STRIPPER SIMULATION FOR CO_2 REMOVAL FROM NATURAL GAS PROCESSING PLANT USING AMINE ABSORPTION PROCESS

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ABSTRACT

Natural gas is consisting of gaseous mixture or hydrocarbon components and mainly contains methane. The gas from reservoir might also contain contaminants (acid gas) such as nitrogen (N_2), carbon dioxide (CO_2) and sulphur compounds. The natural gas should be purified from these contaminants in order to avoid health risk, environment risk and establish the standard specifications of natural gas. In this work, chemical absorption will be used as the method to separate the contaminants especially CO_2 from natural gas processing plant. Chemical absorption processes generally are characterized by highly heat of acid gas absorption and it is required a lot of heat for regeneration. Thus, amount of steam to supply to reboiler will increase as heat of regeneration increase thus increased production cost. The aim of this work is to improve the operation of stripper column to reduce heat of regeneration so that the removal of CO_2 from natural gas using amine absorption will be improved. Aspen Plus simulator is used as a tool to develop the column model. Several process parameters such as concentration, pressure and temperature are varied to determine the optimum process operation at minimum heat of regeneration. Based on the result obtained; the suitable range for each process parameters; DEA concentration, reboiler temperature and stripper pressure is in between 25 wt% and 35 wt%, 118 ^{o}C and 121^{o}C, 1.5 bar and 1.75 bar respectively.

ABSTRAK

Gas asli merupakan campuran gas atau komponen hidrokarbon dan kandungan utamanya ialah gas metana. Gas dari kawasan takungan boleh juga mengandungi bahan pencemar (gas asid) seperti nitrogen (N_2), karbon dioksida (CO_2) dan sebatian sulfur. Gas asli perlu ditulenkan dari bahan pencemar ini bagi menghindari risiko kesihatan, alam sekitar dan mewujudkan spesifikasi gas asli yang mencapai piawaian. Dalam penyelidikan ini, penyerapan kimia akan digunakan sebagai kaedah untuk memisahkan bahan pencemar terutamanya CO_2 dari loji pemprosesan gas asli. Proses penyerapan kimia secara amnya disifatkan mempunyai haba penyerapan gas asid yang tinggi dan memerlukan banyak haba untuk prosess penjanaan semula pelarut. Oleh itu, jumlah stim yang perlu dibekalkan kepada pemanas akan meningkat kerana kadar serapan haba yang tinggi sekaligus mengakibatkan kenaikan kos pengeluaran. Tujuan kajian ini dijalankan adalah untuk menambahbaik operasi “stripper” dan mengurangkan haba dari penjanaan semula agar penyingkiran gas CO_2 daripada gas asli menggunakan serapan amina akan bertambah baik. Perisian Aspen Plus digunakan untuk membangunkan model “stripper”. Beberapa proses parameter seperti kepekatan pelarut, tekanan dan suhu dimanipulasi untuk menentukan operasi proses yang optimum pada kadar minima haba penjanaan semula. Berdasarkan hasil yang diperoleh; kepekatan pelarut, suhu pemanas dan tekanan “stripper” yang sesuai bagi setiap proses parameter adalah di antara 25 kg% dan 35 kg%, 118 ^{o}C dan 121^{o}C, 1.5 bar dan 1.75 bar.

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LIST OF SYMBOLS

a_o	Standard quadratic mixing term
a_1	Additional, asymmetric term
α_i	Temperature function by Soave
$A_\emptyset$	Debye-Huckel parameter
b	constant in equation (2.19)
b_i	Constant in equation (2.26)
d	solvent density
D_s	Dielectric constant of the mixed solvent
D_w	Dielectric constant for water
E	Activation energy
e	Charge of an electron
$fac(i)$	Stream scale factor
$F(i)$	Mass flow of stream i
g^{ex^*}	Molar excess Gibbs free energy
$g^{ex^*,LR}$	Molar excess Gibbs free energy contribution from long range forces
$g^{ex^*,local}$	Molar excess Gibbs free energy contribution from local forces
$g^{ex^*}_{PDH}$	Pitzer-Debye-Hucel contribution
$g^{ex^*,Born}$	Born expression
$h(i)$	Enthalpy of stream i
$H(j)$	Heat flow of heat stream j heat flow of heat stream j
I_x	Ionic strength on a mole fraction basis
k	Rate coefficient
k_B	Boltzmann constant
kij	Binary parameters in equation (2.29)
K_j	Equilibrium constant for thermodynamic model
l_{ij}	Binary parameters in equation (2.31)
m_i	Constant in equation (2.27)
M_s	Solvent molecular weight in kg/kmol
N_o	Avogadro's number
NC	Number of components specified by Comps and Comp-Groups
NH	Number of combined inlet and outlet heat streams
NM	Number of combined inlet and outlet material streams
NSS	Number of sub streams specified
NW	Number of combined inlet and outlet work streams
P_{c_i}	Critical pressure of species i
$q_{reaction}$	Heat of reaction for desorption of CO_2
$q_{reboiler}$	Reboiler duty
$q_{sensible}$	Energy required for sensible heating of the incoming rich amine solution to the stripper operating temperature.

$q_{stripper}$	Energy consumed to generate stripping vapour (steam)
R	Universal gas constant
r_j	Rate of reaction
r_k	Born radius of species k
$sign(i)$	+1 for inlet streams, -1 for outlet streams in equation (3.32) to (3.36)
$s(i,j)$	Mass fraction of sub stream j in stream i
T	Temperature in K
$W(k)$	Work of work stream k
Vm	Molar volume
x_k	Liquid-Phase mole fraction
$z(i,j,k)$	Mass fraction of component k in sub stream j of stream i
z_k	Charge on species k

Greek

α	Non-randomness parameter
ρ	Closest approach parameter
τ	Binary energy interaction parameter
ω_i	Acentric factor

LIST OF ABBREVIATIONS

CO_2	Carbon Dioxide
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Di-isopropanolamine
EOS	Equation of state model
GHG	Greenhouse gas
H_2S	Hydrogen Sulphide
Hg	Mercury
IPAE	2-Isopropylaminoethanol
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
NRTL	Non-random-two-liquid
N_2	Nitrogen
OSHA	Occupational Safety and Health Administration
RK-SOAVE	Redlich-Kwong-Soave equation
SCC	Stress Corrosion Cracking

CHAPTER I

INTRODUCTION

1.1 Research Background

Natural gas is one of vital components of the world's supply of energy. Besides that, it is also source for the petrochemical feed stocks which is hydrocarbons. In natural gas, mainly consist of large quantity of methane along with heavier hydrocarbons. As the component of methane presence in natural gas, it has been contributed for the other potential products such as syngas and high purity hydrogen which lead to undertake natural gas by many researches. It mostly is considered as a "clean" fuel as compared to other fossil fuels (Naturalgas.Org, 2011). Unfortunately, natural gas which found in reservoirs deposit is not really clean and free from impurities. These impurities can be called as contaminating compounds which is considerable amounts of light and heavier non-hydrocarbons such as CO_2, N_2, Hg, H_2S and etc. For CO_2 and H_2S are called as acid gases. The existing of these acid gases can affect health and environment, which lead to establishment of specification for natural gas quality. Besides that, these acid gases also make pipeline corrode during processing and transportation of the gas, hydration of gas may form, and water is likely to condense. Due to these, natural gas needs to be purified by removing the acid gases; CO_2 and H_2S.

As a result many separation processes have been developed and applied for decades. These separation processes can be divided into four types of process; absorption process which is chemical and physical, adsorption process (solid physical); pressure swing and temperature swing adsorption, cryogenic process, and lastly is membrane process. In natural gas processing industries, separation process of chemical absorption have been widely use due to higher rates of CO_2 recovery (98%) can be achieved, and product purity can be in excess of 99% (Wilson *et al.*, 1992).

Chemical absorption process involved an exothermic reaction between the solvent and the gases. This process is being done in counter current flow, which is the solvent enter the absorber column from the top and the gas is enter from the bottom. This process exists in one set processing (absorption and stripping) where it is a continuous processing. As in absorber column the acid gases is being removed from the natural gas, while in stripper these acid gases will be separate from chemical solvent which will be recycle back and enter the absorber back. Chemical absorption processes generally are characterized by highly heat of acid gas absorption and required a lot of heat for regenerate. Thus, amount of steam to supply at reboiler will increase as heat of regeneration increase and this cause increasing of cost for production. In this work, stripper column will be the main focus which is to decrease the heat of regeneration by changing some process parameters.

Chemical solvent that mostly used in gas purification for acid gases (CO_2 and H_2S) removal from natural gas processing industries is amines solution. Amines are compounds formed by replacing hydrogen atoms of ammonia, NH_3 by organic radicals. There are three types of amine that used in this processing; primary amines such as Monoethanolamine (MEA) and diglycolamine (DGA), secondary amine are diethanolamine (DEA) and diisopropanolamine (DIPA), and tertiary amines is methyldiethanolamine (MDEA). Figure 1-1 shows the molecular structure of primary, secondary and tertiary amine. End of 1980's, MEA has been stated to be responsible for stress corrosion cracking (SCC) failure of vessels. Revolution to MDEA eventually leads to low corrosion rates and elimination of SCC.

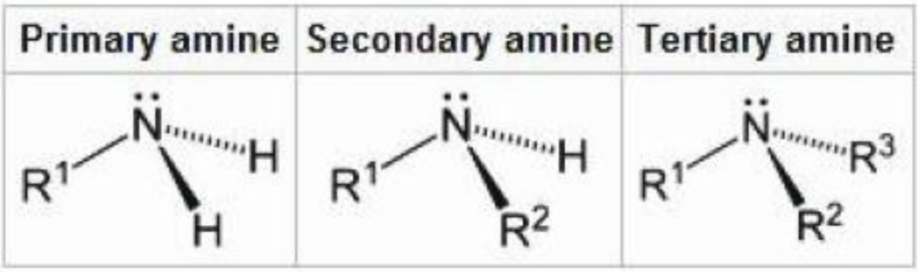

Figure 1-1: Types of amines

1.2 Problem Statement and Motivation

In natural gas exists several contaminants like CO_2, N_2, Hg, and H_2S. Among those contaminants, CO_2 is a part of major provider for the global greenhouse gas (GHG) emissions. This research will be conducted in order to separate the CO_2 from natural gas processing plant using amine absorptions process.

Amine absorption process which involves the removal of carbon dioxide is a technically feasible method of making effective and continuous reductions of CO_2 removal. This can be done by reducing the CO_2 concentration in the natural gas to a controllable level which is focus on the increase of the efficiency of energy conversion and/or utilization in the amine absorption plant (Li, 2008). The main advantage of amine absorption is it can be installed to the existing power plants without major modifications (Arachchige *et al.*, 2012). As stated by Alie *et al.* (2004), amine absorption process involves of an absorber and a stripper as the main unit operations which are important for CO_2 removal. Stripper is especially important in this process to regenerate the amine solvent so that the CO_2 removal percentage is kept in high values. Many researchers have done the studies on the amine absorption process but the studies are mainly focused on chemical reaction mechanism, mass transfer, gas/liquid equilibrium, and other related aspects of CO_2 absorption (Aroonwilas *et al.*, 1999; Soave &Feliu, 2002; Freguia& Rochelle, 2003). However, the most challenging issue is the large quantities of energy required to regenerate the amine solvent within the CO_2 removal process. Chemical absorption processes generally are characterized by highly heat of acid gas absorption and it is required a lot of heat for regeneration especially in the stripper reboiler and CO_2 compression which is higher than capital cost. Thus, amount of steam to supply at reboiler will increase as heat of regeneration increase and this cause increasing of cost for production which is the cost of implementation is too high to be applied in the large scale industry. As action due to this matter, many researchers start to focus on the design of amine scrubbing units which are mainly consists of absorber, stripper and heat exchanger in order to decrease the heat of regeneration and the cost of the process. By varying the stripper parameters in this process, the performance and the cost will be highly affected in the system. Thus, stripper operating parameters have been labelled as the primary factors for the heat of regeneration reducing in the amine scrubbing system.

Recent studies have been done in many aspects in order to reduce the energy consumption of amine scrubbing process. However, there are limitations such as insufficient comparisons between the parameters involved in the studies. Goto *et al.* (2012) work was based on the pilot plant scale experimental method in Japan with 2-Isopropylaminoethanol (IPAE) aqueous solution which only investigated on the types of absorbent that can result the highest CO_2 absorption rate. The pilot plant scale experimental method also done by Cheng *et al.* (2010) where the CO_2 removal percentage was investigated by using more parameters such as types of solvent, speed of the rotation of rotating packed bed column for absorber, temperature, gas flow rate and the liquid flow rate for solvent in the rotating packed bed.

Van Wagener and Rochelle (2011), had introduced an innovative configurations of stripper which might increase the operation cost of the CO_2 removal since the unit operations involved would be increased even though the introduction of more complexity to the process flow by means of splits, recycles, and multiple pressure stages can reduce the existing driving forces to cut down on total energy loss. The reduction of the driving forces and the total compressor work can be done by introducing the more complex configurations with compressor by collecting high-pressure CO_2 (Van Wagener & Rochelle, 2011).

Alternatively, in order to fasten the reaction kinetics; Cullinane and Rochelle (2004) invented the new solvents and additives which are added into the amine solution such as the potassium carbonate/piperazine solvent and it still in research and development progress. Even though it has been established that this solvent can ensure very high CO_2 absorption rate without limiting the lean solvent loading in 0.30 mol CO_2/mol solvent but the expense is much more higher compared to DEA and the stability of the solvent is still under investigation.

There are limited studies by previous researchers focused on the effects of stripper operating parameters on the energy consumption reduction in the CO_2 removal process. Hence, this study aimed to reduce heat regeneration at stripper column in CO_2 removal process, by investigating the effects of stripper operating parameters such as the DEA concentration, reboiler temperature and stripper operating pressure on the heat regenerate of the CO_2 removal process which is directly affecting the operation cost. The optimizing of these parameters not only can reduce the heat regenerate and investment costs but it also can ensure the secure operation safety.

The most precise way to study the effects of the stripper parameters is via experiments. Nevertheless, there are some acute issues regarding experimental procedures since amine scrubbing covers a large range of operation conditions from normal atmosphere to supercritical state, and involve multi-component mixtures (Li, 2008). Based on OSHA (2013), DEA solvent is also hazardous to human body and overexposed to this amine solution would feasibly cause the exasperation of the respiratory system and excretory system. Moreover, a large scale of CO_2 removal plant is very costly to build and time consuming especially for research purposes. Subsequently, process simulation and modelling plays an important role for process optimization and in evaluation of the various process alternatives. In this research, Aspen Plus will be used as the simulation tool to develop the model.

1.3 Research Objectives

The following are the objectives of this research:

- To reduce heat regeneration at stripper column by changing some parameters; amine concentration, reboiler temperature, and stripper pressure.

- To improve amine absorption process for CO_2 removal from natural gas processing plant at stripper column.

1.4 Research Scopes

The following are the scope of this research:

i) Simulation using Aspen Plus, which is will be done based on the industrial CO_2 removal process flow sheet that use amine absorption process.

ii) The result obtained will be compared with data from previous research for validation purpose.

iii) To achieve the objectives, values of some parameter (amine concentration, reboiler temperature and stripper pressure) will be change and record.

1.5 Research Contribution

The contribution of this research is to reduce heat regeneration at stripper column of amine absorption process for CO_2 removal from natural gas processing plant. Several process parameters i.e. amine concentration, reboiler temperature and stripper pressure that effect the heat consumption for solvent regeneration in stripper column are varies in this study. The optimum process operating conditions with minimum heat regeneration are proposed in this work. Thus, CO_2 removal process from natural gas can be improved.

1.6 Chapter Organisation

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the problems, background, and applications of amine scrubbing process for CO_2 removal in natural gas processing. Besides that, general description on the characteristics of the technique, as well as the theories that are related for the modelling are presented.. This chapter also provides a brief discussion on types of separation process for CO_2 removal from natural gas processing plant and which one among those processes most suitable for removing CO_2. Besides that, discussion about chemical solvent as the absorbent in order to remove the $CO_2$from natural gas processing plant also presented. As this research will be done thru simulation, in this chapter also include the discussion on choosing the suitable modelling tools for this research study and a brief discussion of the studies available for the simulation, mentioning their applications and limitations for reducing the heat regeneration analysis. A summary of the previous research work on amine scrubbing as well as in other fields such as CO_2 removal in power plant is also presented.

Chapter 3 gives a review on the procedures and detailed property model with the theory that are applied for the modelling of amine scrubbing process for CO_2 removal from natural gas processing plant. Justifications are stated to clarify the reasons of the usage. This chapter also present, data that have been collected for simulate the CO_2 removal process. A standalone absorber is used as baseline case to obtain the input needed to complete the standalone stripper process modelling. Brief explanation regarding the description of process equipment that will be used in this research also presented. Besides that, the full sequence about this research also presented along with the step required to run the simulation.

Chapter 4 is about the results that have been obtained from simulation regarding this research along with brief discussion by comparing it with previous study. Besides that, expected results for this research, also will be discusses and briefly explain based on results that have been obtained.

Chapter 5 is about the conclusion regarding the simulation of CO_2 removal based on results that have been obtained. Besides that, in this chapter also provides a brief recommendation that can be suggested to improve this research.

CHAPTER II

LITERATURE REVIEW

2.1 Overview

This chapter presents several of information regarding CO_2 removal from natural gas processing plant. This information includes the natural gas composition, type of separation for CO_2 removal, list of chemicals and type of modelling. In this chapter also include discussion regarding the problems and motivations that lead to the development of CO_2 removal by using amine absorption process. Then, the explanation is done to justify the application of this technology should be done in natural gas processing industry and a summary on the limitations based on references from past studies is stated and discussed. Modelling is the best way to know the optimum conditions of stripper to reduce the heat regeneration and the properties of the modelling are explained in the end of this chapter.

2.2 Natural Gas

Natural gas can be found from crude oil wells, gas wells, and condensate wells. Natural gas that found from crude oil wells is known as associated gas. It can exist separately from crude oil due to formation of gas cap or dissolved in the crude oil. While for natural gas that have been found from gas wells and condensate wells is known as non-associated or free gas which is this natural gas has a little or no oil.

Natural gas could be considered as an uninteresting gas because of its characteristics which are colourless, shapeless, and odourless during its pure form. Although it is like that, natural gas is one of vital components of the world's supply of energy that has fulfilled the aforementioned requirement. Compared to the others energy sources, natural gas can be classified as the cleanest, safest, and most useful energy source (Abdel-Aal, 2013).

In natural gas there are a lot of components that is hydrocarbons; methane (CH_4), ethane (C_2H_6), propane (C_3H8) and butane (C_4H_{10}), acid gases; carbon dioxide (CO_2) and hydrogen sulphide (H_2S), inert gas; nitrogen (N_2), and rare gases. Its composition can be changeable, but there is a chart outlining the typical character of natural gas before it is distinguished. Table 2-1 is show the range of typical composition of natural gas.

Table 2-1: Typical Composition of Natural Gas (NaturalGas.org, 2011).

Component	Compound	Percentage
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	Trace

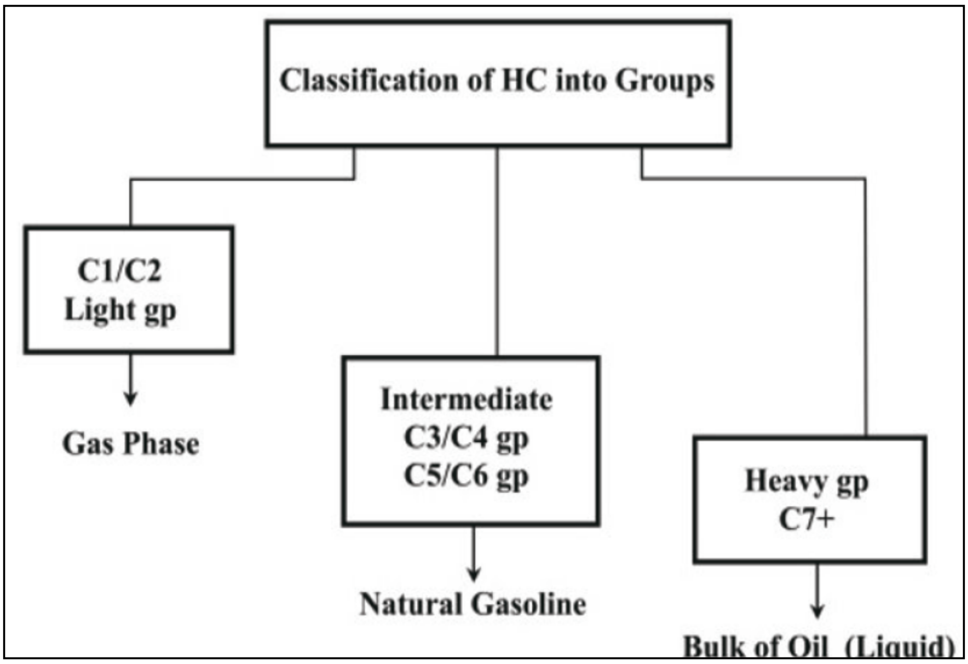

Figure 2-1: Classification of hydrocarbons found in wellhead fluids

2.3 CO_2 Removal Technologies

For operational, economical or environmental reasons acid gases like CO_2 and H2S need to be removed but in selective way from natural gas processing plant. Process of removal the CO_2 always referred as gas sweetening process. Nowadays, there are several methods available for removing this acid gases such as absorption, adsorption, cryogenic methods and membrane separation and between those methods chemical absorption is the most widely used (Kohl and Riesenfeld, 1985).

In order to treat certain types of gas, with the purpose of optimizing capital cost and operating cost, the technologies and their upgrading have been developed over the years by meet gas specifications and environmental purposes (Ebenezer and Gudmundsson, 2006).

2.3.1 Absorption process

Absorption process can be classified into two types which are chemical absorption process and physical absorption process. Basically, these two processes are different in term of their solvent. The chemical absorption and physical absorption or combinations of these two methods have been used extensively in existing base load liquefied natural gas facilities. Each of this method has their own useful used according to different situations.

Chemical absorption processes can be classified as an exothermic reaction. This is can be seen during the reaction of solvent with the gas stream in counter current flow in order to remove the CO_2 present. Most of the chemical reaction is reversible, as in this case at high pressure and rather at low temperature condition is used to remove the CO_2 (Ebenezer, 2005). This type of process is suitable as the CO_2 partial pressure is low. The solvent that used in this process is in dilute state, so with this water content in this solvent it have minimizes the hydrocarbon absorption in natural gas. Therefore, this type of solvent is more suitable for feed gas which contain heavy hydrocarbon. Chemical solvent that mostly have been used for chemical absorption process are amine and carbonate solution.

Rather than react chemically, physical absorption processes is use organic solvents in order to physically absorb the CO_2 gases. Basically, to remove the CO_2 using physical absorption processes is depend on the solubility of CO_2 within the solvents while the solubility of CO_2 is depending on feed gas condition; partial pressure and temperature (Ebenezer, 2005). Complete removal of CO_2 can be achieve if CO_2 condition for partial pressure and temperature is higher and lower respectively which helps the solubility of CO_2 in solvents (absorbents).

2.3.2 Adsorption process

Adsorption process is a process that absorb acid gases (CO_2) component using solid adsorbent. This process can be either by chemical reaction or ionic bonding of solid particle with the CO_2. Iron oxide, zinc oxide and molecular sieve (Zeolite) process are commonly use as adsorption process. Among these three processes, molecular sieve process is more suitable for removal small concentration of CO_2 form natural gas.

The synthetically solid crystalline of Zeolite is used to remove the impurities in natural gas. The crystal structure creates a large number of localized polar charges (active site). H_2S is one polar gas molecule that forms weak ionic bond at the active site. However, CO_2 molecules are non-polar hence it will not bond to active site, but with small concentrations of CO_2, it will trapped in the pores due to linear structure of CO_2. Thus, this process is suitable for low concentration of CO_2.

2.3.3 Cryogenic process

Cryogenic process also can be called as low temperature distillation process is a commercial process that commonly used for CO_2 removal from relatively high purity sources which is more than 90%. This process is involving the cooling of gases to a very low temperature which is lower than -73.3 ^{0}C in order to freeze-out or liquidfied and separated the CO_2.

2.3.4 Membrane process

Commonly, membranes are used in gas field processing for removal CO_2 and water vapour in order to meet the pipeline specification. Before a gas being permeate through a membrane surface, that gas must be dissolve in high pressure side of membranes first. Then diffuse it across the membrane wall and it is evaporate from the low pressure side.