96)	46.14	6	25.17	31.89	27.09	57.85	105.19	79.99	34.21	49.64	14.8
		10	45.61	43.85	6	15.77	12.24	7.44	28.3	73.35	28.8	34.21	54.89	14.8
*		20	33.07	40.46										
	5%	5	79.59(65.74)	35.55	6	22.97	26.59	21.79	50.22	86.97	65.89	34.21	24.01	14.8
		10	54.14	34.70	6	18.43	18.73	13.93	37.57	73.47	40.52	34.21	2.231	14.8
*		20	34.88	32.47										
120kPa	**1.8%**	5	71.95	48.31	8.5	22.05	34.97	30.17	57.89	109.9	88.1	34.21	44.79	14.8
130kPa	**1%**	5	61.84	38.70	6	20.88	23.17	18.37	44.6	84.5	55.66	34.21	54.17	14.8
		10	46.27	54.73	6	15.95	14.43	9.63	30.68	86.61	29.58	34.21	69.73	14.8
*		20	31.94	52.95										
	3%	5	77.77(69.96)	45.24	6	25.17	31.89	27.09	57.85	104.29	79.99	34.21	28.53	14.8
		10	54.32	41.98	6	18.51	18.32	13.52	37.24	80.42	40.88	34.21	12.29	14.8
*		20	38.25	39.70										
	5%	5	87.10(65.74)	34.81	6	22.08	28.66	23.86	51.39	87.4	65.89	34.21	24.01	14.8
		10	59.86	32.98	6	20.86	21.64	16.84	43.01	77.19	51.21	34.21	12.15	14.8
*		20	41.05	29.85										
150kPa	**0.8%**	3	73.4	47.46	6	28.03	37.47	32.67	66.44	115.1	94.79	34.21	51.13	14.8
	1%	5	54.73	61.21	6	17.82	18.25	13.45	36.48	98.89	41.51	34.21	53.83	14.8
		10	44.85	54.00	6	15.62	15	10.2	30.91	86.11	27.92	34.21	-5.973	14.8
*		20	35.78	51.00										
	2.15%	5	71.41	46.17	6	27.39	34.09	29.29	62.32	109.69	85.79	34.21	46.21	14.8
	3%	5	77.19(69.96)	45.24	6	26.51	31.89	27.09	59.19	105.63	79.99	34.21	32.61	14.8
		10	58.33	39.76	6	20.15	21.66	16.86	42.29	83.25	48.07	34.21	-7.793	14.8
*		20	40.07	37.89										
	5%	5	88.87(65.75)	32.81	6	22.07	28.66	23.86	51.38	85.39	65.89	34.21	24.01	14.8
		10	61.93	33.16	6	21.91	23.07	18.27	45.53	79.89	55.83	34.21	13.03	14.8
*		20	44.42	27.39										

Highlighted in grey: best case for overall captures but we still need the data for PSA unit to capture more CO_2 from the depleted gas from the cryogenic section.

Highlighted in light blue: two comparable and considerable cases

* No liquefaction achieved in the cryogenic section at reasonable operating pressure due to low CO_2 composition in the feed gas to this section.

** The power for Dryer is subjected to the amount of hot air to regenerate the adsorbent as well as adsorbent efficiency, pressure drop of adsorber column (Ergun Equation).

*** These depleted gas compositions were obtained from HYSYS simulation (40.21%) however the laboratory experiments verified these values to be lower by about 6% which will improve the capture rate results.

**** Energy correction factor due to *** above is equivalent to **4.8MW** for the cryogenic section

Numbers in red colour means HYSYS value

4.6 Development of refrigeration package R-100

The development of refrigeration package R-100 is very similar to the first stage of the liquefied natural gas (LNG) liquefaction process which is known as the precooling stage. Depending on the precooling technology, the natural gas will be cooled down to -30 ℃ to -50 ℃. In this scenario, a temperature of -55 ℃ is required.

4.6.1 Cascade refrigeration

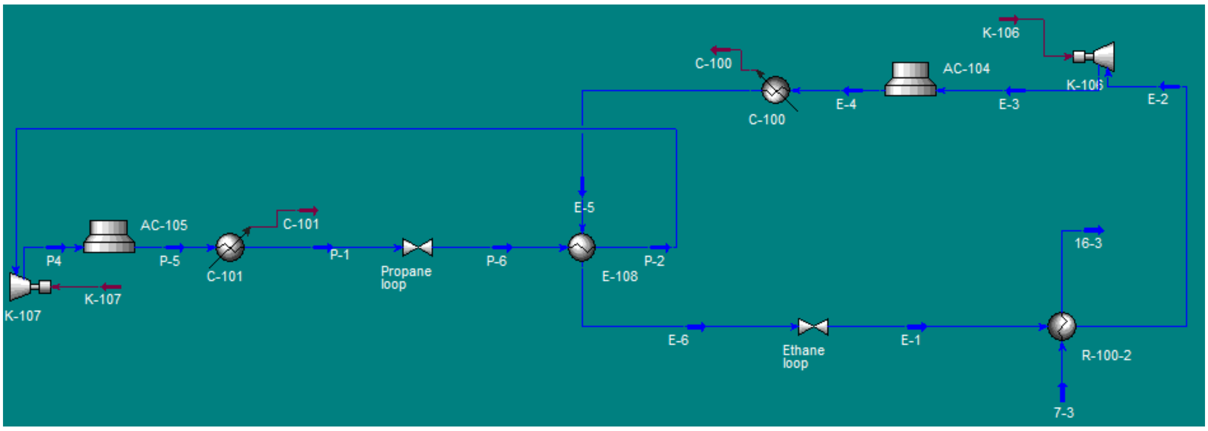


Figure 73 Cascade refrigeration

Results:

Total compression duty (MW)	28.31
Total seawater cooler duty (MW)	27.42
Total duty for cascade refrigeration (MW)	**55.73**
Amount of Ethane required (kg mole/hour)	5510
Amount of Propane required (kg mole/hour)	5359
Pressure drop across the valve for Ethane loop (kPa)	1675
Pressure drop across the valve for Propane loop (kPa)	984

In this cascade refrigeration configuration, one propane cycle is cascaded with one ethane cycle. Joule-Thomson expansion (throttling process) is being used for producing low temperatures. The gases are expanded adiabatically from one constant pressure to another in the way that no external work is done and no net conversion of internal energy to kinetic energy of mass motion occurs.

Firstly, propane gas is compressed to 11bar by K-107 and cools down to 30 ℃ by using an air cooler and a sea water cooler. A valve is used to expand the propane gas from 10.85 bar to atmospheric pressure (1.01 bar) and a temperature of -42.26 ℃ is achieved. Boiling point of propane is approximately -42.1 ℃. Ethane gas, on the other hand, is compressed to 18bar by K-106 and cools down to -35 ℃ by propane loop E-108. Expanding ethane from 18bar to 1.1bar, -87 ℃ is achieved to provide 19.39MW requirement for refrigeration package R-100. Boiling point of ethane is approximately -88.6 ℃.

4.6.2 Mixed refrigerant

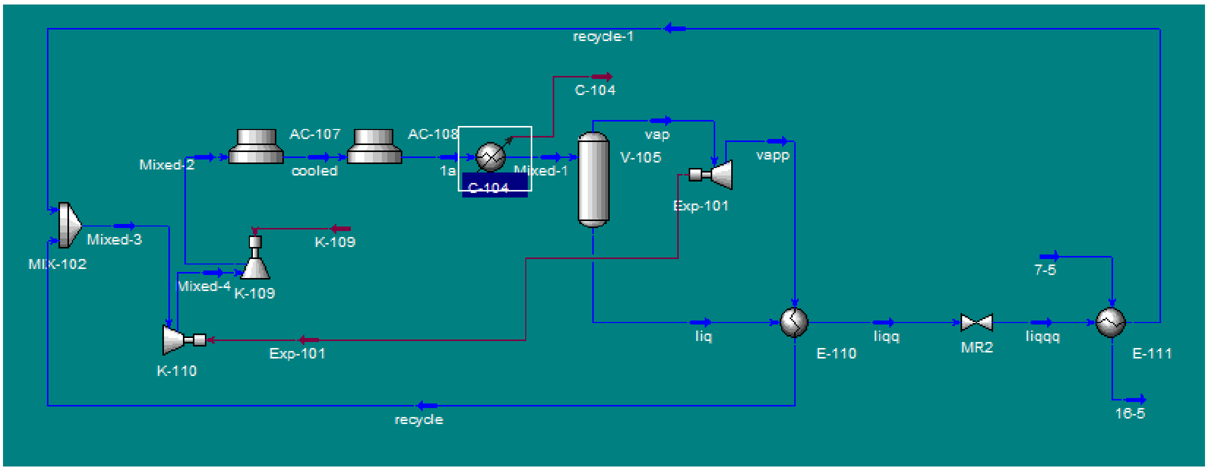


Figure 74 Mixed refrigerant

Mixed refrigerant composition of 65mol% Ethane and 35mol% Propane is used. Heat exchanger E-111 represents the duty required to achieve -55 ℃.

Mol%	Mol%	
Propane	Ethane	Lowest temperature achievable
0.9	0.1	-45.73
0.8	0.2	-49.65
0.7	0.3	-53.63
0.6	0.4	-57.53
0.5	0.5	-61.99
0.45	0.55	-64.19
0.4	0.6	-66.44
0.35	0.65	-66.84
0.3	0.7	-65.48
0.2	0.8	-18.02
0.1	0.9	-13.83

Best results for the energy requirement after the optimization:

Total compression duty (MW)	23.96
Total seawater cooler duty (MW)	24.84
Total duty for mixed refrigeration (MW)	**48.8**
Amount of Ethane required (kg mole/hour)	6093.1
Amount of Propane required (kg mole/hour)	3280.9
Pressure drop across the valve (kPa)	2771

Optimized mixed refrigerant 1

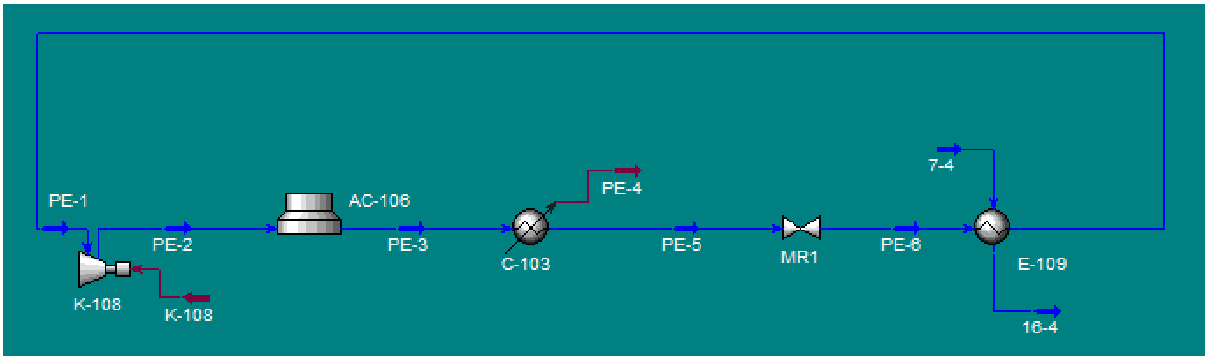


Figure 75 Optimized mixed refrigerant 1

Mixed refrigerant composition of 64mol% Ethane, 31mol% isobutane, 5% Propane is used. Heat exchanger E-109 represents the duty required to achieve -55℃. The optimization was done by adjusting the operating parameters such as temperature, pressures, and flow rates to achieve the lowest possible energy requirement without causing any convergence issue in Aspen HYSYS®.

Mol%	Mol%	Mol%	
Propane	Ethane	isobutane	Power (MW)
0.05	0.7	0.25	25.79
0.05	0.69	0.26	25.43
0.05	0.68	0.27	25.08
0.05	0.67	0.28	24.74
0.05	0.66	0.29	24.41
0.05	0.65	0.3	23.64
0.05	0.64	0.31	23.12
0.05	0.63	0.32	Liquid occur in compressor
0.04	0.64	0.32	Unable to converge
0.06	0.64	0.3	23.45
0.04	0.65	0.31	24.23

Best results for the energy requirement after the optimization:

Total compression duty (MW)	23.12
Total seawater cooler duty (MW)	31.83
Total duty for mixed refrigeration (MW)	54.96
Amount of Ethane required (kg mole/hour)	5120
Amount of Propane required (kg mole/hour)	400
Amount of isobutane required (kg mole./hour)	2480
Pressure drop across the valve (kPa)	2607

Optimized mixed refrigerant 2

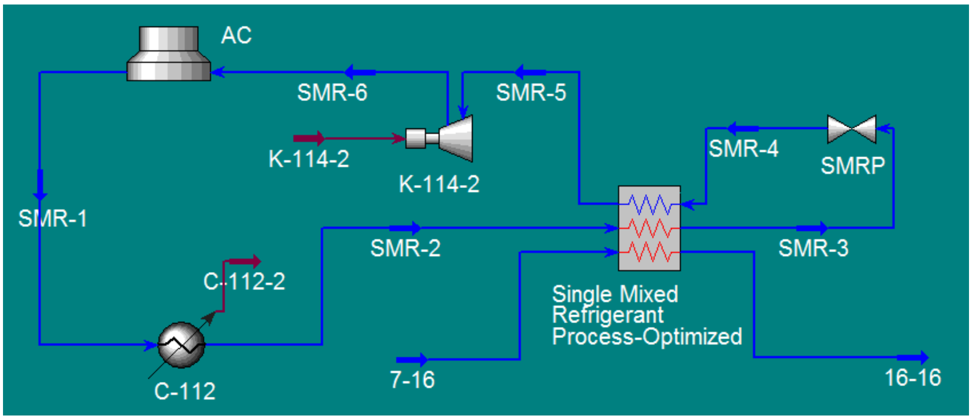


Figure 76 Optimized mixed refrigerant 2

Mixed refrigerant composition of 46% Ethane, 1% Propane, 36% Methane, 17mol% n-Butane is used. LNG Heat exchanger E-109 labelled 'Single Mixed Refrigerant Process-Optimized' represents the duty required to achieve -55℃. The optimization was done by adjusting the operating parameters such as temperature, pressures, and flow rates to achieve the lowest possible energy requirement without causing any convergence issue in Aspen HYSYS®.

Best results for the energy requirement after the optimization:

Total compression duty (MW)	18.84
Total seawater cooler duty (MW)	31.34
Total duty for mixed refrigeration (MW)	50.18
Amount of Ethane required (kg mole/hour)	10877.16
Amount of Propane required (kg mole/hour)	236.46
Amount of Methane required (kg mole./hour)	8512.56
Amount of n-butane required (kgmole/hour)	4019.82
Pressure drop across the valve (kPa)	1745

Conclusion:

Type of refrigeration package	R-100/0.85	Cascade refrigeration	Mixed Refrigeration	Optimized Mixed Refrigeration 1	Optimized Mixed Refrigeration 2
Compression power (MW)	38.35	28.31	23.96	23.12	18.84

4.7 Plot plan

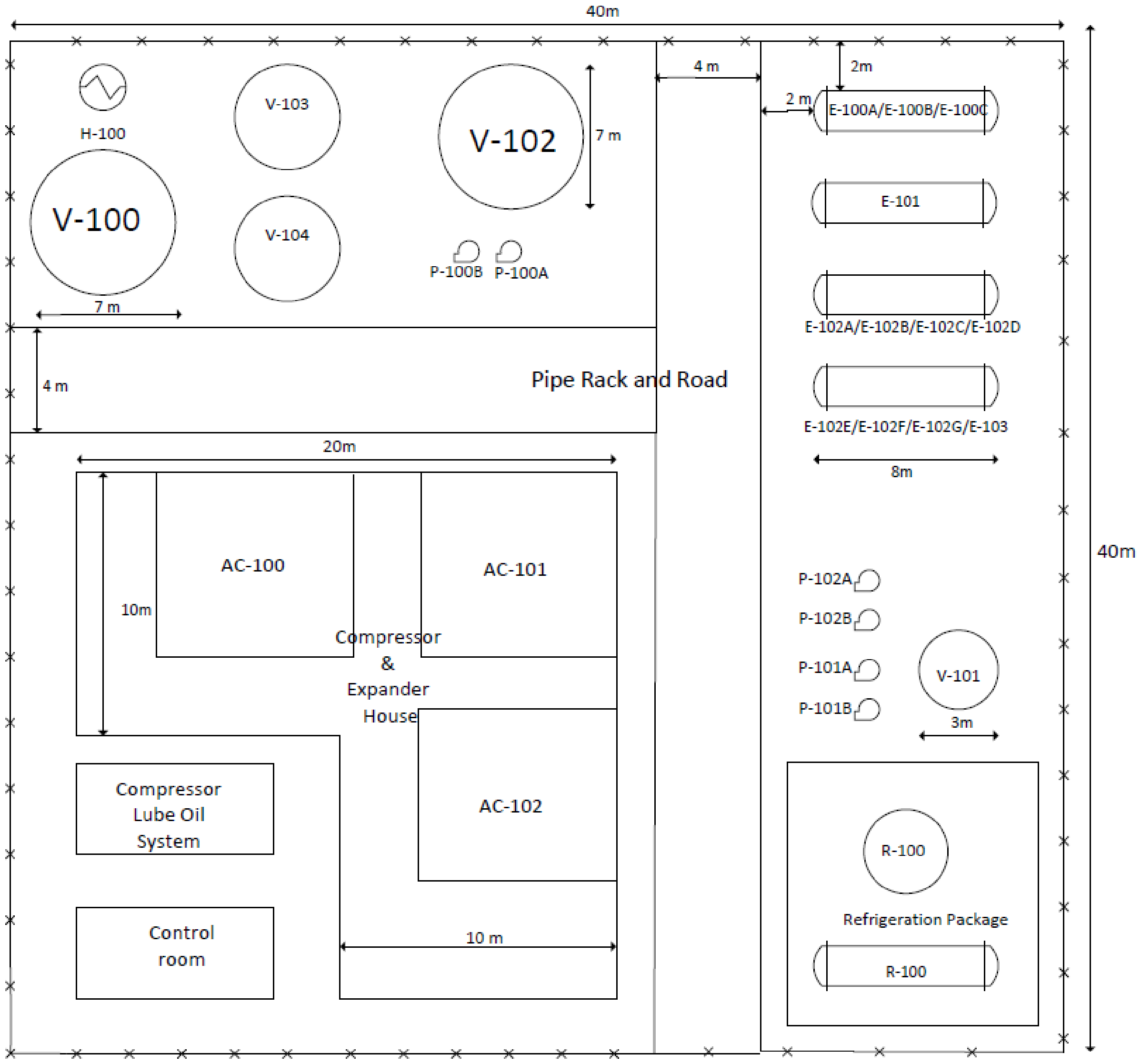


Figure 77 Plot plan for VSA/Cryogenic hybrid process

In order to examine the retrofitting potential of proposed capturing plant to existing power plant, a plot plan shown in Figure 84 was developed based on the equipment sizes and piping arrangement. This plot plan is important because it determines the construction and manufacturing cost before detailed piping, structural and electrical design begins and after the process flow diagrams are completed. A proper plot plan shall include the arrangement of processing areas, storage areas, and handing areas and take into account these factors:

- New site development or addition to previously developed site
- Type and quantity of products to be produced
- Type of process and product control
- Operational convenience and accessibility
- Economic distribution of utilities and services

- Type of buildings required and building code requirements
- Health and safety considerations
- Waste disposal requirements
- Auxiliary equipment
- Space available and space required
- Roads and railroads
- Possible future expansion

A total minimum area of 40 x 40 square metres will be required. Other features of this plot plan include:

- Pipe rack and road for human and crane access will need a width of 4 metres
- All compressors and expander will be stored in the compressor room
- Air coolers will installed on the roof of compressor& expander house for saving space
- Heat recovery exchangers will be stacked one on top of another to maximize space efficiency
- Each pump has a backup pump

4.8 Economic assessment for VSA-Cryogenic hybrid process

The initial scoping-level economic assessment for capturing CO_2 using a hybrid VSA-cryogenic process configuration was summarized by Dr Minh Ho from University of New South Wales. Three cases were presented and compared. It is to be noted that assumptions below were given for the purpose of research and may not be realistic in reality.

- Capture using MEA solvent without heat integration (Benchmark 1)

CO2 is assumed to be captured by a commercially available chemical solvent absorption technology using a mono-ethanol-amine (MEA) solvent. The cost of MEA solvent is assumed to be $1.5 per kg of solvent. The overall CO_2 recovery was assumed to be 90%. Engineering assumptions are given as below:

Table 31 Engineering assumptions for capture using MEA solvent

Parameter	MEA benchmark 1
Separation material	MEA solvent
Pre-treatment NOx and Sox facilities	Yes
Water removal	DCC
Heat integration	N
Absorber height (m)	15
Absorber diameter (m)-single train	22.5
Regenerator height (m)	22
Regenerator diameter (m)-single train	14

- Capture using only VSA 13X without heat integration (Benchmark 2)

CO_2 was assumed to be captured using a 9-step VSA process with 13X zeolite and no heat integration. Zeolite 13X was chosen for this study as it has been shown experimentally to have good adsorption properties for CO_2/N_2 systems. The cost of the zeolite 13X was assumed to be A$6.00 per kg with a life expectancy of 5 years. The overall CO_2 recovery was assumed to be 86%. Engineering assumptions are given as below:

Table 32 Engineering assumptions for capture using only VSA 13X

Parameter	MEA benchmark 1
Separation material	13X zeolite
Pre-treatment NOx and Sox facilities	Yes
Water removal	Dicyclohexylcarbodiimide (DCC)
Heat integration	N
Total adsorbent weight (kg)	4’416’000
Adsorbent bed height (m)	2.3
Number of beds per train	3

Number of VSA trains	20

- Capture using VSA-Cryogenic hybrid without heat integration (Case 1).

The hybrid configuration is where the flue gas enters the VSA unit and is concentrated to a purity of 72 % (dry) before further processing in the cryogenic process. The cost of the zeolite 13X is assumed to be $6 per kg with a life expectancy of 5 years. The hydrate process is then assumed to increase the purity to over 99 % and liquefies the CO_2 ready for transport. The overall CO_2 recovery was assumed to be over 95%. Engineering assumptions are given as below:

Table 33 Engineering assumptions for capture using VSA-Cryogenic hybrid without heat integration

Parameter	MEA benchmark 1
Separation material	Activated carbon+ MEA solvent
Pre-treatment NOx and Sox facilities	Y
Water removal	DCC
Heat integration	N
Total adsorbent weight (kg)	Not simulated-assumed the same as for the VSA 13X Benchmark process
Adsorbent bed height (m)	
Number of beds per train	
Number of VSA trains	

Minh Ho (2015) summarized the breakdown of the equipment component costs for the two standalone Benchmark processes and the VSA-Cryogenic Hybrid process and stated that the absorption and regeneration processes make up 60% of the separation equipment cost (SEC) for the MEA stand-alone process. For the VSA 13X process, VSA adsorber, adsorbent and vacuum pump cost dominate the equipment cost while the CO_2 compressor makes up about 40% of the SEC.

Table 34 Breakdown of the equipment component costs for the two standalone Benchmark processes

Cost parameter ($/ ton CO_2 captured / year)	MEA	VSA benchmark 2 (un-optimized VSA)
Separation-MEA solvent process	41	-
Separation-VSA process	-	47
CO_2 compression	27	30
Separation equipment cost	68	79
Other costs(steam modifications, general equipment, etc)	52	38
Set up cost	130	142
Total capital cost	277	286

Minh Ho (2015) concluded that the hybrid VSA-Cryogenic process may be a competitive process for capturing CO_2 from post-combustion power plant flue gas provided the following can be satisfied:

- The VSA component of the process has much lower cost for the stand-alone VSA 13X process;
- The VSA pumping duty can be decreased;
- The total energy penalty of the Hybrid process can be decreased without increasing the capital cost significantly.

Minh Ho (2015) also agreed with the benefits of hybrid VSA-Cryogenic process compared to conventional solvent absorption processes are as follows:

- Producing a CO_2 production stream of very high purity;
- Using practical equipment with currently available technology;
- Removal of the chemical handling onsite

Cost of CO_2 avoided:

The equation used to calculate the cost of CO_2 avoided in $/tonne is as follows:

$$\text{Avoided cost} = \frac{(\text{FY COE with removal} - \text{FY COE without removal})}{(\text{Emissions without removal} - \text{Emissions with removal})}$$

Where FY COE = first year cost of electricity ($/MWh $_{net}$) and emissions=CO_2 emissions for case (tonnes/MWh $_{net}$)

Cost of CO_2 removed:

The cost of CO_2 removed is calculated based on the equation below:

$$\text{Cost of CO2 removed} = \frac{\text{FY COE with removal} - \text{FY COR without removal}}{\text{CO2 removed}}$$

Where the FY COE= first year cost of electricity ($/MWh) and the CO_2 removal= CO_2 stream leaving the plant (tonnes/MWh$_{net}$). The FY COE for this study does not include a cost for transport, storage and monitoring.

Minh Ho (2015) explained that for VSA 13X* case, the VSA vacuum pump duty was estimated based on the vacuum pump duty from the 2011 La Trobe PCC study for BCIA. This process was highly optimized and considered multiple step changes. The energy for this process was estimated at 0.41 MJ per kg CO_2.

For VSA 13X$^{\#}$ case, a short cut correlation developed by the CO2CRC Adsorption team was used to estimate the energy penalty for the vacuum pump. The energy for this process was estimated at 0.7 MJ per kg CO_2 without optimization.

Table 35 Summary of the energy requirement and engineering results for MEA, VSA 13X*, VSA 13X$^{\#}$ (Minh Ho, 2015)

CO_2 capture technology	**MEA**	**VSA 13X***	**VSA13X$^{\#}$**	**VSA-Cryogenic**
CO_2 mass balance				
Overall CO_2 capture rate (%)	90	86	86	94
CO_2 purity in product (%)	>95	~95	~95	99.9
CO_2 emitted before capture (t/ MWh)	0.89	0.89	0.89	0.89
CO_2 emitted before capture (Mt / yr)	3.32	3.32	3.32	3.32
CO_2 captured (Mt / yr)	2.98	2.85	2.85	3.13
Overall CO_2 captured (kg/s)	94.5	106	106	117
CO_2 emitted after capture (Mt / yr)	0.33	0.46	0.46	0.19
CO_2 factor from electricity and steam use (Mt / yr)	1.05	0.82	1	1.29
CO_2 avoided (Mt / yr)	1.93	2.04	1.85	1.84
CO_2 avoided (% of original emissions)	58%	61%	56%	55%
Energy requirement				
SO_x / NO_x removal pumps (MW_e)	14	14	14	14
Feed gas compressor/blower/pump duty (MW_e)	20	20	20	20
Equivalent electricity use for reboiler (MW_e)	82	N/A	N/A	N/A
VSA vacuum pumps (MW_e)	N/A	46	71	55
Drying (MW_e)	N/A	N/A	N/A	1.8
Cryogenic duty (MW_e)	N/A	N/A	N/A	36.23
CO_2 compressor + pumps(MW_e)	42	46	46	23
Expanders (MW_e)	N/A	N/A	N/A	-4.5
Air coolers (MW_e)	N/A	N/A	N/A	1
Total equivalent electricity used (MW_e)	159	123	150	**155.5**

By using multistage compressor, 23 MW has been evaluated by a formal research fellow (Minh Ho, 2015). All the energy values for drying, cryogenic, CO_2 compressor and pumps and expanders have been adjusted based on 106 kg/s overall CO_2 captured. An overall energy penalty of 155MW has been figured for VSA/Cryogenic hybrid which is lower than the Amine absorption benchmark case 170-175MW.

4.9 Environmental Impact Assessment (EIA) for VSA/Cryogenics Hybrid

This preliminary assessment investigates the possible impacts that the proposed carbon captures technology and transportation, i.e. vacuum swing adsorption and cryogenic hybrid may have on environment in three categories: environmental, social and economic aspects. For example, in Western Australia, the Environmental Protection Act 1986 (Part 4) will provide the legislative framework for the EIA process. Please note that this assessment is just preliminary, specifically for post-combustion power plant and highly subject to the location of the site.

Table 36 Environmental Impact Assessment

Environmental Impact Assessment	Description
Environmental impact	- Minimal environmental effect compared with captured method by MEA solvent - Liquid carbon dioxide is colorless, odorless, nonflammable and slightly acidic liquid and might cause asphyxiation risk if there is massive leak.
Social impact	- Disturbance to local residents, flora and fauna especially during the plant construction phase - Legislative and regulatory challenges - Community leaders and the general public fear the potential impact of carbon capture and the lack of understanding of the concept of carbon capture and sequestration and associated risk/benefits.
Economic impact	- Liquid carbon dioxide can also be used in food industry for freezing purpose, in oil and gas well recovery and other industries such as the production of chemical, plastics, rubber, metals, and electronic components.

CHAPTER 5 LIQUID CO_2 PIPELINE DESIGN

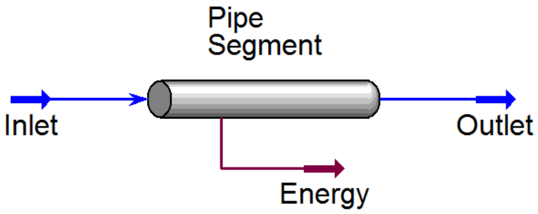
The work in this chapter is the continuation of research work done for CO2CRC in order to complete the unit ChE 491/492 Research project in 2012. The transportation of captured CO_2 from a cryogenic system to a suitable injection point has been published internally in report CO2CRC report no: RPT12-3664. In previous work, the advantages of transporting liquid CO_2 instead of supercritical CO_2 has been investigated by comparing two Aspen HYSYS modelling case studies without considering any elevation of terrain and a constant ground temperature of 20 ℃ was assumed. These assumptions were conservative therefore this chapter will overcome these limitations.

When the CO_2 flows along the pipeline, the fluid will be inevitably influenced by the shear/friction force between the fluid and pipe wall (as a result of viscous nature of real fluid), the heat exchange between the fluid and surrounding soil (due to temperature difference) and any change in elevation.

Zhang et al. (2005) simulated two CO_2 transport scheme using identical pipe diameter for comparison, one is supercritical state transport and one is subcooled liquid transport, and concluded that subcooled liquid transport is more economical. The same study has also proposed that pipeline transportation of liquid CO_2 can be more feasible in areas with cold climate. Consequently, the objective of this chapter is to further strengthen these findings by evaluating the heat transfer process and simulating a liquid CO_2 pipeline using a commercially available process simulator Aspen HYSYS® V7.2.

5.1 Modelling and simulation framework

5.1.1 Pipe segment



The pipe segment is used to simulate a wide variety of piping situation ranging from single/multiphase plant piping with rigorous heat transfer estimation, to large capacity looped pipeline problems.

Step by step procedure:

1) On ‘Parameters’, select **Beggs and Brill (1979)** for pipe flow correlation. Tick the ‘Include Accl. Pr. Drop’ box to include the Beggs & Brill model acceleration pressure drop in the calculation.

2) Go to ‘Rating’ tab and click on ‘Append Segment’, specify its length/equivalent length, elevation and pipe material.

3) Click on ‘View Segment’, specify pipe schedule number and select a nominal diameter required. Calculate the outlet velocity by dividing the volumetric flow rate by cross sectional area of pipe.

4) Go to ‘Heat transfer’ and select the heat transfer specified by ‘estimate HTC’, specify ambient temperature required, tick ‘include pipe wall’ to include the effects of the pipe wall, ‘include inner HTC’ and ‘include outer HTC’ to include the effects of both inner and outer heat transfer coefficient in the heat transfer calculation. Select the ground type required and specify buried depth. A minimum buried depth of 1.2 meter has been suggested by CSBP 2012.

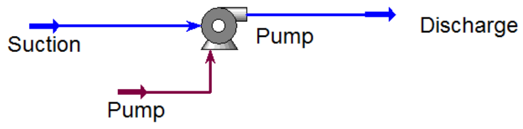
The pipe segment offers four calculation modes: Diameter, Pressure Drop, Flow, and Length. The appropriate mode is automatically selected depending on the information supplied.

Available pipe flow correlations in HYSYS are: Aziz, Govier & Fogarasi, Baxendell & Thomas, Beggs & Brill (1979), Beggs & Brill (1973), Duns & Ros, Gregory Aziz Mandhane, Hagedorn & Brown, HTFS Homogeneous Flow, HTFS Liquid Slip, Olgas2000, Orkisewski, Poettman & Carpenter, or Tulsa99. All methods account for static head losses, while only the Beggs and Brill and OLGAS methods account for hydrostatic recovery. Beggs and Brill calculate the hydrostatic recovery as a function of the flow parameters and pipe angle.

Beggs and Brill (1979) has been selected for the pipe flow correlation due to several reasons:

- It includes Flowmap correction by Payne et al. [1977]
- It includes Frictional Pressure drop correction for rough pipes by Payne et al.[1979]
- It includes Liquid Holdup Correction for uphill & downhill pipes by Payne et al.[1979]
- It gives an option on whether to include Beggs & Brill model acceleration pressure drop in the calculation or not.

5.2.2 Pump



In HYSYS, the pump operation is used to increase the pressure of an inlet liquid stream. Depending on the information supplied, the pump calculates either an unknown pressure, temperature or pump efficiency. The pump operation assumes that the inlet fluid is incompressible. The density is constant, and the liquid volume is independent of pressure. HYSYS uses the following assumptions and equations in calculating the unknown pump unit operation variables:

To calculate the ideal power of the pump required to raise the pressure of the liquid:

$$Power\ Required_{ideal} = \frac{(P_{out} - P_{in}) \times Flow\ Rate}{Liquid\ Density}$$

Where P out = pump outlet pressure, P in= pump inlet pressure

To calculate the actual power of the pump:

$$Efficiency(\%) = \frac{Power\ Required_{ideal}}{Power\ Required_{actual}} \times 100\%$$

Combine the first and second equations leads to the following expression for the actual power requirements of the pump:

$$Power\ Required_{actual} = \frac{(P_{out} - P_{in}) \times Flow\ Rate \times 100\%}{Liquid\ Density \times Efficiency(\%)}$$

The actual power is also equal to the difference in heat flow between the outlet and inlet streams:

$$Power\ Required_{actual} = (Heat\ Flow_{outlet} - Heat\ Flow_{inlet})$$

5.2 Scenario and assumptions

The major assumptions currently used are as follows:

- The product specification of CO_2 captured from the cryogenic section are constant
- After the capture, CO_2 is compressed to 110 bar at the capture site before it enters the transmission pipeline. This pressure ensure that CO_2 remains in a liquid phase throughout the entire transport and storage process
- The shortest possible total distance between the capture site and the sequestration side is **120km**, and it will be divided into short intervals (**30km each).** These intervals are selected for the placement of main line valves. Maintain the fluid velocity at 2m/s by specifying the inner diameter of a pipe (ID: 317.5mm, OD: 355.6mm, Schedule 80), also to keep the pipe size uniform for ease of construction and installation and avoid sudden acceleration/deceleration due to enlargements and contractions.
- Consider only heat transfer from conduction and convection but not radiation.
- **26 ℃** has been selected for the maximum allowable temperature at the sequestration site to provide a 5 ℃ safety margin therefore to avoid the vaporization of liquid CO_2

- Pressure drop due to intermediate cooling station and the design of it is negligible for the purpose of simulation, underground well water is always available for the intermediate cooling station
- The ambient temperature remain constant for every single transmission process is being simulated, assume the ground temperature is the same or at least very close to ambient temperature (as given) in Aspen HYSYS
- 7.38MPa (73.8 bar) is the lowest allowable operating pressure throughout the pipeline
- 1.2 metre buried depth has been assumed and remain unchanged for all simulation
- The amount of pumping capacity being used in HYSYS does not represent the actual quantity of pumping capacity in reality because there will be spare pumps for maintenance or in the event of break down
- At this stage, neglect the pressure losses due to various fittings, valves, bends, inlets and exits
- Default pump adiabatic efficiency of 75%

Scenario 1: To investigate the effect of ground material and ambient temperature to a pipeline system in terms of temperature, pressure and pump duties. No elevation.

Scenario 2: To optimize the pipeline transmission system in scenario 1 in terms of CAPEX and OPEX

Scenario 3: To investigate the impact when there is a change in topography in scenario 2 (at the very last 30km)

Scenario 4: To investigate the impact when there is a variation of feed molar flow rate in scenario 2 (+- 10%, +-20%)

5.2.1 Comparison between buried pipelines for liquid CO_2 and supercritical CO_2

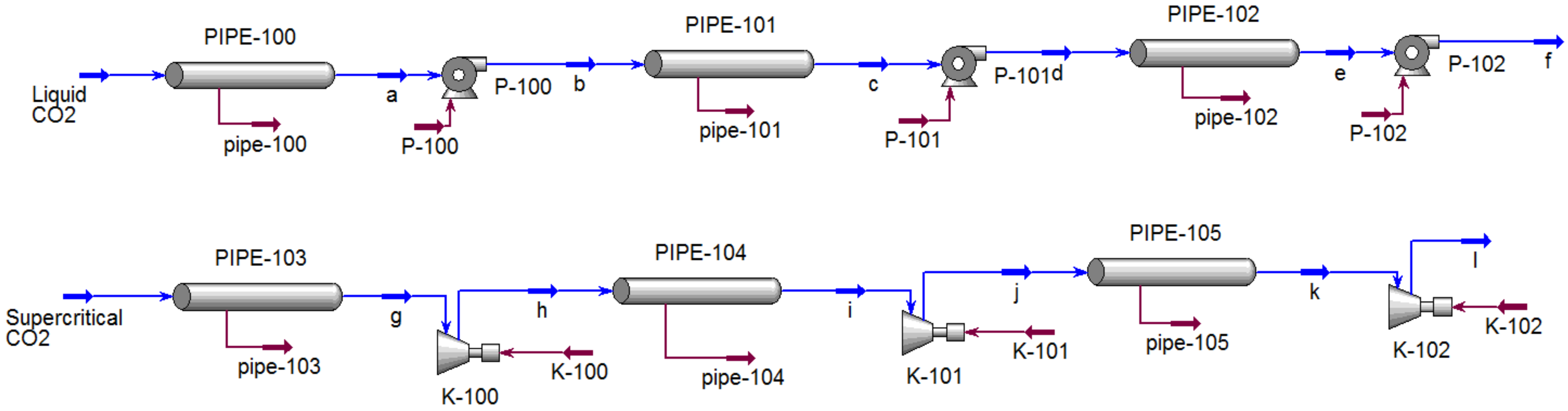
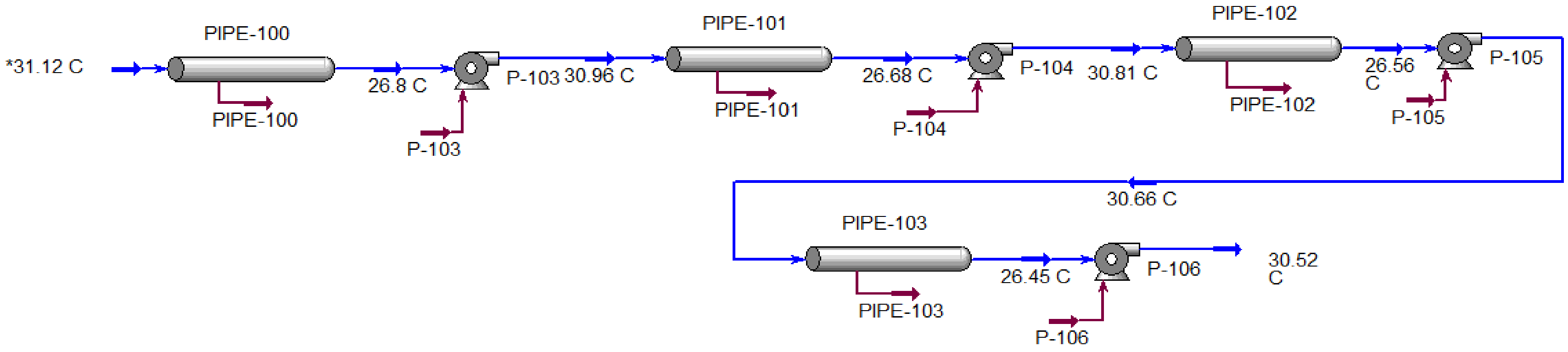
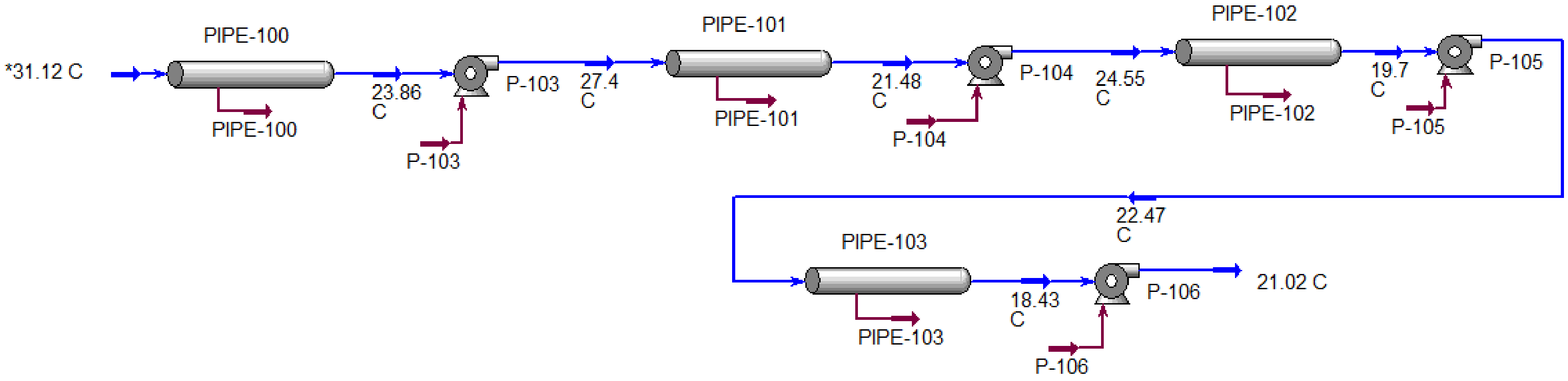


Figure 78 Comparison between buried pipelines for liquid CO_2 and supercritical CO_2

5.2.2 Scenario 1: Dry sand versus wet sand in terms of temperature/Pressure/Pump power

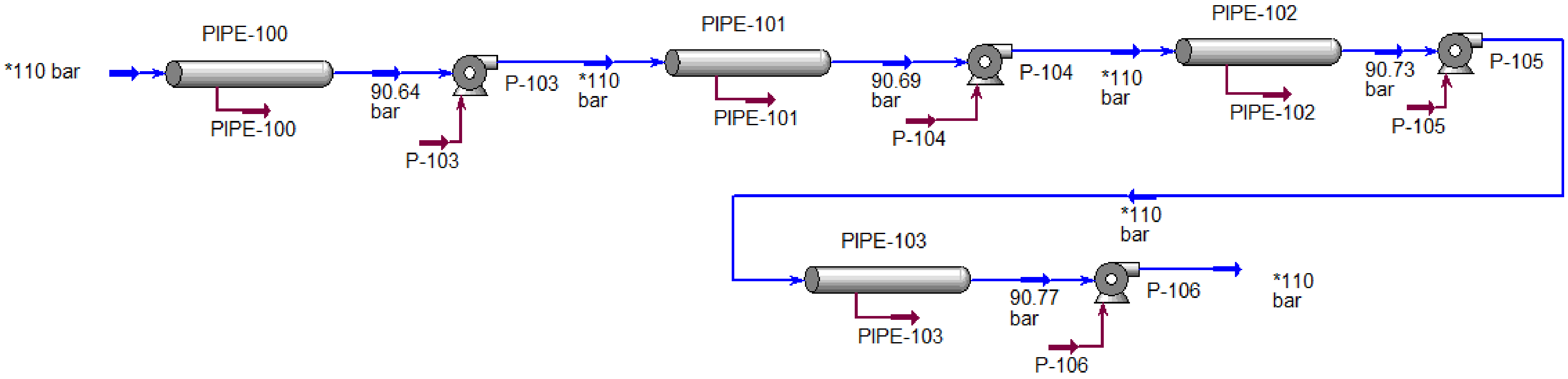


Dry sand

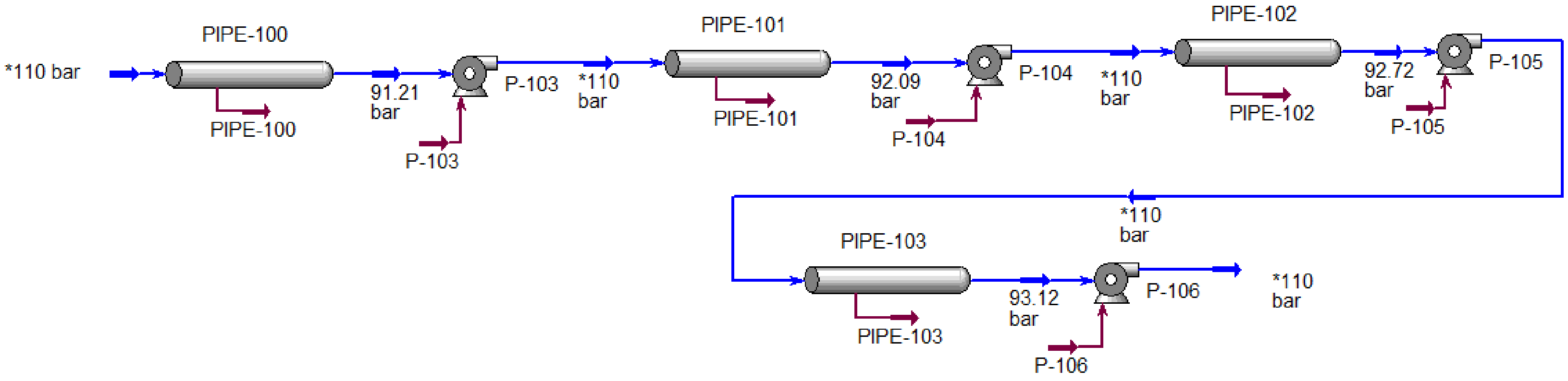


Wet sand

Scenario 1: Dry sand versus wet sand in terms of pressure

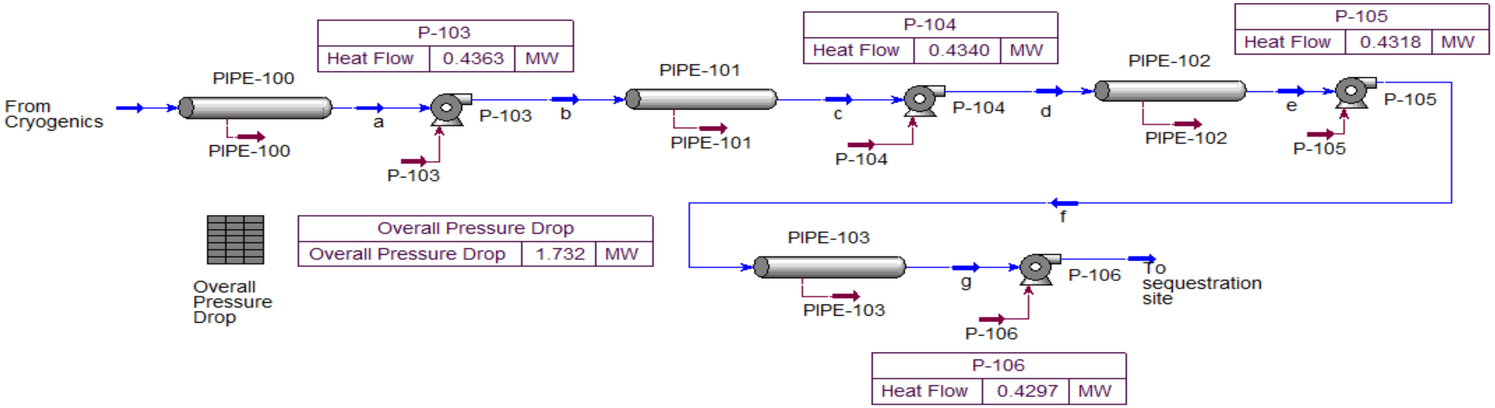


Dry sand

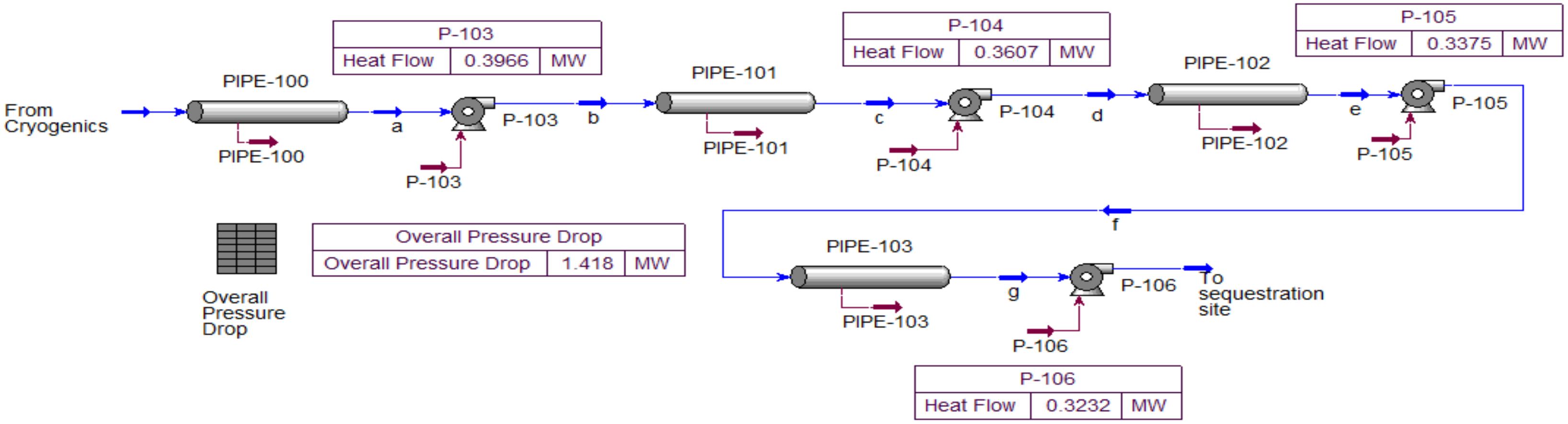


Wet sand

Scenario 1: Dry sand versus wet sand in terms of pump power



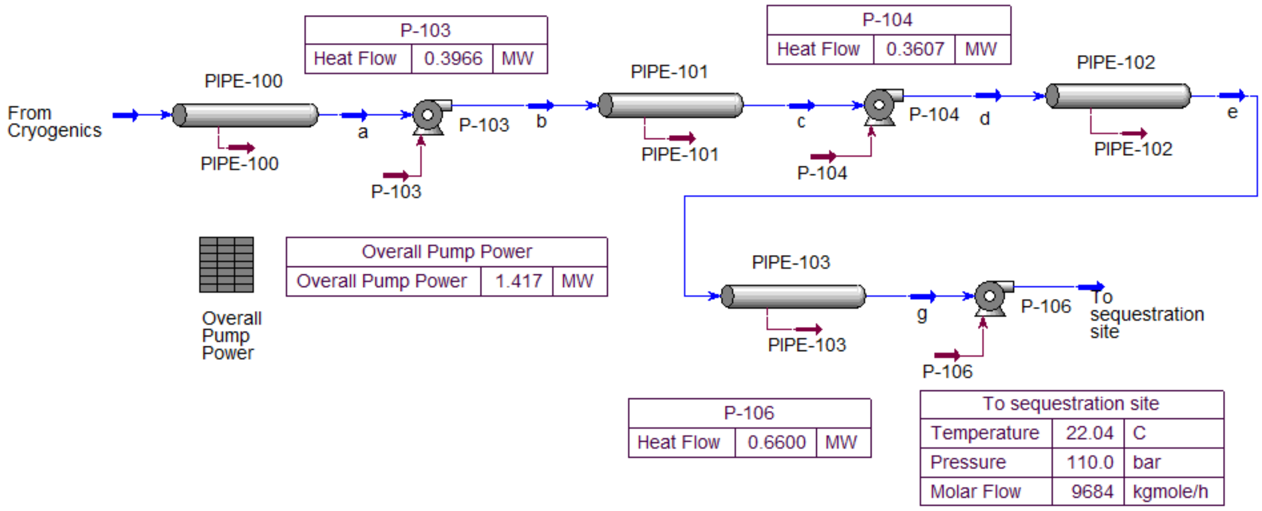
Dry sand



Wet sand

5.2.3 Scenario 2: Optimization of scenario 1 ‘wet sand’ case

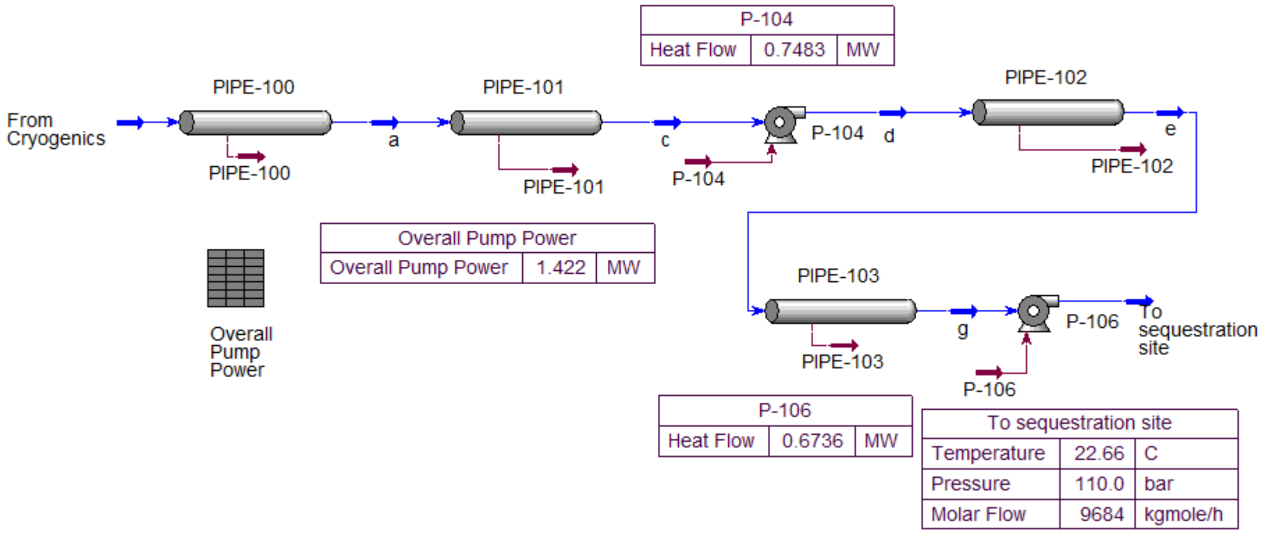
Step 1: reduce the discharge pressure of P-105 and remove it as it does not necessary



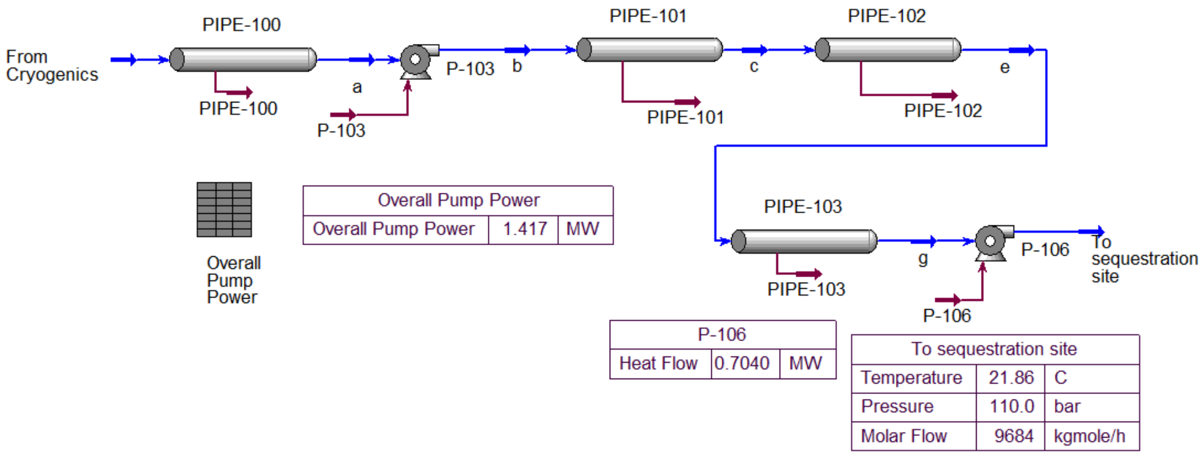
Step 2: Try reducing the discharge pressure for P-104 to 100 bar or increasing it to 120bar. An increase in overall pump power has been observed.

Step 3: Try reducing the discharge pressure for P-103 to 100 bar, the overall pump power has increased. Try increasing the discharge pressure for P-103 to 120 bar, the overall pump power has decreased and result in negative head in P-104. Further increase the discharge pressure for P-103 to 130, the overall power increases.

Step 4: Try removing P-103, overall power increases regardless of increasing or decreasing the discharge pressure of P-104.



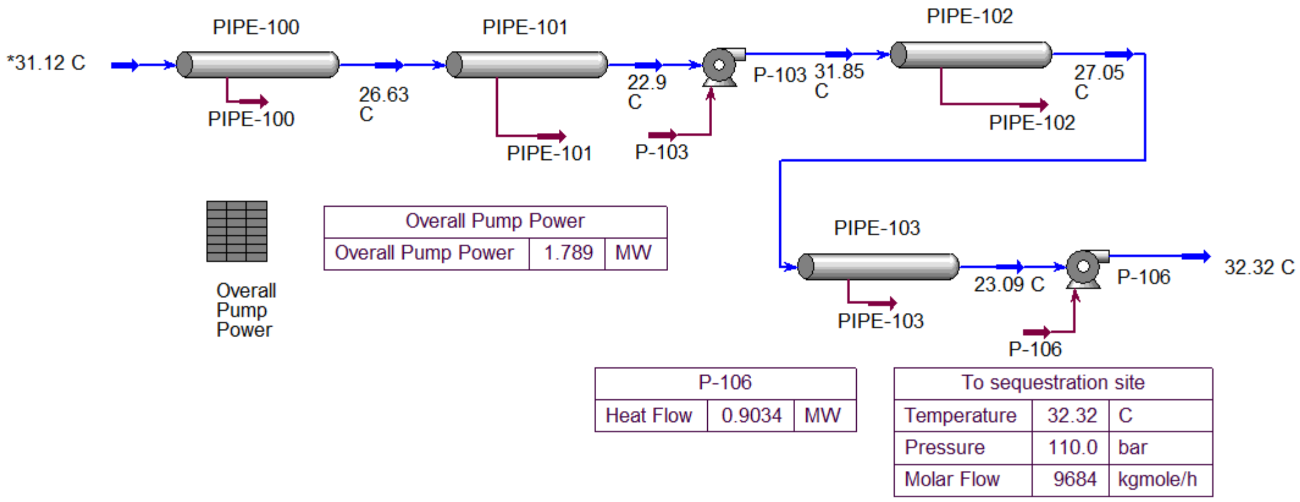
Step 5: Back to step 3. Try removing P-104 and increase the discharge pressure of P-103 to 125 bar



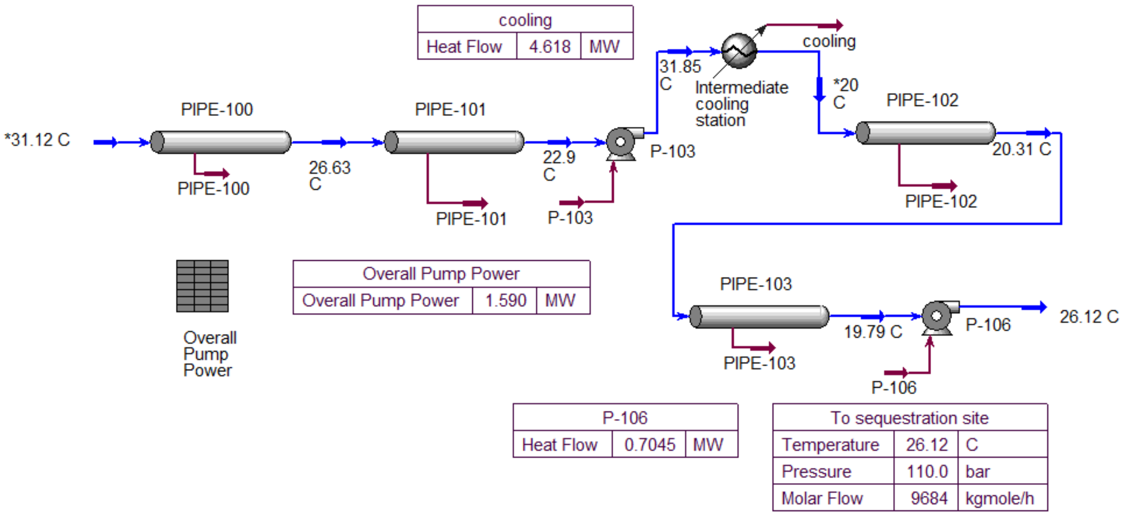
Step 6: Checking the fluid properties for each steam

Stream	Mass density	Temperature	Pressure	Fluid velocity
Unit	Kg/m^3	℃	bar	m/s
A	743.9	23.86	91.21	2.00
B	760	30.12	125	1.95
C	788.3	23.21	107.3	1.88
E	810.2	18.85	90.22	1.83
G	817	15.97	73.38	1.82
To sequestration site	808.4	21.86	110	--

Step 7: Increase the ambient temperature to 25 ℃ and change the position of P-103 is needed



Step 8: Add an intermediate cooling station in the event which the ambient temperature reaches 25 ℃ and to provide a safety margin of 5 ℃



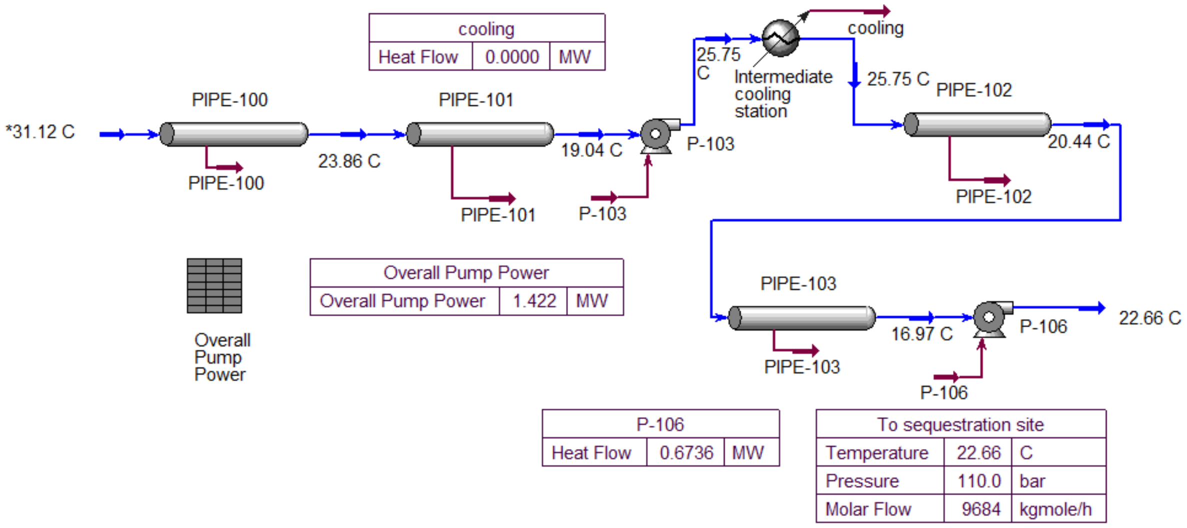
cooling		
Heat Flow	4.618	MW

Overall Pump Power		
Overall Pump Power	1.590	MW

P-106		
Heat Flow	0.7045	MW

To sequestration site		
Temperature	26.12	C
Pressure	110.0	bar
Molar Flow	9684	kgmole/h

Step 9: When the ambient temperature reduces from 25 ℃ to 15 ℃ or below, intermediate cooling station will be shut down as shown below, i.e. 0 MW.



cooling		
Heat Flow	0.0000	MW

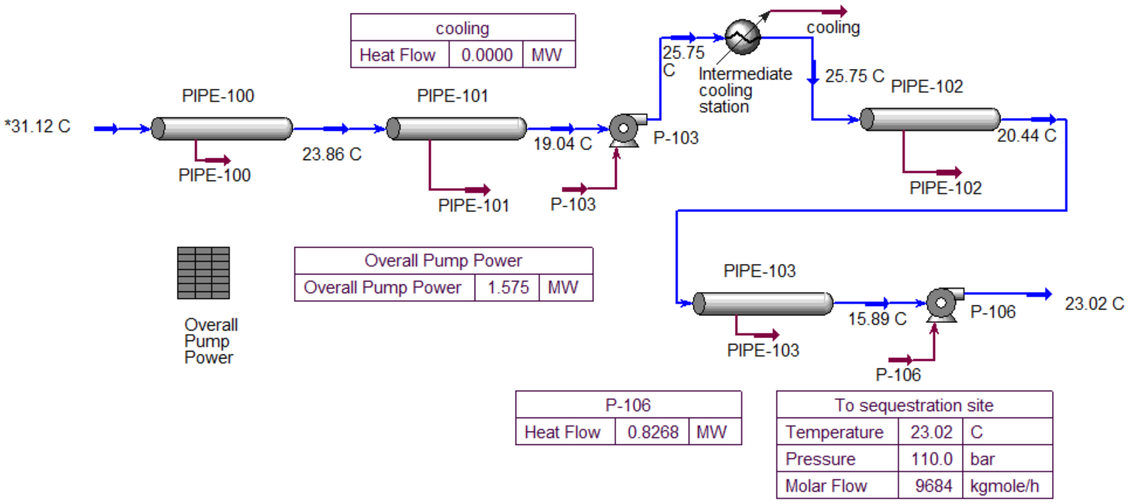
Overall Pump Power		
Overall Pump Power	1.422	MW

P-106		
Heat Flow	0.6736	MW

To sequestration site		
Temperature	22.66	C
Pressure	110.0	bar
Molar Flow	9684	kgmole/h

5.2.4 Scenario 3: To investigate the effect of elevation in scenario 2

Step 1: add 100 metre elevation to PIPE-103 and observe the changes



cooling		
Heat Flow	0.0000	MW

Overall Pump Power		
Overall Pump Power	1.575	MW

P-106		
Heat Flow	0.8268	MW

To sequestration site		
Temperature	23.02	C
Pressure	110.0	bar
Molar Flow	9684	kgmole/h

Step 2: Try out different elevation and observe their changes with respect to PIPE-103

Table 37 Case 1: ambient temperature of 15 ℃, no intermediate cooling is required

Elevation	Outlet temperature	Outlet pressure	Outlet density	Power for P-106	Discharge temperature (to sequestration site)
Metres	℃	bar	Kg/m^3	MW	℃
0	16.97	75.36	807.5	0.6736	22.66
100	15.89	67.49	807.3	0.8268	23.02
150	15.34	63.56	807.6	0.9031	23.2
200	14.77	59.63	808.1	0.9790	23.39
250	Error	Error	Error	Error	Error

*'Error' means that the Aspen HYSYS® wasn't able to converge

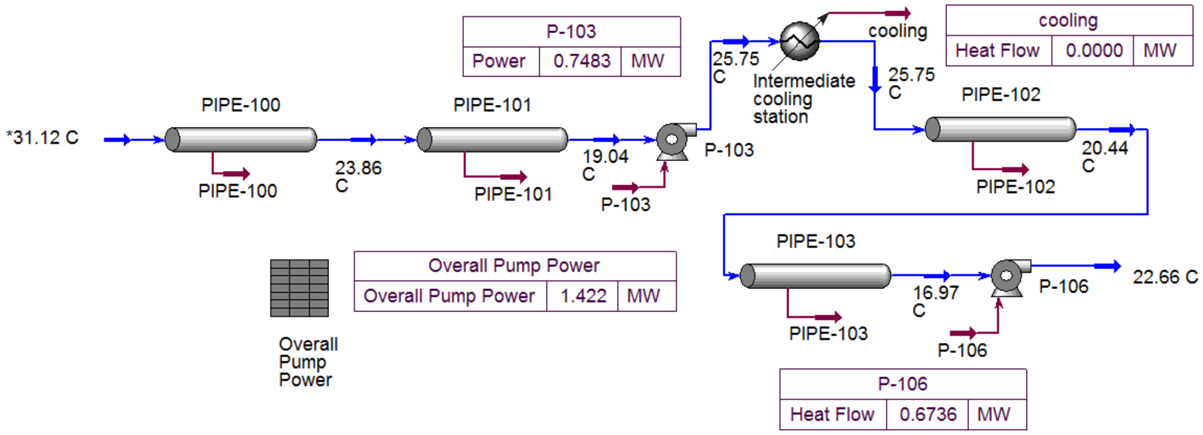
Table 38 Case 2: ambient temperature of 25 ℃ and 26 ℃ as maximum allowable temperature at sequestration site

Elevation	Outlet temperature	Outlet pressure	Outlet density	Power for P-106	Discharge temperature (to sequestration site)	Intermediate Cooling station Duty
Metres	℃	bar	Kg/m^3	MW	℃	MW
0	22.54	92.33	765.7	0.3623	25.69	3.182
100	21.44	84.71	763.8	0.5199	26.02	3.182
150	20.86	80.91	763.2	0.5985	26.19	3.182
200	20.27	77.11	762.8	0.677	26.36	3.182
250	19.67	73.32	762.8	0.7552	26.53	3.182
300	Error	Error	Error	Error	Error	Error

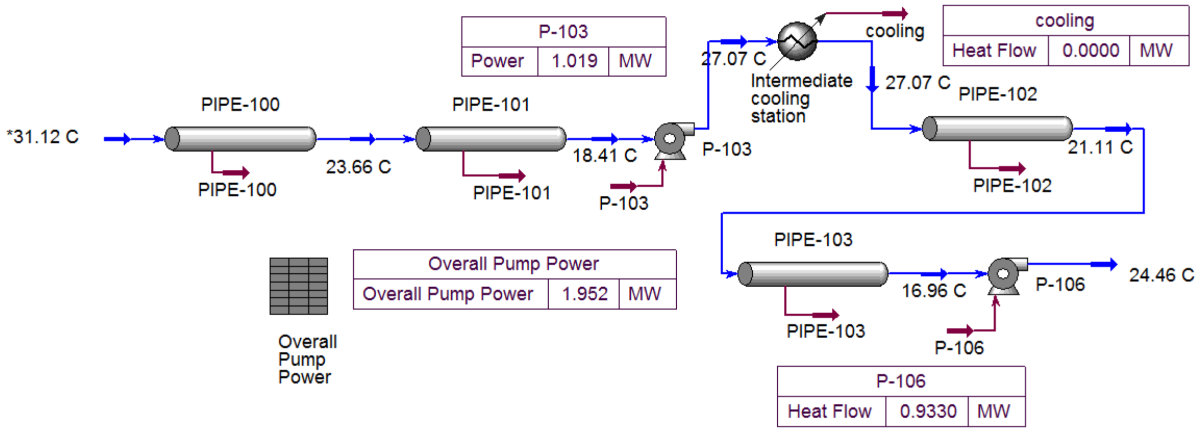
*’Error’ means that the Aspen HYSYS® wasn’t able to converge

5.2.5 Scenario 4: To investigate the impact when there is a variation in feed flow rate

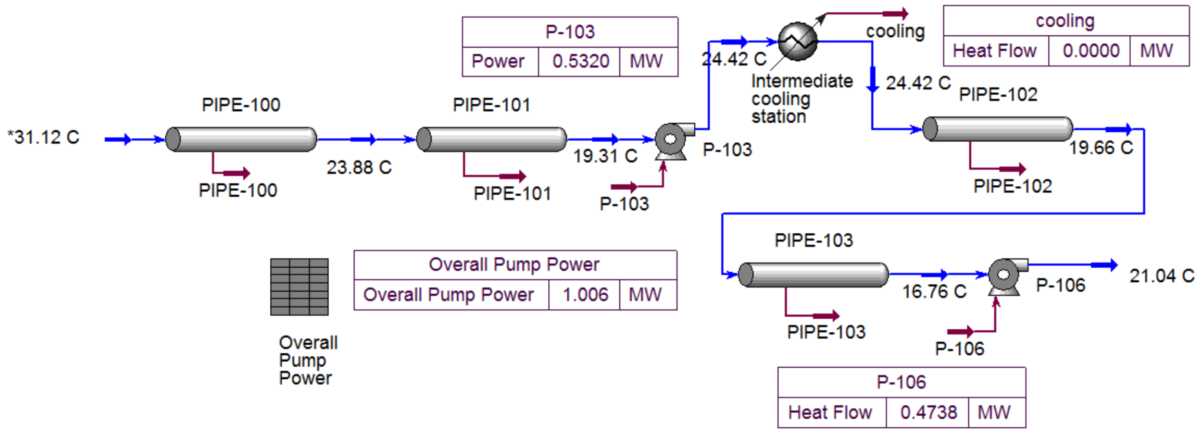
Case 1: 9684 kgmol/hour (original case)



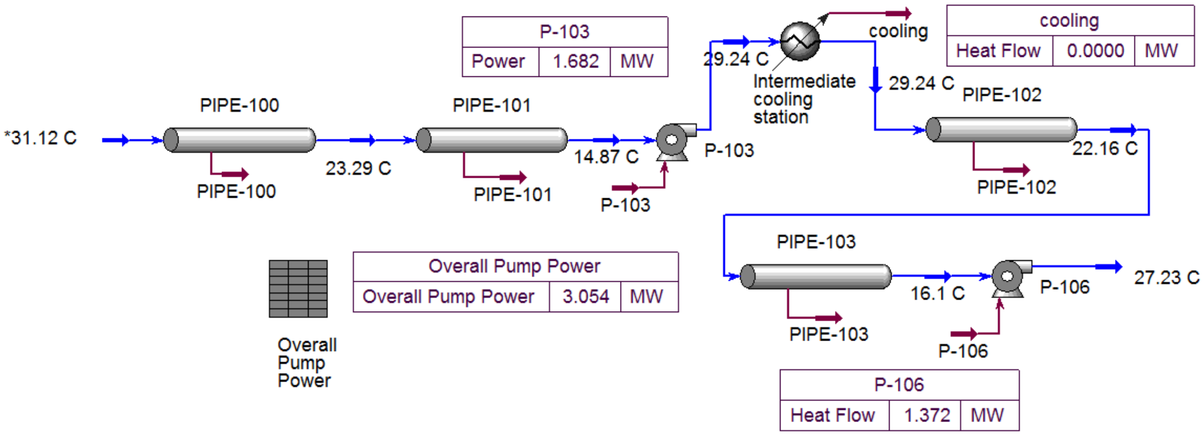
Case 2: 10652.4 kgmol/hour (+10%)



Case 3: 8715.6 kgmole/hour (-10%)



Case 4: 11620.8 kgmole/hour (+20%)



Case 5: 7747.2 kgmole/hour (-20%)

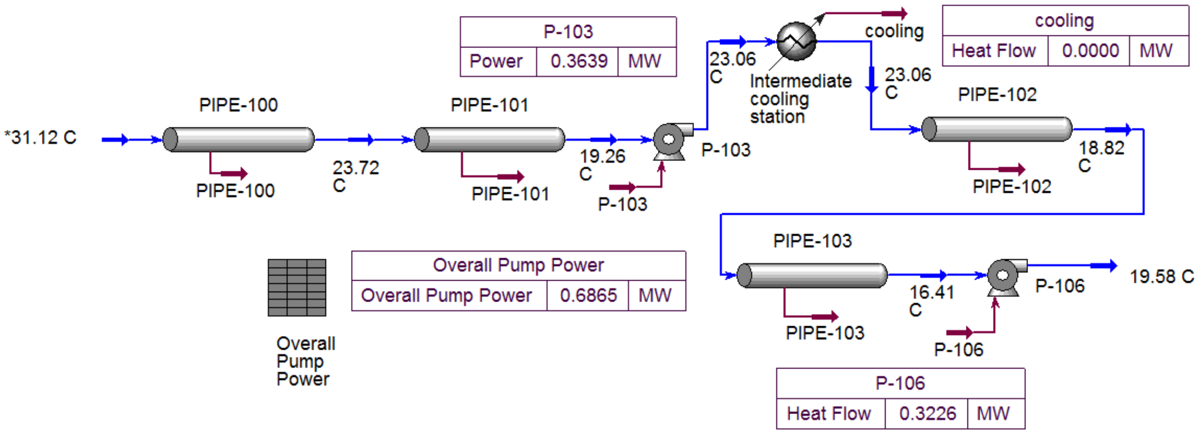


Table 39 Summary for overall pumping power and discharge temperature with respect to various feed flow rate

Case	Overall pumping power	Discharge temperature of P-103	Discharge temperature of P-106
unit	MW	℃	℃
-20%	0.6865	23.06	19.58
-10%	1.006	24.42	21.04
Original	1.422	25.75	22.66
+10%	1.952	**27.07**	24.46
+20%	3.054	**29.24**	**27.23**

*****temperature in bold meaning that it has exceeded the assumed maximum allowable temperature for liquid CO_2

CHAPTER 6 LIQUID CO_2 FLOW LOOP

6.1 Laboratory set-up

The purpose of this laboratory set-up is to investigate the feasibility of pumping liquid CO_2 after the capture in order to retain its liquid phase for pipeline transportation. A packed plunger metering pump (20 to 682 GPH; up to 7200 PSI) is used to pump liquid CO_2 collected at the bottom of gas liquid separator through a close loop back to the feed line of the gas liquid separator. The pump has an accuracy of ±0.5% at steady state and capacity can be manually adjusted. The discharge pressure of the pump can be controlled by an integral bonnet needle valve located on the pump discharge line. One major benefit of using this type of plunger pump is that it provides heavy duty positive displacement for continuous, accurate metering and fast response at higher flow rates and/or pressures can be provided by standard single ball check valve located on both suction and discharge side of the pump.

After successfully collecting pure CO_2 as liquid, valve V-7 can be opened followed by starting the plunger pump. The pump discharge pressure can be controlled by regulating the discharge valve V-8. The suction temperature (i.e. the temperature of separator) has to be maintained by continuously pouring liquid nitrogen so that the CO_2 maintains its liquid phase before establishing a higher liquid pressure. The discharge pressure and temperature will be recorded for analysis.

6.2 Operating procedures

Start-up procedures:

1. All PPE (safety boots, safety goggles, lab coats, heat insulated gloves) must be worn
2. There must be at least 2 people during start up and operations
3. The laboratory sliding door must be opened
4. CO_2 cylinder to be used for gas feeding must be securely placed before connecting with V1.

Operating procedures:

1. Open V1, V3 and V4

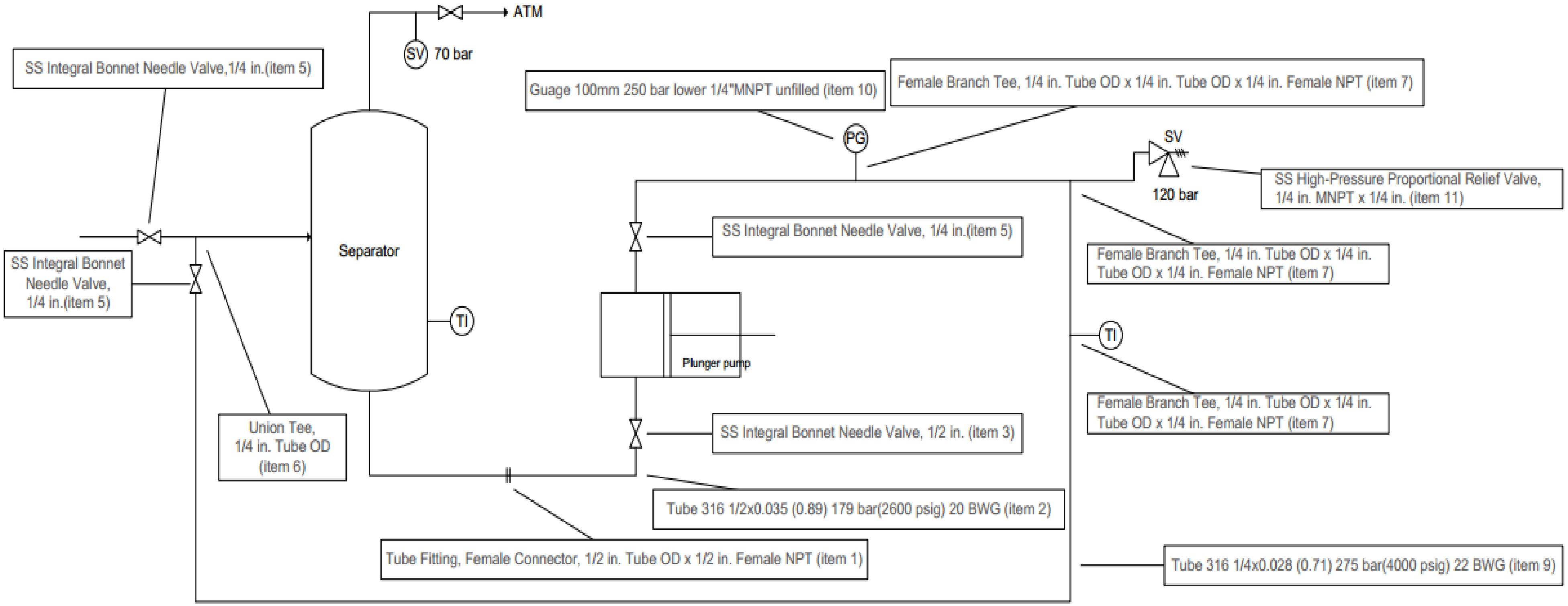
Close V2, V5 and V6

2. Feed CO_2 gas continuously at 30 bar and 10-20C thought ¼ inch PR 101 and ¼ inch PR102 into the separator
3. Observe PG01 at the overhead line of the separator until the pressure reaches 30 bar
4. Start liquefying the CO_2 gas in the separator by pouring liquid N2 to cool down the temperature (observe T-101) to -40C approximately.
5. The level of CO_2 liquid in the separator is estimated to be about ¾ of the separator volume prior to switching on the pump.
6. Close V1 and V3. Open V2 and V6
7. Switch the pump on with the lowest flow rate available for the pump (approximately 10 litres/hour) and continuously operate at 110 bar (observe PG02)
8. Observe the temperature change at the pump discharge line through TI-02 every 1 minute.

Shut down procedures:

1. Switch off the pump
2. Release all gases in the system to atmosphere via V1, V2, V3, V4,V5 and V6 until no pressure indicated in PG01 and PG02.
3. Close V1 and V5 after all gases have been released
4. Remove CO_2 cylinder away and store it in the designated area

6.3 Piping and Instrumentation diagram (P&ID)



SS Nut and Ferrule for ½ and ¼ in. (item 4 and 8)
are also to be purchased.

Figure 79 Piping and Instrumentation diagram (P&ID) for liquid CO_2 flow loop

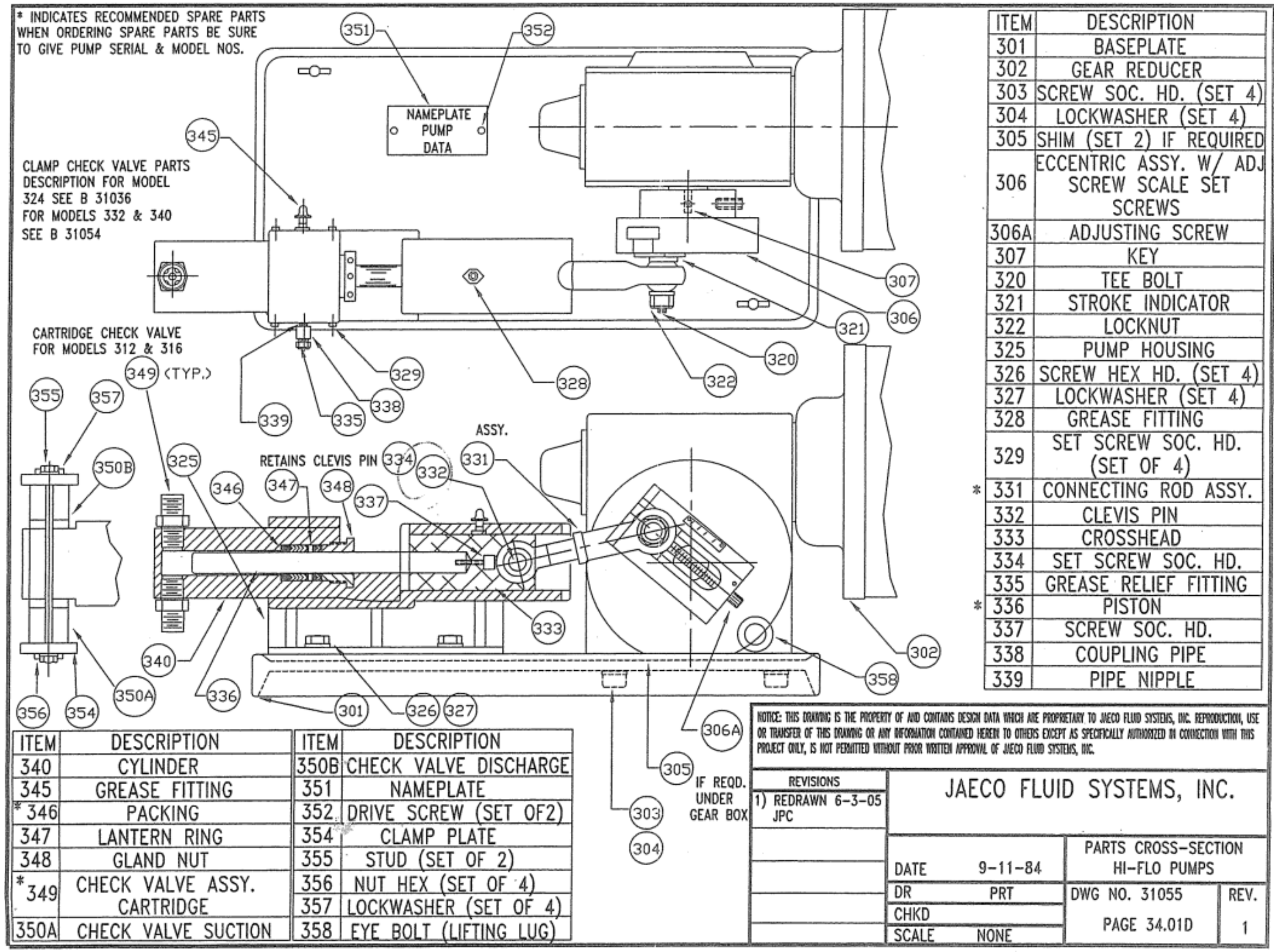
6.4 Hazard and Operability studies (HAZOP) for pumping liquid CO$_2$

Research project	**CO$_2$ handling operation**		Attendees: 1. A/Prof. Ahmed Barifcani: 2. A/Prof. David Pack 3. Lab supervisor: Saif Ghadhban 4. PhD students: Nicholas ChiiJyh Teh (ID: 14200470), Rakpong Peampermpool (ID: 12358487)	
Meeting date	19/08/2013			
Meeting place	Clean Gas Technology Australia, building 614, Curtin University			
Parameter	Cause	Consequences	Protection	Action/Comments
High pressure of the pump discharge	Improperly adjusted operating pressure of the pump	Overpressure in the discharge line	Install SV2 ,pressure set at 120 bar	Observe PG02 while operating pump. The pressure at discharge is to be no more than 110 bar.
Electrical / area classification isolation earthing			The pump will have an adequate earthing protection	Electrician
Low temperature inside the separator	Overcooling by liquid N$_2$	Solidification of CO$_2$ in the separator	Installed TI01	Observe TI01 and adjust the liquid N$_2$ to suit the condition needed for liquid CO$_2$ inside the separator (no lower than -40 ^{0}C at 30 bar). TI01 to be calibrated.

High liquid level in the separator	Freezing of CO_2 in the bottom of separator or malfunction of the pump	Over-filling of the separator with liquid CO_2	CO_2 fed to the separator at between 15-30 bar Control the temperature of separator at no lower than -40 ^{o}C	Switch off the pump Open V3 and V4 to release the over-filling
Power failure		Operation loss of control		Shutdown the system by switching off the pump and releasing all gases to atmosphere
Parameter	Cause	Consequences	Protection	Action/Comments
Leakage of CO_2	Joints loosening	Loss of pressure/flow		Considered leakage If the pressure observed in PG01 is lower than 15 bar after starting operation. Shut down the system by switching off the pump then repair the leaks.
Leakage of CO_2	Venting of CO_2	Asphyxiation	Keep the slide door - open	Switch off the pump and notify the laboratory supervisor
Abnormal noise of operating pump	Pump malfunction	Product loss and/or pump failure	Follow pump operation manual	

Chemical handling				
1. Solid CO_2	Mishandling	Skin freezing	PPE & special gloves	Follow safety data sheet (MSDS) as attached
2. Liquid N_2	Mishandling	Skin cold burn	PPE, clothing & gloves	Follow safety data sheet (MSDS) as attached
Abnormal operation of valve V1 (after starting pump) – V1 opened / leaks	Careless check up / inner valve body leakage	Backflow to the mixing drum leading to overpressure	V1 tested and pre-checked before starting pump	Monitor valve
Abnormal operation of valve V2 (after starting pump) – V2 closed	Careless check up / system malfunction	Pump malfunction and/or over pressure at the discharge line	Pre-check V2 before starting pump	Monitor valve
Abnormal operation of valve V6 (after starting pump) – V6 closed	Careless check up / system malfunction	Pump failure due to low flow of fluid or blockage at the suction	Pre-check V6 before starting pump	Monitor valve

6.5 Technical drawing of Jaeco Pump



ITEM	DESCRIPTION
301	BASEPLATE
302	GEAR REDUCER
303	SCREW SOC. HD. (SET 4)
304	LOCKWASHER (SET 4)
305	SHIM (SET 2) IF REQUIRED
306	ECCENTRIC ASSY. W/ ADJ SCREW SCALE SET SCREWS
306A	ADJUSTING SCREW
307	KEY
320	TEE BOLT
321	STROKE INDICATOR
322	LOCKNUT
325	PUMP HOUSING
326	SCREW HEX HD. (SET 4)
327	LOCKWASHER (SET 4)
328	GREASE FITTING
329	SET SCREW SOC. HD. (SET OF 4)
* 331	CONNECTING ROD ASSY.
332	CLEVIS PIN
333	CROSSHEAD
334	SET SCREW SOC. HD.
335	GREASE RELIEF FITTING
* 336	PISTON
337	SCREW SOC. HD.
338	COUPLING PIPE
339	PIPE NIPPLE

ITEM	DESCRIPTION
340	CYLINDER
345	GREASE FITTING
*346	PACKING
347	LANTERN RING
348	GLAND NUT
*349	CHECK VALVE ASSY. CARTRIDGE
350A	CHECK VALVE SUCTION

ITEM	DESCRIPTION
350B	CHECK VALVE DISCHARGE
351	NAMEPLATE
352	DRIVE SCREW (SET OF2)
354	CLAMP PLATE
355	STUD (SET OF 2)
356	NUT HEX (SET OF 4)
357	LOCKWASHER (SET OF 4)
358	EYE BOLT (LIFTING LUG)

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Figure 807 Technical drawing of Jaeco pump

6.6 Installation and operation of Jaeco pump

Capacity Adjustment

Stop pump; loosen locknut (322) and turn adjusting screw (306B) until required capacity is indicated on the capacity scale. Retighten locknut (322) after adjustment and before starting pump. It is strongly recommended that if the capacity is to be adjusted repeatedly that the locknut be replaced after each adjustment. Failure to do so may generate excessive backlash in the driveline, resulting in premature wear and potential damage.

Pump Servicing – Part Replacement

Packing

- Remove grease relief assembly (335, 338, 339)
- Loosen set screws (329) and remove liquid end assembly
- Remove gland nut (348), packing set (346) and lantern ring (347) taking care not to scratch cylinder walls (340).
- Inspect plunger for scoring/scratches and replace if necessary
- Install, one at a time, the following packing rings: bottom adapter flat side down, V-rings, top adapter flat side up, lantern ring (must line up with grease fitting holes in cylinder), bottom adapter, V-ring and then top adapter.
- Loosely install gland nut.
- Reinstall liquid end assembly
- Tighten set screw (329) and finger tighten gland nut.
- Do not tighten more than one turn past finger tight.
- If a rise in stuffing box temperature is observed, loosen and re-adjust gland nut.
- Packing adjusted too tightly will create excessive friction and heat which will adversely affect the life of the packing, plunger and connecting rod bearings.

Plunger

Remove grease relief assembly (335, 338, 339), loosen set screws (329) and remove liquid end assembly. Remove lock nut (322) and rotate connecting rod assembly (331) off tee bolt (320). Slide plunger/connecting rod assembly out of pump housing end. Remove clevis pin (332) from crosshead and remove retaining screw (337) with an allen wrench. Install new plunger and reinstall liquid end assembly.

Crosshead/Connecting Rod Bearings/Packing

Lubricate each grease fitting once a week with a light hypoid grease until grease appears on outside of bearing area. Lubricate packing with one shot of grease per week.

Connecting Rod Assembly

If connecting rod bearings are worn more than 0.010, replace connecting rod assembly (331).

CHAPTER 7 RESULTS AND DISCUSSION

7.1 Experimental results for CO_2 capture by cryogenics

The analysis of depleted gas composition can be divided into 3 stages:

Stage 1: When the gas mixture starts flowing through the system, the composition of the depleted gas increases from zero and reaches a relatively steady value. Only and most of the CO_2 gets condensed when experiencing the low temperature.

Stage 2: CO_2 continues to get condensed and accumulated at the bottom of the separator. The depleted gas composition remains relatively stable when vapour liquid equilibrium (VLE) is achieved, i.e. the rate of evaporation (liquid changing to vapour) equals to the rate of condensation (vapour changing to liquid) and there is no net vapour-liquid inter-conversion. This is the time when the reading for depleted gas composition shall be taken.

Stage 3: If the depleted gas composition starts increasing, it means that some of the liquefied CO_2 is vaporising due to either due to loss of system pressure and/or temperature. This problem can be solved by pouring more liquid nitrogen onto the separator.

Table 40 Results for capturing CO_2 at different composition and pressure by cryogenic method

Experiment	Feed CO_2 composition (mol %)	Separator pressure (bar)	Separator temperature (℃)	Average Experimental depleted gas composition (mol %)	Theoretical depleted gas composition by HYSYS (mol %)	Experimental Capture Rate/Recovery (%)	Theoretical Capture rate/Recovery by HYSYS (%)	Difference In terms of Recovery (%)
1	85%	15	-53	0.41	0.4335	88.99	87.51	1.48
2	85%	20	-49	0.36	39.91	91.51	89.59	1.92
3	80%	18	-55	0.31	0.3459	89.7	87.75	1.95
4	80%	20	-51	0.33	0.3708	88.73	84.63	4.1
5	75%	20	-52	0.32	0.3572	85	82.55	2.45
6	75%	22	-53	0.25	0.3197	89.59	85.42	4.17
7	75%	24	-55	0.23	0.2778	90.53	88.24	2.29
8	75%	26	-52	0.24	0.2937	90.33	87.37	2.96
9	75%	28	-54	0.23	0.2588	90.57	89.55	1.02
10	75%	30	-47	0.26	0.3179	89.50	86.02	3.48
11	75%	32	-45	0.28	0.3259	88.29	85.61	2.68
12	70%	28	-53	0.25	0.2687	86	85.44	0.56
13	65%	30	-53	0.23	0.2565	84.17	82.6	1.57
14	60%	30	-55	0.23	0.307	80.32	80.22	0.1
						Average improvement		2.2

The results in table 42 are showing a consistent tread that the pressure required to capture CO_2 is directly proportional to the capture rate at a constant operating temperature. More importantly it also indicates that the better performance (higher capture rate, lower depleted gas composition) can be achieved experimentally than the ones from simulation by an average of 2.2%. For experiment 3, 89.7% experimental CO_2 capture rate can be achieved at -55 ℃ and 18 bar for a 80 mol% CO_2 feed. The result given by Xu et al. (2012) has verified that the temperature required by for the same condition to achieve 90% CO_2 separation rate is approximately -55 ℃. For experiment 14, 80% experimental CO_2 capture rate can be achieved at -55 ℃ and 30 bar for a 60 mol% CO_2 feed. The result given by Xu et al. (2012) has confirmed that the temperature required for the same condition to achieve 80% CO_2 separation rate is approximately -52 ℃. It can therefore be concluded that these results are in good agreement with the study of phase transition characteristics of CO_2/H_2 mixture done by Xu et al. (2012).

During the commissioning and operation of pilot plant, engineering issues faced were freezing, condensation of CO_2 in mixing drum, equipment faults, etc. Several solutions have been proposed for these issues:

Temperature control

The temperature of the methanol chiller has to lie between -55 ℃ to -57 ℃ for assisting the liquefaction process. It will subject to the quantity of dry ice and methanol, the frequency of pouring dry ice into the methanol and the accuracy of thermometer. Methanol has a freezing temperature of -98 ℃ it is a suitable cooling medium. The temperature of the gas liquid separator is subject to the quality of insulation, the quantity of liquid nitrogen and the frequency of pouring liquid nitrogen onto the separator. There are also several ways from experience to determine if the CO_2 has become frozen in the system as such:

1) Rapid decrease of depleted gas flow rates observed by the flow meter or zero flow rate

2) Pressure difference between the feed pressure regulator and the depleted gas pressure becomes too large (solid does not exert pressure)

3) The temperature of the separator and/or methanol chiller goes below -57 ℃ for too long

Pressure control

The pressure for capturing CO_2 will be mainly controlled by the *Swagelok*® high pressure regulator (PCV-1). The pressure difference of approximately 1~2 bar between the upstream and downstream of the gas liquid separator shall be taken into account when calculating the capture rate. It can be observed by reading pressure gauges from the corresponding equipment.

CO_2 composition

In order to ensure that feed gas is prepared at the desired composition, sufficient time should be given to allow better mixing of gas. It is also crucial to a feed CO_2 from the top of the drum while N_2 from the bottom to avoid re-condensation of CO_2. The timing of reading the CO_2 composition of the depleted gas is the key to consistent results. The accuracy of composition analyser can be tested by feeding in 100 mol% CO_2.

7.2 VSA/Cryogenic hybrid (Aspen HYSYS) development scheme

The vacuum swing adsorption (VSA) unit separates the CO_2 and water from the nitrogen and oxygen. Two separators V-100 and V-102 are used to knockout the water from the gas and provide energy savings in compression.

The dryer package utilizes physical adsorbent has been proposed and it consists of two bed adsorber columns. Aspen HYSYS is not able to incorporate the aspect of the adsorption process and since water cannot be present in the cryogenic section, a ‘component splitter’ has been used for the dryer. One bed, A-100 dries the gas while the other bed, A-101 goes through a regeneration cycle. The feed gas enters from the top of the column to prevent fluidization.

The dried feed to cryogenic section contains both 77.12% CO_2 and 22.88% nitrogen (refer to stream 29, 35). After passing through a series of compressors, air coolers and heat recovery exchangers, a refrigeration package (R-100) is used for chilling the gas to -55 ℃ using mixed refrigerant to achieve the lowest temperature without freezing. Before entering the refrigeration package, the process stream has also been split into a ratio of 70:30 (by iteration) to increase chilling efficiency. Gas liquid separator V-101 separates the liquid and gaseous CO_2. The gaseous CO_2 is used to chill its feed (at E-103) and expanded by expander (Exp-101) to 165 kPa for further cooling (at E-101). The gaseous stream which has the same pressure as VSA feed (150kPa) is then recycled back to the VSA feed to boost recovery of CO_2 in the VSA process.

Vacuum Swing adsorption recovery

The gaseous stream which has the same pressure as VSA feed (at 150kPa) has been recycled back to the VSA feed to boost recovery of CO_2 in the VSA process.

Compression

The energy from expansion has been re-used to provide compression in one of the process streams. Minimum number of heat recovery exchangers have been used to ensure the overall pressure drop is minimal. The discharge pressure of each compressor has been iterated to ensure the overall duty requirement is minimal and without compromising the overall CO_2 recovery, limitation of discharge temperature for compressor.

Cooling and refrigeration

Air coolers have been used to cool the discharge stream of each compressor. The cryogenic energy of liquid CO_2 has been recycled to chill the feed streams (at E-100 and E-102) and eliminated the use of sea water coolers. Before entering the refrigeration package, the process stream has also been split into a ratio of 70:30 (by iteration) to increase chilling efficiency. The vent from gas liquid separator, at high pressure, has also been used to chill its feed (at E-103) and expanded by expander (Exp-101) to 165 kPa for condensing water at E-101 to reduce energy for drying unit.

Table 41 Summary of the energy requirement for Hybrid VSA-Cryogenic capture

Items	Units	Value	Method proposed by Xu et al. (2012)
Mass flux of CO_2 fed to the cryogenic system	kg/s	148.11	148.11
Mass flux of captured CO_2	kg/s	116.73	128.6
CO_2 recovery ratio for cryogenic section	%	78.81	86.82
Drying	MW	1.67	--
Energy penalty for refrigeration package	MW	38.35	40.99
Energy penalty for compressor intercooler	MW	--	51.27
Energy recovered by heat recovery	MW	34.8	16.88
Compression	MW	32.71	51.15
Pumping	MW	1.311	0.796
Air coolers	MW	1.5	--
Total energy penalty	MW	75.57	144.2
Energy per kg CO_2 captured	MJ/kg CO_2	0.64	1.12

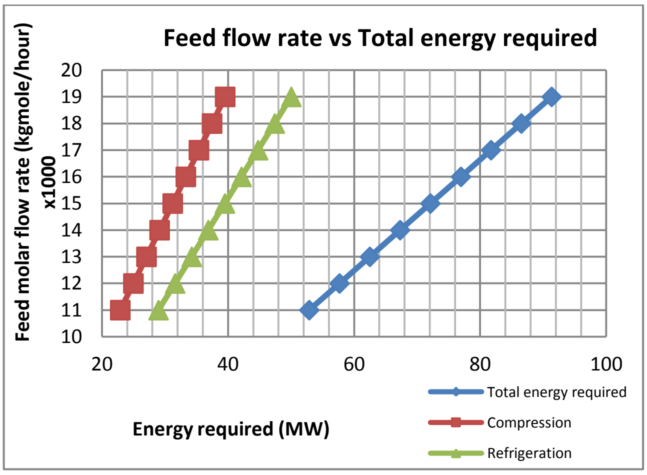

Figure 818 Feed flow rates versus total energy required

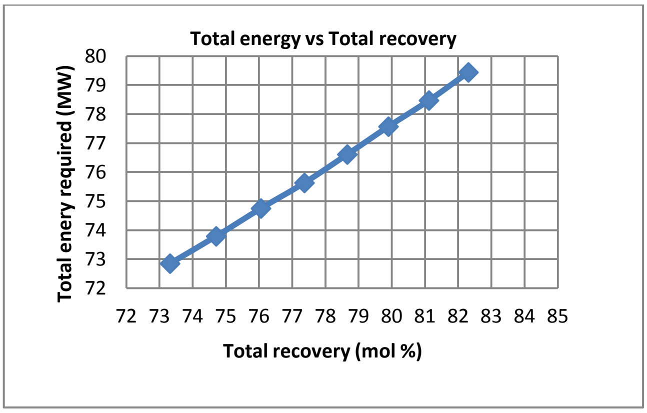

Figure 882 Total energy required versus total recovery

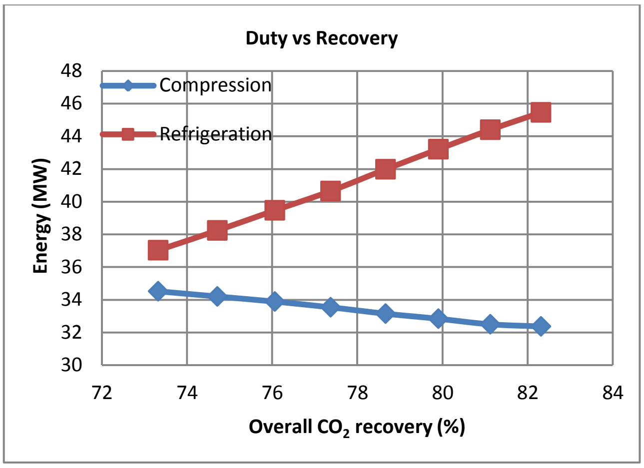

Figure 830 Duty versus total recovery

Figure 88 shows that the total energy required for the cryogenic process is directly proportional to the quantity of feed gas, assuming a constant recovery and feed gas composition. Figure 89 shows that the total energy required is also directly proportional to the total recovery. Figure 90 shows that compression power is inversely proportional to the refrigeration duty to achieve a certain CO_2 recovery. These three figures discover a key finding that is the optimum energy for a cryogenic process is the optimum balance between compression and refrigeration for a given feed CO_2 composition and desired amount of recovery.

This model developed offers several features such as CO_2 is captured as liquid having a purity of 98.6 mole%, 99% by mass. The thermal heat integration between cold and hot streams reduces the cooling duties of auxiliary refrigeration cycles, further providing energy savings in compression power and eliminates the use of sea water coolers. The wastewater separated from the V-100 and V-102 water separator can be treated and reused in other areas of the capture plant. Ultimately the minimal project footprint is reduced as a result of minimum amount of smaller equipment and pipe sizes.

The results for total energy required by the cryogenic liquefaction process. 90% of the cryogenic energy in the liquid product is recovered. From an engineering design point of view, the amount of heat recovery exchangers shall be kept at minimum so that it reduces the overall pressure drop and hence the compression requirement and the cold energy loss to the surroundings. This justifies the reason for not implementing the two stage refrigeration and separation proposed by Xu et al. (2012) because it requires more equipment. Finally, a comparison of the CO_2 recovery between actual experiment and simulation again justifies that higher pressure and/or higher CO_2 mol% in feed will favour the capture rate.

Several highlights for this energy saving scheme are given as follows:

- CO_2 is captured as liquid having a purity of 98.6 mole%
- Thermal heat integration between cold and hot streams contributes to reducing cooling duties of auxiliary refrigeration cycles and thus further savings in compression power
- The wastewater separated from the V-100 and V-102 water separator can be reused
- No seawater cooler is required (except for mixed refrigeration loop) after the recovering available energy in liquid CO_2 product
- Reduced project footprint as a result of using smaller equipment size.
- Environmentally friendly since no solvent such as amine is needed for CO_2 capture in a closed system

VSA recovery	Cryogenic recovery	Overall recovery
95mol%	78.81mol%	94.34mol%

Table 42 A comparison between laboratory result and simulation

Scenarios	Operation of laboratory pilot plant Experiment 3	Energy saving scheme for VSA/Cryogenic hybrid
Feed composition	75mol% CO_2, 25 mol% N_2	77.12 mol% CO_2, 22.88 mol% N_2
Capturing temperature (℃)	-55	-55
Capturing pressure (bar)	20	13.95
Vent gas CO_2 mole composition (%)	31.85	42.6
Liquid CO_2 mole composition (%)	98.6	98.6
Cryogenic capture rate (recovery) (%)	85	78.81

Table 45 above shows that in reality, higher capture rate (recovery) can be achieved and high pressure will favour the cryogenic separation. The energy saving scheme developed in Figure 78 also shows that VSA/Cryogenic hybrid offers an overall CO_2 recovery of 94.34%.

7.3 CO_2 pipeline design

Table 43 Summary of the results for pipeline transportation of liquid CO_2 and supercritical CO2

Design considerations	Liquid CO_2	Supercritical CO_2	Liquid CO_2	Supercritical CO_2
CO_2 inlet condition assumed	25 ℃, 110 bar, 3.7 Mtpa	50 ℃, 110 bar, 3.7 Mtpa	25 ℃, 110 bar, 3.7 Mtpa	50 ℃, 110 bar, 3.7 Mtpa
Change of phase allowed at any stage	No	No	No	No
Pressurization method	Pumps	Compressors	Pumps	Compressors
Minimum pipe size required, inner diameter (mm)	288.9	317.5	288.9	317.5
Pipe thickness (mm)	35	38.1	35	35
Pipe material	Mild steel	Mild steel	Mild steel	Mild steel
Soil material	Dry sand	Dry sand	Dry sand	Dry sand
Fluid velocity (m/s)	2.2~2.3	3.2~3.7	2.2~2.6	3.2~3.9
Total Pipe length assumed (km)	90	90	90	90
Injection pressure (bar)	200	200	200	200
Temperature change due to pressurization (℃)	4.7~4.9	16~17	5~6	17~21
Ambient/soil temperature (℃)	20	20	40	40
Maximum compressor/pump discharge pressure (bar)	110	110	110	110
Compressor/pump adiabatic efficiency (%)	80	80	80	80
Compressor/pump duty (MW)	3.3	5.9	3.7	5.9
Requirement of pipeline insulation for the main trunkline	no	no	no	no
Requirement of intermediate cooling/refrigeration	no	no	no	no

The summarized simulation results in Table 46 show that if transporting the same amount of CO_2 over the same distance at constant ambient temperature, same soil type and same buried depth, liquid CO_2 uses a smaller and thinner pipe compared with the one for supercritical CO_2. Pumps are less energy intensive than compressors and in this scenario consumes about 50% less energy. The temperature rise due to pumping is less significant than the temperature rise due to compression. Considering the same requirement of injection pressure and temperature of a reservoir, it can then be foreseen that the cooling duty required for injecting liquid CO_2 is lower than injecting supercritical CO_2. All these findings conclude that significant cost savings in both capital expenditure and operating expenditures can be attained by transporting liquid CO_2.

The summarized results in Table 45 also show that the temperature of the liquid/supercritical CO_2 will notably decrease as it flows through the pipeline regardless of the ambient temperature (20 ℃ or 40 ℃). The reason is because these two pipelines were buried 1.2 meter underground by dry sand which has a very poor thermal conductivity of 0.5W/mK and act like a thermal insulation. Future research should investigate the effect of buried depth and different soil type. Lower ambient temperature and soil with higher moisture content will improve the heat conductivity of the soil. Thus, it provides better cooling effect to the liquid CO_2, causing the density of liquid CO_2 to rise and it is better for pumps. This will eventually result in a lower pressure drop across the pipeline (ΔP_{loss}) and drive down the pumping power (ΔP_{pump}) and operating cost. It can then be concluded that cold climate is more suitable for liquid CO_2 pipeline while warm climate is more suitable for supercritical CO_2 pipeline without considering thermal insulations.

In scenario 1, the effect of ground material with two significantly different conductivities (dry sand versus wet sand) on a typical liquid CO_s pipeline system is determined. In terms of heat transfer, wet sand offers a higher ground conductivity and result in a much lower outlet temperature for each pipe compared to dry sand. As a result, the overall pressure drop across each pipe is lower for wet sand and lower pump power due to less change in liquid density.

It can also be expected that the pumping power (operating cost) will be higher when there is a significant increase in ambient temperature and/or less moisture content in the surrounding soil.

Table 44 Relationship between different parameters for CO_2 pipeline

Ambient temperature	Moisture content in soil	Ground conductivity
lower	Higher	higher

Ground conductivity	Outlet temperature	liquid density	Pressure drop	Pumping power
Higher	Lower	Higher (more liquid-like)	Lower	Lower

In scenario 2, the objective is to optimize the pipeline in scenario 1, to provide a safety margin of 5 ℃ and for a region where its maximum ambient temperature is 25 ℃ or below. The optimization process is essentially about reducing the pumping requirement/power in order to reduce the operational expenditure and reducing any unnecessary equipment to reduce the capital expenditure. The pipe inner diameter of 317.5mm and mild steel material will remain fixed throughout the whole optimization process in order to satisfy the fluid velocity requirement at 2m/s. It has been noticed that two pumps as a minimum are required for a 120km pipeline system in the simulation however this configuration does not allow any increase in ambient temperature which will consequently causing the CO_2 to vaporize especially due the pumping action **(Step 7)**. As a result, configuration in **Step 5** is suitable for regions where ambient temperatures are usually 15 ℃ and below.

In order to design a pipeline system for a region where its ambient temperature can go up to 25 ℃, the pump has to be repositioned to allow sufficient pipe length and temperature drop before the stream enters the pump **(Step 7)**. It has been noticed that the stream temperature will reaches the critical temperature of CO_2 (31.1 ℃), thus it can be predicted that in extremely warm climates, depending on the availability of underground well water, intermediate cooling station is required to cool and re-liquefy CO_2 **(Step 8)** despite of the fact that it will make the transportation process uneconomical. In reality, the pumping power for P-103 will be higher to overcome the pressure drop across the cooling station. Assuming the maximum allowable temperature at the sequestration site is at 26 ℃ (5 ℃ away from 31 ℃), the cooling duty is 4.62MW.

In scenario 3, the objective is to determine the effect of elevation on the pipeline system. It has been noticed that for both 15 ℃ and 25 ℃ ambient temperature, an increase in elevation will cause the outlet temperature of a pipe to decrease due to pressure loss and result in the relationship as shown below:

Table 45 Relationship between different parameters for CO_2 pipeline

Elevation	Outlet temperature	Pressure drop across that pipe	Outlet density	Power for pump P-106	Discharge temperature of a pump
Increase	Decrease	Increase	Fairly constant	Increase	Increase

The change in elevation does not seem to alter the liquid density due to the fact that liquid is incompressible. It can also be verified that when there is a declination of the land (by entering a negative value for elevation in HYSYS), the result will be the opposite of inclination as the fluid gains potential energy.

In scenario 4, it has been noticed that the overall pumping power is directly proportional to the amount of fluid being compressed. When there is an increase (in this case +10% and +20%), the discharge temperature can go beyond 26 ℃, the maximum allowable temperature assumed therefore intermediate cooling station has to come online. On the other hand, the fluid velocity will also exceed 2m/s when there is an increase in feed molar flow rate. It can be concluded that in the interest of selecting a pipe size which accommodates a range of flow rates, statistical data for the capture rate from the capture site has to be obtained.

These models considering the soil material, soil/ambient temperature and pipeline elevation were developed to evaluate a more effective way to transport CO_2 as liquid mainly the utilization of ground temperature to avoid change in phase. The fluid temperature will eventually reach the soil temperature provided the pipe length is long enough. The results presented in Chapter 5 can help identifying the feasible location for transporting CO_2 as liquid.

Transporting liquid CO_2 via pipeline may provide more energy savings than transporting supercritical CO_2 in such a way that it requires smaller pipe sizes, does not require insulation for the main trunkline and consumes less pumping power. However, to utilize the benefit of lower ambient temperature for maintaining the liquid state, several aspect of the location for transportation have to be properly investigated for example soil type, buried depth and local climate. Another important factor to be taken into consideration is elevation which has substantial impact on the fluid velocity and pressure therefore it changes the density of the fluid.

This model developed in this paper is also currently limited to steady state, fixed amount of CO_2 and fluid composition. Dissimilar assumptions used in other CO_2 transport studies have to be recognized. Future studies should analyse the transient heat conduction model of CO_2 pipeline, forecasting the temperature distribution of CO_2 along the pipeline route especially when there is a change in flow rates and compositions.

More importantly, the simulation developed validates a relationship between several design parameters. Lower ambient temperature and soil with higher moisture content will improve the heat conductivity of the soil. Thus, it provides better cooling effect to the liquid CO_2, causing the density of liquid CO_2 to increase and become more liquid-like and it is better for pumps. This will eventually result in a lower pressure drop across the pipeline (ΔP_{loss}) and drive down the pumping power (ΔP_{pump}) and operating cost. This observation is in line with the model developed by Zhang et al. (2005). The model in Figure 5 and 6 also stresses the importance of pump location which subjects not just to the pressure drop due to altitude, but also in reality the availability of power source and the heat transfer calculation requirement for main trunk line.

Another possible cause for change in phase is elevation (z) which can be further explained by using modified Bernoulli's equation (equation 6). For example when the pipeline unavoidably experiences an increase in altitude (the potential energy term), the fluid velocity (the kinetic energy term) and pressure (the static pressure term) will decrease. By gradually increasing the elevation at two different ambient temperatures, the impact is investigated using the revised model in Figure 4 and the results are summarized in Table 2. The results show that when the ambient temperature is lower, the fluid is able to accommodate more impact of elevation than the one with higher ambient temperature. The pressure drop (ΔP_{loss}) increases dramatically as the elevation increases and results in higher pump duty (ΔP_{pump}). On the contrary, liquid CO_2 will gain kinetic energy converted from potential energy as the terrain declines and result in increased velocity.

Table 46 Effect of elevation on CO_2 pipeline at two different ambient temperatures

Ambient Temperature (℃)	Elevation for PIPE-103	Outlet temperature	Outlet pressure	Outlet density	Power for P-106	Discharge temperature (to sequestration site)	Intermediate Cooling station Duty
15	m	℃	bar	kg/m^3	MW	℃	MW
	0	16.97	75.36	807.5	0.6736	22.66	0
	100	15.89	67.49	807.3	0.8268	23.02	0
	150	15.34	63.56	807.6	0.9031	23.2	0
	200	14.77	59.63	808.1	0.9790	23.39	0
25	0	22.54	92.33	765.7	0.3623	25.69	3.182
	100	21.44	84.71	763.8	0.5199	26.02	3.182
	150	20.86	80.91	763.2	0.5985	26.19	3.182
	200	20.27	77.11	762.8	0.677	26.36	3.182
	250	19.67	73.32	762.8	0.7552	26.53	3.182

By plotting the temperature change against the pipeline distance, it can be anticipated that the location where the change in phase is most likely to happen is at the discharge of the each pump. The location of pump is therefore determines the heat transfer calculation requirement for main trunk line.

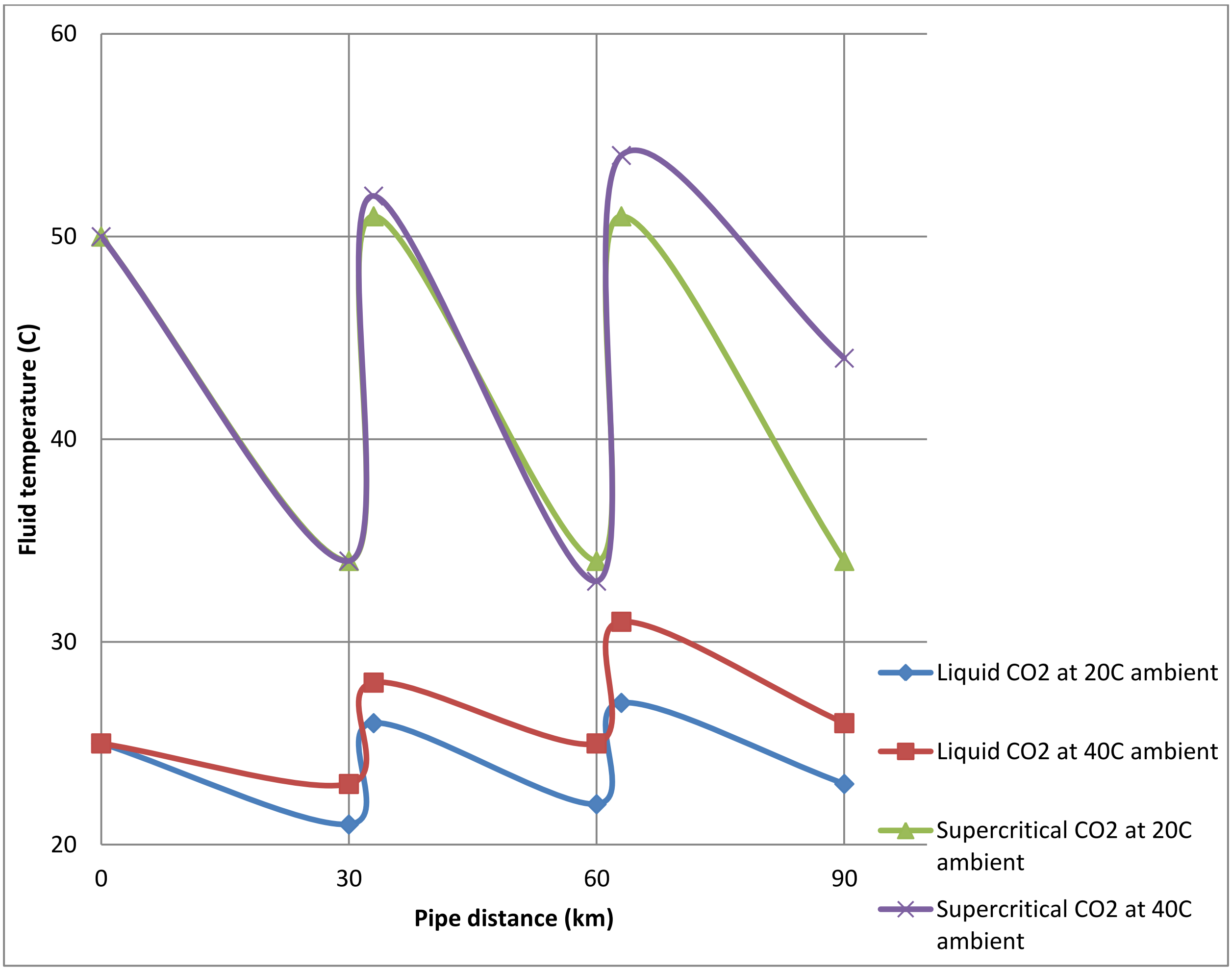

Figure 84 Variation of temperature across the whole transmission length

7.4 Pumping of liquid CO_2

After collecting pure CO_2 as liquid, the pump can be started and the discharge pressure can be controlled by the discharge valve V-2. Decrease the discharge pressure by opening the valve V-2 more; increase the discharge pressure by closing the valve V-2 more. The suction temperature is maintained by pouring liquid nitrogen while the suction pressure is controlled by V-120.

The suction/ discharge pressure and temperature will be recorded. This is to observe the temperature change due to pumping action.

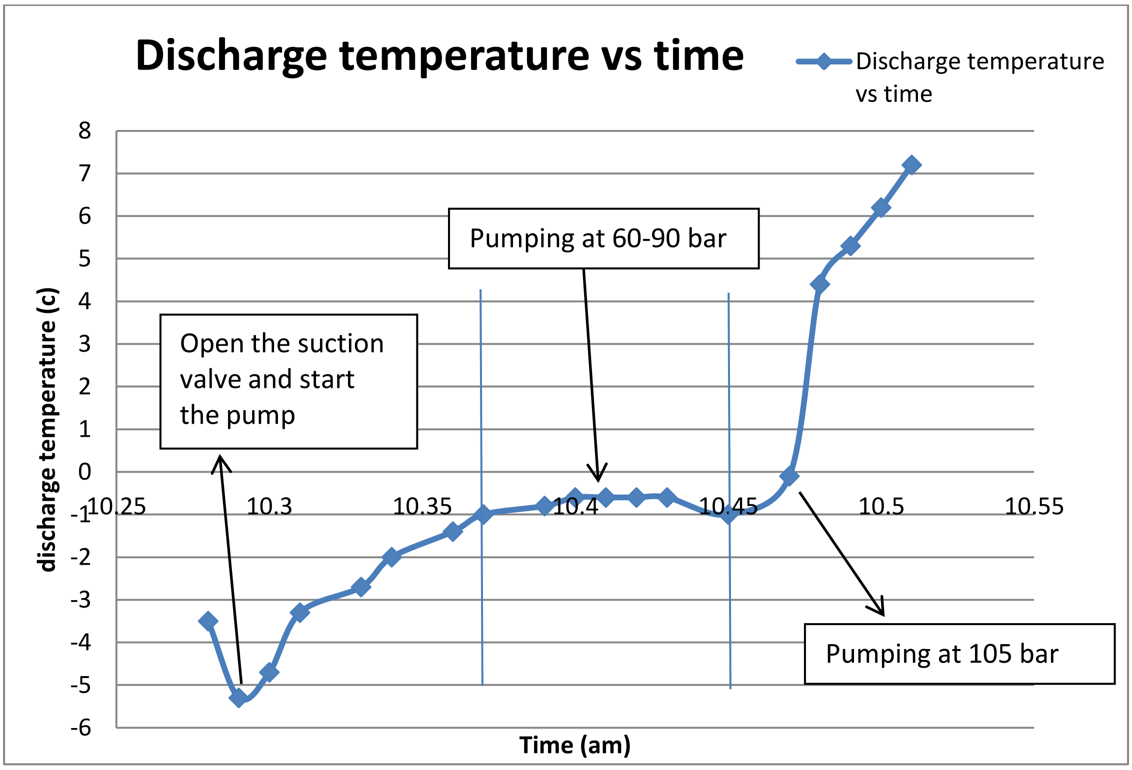

Figure 852 Discharge pressure versus time

From both experiments, there are several observations:

- The discharge temperature will decrease slightly when the pump first started. This is due to the flowing of chilled liquid CO_2.
- When higher discharge pressure is being established, the discharge temperature does not vary too much. Pressure increases, volume decreases therefore the system releases heat to the surroundings.
- When the discharge pressure decreases (say from 105 bar to 60-75 bar), discharge temperature increases (≈1 °C per minute) from 10.48am to 10.51am. This is due to losing of liquid due to expansion therefore it absorbs heat from surrounding.

The pumping action was able to last for 19 minutes for experiment 1 and 13 minutes for experiment 2.

CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This thesis makes significant contribution to the existing knowledge for CO_2 capture by cryogenic and pumping of liquid CO_2. The results of a combination of experimental and simulation studies on the CO_2 capture by cryogenic and the integration of cryogenic process with the vacuum swing adsorption have been presented. On the basis of the characteristic of cryogenic separation, the potential of carbon capture by cryogenic method and the potential of partnering cryogenic with other capturing techniques such as adsorption have been strengthened. The following conclusions are drawn from the theoretical analysis and actual experiments:

- CO_2 will freeze at a temperature of -55 ℃ therefore operating temperatures shall not get below -50 ℃ (5 ℃ buffer). One of the challenges is to avoid over-pouring the dry ice into methanol chiller and over-pouring liquid nitrogen onto the gas liquid separator

- CO_2 can be separated from the flue gas with via cryogenic method at high recovery rate provided the feed is properly conditioned

- Once the CO_2 is liquefied at low temperature and moderate pressure, it has to be pumped to high pressure to retain its liquid phase

- The experimental capture rate (recovery) is comparable with the one given by Aspen HYSYS® simulation tool and some experimental results show that more CO_2 can be captured than the simulation results under the same operating conditions

- For vacuum swing adsorption (VSA), the recovery is inversely proportional to the CO_2 composition in the product. The CO_2 composition in the (VSA) product is then inversely proportional to the energy required in the cryogenic section

- The requirement for refrigeration can be significantly reduced by increasing the CO_2 composition in the feed and feed pressure to achieve a satisfying recovery

- The optimum energy required for the cryogenic condensation process is a balance between compression and refrigeration

In order to ensure a smooth transportation of liquid CO_2 from the capture site to sequestration site, some preliminary conclusions can be drawn on the basis of the above numerical study and discussion, they include:

- The ambient temperature will significantly change the ground temperature around the pipe and cause the fluid to change phase. In order to prevent CO_2 vaporisation, the region with ambient temperature below 25 ℃ is desirable and reliable air/soil temperature data has to be obtained.

- The importance of ambient and ground temperature in CO_2 pipeline design shall be highlighted because it will significantly determine the size of the pipe and therefore the capital and operational cost.

- A ground material with higher conductivity (e.g. when it is wet) will promote the heat transfer from the fluid to the ground. However the presence of water will lead to corrosion problem to the steel pipe.

- An intermediate cooling station is required to maintain the maximum allowable fluid temperature in particularly when there is an increase in feed flow rate, at the discharge of the pumping station, at a terrain where there is a significant decrease in elevation, and at the tee junction where two separate lines meet and the likelihood for phase change is higher. The availability of process water or underground well water has to be assessed before the installation of cooling station.

On the basis of the characteristic of liquid CO_2, the following conclusions are drawn from the actual experiments:

- Liquid CO_2 can be pumped to high pressure to maintain its liquid phase without significant variation of temperature
- It is however very challenging prolong the experiment due to external factors such as losing of operating pressure due to exhaustion of feed gas from the feed drum, the effectiveness of insulation on the pumping loop and running out of liquid nitrogen for maintaining the operating temperature of the gas liquid separator.

8.2 Recommendations

With the increasing recognition of the significance of the CO_2 capture by cryogenic and transporting CO_2 in liquid phase, several perspectives which provide directions for future research work are as follows:

- Process improvements on the cryogenic capture section can be investigated. For example using two stage separations which offers the advantage of reducing the cryogenic energy demand (Xu et al. 2012), three stage refrigeration, better insulation material, more sensitive feed gas composition, cooling system for the feed drum, using air coolers etc.
- Investigate more potential methods for establishing sub-zero temperatures for example creating isenthalpic flash using Joule Thomson valve however this will product liquid CO_2 at low pressure. (Hart and Gnanendran 2009).
- More detailed investigation of relationship between pressure, temperature and feed gas composition for cryogenic operation. Perform sensitivity analysis to determine an optimal configuration.
- Investigation of level of impurities present in the flue gas and their effect on cryogenic separation (CO, O_2, $NO_{x,}$ SO_x and particulate matter may exist and must be minimal).
- Consider scaling up the existing facility to capture CO_2 at higher flow rate and to investigate the impact of flow rates to the capture rate.
- Freezing of CO_2 may have occurred due to the non-ideal behaviour of gas mixture, i.e. the formation of dry ice has to be avoided at any stage of the cryogenic operation. However, Aspen HYSYS does not have vapour-liquid-solid thermodynamic equilibrium (VLSE) flash calculation capabilities. Multiphase flash prediction software such as STFlash® developed by Shell Research and Technology Centre can be used to predict solid CO_2 formation at various conditions (Hart and Gnanendran 2009).
- Investigation of specific sealing materials and gaskets required for CO_2 pumps and pipe fittings because some petroleum based and synthetic lubricants can be harden and become ineffective (Zanganeh, Shafeen, and Salvador 2009).
- The optimization of vacuum swing adsorption shall be investigated since the VSA vacuum pump is the major contributor in both energy penalty and capital cost (Fong et al. 2013)
- Consider using multistage compressor with intercooling features therefore it provides isothermal compression
- Investigation of cost and energy efficient mixed refrigerant system and other type of refrigeration technology for cryogenic separation
- Consider a more comprehensive hybrid process such as VSA/Cryogenic/Membrane or VSA/Membrane/Cryogenic hybrid for CO_2 capture at high recovery. In this paper, membrane unit can be utilized after the cryogenic section for boosting the overall CO_2 rate

- Consider using *Aspen Adsorption* for simulating the VSA process and *Aspen Heat Analyzer* for optimizing heat integration process
- Consider simulating the VSA process using Visual Basics Language in Microsoft Excel and run within Aspen HYSYS with the use of a User Unit Operation.
- The selection of pipe material with more accurate input of pipe wall conductivity, roughness etc will result in more realistic simulation.

- Depending on the capturing technology (pre-combustion, post-combustion, or oxy-fuel process), impurities such as H2O, H2S, SOx, NOx, O2 , Glycol may exist and affect the phase diagram of $CO_{2.}$

- The determination of thermal conductivity of soils at desired moisture-density content.

- The consideration of thermal conductivity of pipeline coating.

- The consideration of pressure losses due to various fittings, valves, bends, elbows, tees, inlets, exits and etc. in addition to the pipes because of the flow separation and mixing they induce.

- The identification of locations where heat insulations should be considered such as above ground facilities, together with type of insulation.

- Aspen HYSYS-PIPESYS, proprietary software developed by *Neotechnology Consultants Ltd* and *Hyprotech* should be used for further research development because it is able to accurately model single and multiphase flow, debottleneck and optimize pipeline systems. Other commercial process simulation tools such as, ProVision, ProMax, etc can also be used.
- Considering other pump types such as triplex positive displacement plunger pumps or Teledyne Isco syringe pumps
- To ensure the optimum performance and working life of pump seals, a seal condition monitoring system can be incorporated.
- Perform liquid CO_2 pumping loop testing such as measuring pump efficiency, validating pump design, measuring NPSH requirements for preventing cavitation, investigating gas entrainment effects, and etc.

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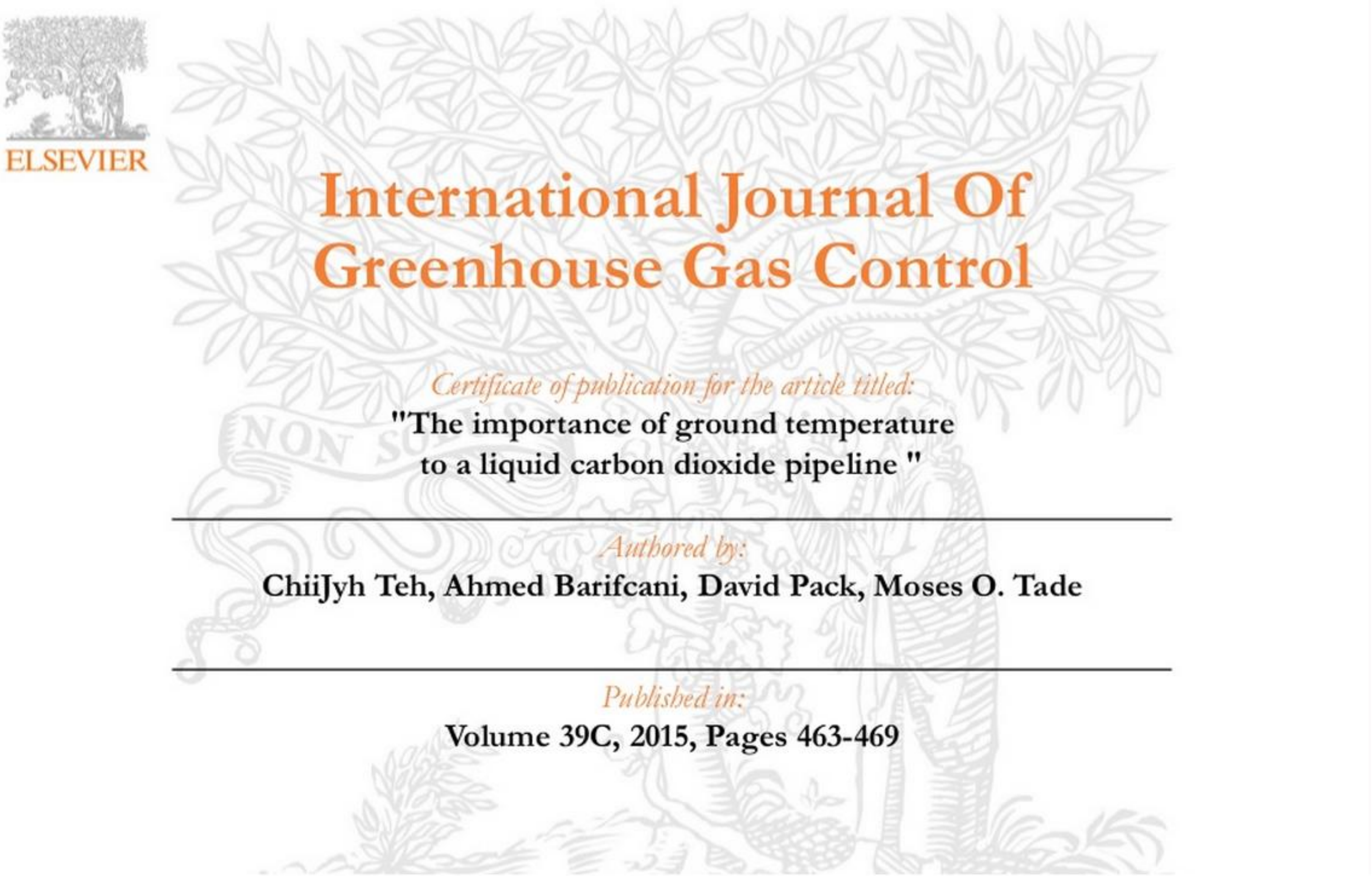
APPENDIX A



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International Journal Of
Greenhouse Gas Control

Certificate of publication for the article titled:

**"The importance of ground temperature
to a liquid carbon dioxide pipeline "**

Authored by:

ChiiJyh Teh, Ahmed Barifcani, David Pack, Moses O. Tade

Published in:

Volume 39C, 2015, Pages 463-469

Abstract for CO2CRC Annual Research Symposium 2014

Developing an energy efficient carbon capture process via VSA/Cryogenic hybrid method is essentially an optimum balance between the capture rate and overall power consumption. The better the CO_2 recovery, the higher the overall power consumption required. However, there are technological constraints such as freezing of CO_2 at -57 °C and limitation of compressors's discharge temperature that must not be compromised.

The overall power consumption consists of two major components which are the compressor power and refrigeration duty. One major benefit of using cryogenic method is that CO_2 captured as liquid could be pumped to high pressure and act as refrigerant for heat recovery before it enters the pipeline to sequestration site. Liquid CO_2 also provides energy savings in transportation by using pumps instead of compressors and using smaller pipe sizes.

Different VSA product specifications,as supplied by the University of Melbourne, have been applied experimentally as feed to the cryogenic section. Energy savings were achieved by several methods for example using air coolers, expanders, knockout drum for removing free water, multistage intercooled compressors, mixed refrigerant and split streams for better cooling. Minimum number of heat recovery exchangers and space efficiency have been taken into consideration so that the project footprint is minimal and can be retrofitted to an existing 500MW power plant.

The result shows that a total power consumption of 162 MW (VSA+Drying+Cryogenics) is the optimal for a total recovery of 94.3 %.

Abstract for CO2CRC Annual Research Symposium 2013

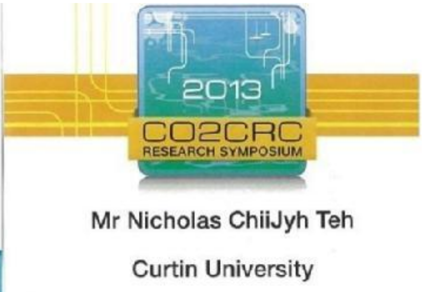
A laboratory pilot plant has been designed and built for CO_2 capture by cryogenics in Clean Gas Technology Australia at Curtin University since 2008. The laboratory pilot plant was operated between 6 and 57 bar according to the flue gas conditions requirements. The feed gas flow rates were varied from 1,000 – 4,000 ncc/min. This laboratory pilot plant was successfully operated for CO_2 capture by cryogenics for oxyfuel, IGCC GE, IGCC Shell, and now extended topostcombustion flue gases. The laboratory pilot plant was operated at various pressures and temperatures down to -55 ^{0}C to achieve 90% CO_2 capture rate from the feed flue gases.

Based on the results obtained from the experiments, the optimum pressure was found to be 16 bar at a temperature of -45 ^{0}C for the oxyfuel flue gas feed . Using HYSYS simulation, energy saving schemes were developed to obtain the optimum enegy consumption for each process. The compression stage for the final delivery of CO_2 to 110 bar is eliminated by pumping liquid CO_2 at low temperatures and using it to chill the feed lowering CAPEX and OPEX costs.

Abstract for CO2CRC Annual Research Symposium 2012

The transportation of captured CO2 to a storage location must be performed safety, reliably and as economically as possible. For the majority of carbon capture and storage (CCS) projects large continuous volumes of CO2 are required to be transported to storage sites. High pressure transmission pipelines have been proven to be the most economical method. Any transportation process requires energy input, pipelines are no exception. However, the transportation process can be designed to minimize the amount of energy required for the operational purposes. The transportation of liquid CO2 meets this energy minimization requirement. An integral part of this energy minimization relates to the conditions at which the captured CO2 is presented for transportation. Consideration must be given if, and to what extent, compression is required to bring the CO2 stream to required phase conditions prior to entry to the transmission pipeline system. This can be a high energy demand process.

This paper takes a holistic approach to the energy requirements for the captured CO2 transportation process, together with considerations to make a high-pressure CO2 transmission pipeline more acceptable to community stakeholders. As the operating temperature of transmission pipelines are influenced by ground temperature conditions the transported CO2 phase behaviour requirement have to be carefully considered to ensure two-phase flow conditions do not exist. The range of suitable pipeline operating conditions together with contaminants that could potentially be transported within CO2 streams is discussed.



APPENDIX B

The operation of laboratory pilot plant for cryogenic separation of CO_2

Hazard and Operability studies (HAZOP) for Cryogenic experiment

Research project	**Operation of pilot laboratory pilot plant for cryogenic carbon capture**	Attendees: 1. A/Prof. Ahmed Barifcani; A/Prof. David Pack 2. Lab supervisor: Saif Ghadhban 3. PhD students: Nicholas ChiiJyh Teh (ID: 14200470), Rakpong Peampermpool (ID: 12358487)
Meeting place	Clean Gas Technology Australia, building 614, Curtin University	

Parameter	Cause	Consequences	Protection	Action/Comments
No flow of CO_2 /N_2/H_2 mixture	Empty gas cylinder, close valves, reversed check valve	No flow to the system	N/A	Always ensure the pressures of CO_2 and N_2 are available at the feed station, ensure check valve is in right direction
Reverse flow	Failure of check valve	Mixing of gases in cylinder	2 check valves available on each gas line	Ensure check valves are in good conditions
Low temperature	Over pouring of liquid nitrogen and dry ice	Line blockage caused by frozen CO_2	--	Follow operating procedures
High temperature	N/A	--	--	--
Low pressure	Running out of feed gas, leakage, over pouring of	Unable to maintain operating pressure,	--	Follow operating procedures, always check relevant pressure gauges

	liquid nitrogen and dry ice	line blockage caused by frozen CO_2		
High pressure	Failure of pressure safety valve (PSVs), failure of regulator	Rupture of feed gas tank and separator	Pressure safety valve on feed tanks and gas liquid separator	Ensure PSVs are regularly calibrated, pressure regulator is in good condition
High level of CO_2 in the separator	N/A	N/A		Unlikely due to quantity of feed gas and liquid nitrogen available
Leaks	Untightened tubing and fittings	Noise, unable to maintain operating pressure	Always ensure tubing and fittings are fully tightened but not overtightened, gas detectors installed	Refer to Swagelok Tube Fitter's manual, a tube fitting pocket guide, operators must have attended the Swagelok Tube Fitting and Installation Training
Power failure	Power failure from main power grid, overconsumption of power limit at building 614	Loss of control and operation. deviation from normal operating conditions	Avoid operating during extreme weather conditions. (such as heavy rain, strong winds, storm and heatwave conditions)	Monitor consumption of power consumption in building, Have back up power for emergency shut down operations. Implement safe guard to avoid power surges.
Fire	Electrical fault,, leakage of hydrogen/ overspilling methanol with sparks, extreme	Personal injury, loss of equipment	CO_2 and powder fire extinguisher available in the laboratory	Ensure fire extinguisher are certified and in working Condition. Call 000 for emergency situation and Curtin Emergency Services 08-9266 4444. Fire emergency response training. Upgrade or review

	weather conditions			building emergency plan.

Operating procedure for cryogenic experiment

Pre-start up procedure

Step 1: Purge the whole system using N_2 gas to blow out any water vapour or impurities within the system.

Step 2: Fill the chiller with methanol (at least half full) and dry ice, start the stirrer and read the temperature meter Q1437 for the desired temperature -55 ℃, also fill the dry ice around the bottom of the separator. Make sure the dry ice covers around the bottom of the separator; fail to do so will result in vaporisation of liquid CO_2 when it reaches the bottom.

Step 3: Fill the heater with hot water to promote gas flow. Feed the CO_2 gas from the BOC gas cylinder the mixing drum. The CO_2 will be fed from the top. Read the pressure from the pressure meter (PI-107 and PI-104 in psi and PG102 in kPa).

Step 4: Always check the label on gas cylinders to identify the contents of cylinders, common layout of labels is given in appendix. Load the N_2 gas from the BOC gas cylinder to the mixing drum. The N_2 gas will be fed from the bottom to avoid the condensation of CO_2 due to high pressure. Read the pressure from the pressure meter PI-107 and PI-104.

Step 5: Allow sufficient time for the gas mixture to mix and reach equilibrium, preferably at least 2-3 hours. Record the pressure from pressure gauges. Analyse and record the initial gas composition from the top and bottom of the drum by passing a small amount of gas (slip stream) to the composition analyser.

Start-up procedure

Step 1: Run the hydrogen (H_2) gas as an imitation gas from the gas cylinder to the system. Ensure the flow rate is around 0.2-0.3 kg/hour (read the flow meter ‘Supply Gas’ MT-01) by controlling the V-216 to control the flow to vent. Adjust V-120 for controlling the feed pressure to the separator.

Step 2: Start chilling the separator by pouring liquid nitrogen (both at the top and middle of the separator) to reach the desired temperature -55 ℃ and maintain the temperature in the methanol chiller by adding dry ice.

Step 3: Once the desired temperature is reached, switch the imitation gas to the gas mixture prepared in the mixing drum by opening V1 and closing V2 in Figure 58.

Step 4: Read temperatures from TI-207B for temperature in the separator, TI-204A for temperature of the inlet to the separator. Record the several temperatures (temperature in the heat exchanger, temperature in the separator, temperature of the inlet to the separator), and also depleted gas composition while maintaining the pressure using V-102 (read the pressure gauge PG106B) and temperature in the separator (TI-207B) for capturing CO_2.

Shut down procedure

Step 1: Once the desired pressure cannot be maintained, stop the experiment by venting all the remaining gas to the atmosphere and stop the chilling process. The result of cryogenic experiment can be further confirmed by closing the feed valve to the separator and vent valve from the separator to isolate the separator as one system. Monitor the vent gas composition the next day. If the composition reaches 99mol%, it means CO_2 has been successfully liquefied.

Emergency and evacuation procedure

Step 1: if possible, turn off the main power switch on the wall that supplies electricity to the composition analyser, pressure transmitters. Vent the gas in the feed gas drum.

Step 2: For life threatening emergencies, dial 000 (0000 from an internal phone), for all other assistance, call security on (08) 9266 4444. For gas cylinder related emergency, call BOC on the Emergency Response Line 1800-653-572. Remain calm and alert other occupants in the area and commence evacuation of the building. Follow instructions from Wardens, Security and other Emergency Personnel and move directly to assembly area.

Step 3: Always refer to the evacuation diagram which shows the position of each fire extinguisher. Note that fire extinguishers and fire hoses are to be used only by those who have received the appropriate training.

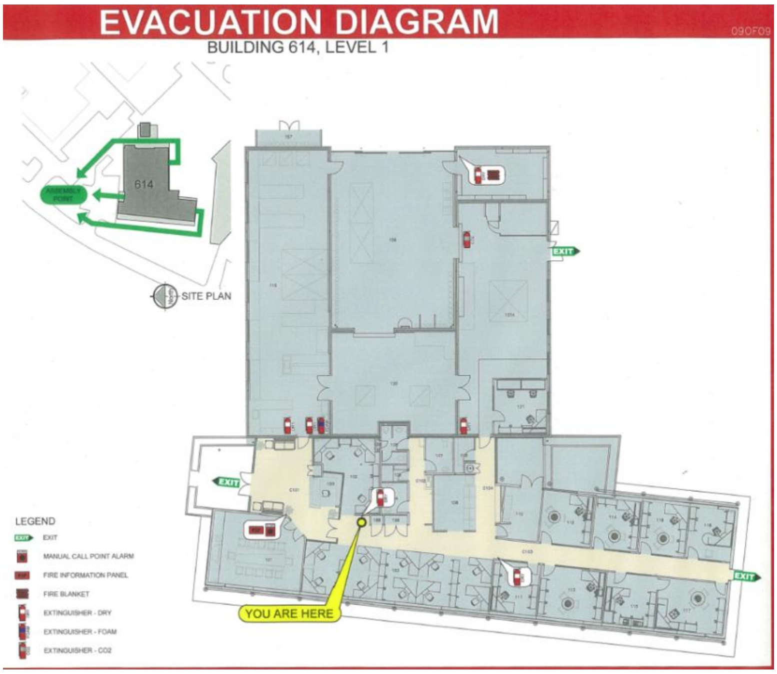
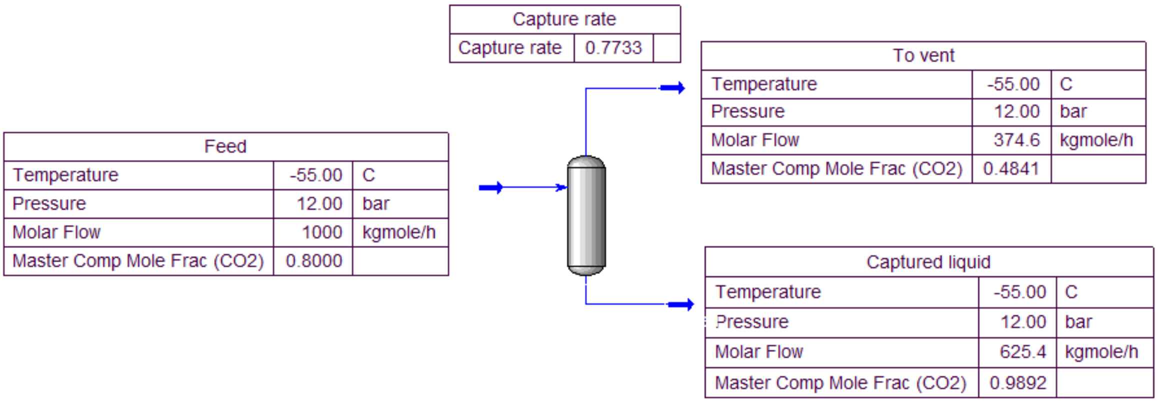


Figure 86 Evacuation diagram of building 614

Sensitivity analysis by HYSYS

Aspen HYSYS® was used to estimate the capture rate, i.e. how much liquid CO_2 can be liquefied at a certain composition and operating conditions. There were three main variables which are the feed composition, feed pressure and feed temperature. Several assumptions were made to simplify the analysis:

- Negligible pressure drop across the separator
- Negligible temperature change to the surrounding
- Freezing temperature of CO_2 is -57 ℃, therefore the lowest possible chilling temperature is set at -55 ℃ to avoid freezing of CO_2



Capture rate		
Capture rate	0.7733	

To vent		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	374.6	kgmole/h
Master Comp Mole Frac (CO2)	0.4841	

Feed		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	1000	kgmole/h
Master Comp Mole Frac (CO2)	0.8000	

Captured liquid		
Temperature	-55.00	C
Pressure	12.00	bar
Molar Flow	625.4	kgmole/h
Master Comp Mole Frac (CO2)	0.9892	

Figure 87 Estimating capture rate using HYSYS at different operating conditions

For 85% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
8.9	-55	62.90	99.42	70.77
9.51	-55	59.31	99.32	75.02
10	-55	56.74	99.25	77.63
11	-55	52.20	99.08	81.55
12	-55	48.41	98.92	84.30
13	-55	45.21	98.76	86.33
14	-55	42.47	98.60	87.89
15	-55	40.10	98.43	89.13
16	-55	38.03	98.27	90.14
17	-55	36.21	98.11	90.98
18	-55	34.59	97.95	91.69
19	-55	33.14	97.78	92.29
20	-55	31.85	97.62	92.81

For 80% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
10.34	-55	55.09	99.19	70.03
11	-55	52.20	99.08	73.44
11.37	-55	50.72	99.02	75.03
12	-55	48.41	98.92	77.33
13	-55	45.21	98.76	80.20
14	-55	42.47	98.6	82.41
15	-55	40.1	98.43	84.16
16	-55	38.03	98.27	85.58
17	-55	36.21	98.11	86.76
18	-55	34.59	97.95	87.75
19	-55	33.14	97.78	88.60
20	-55	31.85	97.62	89.34

For 75% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
11	-55	52.2	99.08	64.25
12	-55	48.41	98.92	69.43
12.14	-55	47.93	98.90	70.03
13	-55	45.21	98.76	73.25
13.57	-55	43.60	98.67	75.01
14	-55	42.47	98.6	76.19
15	-55	40.10	98.43	78.52
16	-55	38.03	98.27	80.41
17	-55	36.21	98.11	81.98
18	-55	34.59	97.95	83.30
19	-55	33.14	97.78	84.42
20	-55	31.85	97.62	85.40

For 70% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
11	-55	52.20	99.08	53.75
12	-55	48.41	98.92	60.40
13	-55	45.21	98.76	65.31
14	-55	42.47	98.60	69.08
14.3	-55	41.73	98.55	70.05
15	-55	40.10	98.43	72.07
16	-55	38.03	98.27	74.50
16.23	-55	37.59	98.23	75.00
17	-55	36.21	98.11	76.51
18	-55	34.59	97.95	78.21
19	-55	33.14	97.78	79.65
20	-55	31.85	97.62	80.89
21	-55	30.68	97.46	81.98
22	-55	29.62	97.29	82.93
23	-55	28.66	97.13	83.78
24	-55	27.78	96.97	84.53
25	-55	26.97	96.80	85.21

For 65% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
16.91	-55	36.36	98.12	70.00
20	-55	31.85	97.62	75.70
21	-55	30.68	97.46	77.06
22	-55	29.62	97.29	78.25
23	-55	28.66	97.13	79.31
24	-55	27.78	96.97	80.25
25	-55	26.97	96.8	81.10
26	-55	26.23	96.64	81.86
27	-55	25.55	96.48	82.25
28	-55	24.92	96.31	83.18
29	-55	24.34	96.15	83.76
30	-55	23.80	95.98	84.28
31	-55	23.30	95.82	84.77
32	-55	22.83	95.66	85.21

For 60% CO2 feed,

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
20.21	-55	31.59	97.58	70.01
23.76	-55	27.98	97.01	75.00
29	-55	24.34	96.15	79.58
30	-55	23.8	95.98	80.22
31	-55	23.3	95.82	80.82
32	-55	22.83	95.66	81.37
33	-55	22.4	95.49	81.88
34	-55	21.99	95.33	82.35
35	-55	21.61	95.16	82.78
36	-55	21.25	95.00	83.19
37	-55	20.92	94.83	83.57
38	-55	20.60	94.67	83.93
39	-55	20.31	94.50	84.26
40	-55	20.03	94.34	84.57
41	-55	19.77	94.17	84.86

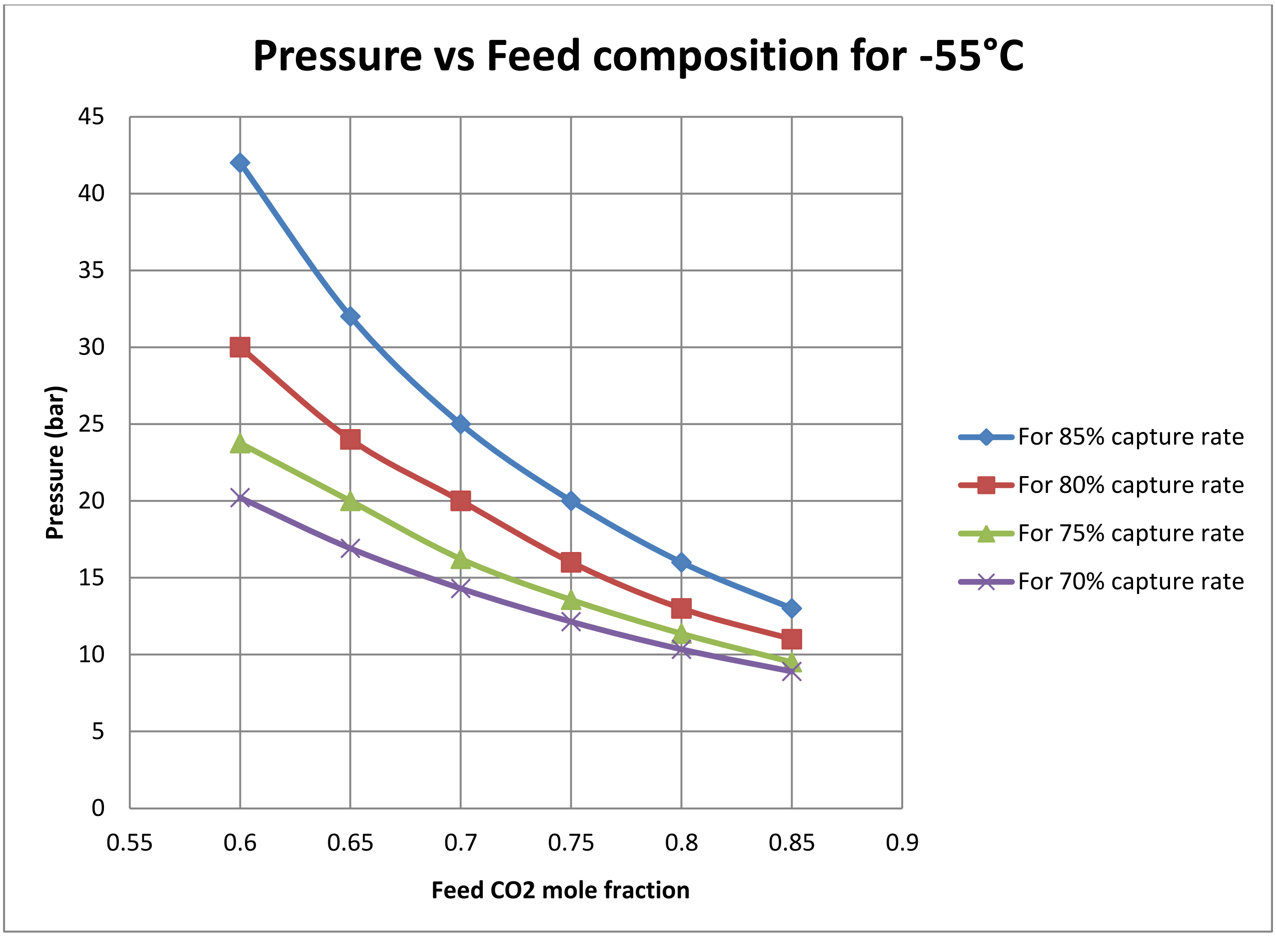


Figure 88 Effect of pressure on capture rate

Assuming the two capture rates (80% and 85%) are desirable for different compositions; the capture pressure is inversely proportional to the feed composition by keeping the refrigeration temperature constant. The higher the CO_2 composition in the feed, the lower the pressure required achieving the same capture rate and the relationship is not linear.

For 11bar, to achieve high capture rate say above 80%, the temperature has to go below -55C which would cause freezing. At 15 bar, capture rate above 80% can be achieved by any temperature between -47C to -55C. Therefore it can be concluded that the capture rate is more sensitive to the change of pressure.

Effect of temperature on capture rate:

85 mol%, 11 bar

Pressure (bar)	Temperature (℃)	Vent composition (mol %)	Liquid composition (mol %)	Capture rate (%)
11	-55	52.20	99.08	81.55
11	-54	54.29	99.12	79.88
11	-53	56.45	99.16	77.98
11	-52	58.66	99.20	75.83
11	-51	60.94	99.24	73.35
11	-50	63.27	99.28	70.49
11	-49	65.65	99.32	67.14
11	-48	68.10	99.37	63.18
11	-47	70.61	99.41	58.43
11	-46	73.17	99.46	52.64
11	-45	75.80	99.51	45.43

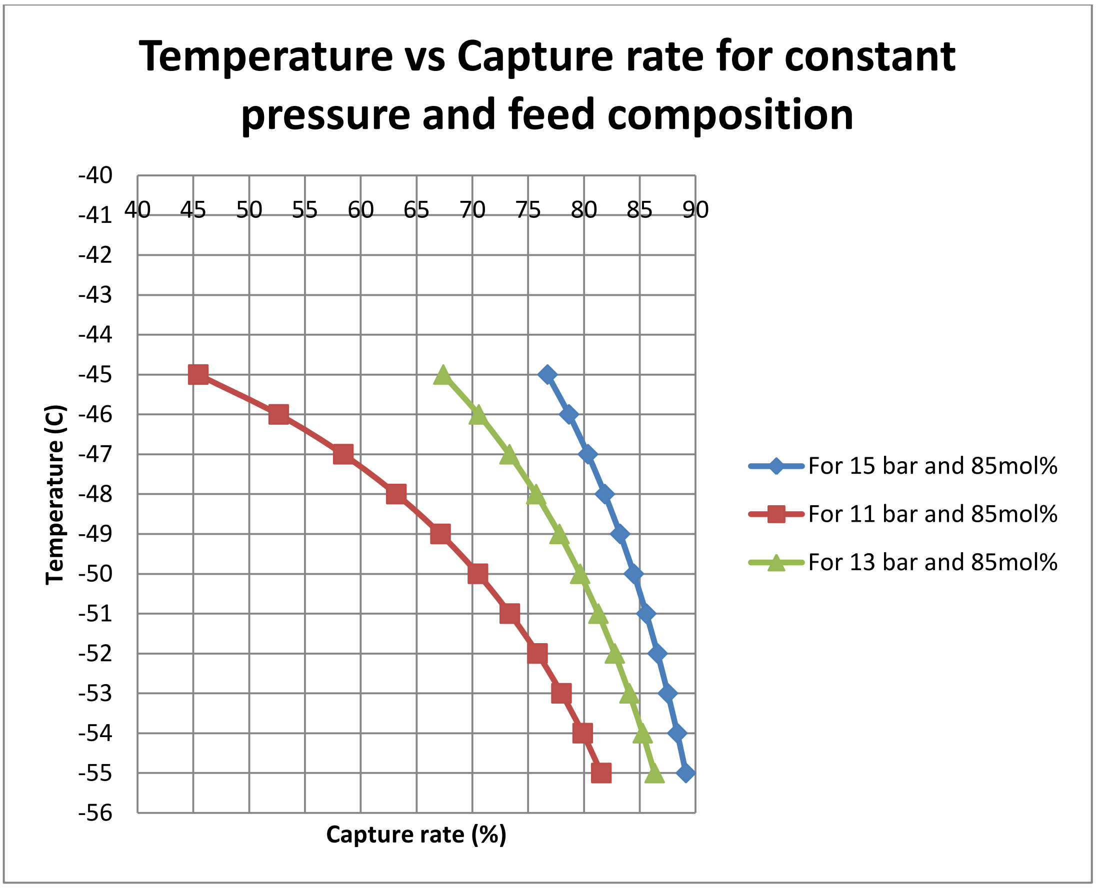


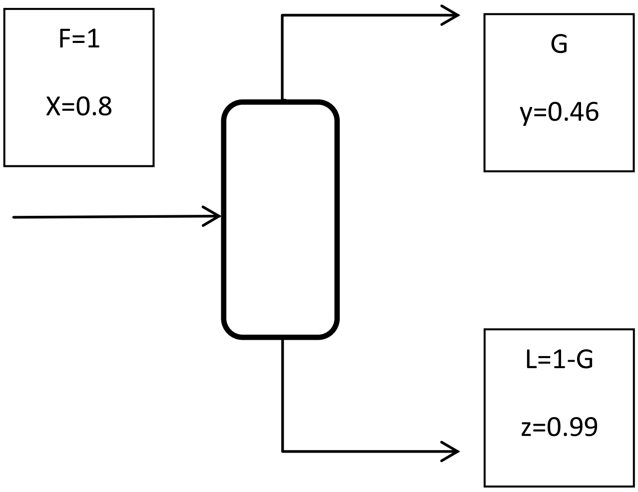
Figure 89 Effect of temperature on capture rate

Experiment 1

Date: 1-11-2013

Initial composition: 80% mol   Pressure: 18 bar

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
10.30	0.18	-54.8	-55	-48	--	--
10.30	0.35	-53	-54	-45	--	0.26
10.33	0.203	-52.3	-47	-50	--	0.36
10.37	0.177	-52	-55	-50	--	0.41
10.40	0.164	-52.7	-53	-50	--	0.45
10.41	0.169	-53.7	-49	-51	--	0.46
10.43	0.16	-54.5	-55	-52	--	0.41
10.46	0.156	-54.9	-52	-53	--	0.37



Overall Material Balance:

F=G+L

Where L=1-G

Component material balance:

xF=yG+zL

Therefore,

Average depleted gas composition= 0.388

0.81 (1) = 0.388 G+ 0.99 (1-G)

So G= 0.3156

Capture rate= L/F= 0.99(1-G)/ (0.8) (1) = 84.7% (experiment)

Capture rare= 88.58% (HYSYS)

Experiment 2

Date: 5-12-2013

Initial composition: 70% mol Pressure: 28 bar P_{drum}: 793 psi, P_{line}: 815 psi

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
11.30	0.25	-54.3	-52	-50	30	--
11.34	0.195	-53.4	-47	-50	30	0.4
11.39	0.16	-44.1	-56	-52	30	0.31
11.40	0.139	-44.4	-47	-51	30	0.36
11.42	--	--	--	--	--	0.41
11.44	0.14	-53	-50	-49	30	0.42
11.46	0.2	-50.5	-53	-50	30	0.39

Component material balance:

$xF=yG+zL$

Therefore,

Average depleted gas composition= 0.38

$0.7\ (1) = 0.38\ G+ 0.99\ (1-G)$

So $G= 0.477$

Capture rate= $L/F= 0.99(1-G)/\ (0.7)\ (1)$ = 74% (Experiment)

Capture rate= 86.45% (HYSYS)

Experiment 3

Date: 21-3-2014

Initial composition: 85% mol Pressure: 20 bar

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
10.03am	0.28	-55	-44	-47	20	
10.11am	0.138	-46	-43	-48	20	60
10.14am	0.135	-42	-50	-45	20	57
10.16am	0.131	-53	-68	-51	20	51
10.18am	0.119	-53.3	-63	-51	20	49
10.20am	0.120	-51	-55	-50	15	48
10.22am	0.100	-50	-55	-49	15	47
10.24am	0.083	-52.7	-59	-49	12	48
10.26am	0.077	-55	-55	-51	10	54

Component material balance:

$xF=yG+zL$

Average depleted gas composition= 0.5175

Therefore,

$0.85\ (1) = 0.5175\ G + 0.98\ (1-G)$

So $G= 0.2963$

Capture rate= $L/F= 0.99(1-G)/\ (0.85)\ (1) = 81.9\%$ (experiment)

Capture rare= 89.13% (HYSYS)

Experiment 4

Date: 1-7-2014

Initial composition: 75% mol   Pressure: 20 bar P_{drum}: psi P_{line}: psi

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
10.56am	0.169	-53	-40		20	15
11.03am	0.18	-50	-45		20	17
11.10am	0.164	-51	-50		20	20
11.12am	0.166	-53	-55		20	23
11.21am	0.107	-55	-55		20	27
11.23am		-55	-55		20	30
11.25am	0.248	-55	-55		20	29
11.26am		-55	-55		20	30
11.27am		-55	-55		20	30
11.28am	0.165	-55	-55		20	31

Component material balance:

xF=yG+zL

Therefore,

0.75 (1) = 0.31 G+ 0.99 (1-G)

So G= 0.35

Capture rate= L/F= 0.99(1-G)/ (0.75) (1) = 85.4% (experiment)

Capture rare= 85.4% (HYSYS)

Lesson learnt: it is very important to control the temperature of the separator by the frequency of pouring liquid nitrogen, overchilling will result in freezing of CO2.

Experiment 5

Date: 5-5-2014

Initial composition: 55% mol   Pressure: 30 bar

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
10.39am	0.12		-40	-21		
10.42am	0.3		-53	-19	35	32
10.44am	0.29		-45	-21	35	35
10.46am	0.322		-43	-25	35	40
10.48am	0.271		-55	-28	35	39
10.49am	0.291		-49	-27	35	43
10.51am	0.291		-55	--	35	44
10.52am	0.296		-57	-27	35	45
10.52am	0.27		-45	-	35	46
10.55am	0.247		-41	-26	35	47
10.56am	0.247		-44	-25	35	48
10.58am	0.286		-46	-24	35	46

Component material balance:

xF=yG+zL

Therefore,

0.55 (1) = 0. 32 G+ 0.99 (1-G)

So G= 0.6567

Capture rate= L/F= 0.99(1-G)/ (0.55) (1) =61.79% (experiment)

Capture rare=78% (HYSYS)

Lesson learnt: the insulation of separator needs to be fixed. There was no CO2 liquid collected due to the improper insulation of separator. The bottom of the separator should also be fully blanketed by dry ice.

Experiment 6

Date: 18-6-2014

Initial composition: 60% mol   Pressure: 30 bar

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
2.01pm	0.1	-55.3	-50	-54	30	16
2.03pm	0.1	-50	-49	-54	30	17
2.05pm	0.08	-50	-48	-49	30	20
2.06pm	0.08	-50	-48	-49	30	23
						25
2.07pm	0.7	49.5	-48	-51	30	28
2.09pm	0.6	-48.5	-47	-55	30	33
		-48.5	-46	-53	30	34
		-47	-46	-52	30	35
	0.3	-47	-46	-50	30	36
2.19pm	0.29	-55	-51	-55	30	27
		-55	-54	-55	30	26

Component material balance:

xF=yG+zL

Therefore,

0.6 (1) = 0. 23 G+ 0.99 (1-G)

So G= 0.513

Capture rate= L/F= 0.99(1-G)/ (0.6) (1) =80% (experiment)

Capture rare=80% (HYSYS)

Lesson learnt: it is important to maintain the temperature of the separator by consistently pouring liquid nitrogen and also to cover the bottom of separator with sufficient dry ice.

Experiment 7

Date: 5-6-2014

Initial composition: 65% mol, top composition: 65% Bottom composition: 65% Pressure: 30 bar

Time	Flow rates	Heat exchanger temperature	Separator temperature	Inlet line temperature	Pressure of the separator	Depleted gas composition
	Kg/hour	℃	℃	℃	bar	Mol%
10.54am						
11.20am	0.16	-48	-55	-52	30	6
11.23am	0.106	-55	-54	-52	30	17
11.25am	0.08	-58	-55	-52	30	23-27
11.26am	0.06	-55	-53	-51	30	30
11.26am	--	-51	-53	-48	30	33
11.27am	0.3	-50	-52	-50	30	35
11.30am	0.345	-55	-51	-50	30	37
11.33am	0.336	-48	-50	-49	30	39
11.34am	0.3	-49	-58	-49		34
11.37am	0.272	-47	-55	-46	28	31
11.39am	0.27	-46	-55	-45	22	30

Component material balance:

$xF=yG+zL$

$0.65 (1) = 0. 23 G+ 0.99 (1-G)$

So $G= 0.447$

Capture rate= $L/F= 0.99(1-G)/ (0.65) (1) =80\%$ (experiment)

Capture rare=84% (HYSYS)

Lesson learnt: pour the liquid nitrogen both at the top and bottom of the separator to prevent liquid CO2 from vaporising again. Blanket the bottom of the separator with enough dry ice.

Installation and dismantling procedure for band lock closure doors

Installation procedure for closure door and GD locks

Warning: the closure door is very heavy and should be handled with care. Always ensure safety goggles and safety shoes are worn.

Figure 90 Closure doors and GD locks

Step 1: install the new seal (Bandlock 2 closure 8” viton seal, part no. 3131-0001-03) and apply small amount of grease (Molykote supplied by Dow Corning Australia Pty. Ltd.) onto the seal and inner surface of the vessel where only seal will come in contact to.

Step 2: Ensuring the alignment of closure door by using a C clamp to clamp the forklift while the forklift is clamping the wooden part of the closure door, so that the closure door doesn’t wobble at all. When locking the locking ring using the metal rod, ensuring the position of the gap left is situated next to the hole (for the bolt to go in). Lift the closure door until it sits perfectly in the bottom of vessel. When the seal is new, the lifting action should strong as possible to suppress the seal and allow the door to be closed.

The ring must be placed on the 5mm ledge just below the main body of the door. Close the ring against the 5mm ledge before lifting the door into position in the bottom of the vessel.

Step 3: releasing the locking ring and ensuring the the locking ring sits inside the gap in the housing without sticking out (may use a hammer with a 1” x 1” piece of wood to knock it in place gently)

Step 4: installing the bolt: Install the small curved plate attached to the bolt into the cavity next to the main retaining ring and turn the bolt in a clockwise rotation until it becomes tight. Then use the round bar handle to tighten the bolt.

Step 5: Pressure test the vessel

The final condition for both vessels is shown as below:

Figure 91 Left vessel (the vessel which is closer to the garage door)

Figure 92 Right vessel (the vessel which is closer to the main power board on the wall)

Dismantling procedure for closure door of vessel

Step 1: Removing the bolt using the metal rod

Step 2: Ensuring the C clamp is securely clamping the wooden part of the closure door before unlocking the locking ring

Step 3: unlock the locking ring and slowly lower the forklift

BOC Gas Cylinders

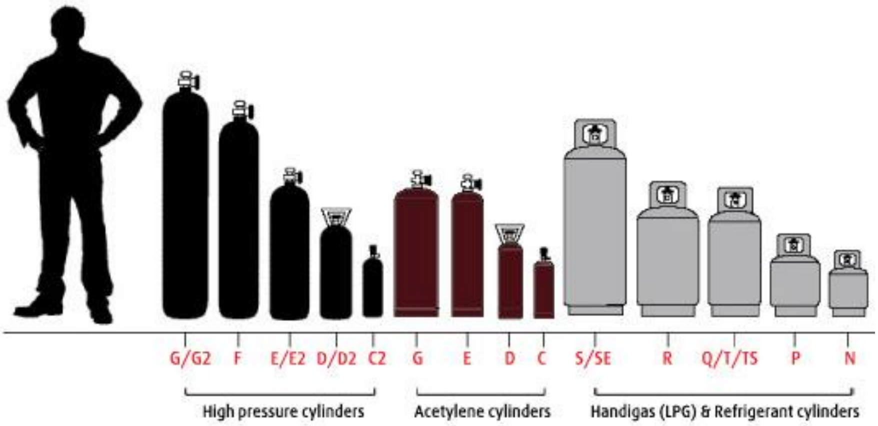


Figure 93 BOC gas cylinder size identification (BOC 2015)

BOC cylinder sizes are denoted by a letter code. The gas content of cylinders is measured in cubic metres, litres or kilograms. If volume unit is given, it refers to standard temperature and pressure of 15 ℃ (101.3 kPa).

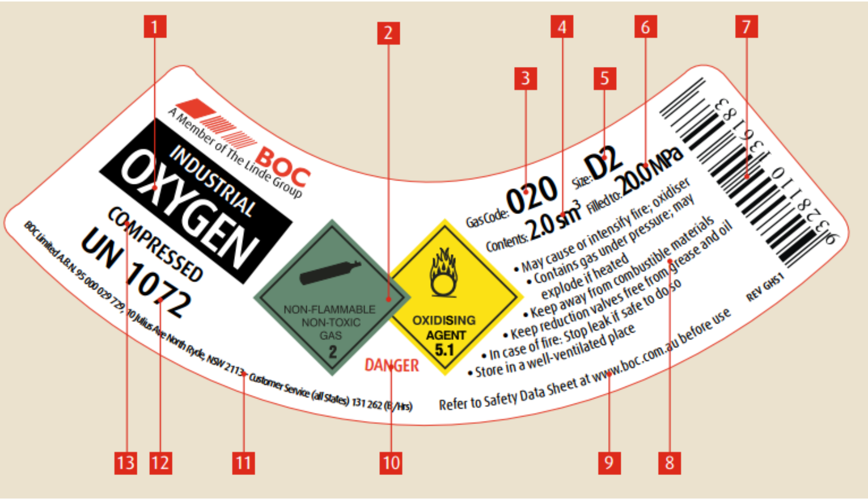


Figure 94 BOC Gas Cylinder's label (BOC 2015)

Common layout of cylinder label:
1: gas name
2: dangerous good classification
3: BOC gas code
4: contents of cylinder at standard temperature
5: cylinder size
6: cylinder pressure
7: material barcode
8: hazard and precaution statements
9: safety data sheet location
10: signal word
11: customer engagement centre contact details
12: United Nations numbering systems for safe handling, transport and storage
13: gas grade

Chemical Risk Assessments (CRA forms)

Chemical Risk Assessment for Hydrogen gas

Worksheet

Curtin University

INTRODUCTION
The questions in this *Worksheet* are designed to prompt you to think about the risks you face when using chemicals and whether you believe the current controls will adequately protect you. You should not proceed with the use of a product if you believe it is unsafe. There are two elements to the *Risk Assessment*: You will need a *Safety Data Sheet (SDS)* for the product (obtained from **Chem Alert** or from the supplier); and you will need to consider circumstances of use in your area. Complete the *Risk Assessment* in consultation with your supervisor.

SECTION 1: SUMMARY (from SDS)

Chemical / Product Name	**Storage Location**
Compressed Hydrogen	Building: 614 Room: Back yard
Manufacturer / Supplier	**Lab for Intended Use**
BOC	Building: 614 Room: Back yard
Safety Data Sheet	**Hazardous and Dangerous Goods**
Is a current SDS Available? *(You must obtain it)* ☒ Yes ☐ No	Is the chemical classified as Hazardous? ☒ Yes ☐ No
Assessment Date: 6 December 2012	Is the chemical classified as Dangerous Goods? ☒ Yes ☐ No *(if applicable)* Class: Sub Class:
Assessor	**Supervisor**
Nicholas ChiiJyh Teh	Ahmed Barifcani, David Pack

SECTION 2: USE

Task Description: (Including any storage or disposal requirements)	dummy gas

Concentration: (%)	>99.5	Quantity: (including units)	G cylinder	Duration of Use:	10min	Frequency of Use:	Regular

Note: Substances that are not classified as a **Hazardous Substance** or **Dangerous Good** require **no further assessment** (i.e. you do not need to compete the remaining sections).

SECTION 3: HOW CAN EXPOSURE OCCUR?

☐ Dermal (Skin):	☐ Eyes:	☒ Inhalation:	☐ Ingestion:	☐ Injection:
Solid	Dust	Vapour Aerosols	Dust	Pressure
Aerosol	Aerosol	Gas	Aerosols	Sharp objects
Liquid	Liquid	Dust	Liquid	Open wounds
			Hygiene	

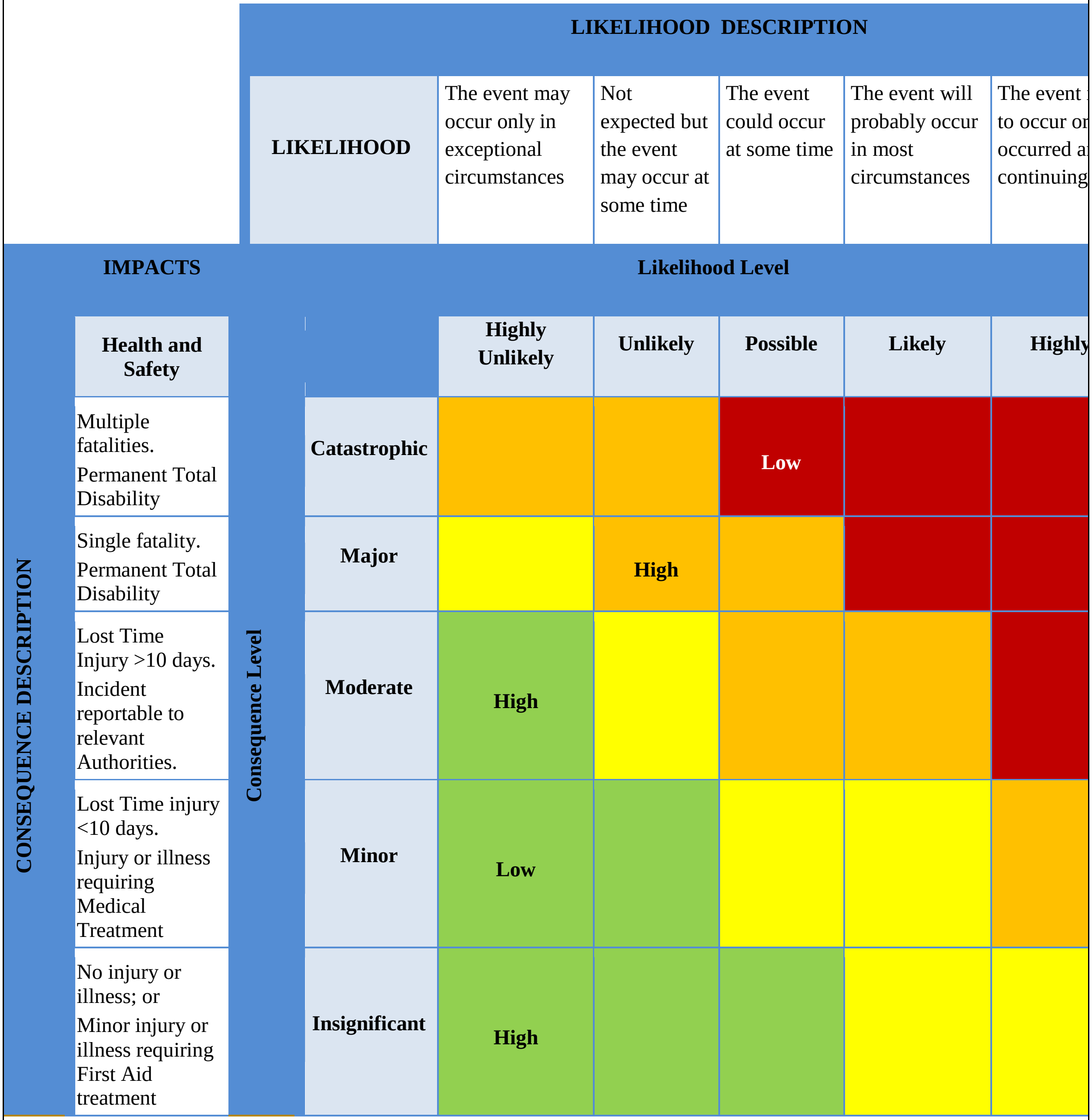
Who is potentially exposed? : *(e.g. Students, Lab Staff, Researchers, Others)*	Students, supervisors

SECTION 4: POTENTIAL HEALTH EFFECTS

Acute (Immediate) Effects	**Chronic (Delayed) Effects**
☐ Eye and skin Irritant / Corrosion	☐ Sensitising Agent (Skin/Inhalation)
☐ Central Nervous System	☐ Carcinogenic
☒ Asphyxiant (Inhalation)	☐ Liver/Kidney Disease
☐ Respiratory Tract Irritant	☐ Brain/Nerve Disease
☐ Toxic by Skin Exposure	☐ Respiratory Disease
☐ Toxic by Ingestion	☐ Reproductive System Disease
☐ Other (Specify):	☐ Other (Specify):

SECTION 5:	**RISK RANKING WITH EXISTING CONTROLS IN PLACE**

Risk Matrix



				LIKELIHOOD DESCRIPTION				
			LIKELIHOOD	The event may occur only in exceptional circumstances	Not expected but the event may occur at some time	The event could occur at some time	The event will probably occur in most circumstances	The event to occur or occurred a continuing
IMPACTS				**Likelihood Level**				
	Health and Safety			**Highly Unlikely**	**Unlikely**	**Possible**	**Likely**	**Highly**
CONSEQUENCE DESCRIPTION	Multiple fatalities. Permanent Total Disability	**Consequence Level**	**Catastrophic**	🟧	🟧	🟥 **Low**	🟥	🟥
	Single fatality. Permanent Total Disability		**Major**	🟨	🟧 **High**	🟧	🟥	🟥
	Lost Time Injury >10 days. Incident reportable to relevant Authorities.		**Moderate**	🟩 **High**	🟨	🟧	🟧	🟥
	Lost Time injury <10 days. Injury or illness requiring Medical Treatment		**Minor**	🟩 **Low**	🟩	🟨	🟨	🟧
	No injury or illness; or Minor injury or illness requiring First Aid treatment		**Insignificant**	🟩 **High**	🟩	🟩	🟨	🟨

So the questions are: based on the above matrix:

What could be the consequences?	Hydrogen will form explosive mixtures in air and add fuel to a fire. Temperatures in a fire may cause cylinders to rupture and internal pressure relief devices to be activated.
What is the likelihood of that happening?	Rare
What is the risk rating? ***Note**: If the rating is above **LOW**, Risk Management action is required.*	Low

Risk Management Action

Risk Level	**Response**
Extreme	Immediate action required to reduce exposure. A detailed mitigation plan must be developed, implemented and monitored by senior management to reduce the risk to as low as reasonably practicable.

High	A mitigation plan shall be developed and authorised by area manager or supervisor to reduce the risk to as low as reasonably practicable. The effectiveness of risk control strategies shall be monitored and reported to management and relevant committee.
Medium	A mitigation plan shall be developed. Control strategies are implemented and periodically monitored.
Low	Manage by documented routine processes and procedures. Monitor periodically to determine situation changes which may affect the risk.

SECTION 6: REQUIRED CONTROL MEASURES TO REDUCE RISK

Control	Example	Intention to apply
1. Elimination	Eliminate materials or elements of the process that carry significant risk.	☐
2. Substitution	Substitute a safer chemical or safer process.	☐
3. Isolation	Barriers, enclosures, remote operation.	☒
4. Engineering	Local exhaust ventilation, dilution ventilation.	☒
5. Administrative	Supervision, use of safe work procedures, housekeeping, organisation of work to limit contact, standards, training, signage.	☒
6. PPE	Face shields, safety glasses, goggles, gloves, aprons.	☒

SECTION 7: SPECIFIC ACTIONS TO REDUCE RISK

List specific actions that will be carried out for each of the controls you nominated in Section 6.

Control	Action
1. Elimination	
2. Substitution	
3. Isolation	If the cylinder is leaking, eliminate all potential ignition sources and evacuate area of personnel. Prevent spreading of vapours through drains and ventilation systems. Inform manufacturer/supplier of leak. Use personal protective equipment. Carefully move material to a well ventilated remote area, then allow to discharge. Do not attempt to repair leaking valve or cylinder safety devices.
4. Engineering	Provide suitable ventilation to minimise or eliminate exposure. Confined areas (eg. tanks) should be adequately ventilated or gas tested. Flammable/explosive vapours may accumulate in poorly ventilated areas. Vapours may also travel some distance to an ignition source and flash back.
5. Administrative	Follow operating procedures
6. PPE	Wear safety glasses, leather gloves, safety boots and self-contained breathing apparatus (SCBA) where an inhalation risk exists

Note: If after the implementation of all of the controls above, the risks of using the assessed chemical remain MODERATE or higher (based on the *Risk Matrix* in Section 5); expert advice must be obtained so as to reduce risk before proceeding.

The *Occupational Health and Safety Regulations (1996)* require that *Risk Assessments* are retained. *Risk Assessments* must be revised if procedures change and are to be reviewed every 5 years. Save a copy of this *Risk Assessment*, to be retained in your area. Give it a unique name (eg CRA + product name + your name). Send a copy to Health and Safety. Any queries should be directed to the Curtin Health and Safety Ext. 4900.

Plant Risk Assessment

- **SCOPE**
- This document defines the risks associated with the selected item of plant.
- Refer to the Plant Risk Assessment Procedure for instructions on completing the assessment. You will need a University Health and Safety Risk Matrix.
- **Application**

Location name: Clean Gas Technology Australia	**Building No.: 614**	**Date: 15/12/12**
Assessed By: Nicholas ChiiJyh Teh	**Health and Safety Representative(s):**	
Users of the plant: PhD Students Rakpong Peampermpool, Nicholas ChiiJyh Teh, Authorised Staff Ahmed Barifcani, David Pack	**Plant (Manufacturer's name and model no): JAECO pump, MSR Gas Analyzer, Maximator pump, Heidoath mixer, Dick Smith thermometer, Methanol bath, Gas separator, Hydrate Chiller**	

Purpose of plant: The purpose of the plant is to capture CO2 by liquefaction and pumping liquid CO2 using the Jaeco pump

Description of how plant is used: The flue gas is prepared in the mixing drum and keeps it for a period of time for a better mixing. The pilot plant is operated by running the dummy gas (H2) and chilling the separator by using liquid nitrogen and dry ice. When the desired temperature is achieved, dummy gas will be replaced by the flue gas. Then the depleted gas composition is analysed before venting it to the roof of the building. The liquefied CO2 is also pumped around the separator.

Does the operator require a licence or competency? Yes	External licence	Specify: n/a
	Internal competency	Specify: laboratory induction and regular safety training
	No specific competency	Supervision until deemed competent

Workplace conditions (Describe layout and physical conditions – including access and egress). Use extra page for diagram space if needed.

Eg. Located in under cover area, no equipment nearby, chemical cabinet 3 metres away, no fire extinguisher in area

There is a noisy compressor just outside the lab and the roller doors are always kept open during experiments. Computer where readings would be taken presents an ergonomic hazard.

Consider operation outside of normal conditions • Cleaning • Non-standard use • Breakdown and repair • Maintenance • Commissioning • Emergency situations	Which could apply? • Cleaning • Maintenance • Commissioning • Emergency situations
List systems of work for using the plant: • Training Procedure • Safe Work Procedures • Manufacturer’s information and instructions • Pre-start inspections	What is in place already? • Training procedure I was trained to meet the safety procedures and also operated the plant for several times under the supervision of Rakpong who was the PhD in last 3 years and Ahmed Barifcani (supervisor) without any incident. I have also participated in the HAZOP studies and the lab safety induction provided by Saif.
Is there past experience or background material regarding the plant operation that may assist in the assessment? • Existing controls • Safe Work Procedures • Standards (Internal, Australian Standard, National) • Codes of Practice (State, National) • Previous incidents including near miss/hit • Legislation & subsidiary guidance material	What is relevant? The pilot plant has been operated for the past 5.5 years without any incident by PhD student Daria Surovtseva in 2010 and Rakpong who is in the process of completing his PhD. Saif Ghadhban also utilized this pilot plant for his research project. I am a currently using this facilities for experiments.

Identify hazards and associated risk and controls

For each of the following prompts:

- **Check the box** for each hazard that may potentially exist for the plant;
- Using the **Health and Safety risk matrix**, determine and record the likelihood, consequences and the **risk level**
- In the **comments** box, describe when and where the hazard is present;
- Specify the risk **control type** from the hierarchy of control at right, for each current or proposed risk control. e.g. Number 1-6;
- Provide a **control description** for each current or proposed risk control.

Risk Control Measures

1. **Eliminate,** e.g.: eliminate task, remove hazard
2. **Substitute** e.g.: replace with less hazardous process, material
3. **Isolate** e.g.: enclosures, restricted access;
4. **Engineering** e.g.: guarding, separation, redesign;
5. **Administrative** e.g.: Safe Work Procedure, training;

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	**L**	**R**				**C**	**L**	**R**
Can the following items become ENTANGLED with moving parts of the plant, or materials in motion: ☐ Hair ☐ Rags ☐ Jewellery ☐ Gloves ☐ Clothing ☐ Other materials – specify:________________	**Major**	**Possible**	**High**	Contact with the stirrer could cause friction injuries. The pump, a standard Australian pump has a moving part and safety guard and protection device during operation.	Engineering	Operators trained to stay clear of rotating parts. Loose clothing and any items that could get caught in the stirrer should not be worn. Lab coats should be placed on the hanger provided. Operators are trained in the Safe work procedure of the plant. The pump maintenance will be carried out by the electrical department at Curtin University regularly. 2 people must work together in the lab at all times.	**Moderate**	**Unlikely**	**Medium**

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	L	R				C	L	R
SHEARING – Can anyone's body parts be cut off between: ☐ Two parts of the plant ☐ A part of the plant and a work piece or structure ☐ Other factors – specify: ___________________				N/A	N/A	N/A			
Can anyone be CUT, STABBED or PUNCTURED by coming in contact with: ☐ Moving plant or parts ☐ Sharp or flying objects ☐ Work pieces disintegrating				N/A	N/A	N/A			

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	L	R				C	L	R
Can anyone be CRUSHED due to: ☐ Falling, uncontrolled or unexpected movement of plant ☐ Lack of capacity to slow, stop or immobilise the plant ☐ Falling, uncontrolled or unexpected movement of the plant's load ☐ Under or trapped between plant and materials or fixed structure ☐ Contact with moving parts during testing, inspection, repair, maintenance or cleaning ☐ Tipping or rolling over ☐ Parts of plant collapsing ☐ Being thrown off ☐ Other factors – specify:_____ __________				N/A	N/A	N/A			
FRICTION - Can anyone be injured due to: ☐ Contact with moving parts or surfaces of the plant ☐ Material handled by the plant	**Moderate**	**Unlikely**	**Medium**	Contact with the stirrer could cause friction injuries	Administrative	Operators trained to stay clear of rotating parts. Operators are trained in the Safe work procedure of the plant.	**Moderate**	**Rare**	**Low**

☐ Other factors – specify: ______________

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	L	R				C	L	R
EMERGENCY STOP BUTTONS - can injury from interaction with the plant be caused by: ☐ Lack of proud mushroom-type emergency stop ☐ Emergency stop not being fail safe ☐ Emergency stop not red in colour ☐ Stored energy being released slowly or at a subsequent time ☐ Lack of clarity of emergency stop markings ☐ Restarting plant by resetting the emergency stop button ☐ Other factors – specify: _____________				Emergency stop buttons are installed the authorized electrician at Curtin University and are functional.	Isolation	The power supply is controlled by On Off switches installed by electricians from Curtin University.			
Can anyone be STRUCK by moving objects due to: ☐ Plant or work pieces being ejected or disintegrating ☐ Mobility ☐ Uncontrolled or unexpected plant movement									

☐ Other factors – specify: _______________

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	L	R				C	L	R
Can anyone be injured by ELECTRICAL shock or burnt due to: ☐ Damaged/poorly maintained leads or switches ☐ Working near or contact with live electrical conductors ☐ Water near electrical equipment ☐ Lack of isolation procedures and/or equipment e.g. locks, tags ☐ Overload of electrical switches ☐ Lack of RCD protection – portable or building ☐ Other factors – specify:_______________	**Major**	**Unlikely**	**High**	Plant is connected to a 3 phase high voltage electrical point. Damaged or frayed electrical cords would pose an electrical hazard. **Risk**	Administrative	Operator to check for damaged electrical cords prior to use. Make sure equipment is serviced on a regular basis, tested & tagged and appropriate isolation procedures (e.g. lock out tags) are in place.	**Moderate**	**Unlikely**	**Medium**
Can anyone be injured by an explosion of the following triggered by plant operation? ☐ Gas ☐ Vapours ☐ Dust ☐ Liquids ☐ Other factors – specify:________________	**Major**	**Possible**	**High**	Small blasts could occur with low pressure and a small amount of gas can be released.	Administrative	Operators are trained prior to using the equipment. Gas detectors are present which could identify when there is a leak. Room is well ventilated and the roller doors are always kept open during the experiment. Ignition sources are minimised as reasonably practicable e.g. light fittings in the lab are	**Moderate**	**Unlikely**	**Medium**
Can anyone be SUFFOCATED due to: ☐ Lack of oxygen ☐ Atmospheric contamination ☐ Other factors – specify: _______________	**Major**	**Possible**	**High**	Gas leakage could occur by human error	Engineering and Administrative	Room is ventilated. Roller doors are always kept open during the experiment. Local extraction present. There are gas detectors and an alarm goes off when there is a leak.	**Moderate**	**Unlikely**	**Medium**

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	L	R				C	L	R
HIGH TEMPERATURE OR FIRE – Can anyone: ☐ Come into contact with objects at high temperature ☐ Be injured by fire ☐ Other factors – specify: _______________	**Moderate**	**Possible**	**High**	Skin burns could occur.	Administrative	Reactor chamber is always closed whilst it is in operation. Operators are not allowed to open the chamber whilst it is hot to prevent burns from occurring. Temperature gauge available to indicate the temperature within the chamber. Consider placing signage which states ‘do not open whilst in operation’	**Moderate**	**Unlikely**	**Medium**
TEMPERATURE (Thermal Comfort) – Can anyone suffer ill health due to: ☐ Exposure to high temperatures ☐ Exposure to low temperatures ☐ Other factors – specify: _______________									
Can anyone come into contact with FLUIDS or GASES under HIGH PRESSURE due to: ☐ Failure of the plant ☐ Misuse of the plant ☐ Other Factors – specify:_______________	**Major**	**Unlikely**	**High**	Potential hazard could exist when filling the gas from the gas cylinders into gas bottles. Also when operating the pump up to 100 bar.	Engineering, Administrative	Operators trained in the safe work procedure and they are supervised until certified competent. Pressure relief valves are present, Pressure gauge indicates the pressure within the chamber, and if noted that this is higher than the required pressure. Pump is switched off when this occurs.	**Moderate**	**Unlikely**	**Medium**

	Risk Level			**Comments (when and where hazard is present)**	**Control type**	**Control description (current & proposed)**	**Residual Risk Level**		
	C	**L**	**R**				**C**	**L**	**R**
RADIATION Can anyone be injured/ suffer ill health due to: ☐ Ionising radiation e.g. x-ray, infrared light ☐ Lasers ☐ Ultraviolet light ☐ Microwaves				N/A	N/A	N/A			
Ergonomic – Can anyone be injured due to: ☐ Seating design ☐ Excessive effort ☐ Repetitive body movement ☐ Constrained posture ☐ Poor lighting ☐ Poor workplace or plant design ☐ Controls layout and design				N/A	N/A	N/A			

	Risk Level			Comments (when and where hazard is present)	Control type	Control description (current & proposed)	Residual Risk Level		
	C	**L**	**R**				**C**	**L**	**R**
Can anyone be injured or suffer ill health from exposure to OTHER HAZARDS: ☐ Chemicals ☐ Fumes ☐ Dusts ☐ Vibration ☐ Noise ☐ Biological exposure ☐ Toxic gases or vapours ☐ Other factors – specify_______________	**Moderate**	**Possible**	**High**	Chemicals such as methanol and dry ice and gases (carbon dioxide, oxygen, nitrogen, hydrogen) are used in the experiment. There is noisy air compressor outside the lab.		Appropriate PPE such as safety glasses, respirators, ear plugs when air compressor is running. Gloves should be used when handling dry ice. Room is well ventilated to prevent inhalation of CO from dry ice and other gases. Gas detectors and extraction fans are available to reduce the effect or detect gas leaks. Pressure gauge indicates if there is a leak when it goes below the required pressure. It should be monitored during the research/experiment. Chemical risk assessments should be carried out for chemicals used for the research and the MSDS should be read and understood	**Moderate**	**Unlikely**	**Medium**

What is the highest risk score from the initial risk assessment?	High
What is the highest residual risk assessment score? (This the overall risk rating for the plant to add to the risk register)	Medium

▪ **FURTHER RISK CONTROLS REQUIRED**		▪
▪ **Control**	▪ **Person Responsible**	▪ **Date Due By:**
▪ Eg. Guard to be purchased for pedestal drill	▪ e.g. John Smith	▪
1.	▪	▪
2.	▪ ▪	▪
3.	▪ ▪	▪
4.	▪ ▪	▪
5.	▪ ▪	▪

Name: Nicholas ChiiJyh Teh ____Signature(s):_________________________________Date: ____/_____/_____

Name: ____Signature(s):_________________________________Date: ____/_____/_____

Name: ____Signature(s):_________________________________Date: ____/_____/_____

APPENDIX C

Energy saving scheme for CO_2 capture by hybrid method of VSA/Cryogenic

Equipment list and sizing

Recovery exchangers, air coolers, and refrigeration chillers

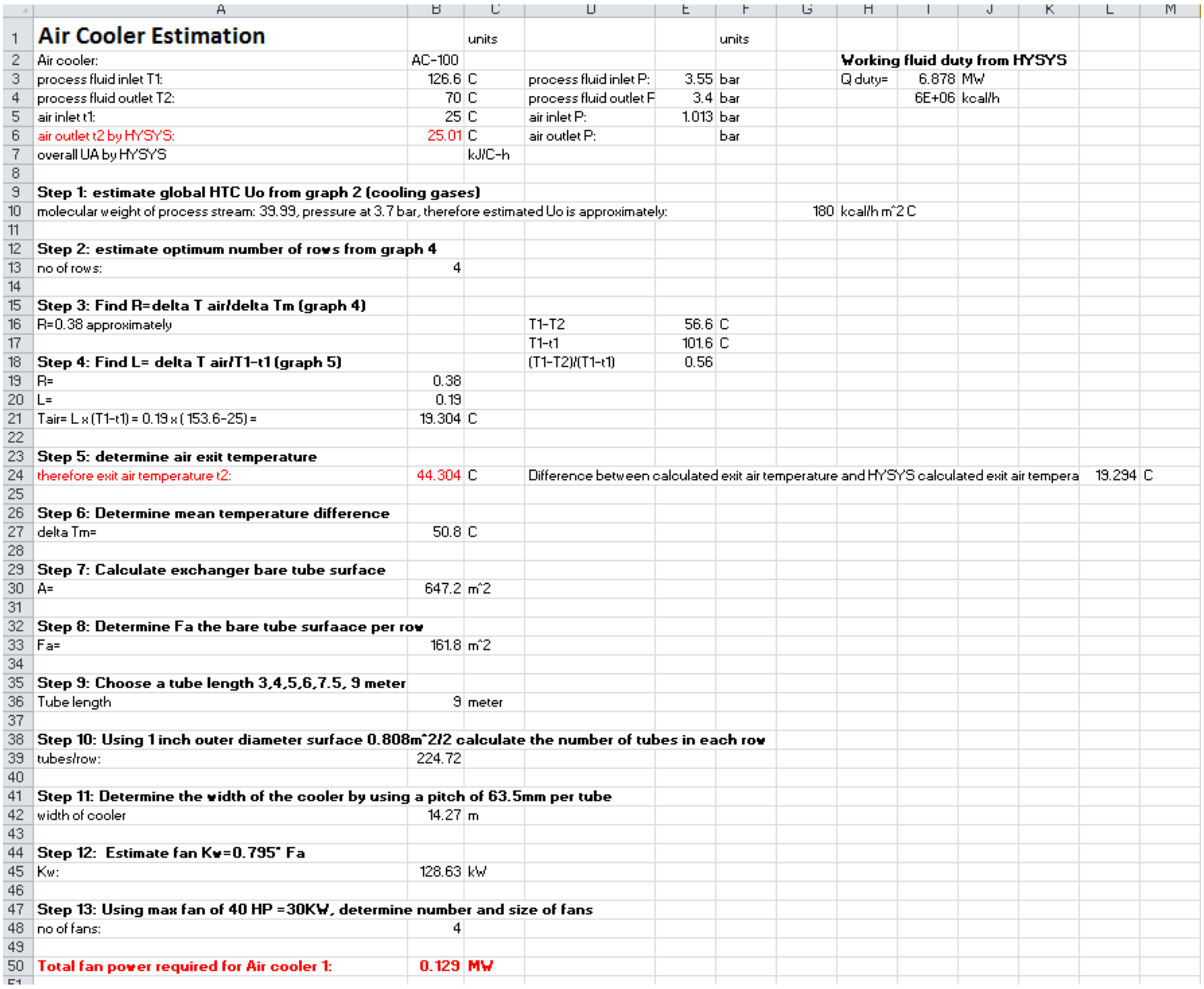
Tag	Heat Loads (MW)	Material	LMTD (℃)	Heat transfer area required (m^2)	No of tubes	Shell diameter (mm)	Heat exchanger tube length (m)
Feed Gas (CO_2 Mole %)	**77.12%**						
E-100A/E-100B/E-100C	7.55	CS	6.398	3933.52	1044	2417	8
E-101	6.41	CS	11.12	1921.46	1528	2841	8
E-102A/ E-102B/ E-102C/ E-102D/ E-102E/ E-102F/ E-102G	14.73	3.5Ni	5.023	9775.03	1112	2482	8
E-103	5.683	3.5Ni	7.3	2594.97	1032	2406	8
AC-100 (3 bays, 6 bundles, 6 fans)	0.1398	CS	37.59	--		--	9.91
AC-101 (2 bays, 4 bundles, 4 fans)	0.1052	CS	4.754	--		--	10.57
AC-102 (1 bays, 1 bundle, 2 fans)	0.0606	CS	28.3	--		--	11.29
PA (R-100) at 80% efficiency	48.01						

Table 47 List of heat exchangers, air coolers and refrigeration package

The preliminary sizing of heat recovery exchanger has been done in several steps using Microsoft Excel:

1) Extracting data such as heat loads and log mean temperature difference (LMTD) from HYSYS.
2) Assume U, the overall heat transfer coefficient as 300 W/m^2 ℃
3) From Q=UAΔT, calculate A the heat transfer area required in metre square
4) By assuming the outer diameter and length of tube, number of tubes can be calculated based on heat transfer area required.
5) From number of tubes, the shell diameter can be calculated.

The preliminary sizing of air coolers has been done in several steps using *Hudson methods* in Microsoft excel:



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Air Cooler Estimation**		units			units							
2	Air cooler:	AC-100						**Working fluid duty from HYSYS**					
3	process fluid inlet T1:	126.6	C	process fluid inlet P:	3.55	bar		Q duty=	6.878	MW			
4	process fluid outlet T2:	70	C	process fluid outlet F	3.4	bar			6E+06	kcal/h			
5	air inlet t1:	25	C	air inlet P:	1.013	bar							
6	air outlet t2 by HYSYS:	25.01	C	air outlet P:		bar							
7	overall UA by HYSYS		kJ/C-h										
8													
9	**Step 1: estimate global HTC Uo from graph 2 (cooling gases)**												
10	molecular weight of process stream: 39.99, pressure at 3.7 bar, therefore estimated Uo is approximately:						180	kcal/h m^2 C					
11													
12	**Step 2: estimate optimum number of rows from graph 4**												
13	no of rows:	4											
14													
15	**Step 3: Find R=delta T air/delta Tm (graph 4)**												
16	R=0.38 approximately			T1-T2	56.6	C							
17				T1-t1	101.6	C							
18	**Step 4: Find L= delta T air/T1-t1 (graph 5)**			(T1-T2)/(T1-t1)	0.56								
19	R=	0.38											
20	L=	0.19											
21	Tair= L x (T1-t1) = 0.19 x (153.6-25) =	19.304	C										
22													
23	**Step 5: determine air exit temperature**												
24	therefore exit air temperature t2:	44.304	C	Difference between calculated exit air temperature and HYSYS calculated exit air tempera								19.294	C
25													
26	**Step 6: Determine mean temperature difference**												
27	delta Tm=	50.8	C										
28													
29	**Step 7: Calculate exchanger bare tube surface**												
30	A=	647.2	m^2										
31													
32	**Step 8: Determine Fa the bare tube surfaace per row**												
33	Fa=	161.8	m^2										
34													
35	**Step 9: Choose a tube length 3,4,5,6,7.5, 9 meter**												
36	Tube length	9	meter										
37													
38	**Step 10: Using 1 inch outer diameter surface 0.808m^2/2 calculate the number of tubes in each row**												
39	tubes/row:	224.72											
40													
41	**Step 11: Determine the width of the cooler by using a pitch of 63.5mm per tube**												
42	width of cooler	14.27	m										
43													
44	**Step 12: Estimate fan Kw=0.795* Fa**												
45	Kw:	128.63	kW										
46													
47	**Step 13: Using max fan of 40 HP =30KW, determine number and size of fans**												
48	no of fans:	4											
49													
50	**Total fan power required for Air cooler 1:**	**0.129**	**MW**										

Tag	Heat Loads (MW)	Material of construction	Amount of low pressure steam /cooling water required (kg/hour)
H-100	1.115	CS	1827

Table 48 List of heater and coolers

Compressors and pumps

Tag	Power Load (MW)	Pressure ratio	ΔP (kPa)	Outlet Temperature (℃)
Feed	**77.12% Gas (CO_2 Mole %)**			
K-100	15.68	2.822	939.5	144.2
K-101 (Exp-100)	5.955	1.611	195.5	46.6
K-102	11.19	2.121	185	117.3
K-103	0.55	1.974	98.7	100.9
K-104	5.845	1.481	65	76.07
P-100	0.00012	1.067	10	50.19
P-101	0.92	6.509	7685	-51.72
P-102	0.3897	1.215	1950	31.12

Table 49 Centrifugal compressors and Pumps

*All compressors and pumps have 85% adiabatic efficiency. K-101 uses energy from expansion
*All power loads have been extracted directly from energy streams in HYSYS. Energy stream is used to simulate the energy travelling in and out of the simulation boundaries and passing between unit operations.

Vessel sizing (Manual calculation based on ellipsoidal head)

Feed Gas (CO2 Mole %)	Tag	Diameter (m)	Height (m)	Shell Thickness (mm)	Material of construction	Operating pressure (bar)	Operating temperature (℃)	% of water separation
77.12%	V-100	7	21	8	SS	1.5	50.19	58.7
	V-101	2	6	25	SS	13.95	-55	N/A
	V-102	7	21	8	SS	1.35	42.01	28.79

Table 50 Liquid separators

The preliminary sizing of gas liquid separator has been done in several steps:

1) Extracting data such as liquid density, gas density from HYSYS, the allowable vapour velocity V can be calculated using *Souder's- Brown equations*.

$$V = (k)\sqrt{\frac{\rho_L - \rho_V}{\rho_V}}$$

V=maximum allowable vapour velocity (m/s)
ρL= liquid density (kg/m3)
ρv= vapour density (kg/m3)
k: 0.35 for a vertical drum with a wire mesh

2) Diameter of the drum can be calculated by dividing the volumetric flow rate by V.
3) The height is calculated based on a ratio of height/diameter=2.5

Step 1: Calculate settling velocity u_t for estimating the settling velocity of the liquid droplets, for the design of separating vessel:

U t= 0.07 [(ρ L-ρ v)/ ρ v] $^{0.5}$

ρ L= liquid density= 1155kg/m^3

ρ v= vapour density= 31.12 kg/m^3

Therefore U t= 0.421m/s

Assume a demister pad is not used, Ut= 0.421x0.15=**0.0652m/s** for providing a margin of safety and allow for flow surges.

Step 2: Calculate the minimum vessel diameter Dv

$$D_v = \sqrt{\left(\frac{4V_v}{\pi u_s}\right)}$$

Vv= gas or vapour volumetric flow rate= 4368 m^3/hour=1.21 m^3/sec

Us=ut= 0.0652m/s, assume demister pad is used.

Therefore Dv= 4.867meter ≈ 5meter

For the height, according to Coulson and Richardson page 462, the height is equal to the diameter of the vessel or 1m; whichever is the greatest should be used.

Select 5m as Dv,

Step 3: calculate the minimum liquid level by allowing 10 minutes necessary for smooth operation and control.

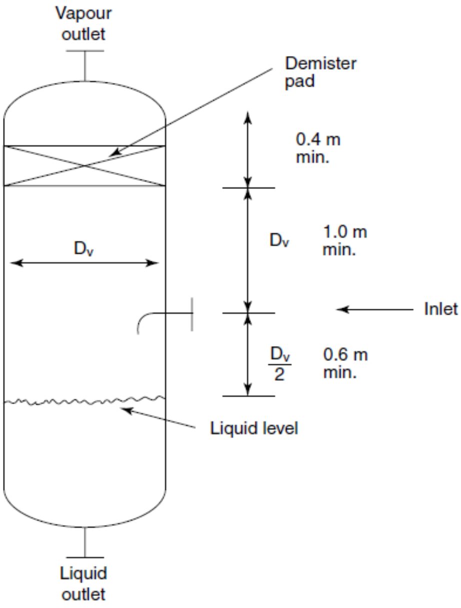
Liquid volume held in vessel= liquid volumetric flow rate x 10 minutes= 179.2 m^3/hour x 10 minutes= 29.86m^3

Liquid depth required= volume held up/ vessel cross sec area= 29.86/ (pi x 5^2/4) =1.52m

**Increase 0.15m to allow space for positioning the level controller.

Therefore the total Tan to Tan height of V-100 is 0.15m+ 5m+2.5m+1.52+0.4=9.57meter ≈ 9.6 **meter**

Comment: a demister pad is used because the separation is likely to be critical.



V-101 separator thickness and head thickness

Using AS1210 section 3.7.3

(a) Based on circumferential stress (longitudinal joints):

$$t = \frac{PD}{2f\eta - P} = \frac{PD_m}{2f\eta} = \frac{PD_o}{2f\eta + P}$$

D=inner diameter of shell=3m=3000mm
f= design tensile strength at design temperature (-54.6 ℃) = 1150kg/cm^2=113MPa
P= design pressure=14.81bar=1.481Mpa
Ƞ=welded joint efficiency=100% (ASME VIII, Div 1, UW-12, 2004)
Circumferential t=19.78mm≈20mm

(b) Based on longitudinal stress (circumferential joints):

$$t = \frac{PD}{4f\eta - P} = \frac{PD_m}{4f\eta} = \frac{PD_o}{4f\eta + P}$$

Longitudinal t≈9.9mm

Take average of circumferential and longitudinal stress= (20+9.9)/2=**15mm**

Head thickness and head type

Ellipsoidal head

Sinnott (2005) has proposed that the standard ellipsoidal head with major axis: minor axis=2:1,
The minimum thickness required can be calculated by e = (Pi*Di/ [2*J*F – 0.2* Pi]) +C

Pi = Design pressure = 1.481N/mm^2
Di = Inner diameter of the column = 3000mm
J = the weld joint efficiency = 100%. The weld joint is double welded butt joint and radio graphed.
f or S = the design stress of the material of construction=113N/mm^2
Therefore e= (1.481*3000/ (2*1*113-0.2*1.481)) =19.78 **mm=20mm**

Capacity as volume in head= $\pi D_{\text{major axis}}^3/24 = \pi 3^3/24 = 3.53 m^3$

Heat exchanger sizing

For example for E-100

Calculate log mean temperature difference (LMTD)

$$\Delta T_{LM} = \frac{(T_{h,i} - T_{c,o}) - (T_{h,o} - T_{c,i})}{ln\left(\frac{T_{h,i} - T_{c,o}}{T_{h,o} - T_{c,i}}\right)} = \frac{\Delta T_2 - \Delta T_1}{\ln\,(\Delta T_2/\Delta T_1)} = \frac{27.7 - 16.51}{\ln\,(27.7/16.51)} = 21.624℃ \approx 29.25℃$$

$\Delta T_m = F_t\,\Delta T_{LM} = 0.9\text{x}21.62 = 19.46℃$ where F_t is the temperature correction factor

Total Heat Transfer Area Required

By Q= 14446800kJ/hour = 4147W =UA ΔT_M

For U, Coulson and Richardson page 654 stated that for gas as hot fluid, water as cold fluid, the U is between 20-300 W/m^2 ℃, therefore assume 1st trial U=300W/m^2°C, ΔT_M calculated=19.46 ℃

Therefore 1st total heat transfer area estimated = 618.7 m^2 ≈ **620m^2**

No of tubes required

By $A=N_{tube}\,(\pi\,D_{outer})\,L_{tube}$, take total tube length as 7.2m, tube outer diameter as 23mm.

One whole tube is 7.2m but divided into 2, therefore 1 section is 3.6m

Allowing for tube sheet thickness,
Take L=7.2m, area of one tube=7.2*0.023*3.1415=0.52m^2
Number of tube=620/0.52=**1193 tubes**.

N_t =1193,
D_b=bundle diameter= 0.023*(1193/0.156)$^{1/2.291}$=1.139m=1139mm
d_o = tube outer diameter= 23mm=0.023m

$$N_t = K_1\left(\frac{D_b}{d_o}\right)^{n_1},$$

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{1/n_1},$$

For square pitch, p_t=1.25d_o=1.25*0.023=0.028m

From table 12.4, for four pass, K_1=0.156, n_1=2.291

Assume the bundle diametrical clearance is about 40mm.

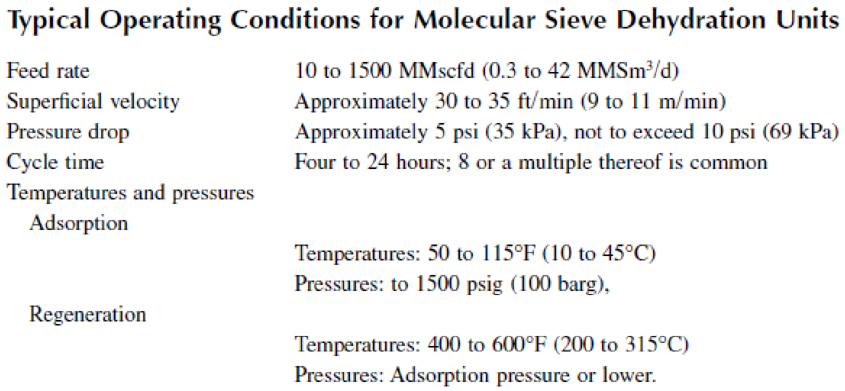
Shell diameter D_s=1139+80=**1219mm**

**Shell size should be read from standard tube count tables.

Dryer design

Data of molecular sieve

Shape	Pellets (extruded cylinders) and beads
Regeneration temperature (℃)	200-315
Packed bed % voids	35
Particle size (mm)	1.6, 3.2, 6
Bulk density (kg/m^3)	640-720
Specific heat (kJ/kg-K)	1
Pore volume (cm^3/g)	0.28
Surface area (m^2/g)	600-800



Typical Operating Conditions for Molecular Sieve Dehydration Units

Feed rate	10 to 1500 MMscfd (0.3 to 42 MMSm³/d)
Superficial velocity	Approximately 30 to 35 ft/min (9 to 11 m/min)
Pressure drop	Approximately 5 psi (35 kPa), not to exceed 10 psi (69 kPa)
Cycle time	Four to 24 hours; 8 or a multiple thereof is common
Temperatures and pressures	
Adsorption	
	Temperatures: 50 to 115°F (10 to 45°C)
	Pressures: to 1500 psig (100 barg),
Regeneration	
	Temperatures: 400 to 600°F (200 to 315°C)
	Pressures: Adsorption pressure or lower.

Process stream data:

7.002kgmole/hour, 2.25 bar, 54.92C, 69.18% CO2, 26.97% N2, 3.85% H2O

$$L_{MTZ}\,(\text{ft}) = 2.5 + 0.025\,V_S\,(\text{ft/min}),$$

Volumetric flow rate= 7.002kgmole/hour *22.4/ 36= 4.35m^3/hour=0.00121 m^3/s

Choosing 9m/min as superficial velocity, 9m/min= 0.15m/s

Velocity= volumetric flow rate/ cross sectional area

0.15m/s= 0.00121(m^3/s)/ x m^2

X= 0.00806m^2= Pi * D^2/4

Therefore D=0.101m≈0.1m

L/D= 2.5

Therefore L=0.25m

APPENDIX D

Chapter 5 CO_2 pipeline design

Table 51 Liquid CO2 versus supercritical CO2 at 20 ℃ ambient temperature

		Liquid CO_2,			Supercritical CO_2,		
Design parameters	Units	Pipe-100	Pipe-101	Pipe-102	Pipe-103	Pipe-104	Pipe-105
Inlet pressure	bar	110	110	110	110	110	110
Outlet pressure	bar	81.8	81.35	80.91	78.91	78.31	77.6
Inlet temperature	℃	25	26	27	50	51	51
Outlet temperature	℃	21	22	23	34	34	34
Inlet velocity	m/s	2.25	2.3	2.3	3.234	3.3	3.3
outlet velocity	m/s	2.26	2.3	2.3	3.6	3.7	3.7
Inlet density	kg/m^3	803.1	790.2	777.8	462.2	454.7	446.4
Outlet density	kg/ m^3	796.5	784	772.2	415.1	405.3	394.1

Table 52 Liquid CO2 versus supercritical CO2 at 40 ℃ ambient temperature

		Liquid CO_2,			Supercritical CO_2,		
Design parameters	Units	Pipe-100	Pipe-101	Pipe-102	Pipe-103	Pipe-104	Pipe-105
Inlet pressure	bar	110	110	110	110	110	110
Outlet pressure	bar	81.41	80.11	78.74	78.15	75.95	92.83
Inlet temperature	℃	25	28	31	50	52	54
Outlet temperature	℃	23	25	26	34	33	44
Inlet velocity	m/s	2.2	2.3	2.4	3.2	3.4	3.6
outlet velocity	m/s	2.3	2.4	2.6	3.8	4.2	3.9
Inlet density	kg/ m^3	803.1	768.7	741.0	462.2	437.2	409.9
Outlet density	kg/ m^3	774.2	739.1	703.2	393.3	360.3	380.0

Fourier's law states that the transfer of energy ($q_{\text{conduction}}$) through the pipe wall via conduction is directly proportional to the driving force i.e. the temperature gradient (rate of change of temperature with respect to x) where k is the conductivity of the pipe wall (W/mK). The negative sign indicates that the heat is transferred in the direction of decreasing temperature.

$$q = -k\frac{dT}{dx}\ (1)$$

For convection, Newton's law of cooling shown in equation 2 is used, where h is the heat transfer coefficient of CO_2 fluid (W/m^2K), T_s is the surface temperature of inner pipe wall and $T\infty$ is the temperature of the CO_2 fluid in the middle of pipe.

$$q = h(Ts - T\infty)\ (2)$$

Similar equations are used for convection from the ground surface to the air and conduction across the soil. Based on the first law of thermodynamics for conservation of energy, the four q values should be equal ($q_{\text{Convection from CO2 fluid to pipe wall}} = q_{\text{Conduction-pipe wall}} = q_{\text{conduction-soil}} = q_{\text{convection from ground surface to air}}$). By performing an energy balance, the temperatures at the ground surface and the temperature on outer and inner pipe wall can be estimated.Bernoulli's principle which can be derived from conservation of energy applies for incompressible, steady and non-rotational flows. This principle states that the sum of kinetic energy, potential energy and internal energy remains constant at all points of that streamline. This principle can be expressed as:

$$\Delta\left(P + \rho g z + \frac{1}{2}\rho\, v^2\right) = 0\ (3)$$

Where

P= pressure (kPa)

z= elevation (m)

v= velocity of fluid (m/s)

ρ=density of fluid (kg/m^3)

g=acceleration due to gravity (9.81 m/s^2)

The pressure drop Δ P $_{\text{loss}}$ can be due to pressure drop in straight pipes called major loss and pressure drop due to piping components called minor loss. The minor loss is not taken into account in this paper.

$$\Delta P\ loss = \Delta P\ major + \ \Delta P\ minor \text{ (4)}$$

The major pressure drop Δ P $_{\text{major}}$ can be expressed as:

$$\Delta P\ major = f\,\frac{L}{2D}\ \rho\ v^2 \text{ (5)}$$

Where

f= friction factor can be obtained from Moody diagram by calculating Reynold's number and using the curve (roughness ε/diameter D)

L: pipe length (m)

D: inner diameter of pipe (m)

v= velocity of fluid (m/s)

ρ=density of fluid (kg/m^3)

By taking into account the energy due to pumping Δ P $_{\text{pump}}$, Bernoulli's Equation can be further modified into:

$$\Delta\left(P\ +\ \rho g z\ + \frac{1}{2}\rho\ v^2\right) + \Delta P\ pump\ - \Delta P\ loss\ = 0 \text{ (6)}$$

The optimum economic pipe diameter (D$_{\text{i, opt}}$) referenced by Zhang et al. (2005) is given as:

$$Di, opt = 0.363\ m^{0.45}\ \rho^{0.13}\ \mu^{0.025}\text{(7)}$$

Where m is the volumetric flow rate (m^3/s), ρ is the density of fluid (kg/m^3) and μ is the viscosity (Pa.s)

APPENDIX E

Liquid CO_2 flow loop
Date: 16-8-2013

Table 53 Experiment 1 for pumping liquid CO2

Time	suction T	suction P	CO2 state at suction by HYSYS	discharge T	discharge P	CO2 state at Discharge by HYSYS	Description
	C	bar	--	C	bar	--	--
n/a	16	40		14.4	35		Initial condition
n/a	-29	25		9.5	11		Chilling the separator using liquid N2
n/a	-30	40		9.9	31		Chilling the separator using liquid N2, increase the pressure back to 40 bar using nitrogen blanket
10.28 am	-26	40	Liquid	-3.5	45	Liquid	Start the pump, the discharge temperature decrease rapidly due to flowing of liquid CO2
10.29 am	-19	45	Liquid	-5.3	50	Liquid	Discharge temperature become steady while discharge pressure of 50 bar was being established
10.30 am	-17	45	Liquid	-4.7	50	Liquid	Discharge temperature started to increase
10.31 am	-21	45	Liquid	-3.3	50	Liquid	Chilling the separator using liquid N2, maintain the pressure using discharge valve
10.33 am	-18	45	Liquid	-2.7	65	Liquid	Close the discharge valve a bit to increase discharge pressure
10.34 am	-21	50	Liquid	-2	70	Liquid	
10.36 am	-23	50	Liquid	-1.4	90	Liquid	
10.37 am	-19	50	Liquid	-1	75	Liquid	
10.39 am	-20	50	Liquid	-0.8	70	Liquid	
10.40 am	-23	50	Liquid	-0.6	70	Liquid	
10.41 am	-21	50	Liquid	-0.6	65	Liquid	
10.42 am	-17	50	Liquid	-0.6	64	Liquid	
10.43 am	-23	50	Liquid	-0.6	60	Liquid	
10.45 am	n/a	50	Liquid	-1	N/A	Liquid	
10.47 am	-19	50	Liquid	-0.1	105	Liquid	
10.48 am	-22	50		4.4	60	--	
10.49 am	-24	50		5.3	70	--	
10.50 am	-21	50		6.2	75	--	
10.51 am	-19	50		7.2	75	--	

Date: 29-8-2013

Table 54 Experiment 2 for pumping liquid CO2

Time	suction T	suction P	CO2 state at suction by HYSYS	discharge T	discharge P	CO2 state at Discharge by HYSYS	Description
	C	bar	--	C	bar	--	--
11.21am	19	45	Gas	17.2	40	Gas	Initial condition
12.01pm	-32	20	Liquid	12.6	13	Gas	Chilling the separator using liquid N2
12.04pm	-28	20	Liquid	11.6	14	Gas	
12.27pm	-2	35	Liquid	9.7	29	Gas	
12.31pm	-1	35	Liquid	10.3	29	Gas	
12.53pm	-2	40	Liquid	13.5	25	Gas	
12.58pm	-2	40	Liquid	14	34	Gas	Start the pump, the discharge temperature decrease rapidly due to flowing of liquid CO2
1.00pm	-4	40	Liquid	6.4	40	Gas	
1.01pm	-5	40	Liquid	2.8	60	Liquid	Close the valve a bit
1.03pm	-4	40	Liquid	2.8	70	Liquid	
1.05pm	-5	40	Liquid	3.9	74	Liquid	Pour liquid nitrogen
1.08pm	-10	40	Liquid	4.9	75	Liquid	Pour liquid nitrogen
1.09pm	6	40	Liquid	5	75	Liquid	Close valve a bit
1.11pm	0	40	Liquid	5.6	100	Liquid	Close valve a bit
1.13pm	3	40	Liquid	7.3	105	Liquid	