Optimization of High Content Sour Gas Treating Unit using Amine Solution

By

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CERTIFICATION OF APPROVAL

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Approved by,

____

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UNIVERSITI TEKNOLOGI PETRONAS
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September 2012

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons**.**

NUR SYAFIQAH ABDUL MANAN

ABSTRACT

The removal of sour gas or acid gas such as hydrogen sulfide ,carbon dioxide and carbonyl sulfide from gas and liquid hydrocarbon streams always know as sweetening process is a vital process used for natural gas treatment. Although there is already an established treatment process widely used in industry since 1960's to 70's which is known as amine treatment this process is still becoming an issue for improvement. The purpose of this paper is to further research on the removal of high content sour gas by using the established amine treatment. With the used of HYSYS simulator this project will involve the development of the conventional amine treatment units, the evaluation on the efficiency of the treatment unit, and the analysis on the best parameter and specifications in both plant operation and amine solutions for maximum efficiency of CO_2 removal. From the study, it is shown that the performance of acid gas removal can be increased and advantageous by increasing the amine concentration if and only if the concentration does not exceed the corrosion limits apart from increasing the contactor pressure. MEA shows the best performance in acid gas removal followed by DEA and MDEA solvent. In improving the single amine performance, mixtures of amines is identified to be one of the best alternatives in increasing CO_2 absorption by using DEA/MDEA mixture.

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Last but not least, a million thanks to my parent and colleagues for supporting me to successfully completing this Final Year Project within allocated time.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULT AND DISCUSSION

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

LIST OF FIGURES

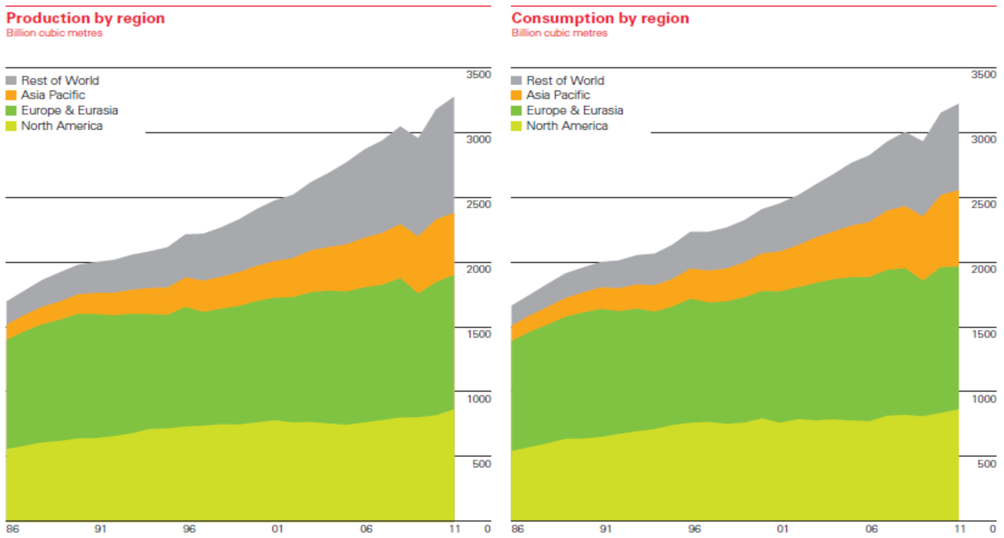
LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Natural gas is one of the world highest demand of energy resources. Recent study in 2012 has shown that the world natural gas consumption grew by 2.2 % while the gas production grew by 3.1%.Natural gas found underground is not exactly the same with gas transported and consumed in homes. It comes associated with variety of other trace compounds and gases and must first be purified to meet the purity specification before being consumed by public. Figure 1.1 shows the trend of production and consumption of world natural gas by region.



World natural gas production increased by 3.1% in 2011. While the US saw the largest national increase, the Middle East recorded the largest regional increment to production. Production growth in Russia and Turkmenistan was partly offset by a large decline in European production. Natural gas consumption increased by 2.2%, with below-average growth in all regions but North America. The European Union experienced the sharpest decline in natural gas consumption (–9.9%) on record.

Figure 1.1 World production and consumption of natural gas.

Reproduced from ref [9]

As for every country in the world, the natural gas consumption varies widely from each other. (Figure 1.2). Some country with large own reserves tend to more generously handle the raw material natural gas, while some country with scarce or lacking resources are more economical. This however, is enough to show on how the market demand welcome more improvement and technologies for higher natural gas processing efficiency.

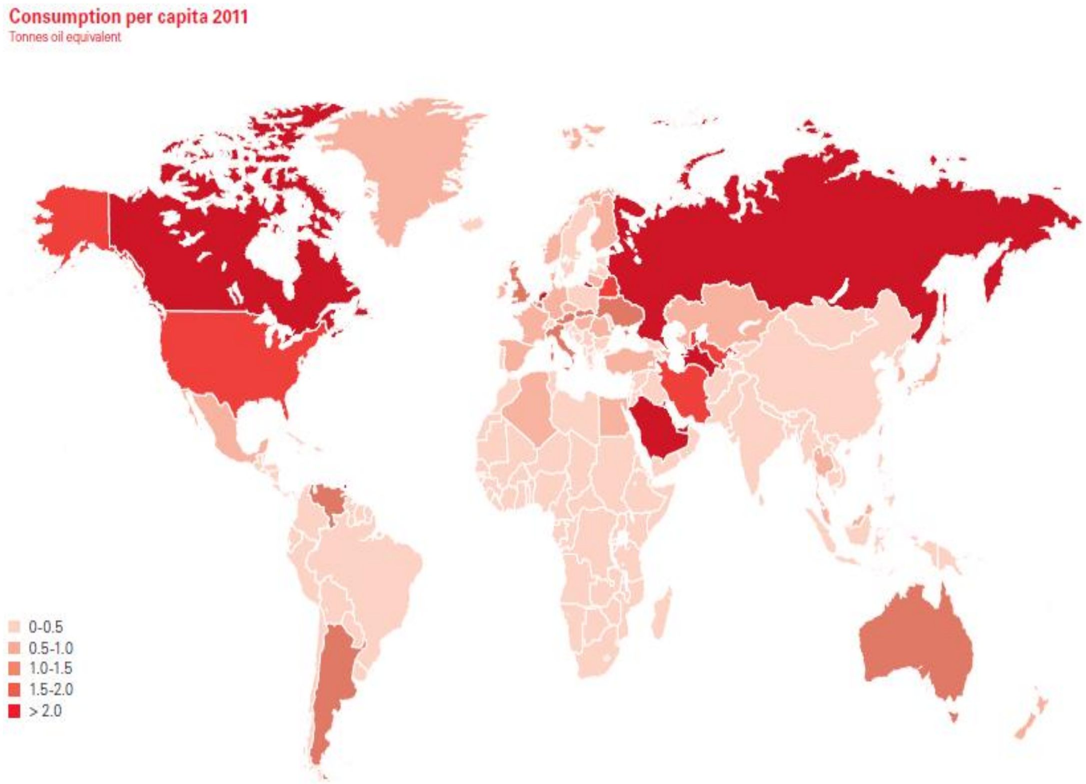


Figure 1.2 Natural Gas consumption per capita in 2011.*Reproduced from ref [9]*

1.2 Problem Statement

Natural gas can account between 1% to 99% of non hydrocarbon gases (CO_2, N_2, H_2S) from overall composition. Diverse areas including South China Sea, Gulf of Thailand, Central European Pannonian basin, Australian Cooper-Eromanga basin, Colombian Putumayo basin, Ibleo platform, Sicily, Taranaki basin, New Zealand andNorth Sea South Viking Graben encountered high carbon dioxide concentration.

CO_2 composition can reach as high as 80% in certain natural gas wells such as in Natuna production field in Indonesia.

High CO_2 concentration in the natural gas composition is the main problem focused in this project. With the used of the conventional amine treatment unit which had established since 1960's and 1970's the efficiency of removing the high content acid gases still becoming an issues in the industry.

This paper will present briefly on the removal of high content carbon dioxide from the natural gas resource . HYSYS software will be used in this project to study on the effectiveness of the conventional sour gas treatment and the problems identified from the simulation.

1.3 Aims and Objectives

The aims and objectives of this projects are :

a) To develop the flow sheet of the conventional amine treatment units by using HYSYS simulator.
b) To evaluate the efficiency of the conventional gas treatment unit in removing high content CO_2 using various amine solutions .
c) To analyze on the best parameter and specifications in both plant operation and amine solutions for maximum efficiency of CO_2 removal.

1.4 Scope of study

The main focus of this project will be on sour gas treating unit by using amine solution for high content CO_2 removal. By using HYSYS software as the simulator, the efficiency of the treatment unit is analyze and best suited parameter and specification in both plant operation and amine solutions are identified. The detail scope of study is as followed :

a) To study on the previous journals and related article
b) To identify the conventional amine treatment process flow and units

c) To construct the flow sheet by using HYSYS
d) To evaluate the efficiency of the treatment unit.
e) To analyze on process optimization by varying the input variables
f) To document the findings of project

CHAPTER 2

LITERATURE REVIEW

2.1 Sour Gas

The source of natural gas commonly exists in mixtures of hydrocarbons, water vapor , hydrogen sulfide (H_2S), carbon dioxide (CO_2), helium, nitrogen and other compounds. It is often the case that heavier natural gas, rich in higher hydrocarbons can be found in deep reservoirs and vice versa. The typical composition of natural gas can be obtain as in Table 2.1 below.

Table 2.1 Typical composition of natural gas. *Reproduced from ref* [14]

Components	Typical	Extreme	
Methane	80-95	50-95	% Mol. Frac
Ethane	2-5	2-20	% Mol. Frac
Propane	1-3	1-12	% Mol. Frac
Butane	0-1	0-4	% Mol. Frac
C_5 Alkanes and higher hydrocarbons	0-1	0-1	% Mol. Frac
Carbon Dioxide CO_2	1-5	0-99	% Mol. Frac
Nitrogen , N_2	1-5	0-70	% Mol. Frac
Hydrogen Sulfide, H_2S	0-2	0-6	% Mol. Frac
Oxygen , O_2	0	0-0.2	% Mol. Frac
Helium	0-0-1	0-1	% Mol. Frac
Other inert gases	traces		% Mol. Frac

Hydrogen Sulfide and Carbon dioxide presence in quiet a significant amount in the natural gas which is commonly called as ‘Sour Gas’ because of the rotten smell provided by the sulfur content [1]. Gas with H_2S content more than 5.7 milligrams per meter cubic of natural gas (4 ppm H_2S by volume) is usually considered sour[2].

H_2S can be extremely corrosive to equipment, harmful and even lethal to breath which make it undesirable[22].CO_2 on the other hand, combines with water to form carbonic acid which is also corrosive and unmarketable for concentration more than 2% to 3%[15,16] The removal of this contaminants will allowed the gas to be marketable, suitable and reduces the gas volume to be transported apart from increasing the calorific value of sold gas stream [3,11]. Table 2.2 shows some of the available information of the natural gases as the feed streams which required a treatment process .

Table 2.2 Natural gas feed streams. *Reproduced from ref.* [4]

	Case 1 A Natural gas from Canada (Alberta)	**Case 2 A Natural gas from Miskar Field Tunisia**	**Case 3 A Natural Gas from western Colorado**
Components	Mole percent	Mole percent	Mole percent
Helium	0	0	0
Nitrogen	3.2	16.903	26.1
Carbon dioxide	1.7	13.588	42.66
Hydrogen Sulfide	3.3	0.092	0
Methane	77.1	63.901	29.98
Ethane	6.6	3.349	0.55
Propane	3.1	0.96	0.28
Butane	2	0.544	0.21
Pentane	3	0.63	0.25

2.2 Sour Gas Treatment

Natural gas treatment is usually takes place on the basis of thermal process engineering in there steps as shown in Figure2.1. The first step serves the preparation of the crude gas for it processing followed by the central process whereby the pre-treated natural gas is separated into a light and heavy fraction in the third step. The light fraction always contains methane and nitrogen ,sometimes even lighter hydrocarbons. It is either be compresses to pipeline pressure or liquefied and use as LNG for further use. [14]

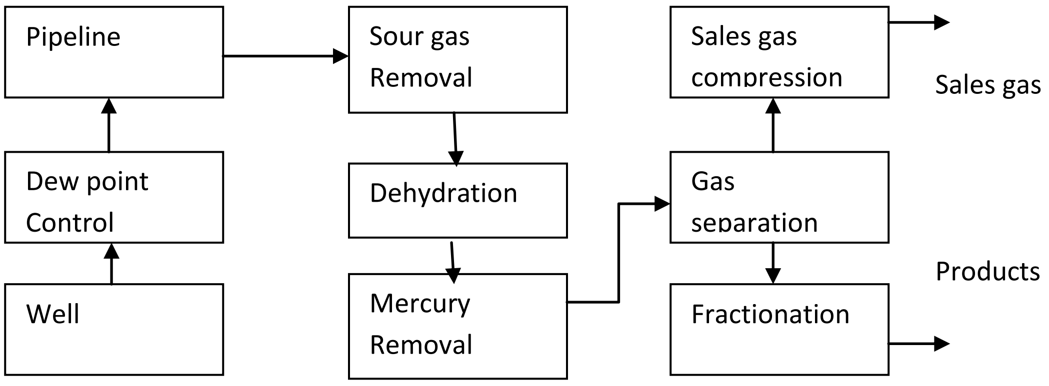


Figure 2.1Natural gas treatment. *Reproduced from ref.* [14]

The removal of sour gas or acid gas such as hydrogen sulfide ,carbon dioxide and carbonyl sulfide from gas and liquid hydrocarbon streams always know as sweetening process is a vital process which constitutes about 70% of the processes used for treating natural gas [4,5]. This process is a part of the first step in natural gas treatment which is very important especially with the increase of stringent environmental consideration and higher sulfur and carbon dioxide content in natural gas and crude oil. It is also very important in meeting the tightly controlled pipeline specifications (Table 2.1) and CO_2 requirement of 2 volume % in sale natural gas.[5,11,14]. Table 2.3 shows the pipeline specification required in industry.

Table 2.3 : Pipeline specification. *Reproduced from ref.* [14]

Component	**CO_2**	**Total Water**	**H_2S**	**Total C3+ content**
Specification	< 2%	< 120 ppm	< 4ppm	950-1050 Btu/scfDew point : -20^{0}C

A numbers of ways are available today to accomplish the removal of acid gases. These processes have been developed in years in the aim of optimizing the capital and operating cost, meet gas specification and environmental purpose..The primary operation of gas purification and preferred area of application for each process type is shown in figure 2.4 below and can be classified as followed [8,13] :

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)

Absorption

Refers to the transfer of a component of a gas phase to a liquid phase in which it is soluble. The reverse of this process is known as stripping, the transfer of a component from a liquid phase in which it is dissolved to a gas phase. It is a widely used process in industry and the single most important operation of gas purification process.

Adsorption

Adsorption involved the selective concentration of one or more components of a gas at the surface of micro porous solid. It consist of an adsorbate, the mixture of adsorbed component and adsorbent which is the microprous solid. Both the adsorbate and adsorbent of are weakly hold compared to those of chemical bonds. The raise of temperature and reduction of partial pressure can generally releasing (desorbed) the absorbate. Desorption is however not possible for adsorbed components which chemically react with the solid. (chemisorptions)

Membrane permeation

It is a relatively new technology of gas purification. Polymeric membranes is used to separate gases by selective permeation of one or more gaseous components from one side of the membrane barrier to the other side .

Table 2.4 Preferred areas of application for each process type.

Reproduced from ref.[13]

Type of process	Acid gas		Plant Size	Partial Pressure	Sulfur Capacity
Absorption in Alkaline Solution	**A**	**A**	**H**	**L**	**H**
Physical Absorption	**A**	**A**	**H**	**H**	**H**
Absorption/ Oxidation	**A**	**-**	**H**	**L**	**L**
Dry Sorption/ Reaction	**A**	**-**	**L**	**L**	**L**
Membrane Permeation	**A**	**A**	**L**	**H**	**L**
Adsorption	**A**	**A**	**L**	**L**	**L**
Methanation	**-**	**A**	**L**	**L**	**-**

A : Applicable H : High L : Low
*Dividing line between high and low is roughly 20 MMscfd for plant size, 100 psia for partial pressure and 10 tons/day for sulfur capacity.

2.2.1 Factors for process selection

Every single process is ideal only for certain application. In optimizing the purification, selection of the most ideal process becomes an important issue. Thus, in selecting the process, the following factors should be considered [5] :

- Feed parameter such as composition, pressure, temperature and nature of the impurities
- Acid/ Sour gas percent in the feed
- Content of $C3^+$ in the feed gas and the size of the unit
- Process economics, reliability, versatility and environmental constraints.

2.2.2 Amine treatment Process

In industry, the most widely employed gas treating process is known as ‘amine process’ which is a chemical solvent process by using various alkanolamines to removed the gases [5]. Almost 95% of the process is used in U.S for gas sweetening operations [3] .Alkanolamine solvent such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamin (MDEA) and diglycolamine (DGA) [5,16,17,18] are utilize as solvent which react with the acid gas constituents to form a chemical complex or bond which subsequently reversed in the regenerator at elevated temperatures and reduced acid gas partial pressures releasing the acid gas and regenerating the solvent for reuse. Figure 2.2 below shows the typical process flow of the amine treatment units.

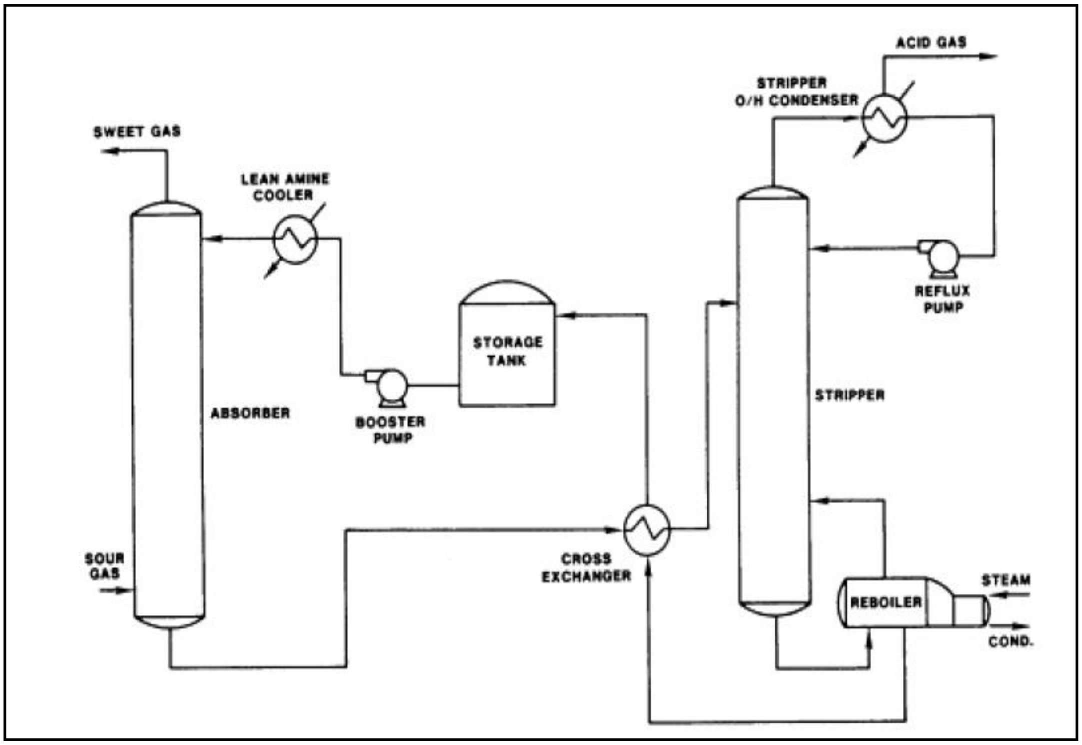


Figure 2.2 Typical amine process unit. *Reproduced from ref.* [5]

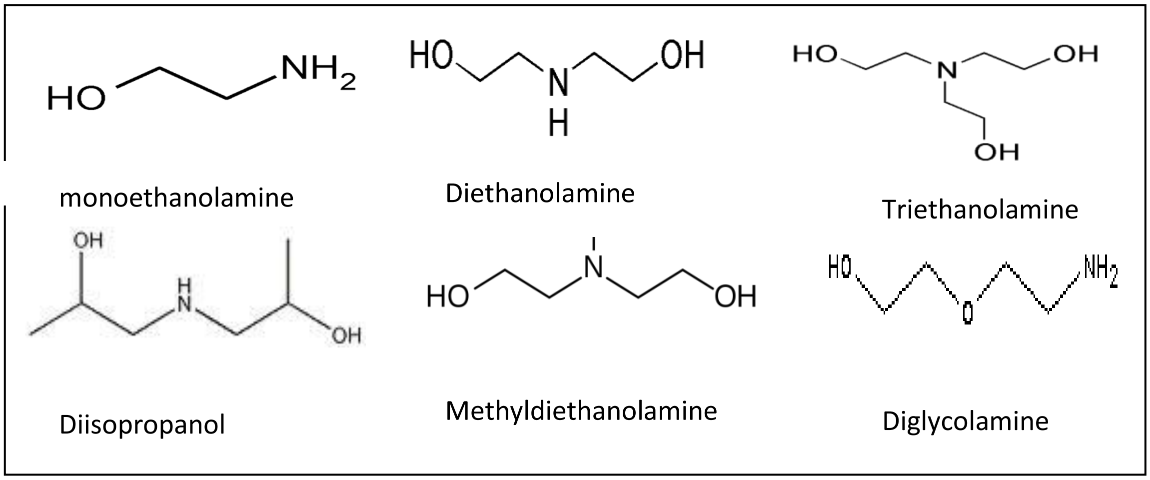
Sour gas is introduced at the bottom of the absorber and the gas is contacted counter currently with aqueous amine solution absorbing the acid gas, leaving sweet gas at the top stream for further processing. Rich amine from the bottom of the absorber is heated by flowing through lean/rich heat exchanger with lean solution from the bottom of the stripping column. The rich amine is then fed to the stripping column at the same point near the top and is stripped at low pressure removing the absorbed acid gases , dissolved hydrocarbons and some water. Lean amine from the stripper on the other hand, is sent back to the absorber through lean/ rich heat exchanger decreasing its temperature. After partial cooling in the lean/rich exchanger, lean amine is further cooled by heat exchanger with water or air, and fed into the top of the absorber with the help of booster pump to increase the pressure greater than the absorber columns.[5,6,17,21,23].

2.3 Alkanolaminesolvent chemistry

Acid gases will dissociated to form weak acids in water or an aqueous solution. This property suited hydrogen sulfide (H_2S) and carbon dioxide (CO_2) to be called as acid gases. An acid-base complex, a salt, is formed when the acid gas containing H_2S and CO_2 react counter currently with the aqueous alkanolamine solution. In stripper, the acid-base complex is reversed when rich amine is stripped by steam, to release the acid gas at the top of the column and the amine solution is regenerating for reuse. [5]

Alkanolamines are classified as primary, secondary, or tertiary according to the degree of substitiutional on the central nitrogen (number of carbons bonded directly to nitrogen atom) [5,7,21]. The alkanolamines consist of at least one hydroxyl group and one amino group.[5]

Primary amines refer to amines with one carbon bonded to a nitrogen atom, such as MEA and DGA and are generally the most alkaline. Secondary amines represent by DEA and DPA have two carbons bonded to a nitrogen atom while tertiary amines such as TEA and MDEA represent three carbon atoms bonded to a nitrogen atom[5,7]. Figure 2.3 below shows the structural formulae of Alkanolamine used in gas treating unit [13].


monoethanolamine

Diethanolamine

Triethanolamine

Diisopropanol

Methyldiethanolamine

Diglycolamine

Figure 2.3 Structural formulae of Alkanolamine used in gas treating

2.3.1 Ganeral Chemistry

The absorption of acid gases into aqueous amine solution can be described by the following chemical reactions :

Description	Reaction
Ionization of water	$H_2O = H^+ + OH^+$
Dissociation of carbon dioxide	$CO_2 + H_2O = HCO_3^- + H^+$
Dissociation of bisulfide	$H_2S \rightarrow H^+ + HS^-$

A soluble acid-base complex, a salt is formed in the treating solution when a gas stream containing acid gases, H_2S/CO_2 contacted by an aqueous amine solution. The reaction between the gases is exothermic and liberating a considerable amount of heat. H_2S will react instantaneously with amine solution regardless of the structure via a direct proton transfer to form amine hydrosulfide as shown in the equation below.

$R_1R_2R_3N + H_2S \rightarrow R_1R_2R_3NH + HS$

A more complex reaction will occur between the amine and CO_2via two different reaction mechanism. For the first mechanism,CO_2hydrolyses to form carbonic acid in water which slowly dissociates to bicarbonate and undertakes an acid-base reaction with amine to yield the equation as followed [4,17,19] :

$CO_2 + H_2O \rightarrow H_2\,CO_3$ (carbonic acid)

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ (bicarbonate)

$H^+ + R_1R_2R_3N \rightarrow R_1R_2R_3NH^+$

$CO_2 + R_1R_2R_3N \rightarrow R_1R_2R_3NH + HCO_3$

This mechanism is slow kinetically because of the carbonic acid dissociation step to bicarbonate is relatively slow. For the second reaction mechanism, a labile hydrogen in amine molecular structure is required.

$CO_2 + R_1R_2NH \rightarrow R_1R_2N + HCOO^-$

$R_1R_2N + HCOO^- + R_1R_2NHR_1 \rightarrow R_2NCOO^- + R_1R_2NH_2$

$CO_2 + 2\,R_1R_2NHR_1 \rightarrow R_2NH_2 + R_1R_2NCOO^-$

This second reaction mechanism for CO_2 is called as carbamate formation due to the formation of amine salt of a substituted carbamic acid and may only occur in primary and secondary amine. A carbamate intermediate is formed when CO_2 reacts with one primary or secondary amine which then reacts with a second amine to form amine salt. This mechanism is rapid, much faster than the first CO_2 hydrolysis reaction. The significantly different kinetics characteristics which occur by the two mechanism result in great impact on the relative absorption rates of H_2S and CO_2 among different alkanolamines. [11,12,25].

2.4 Selection of process Solution

Various available alkanolamine solution can be choose in conducting the treatment process depending on the pressure and temperature conditions at which the gas to be treated is available, its composition with respect to major and minor constituents , and the purity requirement of the gas[13,5,21]. Consideration should also be given to whether simultaneous H_2S and CO_2 removal or selective H_2S absorption is required. [13, 5, 24]

Monoethanolamine (MEA)

MEA is a well established solution used in gas treating application and the subject of tremendous amount of literature. However, it use has declined in recent years and is no longer the predominant gas treating alkanolamine.

The use is preferable for the treatment of gas stream containing low concentration of CO_2 and H_2S with no minor contaminants such as COS and CS_2. This is more suitable especially for treatment at low pressure and maximum removal of H_2S and CO_2. MEA with low molecular weight on the other hands will result in high solution capacity at moderate concentration. However, it is more corrosive than solution of most other amines, particularly if the amine concentration exceed 20% and the solution are highly loaded with acid gas [5,13] .It also produce undesirable high heat of reaction with CO_2 and H_2S which lead to higher energy requirements for stripping in MEA system [5,13,16].

Diethanolamine

DEA is a less reactive secondary amine than MEA and the reaction products are not particularly corrosive [16, 20]. Stream with appreciable amounts of COS and CS_2 besides H_2S and CO_2 can be treated successfully such as in refinery gas stream. It is suitable for low-pressure operations as vaporization losses are quiet negligible. A study by Sociate Nationale des Petroles d' Aquitaine (SNPA) of France recognized that relatively concentrated DEA solutions (25%-30%) can absorb acid gases up to stoichiometric molar ratios as high as 0.70 to 1.0 Mole of acid gas per mole of DEA provided that the partial pressure of the acid gases in the feed gas to the plant is sufficiently high.

The disadvantages of this solution is that the reclaiming of contaminated solutions may require vacuum distillation and undergoes numerous irreversible reactions with $CO_{2,}$ forming corrosive degradation products, and for that reason, DEA may not be the optimum choice for treatment of high content CO_2. [5,13]

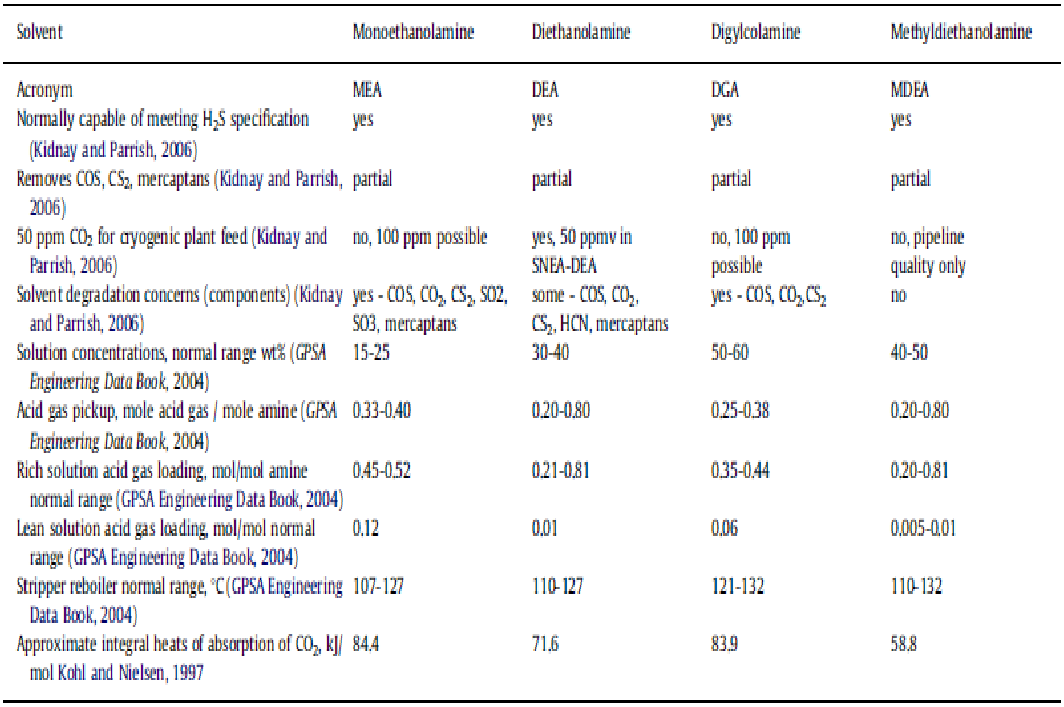
Diglycolamine (DGA)

This solvent in many aspect similar to MEA . However DGA low vapor pressure permits its use in relatively high concentrations, typically 40-60 % which result in lower circulation rates and steam consumption compare to MEA [19]. Treatment of low pressure associated gas in Saudi Arabia is proven to be effective by using DGA as it can operate at high ambient temperature and can produce sweet gas at moderate pressure[13].

Methyldiehtanolamine (MDEA)

MDEA is the solvent with selective absorption of hydrogen sulfide in the presence of carbon dioxide[20]. This is especially for the case whereby the ratio of carbon dioxide to hydrogen sulfide is very high. However with proper design , selective solvents can yield H_2S concentration as low as 4 ppmv in the treated gas while permitting a major fraction of CO_2 to pass through unabsorbed. Due to the low vapor pressure, it can be used in concentrations up to 60% in aqueous solution without evaporation losses. Apart from that it is, resistance to thermal and chemical degradation , non corrosive and has low specific heat and heats of reaction with H_2S and $CO_{2.}$ [13, 5,25]

Table 2.5Properties of common aqueous amine solvent for acid gas treating. *Reproduced from ref* [12].



Solvent	Monoethanolamine	Diethanolamine	Digylcolamine	Methyldiethanolamine
Acronym	MEA	DEA	DGA	MDEA
Normally capable of meeting H_2S specification (Kidnay and Parrish, 2006)	yes	yes	yes	yes
Removes COS, CS_2, mercaptans (Kidnay and Parrish, 2006)	partial	partial	partial	partial
50 ppm CO_2 for cryogenic plant feed (Kidnay and Parrish, 2006)	no, 100 ppm possible	yes, 50 ppmv in SNEA-DEA	no, 100 ppm possible	no, pipeline quality only
Solvent degradation concerns (components) (Kidnay and Parrish, 2006)	yes - COS, CO_2, CS_2, SO2, SO3, mercaptans	some - COS, CO_2, CS_2, HCN, mercaptans	yes - COS, CO_2,CS_2	no
Solution concentrations, normal range wt% (*GPSA Engineering Data Book*, 2004)	15-25	30-40	50-60	40-50
Acid gas pickup, mole acid gas / mole amine (*GPSA Engineering Data Book*, 2004)	0.33-0.40	0.20-0.80	0.25-0.38	0.20-0.80
Rich solution acid gas loading, mol/mol amine normal range (GPSA Engineering Data Book, 2004)	0.45-0.52	0.21-0.81	0.35-0.44	0.20-0.81
Lean solution acid gas loading, mol/mol normal range (GPSA Engineering Data Book, 2004)	0.12	0.01	0.06	0.005-0.01
Stripper reboiler normal range, °C (GPSA Engineering Data Book, 2004)	107-127	110-127	121-132	110-132
Approximate integral heats of absorption of CO_2, kJ/mol Kohl and Nielsen, 1997	84.4	71.6	83.9	58.8

CHAPTER 3

METHODOLOGY

This chapter will cover a detail explanation on the methodology to ensure this project to be successfully completed in achieving its objectives.

3.1 Research Methodology

In conducting this project, a few methodology are identified to be carried out. The methodology identified are as followed :

3.1.1 Case study

Conduct a through study on the background, current condition and environmental interactions of the existence gas treating unit by using various amine solution by referring to numbers of related articles and journals to be summarize in a literature review.

3.1.2 Analysis

Collect and analyze classes of data which consist of the composition data of high content CO_2 in natural gas stream, the operating parameter and related variables which will affect the efficiency of the treatment unit. A case study referring to the literature has been used as a reference in constructing a basic conventional amine treatment flow sheet. The work progress of the flow sheet development is shown in **Appendix A**.

3.1.3 Evaluation

Determine whether the outcome of the stimulated process meet the prescribed hypothesis

3.2 Project Activities

Proposal preparation

- Do research on related journals and articles
- Understand on the objectives and scope of study of the project

Project study

- HYSYS simulator familiarization
- Suitable data findings for gas with high CO_2 content.

Designing

- Construct flowsheet of the process (Appendix A)
- Test on the convergence of the simulation

Data analyzing

- Optimizing process for maximization of $C0_2$ capture by adjusting the variables.
- Discuss and propose framework for the application in industrial case study.

Report writing

- Report the findings of the whole study and outcomes of the project

3.3 Project Tools

Process simulator enable various process alternatives and variable modification to be evaluated easily in a shorter time. The output of the process plant will be simulated in response to changes in the input variable.

In CO_2 capture process, HYSYS process simulator is selected as the detailed mechanism of CO_2 absorption into amine solvent are complex. This is because HYSYS can offer a good user –interface and reliable property packages for simulation of such complex process.

3.4 Gantt Chart

No	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
Final Year Project I									Mid semester break								
1	First meeting with coordinator and supervisors	🟩	🟩														
2	Preliminary research work		🟩	🟩	🟩	🟩											
3	Submission of Extended proposal Defence						🟥										
4	Proposal Defence									🟩	🟩						
5	Project Study and Designing (Simulation work)											🟩	🟩	🟩	🟩		
6	Submission of Interim Draft Report														🟥		
7	Submission of Interim Report																🟥
Final Year Project II																	
1	Data Analyzing (Simulation work)	🟩	🟩	🟩	🟩	🟩	🟩	🟩		🟩	🟩	🟩	🟩	🟩			
2	Submission of Progress Report									🟥							
3	Pre-EDX												🟥				
4	Submission of Draft Report													🟥			
5	Submission of Dissertation (Soft Bound)														🟥		
6	Submission of Technical Paper														🟥		
7	Oral Presentation															🟥	
8	Submission of Dissertation (Hard Bound)																🟥

🟩 **Process** 🟥 **Suggested Mileston**

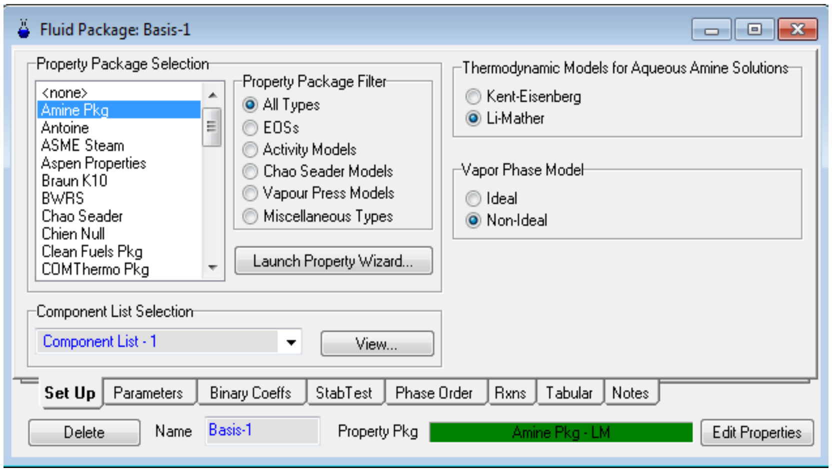
CHAPTER 4

RESULT AND DISCUSSION

4.1 Simulation of Sour Gas Treating Unit

The simulation work for amine gas sweetening plant is conducted by using Aspen HYSYS software. An aqueous amine solution is used as an absorbent to remove acid gases from sour gas stream. In this project , different amine solution which are diethanolamine (DEA), monoethanolamine (MEA), diglycolamine (DGA) and methyldiethanolamine (MDEA) are used in different range of concentration.

A gas stream composition and conditions are first added for a case study and suitable Hysys fluid package is chosen. In this case, Amine Pkg is used based on the literature studied.


Fluid Package: Basis-1

Property Package Selection: Amine Pkg

Property Package Filter: ● All Types

Thermodynamic Models for Aqueous Amine Solutions: ○ Kent-Eisenberg ● Li-Mather

Vapor Phase Model: ○ Ideal ● Non-Ideal

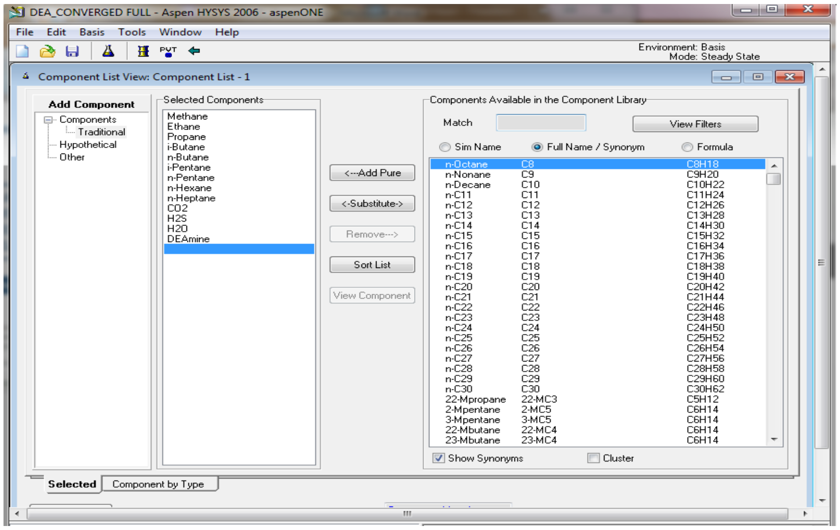
Component List Selection: Component List - 1

Name: Basis-1

Property Pkg: Amine Pkg - LM

Figure 4.1 Hysys fluid package window

The component of the fluid is selected from the component lists provided in HYSYS simulator. Then, the simulation environment is entered and proceeded with the construction of other required equipments. In removing undesirable impurities such solid particles and liquids a gas separator is used before the absorber. In the absorber also known as gas contactor, some specifications such as temperature, pressure and amine concentration is specified followed by the installation of rich-lean heat exchanger.



Environment: Basis
Mode: Steady State

Selected Components
Methane
Ethane
Propane
i-Butane
n-Butane
i-Pentane
n-Pentane
n-Hexane
n-Heptane
CO2
H2S
H2O
DEAmine

Components Available in the Component Library

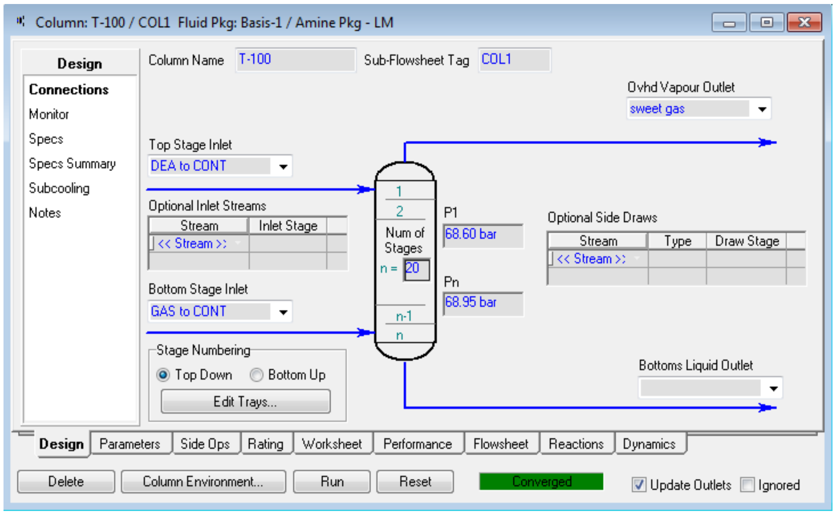
Match

○ Sim Name ● Full Name / Synonym ○ Formula

n-Octane	C8	C8H18
n-Nonane	C9	C9H20
n-Decane	C10	C10H22
n-C11	C11	C11H24
n-C12	C12	C12H26
n-C13	C13	C13H28
n-C14	C14	C14H30
n-C15	C15	C15H32
n-C16	C16	C16H34
n-C17	C17	C17H36
n-C18	C18	C18H38
n-C19	C19	C19H40
n-C20	C20	C20H42
n-C21	C21	C21H44
n-C22	C22	C22H46
n-C23	C23	C23H48
n-C24	C24	C24H50
n-C25	C25	C25H52
n-C26	C26	C26H54
n-C27	C27	C27H56
n-C28	C28	C28H58
n-C29	C29	C29H60
n-C30	C30	C30H62
22-Mpropane	22-MC3	C5H12
2-Mpentane	2-MC5	C6H14
3-Mpentane	3-MC5	C6H14
22-Mbutane	22-MC4	C6H14
23-Mbutane	23-MC4	C6H14

☑ Show Synonyms ☐ Cluster

Figure 4.2 Components selection window



Column Name T-100 Sub-Flowsheet Tag COL1

Ovhd Vapour Outlet: sweet gas

Top Stage Inlet: DEA to CONT

Optional Inlet Streams

Stream	Inlet Stage
<< Stream >>	

Bottom Stage Inlet: GAS to CONT

n = 20

P1: 68.60 bar

Pn: 68.95 bar

Optional Side Draws

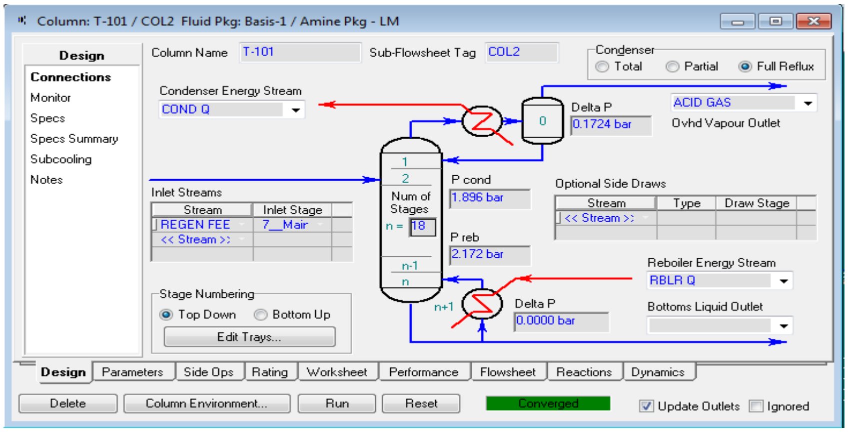
Stream	Type	Draw Stage
<< Stream >>		

Bottoms Liquid Outlet:

Stage Numbering: ● Top Down ○ Bottom Up

☑ Update Outlets ☐ Ignored

Figure 4.3 Amine contactor column window



Column: T-101 / COL2 Fluid Pkg: Basis-1 / Amine Pkg - LM

Column Name T-101

Sub-Flowsheet Tag COL2

Condenser: ○ Total ○ Partial ● Full Reflux

Condenser Energy Stream COND Q

Delta P 0.1724 bar

Ovhd Vapour Outlet ACID GAS

P cond 1.896 bar

Num of Stages n = 18

P reb 2.172 bar

Inlet Streams

Stream	Inlet Stage
REGEN FEE	7__Main
<< Stream >>	

Optional Side Draws

Stream	Type	Draw Stage
<< Stream >>		

Reboiler Energy Stream RBLR Q

Delta P 0.0000 bar

Bottoms Liquid Outlet

Stage Numbering: ● Top Down ○ Bottom Up

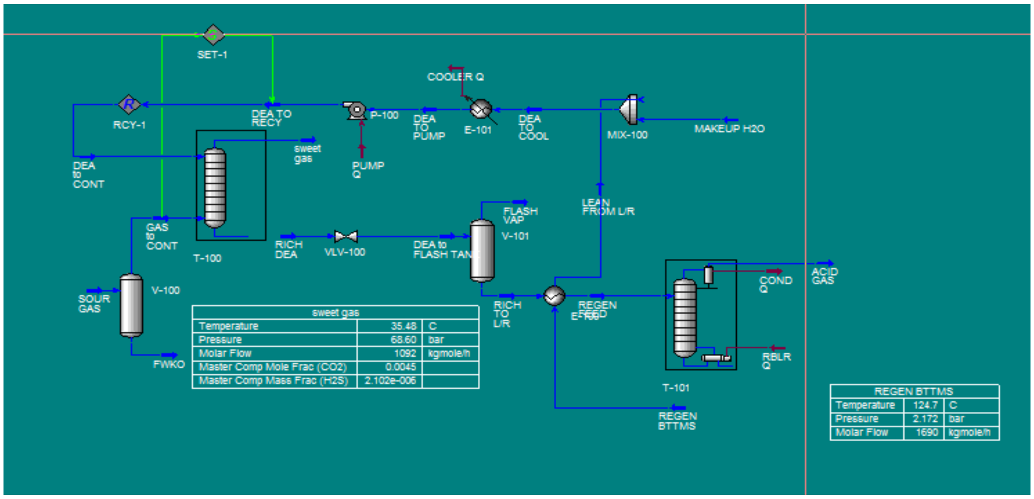
Converged

☑ Update Outlets ☐ Ignored

Figure 4.4 Amine contactor and regenerator column window

In regenerating the amine solution, a regeneration column is installed to strip off the acid gases from amine solution which leave at the top of the column with some specifications which are the top temperature, reboiler duty, reflux ratio and overhead vapor rate. The regenerated amine solvent leave the column, flowing through the rich-lean heat exchanger to exchange heat with the C02 enriched amine

A few others equipment such as water make up, cooler and pump are installed to maintain back the amine solution at acceptable concentration and parameters values because of water and amine losses with sweet gas.



sweet gas		
Temperature	35.48	C
Pressure	68.60	bar
Molar Flow	1092	kgmole/h
Master Comp Mole Frac (CO2)	0.0045	
Master Comp Mass Frac (H2S)	2.102e-006	

REGEN BTTMS		
Temperature	124.7	C
Pressure	2.172	bar
Molar Flow	1690	kgmole/h

Figure 4.5 Process flow diagram

4.2 Data Validation

In the designing phase, scheduled to be conducted before data analysis, a full process flow of amine sweetening plant is first constructed by using a specific case study as shown in table 4.1.

Table 4.1 Case study

Parameter	Value
Molar Flow	25 MMSCFD
Temperature	86 F
Pressure	1000 psia
CO_2	0.0413
H_2S	0.0172
C1	0.8706
C2	0.0394
C3	0.0093
iC4	0.0026
nC4	0.0029
iC5	0.0014
nC5	0.0012
nC6	0.0018
nC7	0.0072
H_2O	0.005
DEA Concentration	30 %

Based on the data obtained, for DEA 30% concentration, it can be observed that the CO2 concentration decrease up to 0.5 mole percent concentration in the sweet gas after the treatment process with acid gas loading of 0.379 .

The validation of this convergence flow however need to be tested by comparing the simulated result with a previous study. The validation test result obtained is as followed :

Table 4.3 Validation test result

	P.Lars, 2011 (11)	Simulated Result
Flow (kmol/h)	1183	1180.63
Temperature (°C)	33.7	33.3
Pressure (bar)	89.5	89.5
Acid gas loading (mole acid gas/mole amine)	0.62	0.65

With an acid gas loading of 0.65 for the simulated result and 0.62 for the study done by P. Lars, 2011, the result shows an acceptable tolerance which indicate the validity of the flow sheet constructed for simulation process. The difference results in the mole fraction of acid gases may because of a few different in specifications specified in both studies.

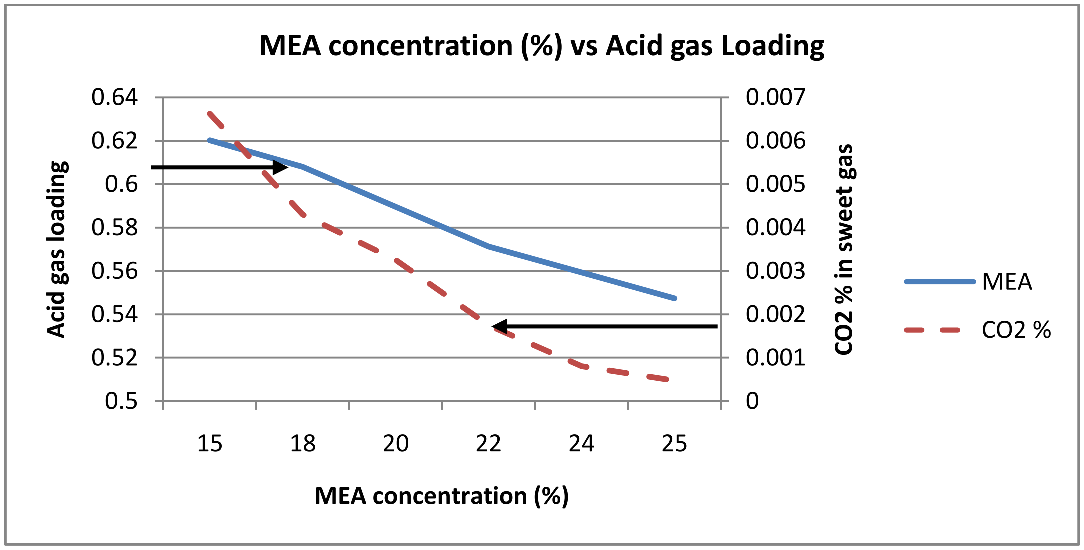
4.3 Amine concentration

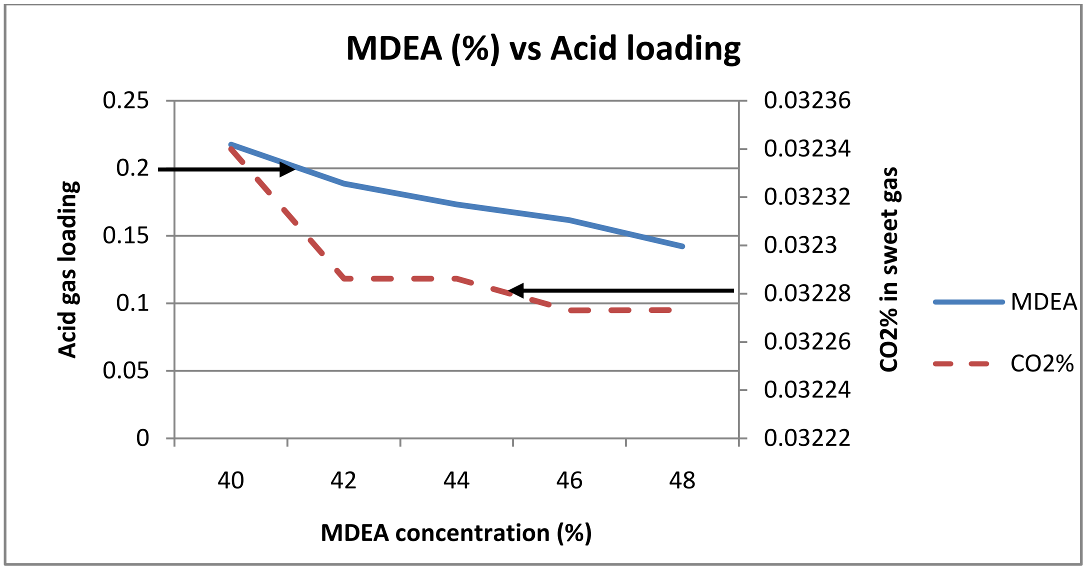
In order to investigate the effect of different amine concentration on the removal of high content acid gas, three different type of amine , DEA, MDEA and MEA are used and simulated at different suggested range of concentration as shown in table 4.4.

Table 4.4 Amine solvent concentration

Amine Solvent	Concentration (%)
MEA	15-25
MDEA	30-40
MEA	40-50

The acid gas concentration in the sweet gas results for 6% acid gas feed concentration as a function of amine solvent concentration, wt% percent are identified. The simulated result of the study are transformed into plotted graph as shown in Figure 4.1 , holding the other variables constant :





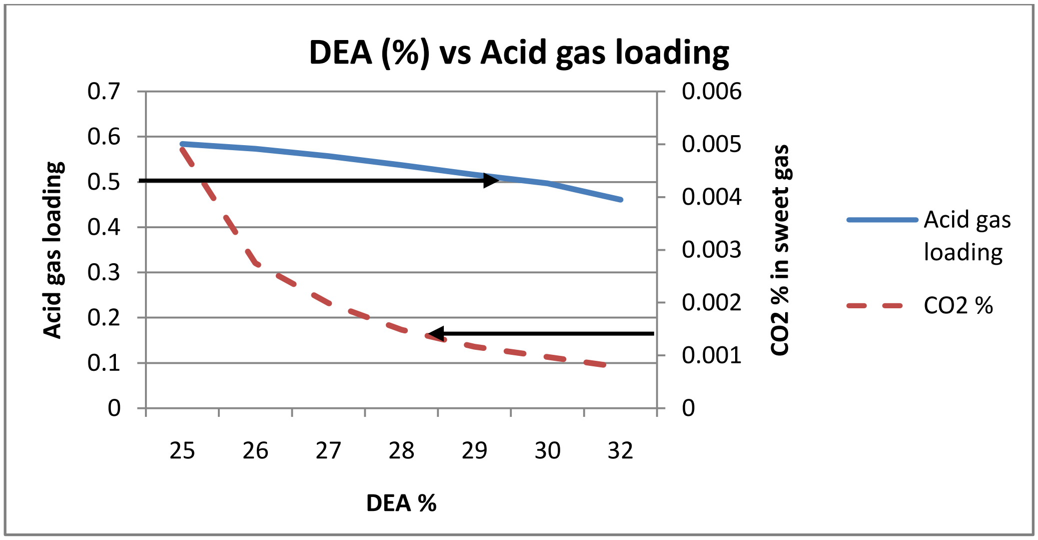


Figure 4.6 Trending of acid gas removal and loading

From figure 4.6, CO_2 concentration left in sweet gas decreased with increasing amine concentration for all amine solution used. For all amines studied, the CO_2 concentration in sweet gas are well within the required specification except for MDEA which is a selective solvent to H_2S with the presence of CO_2.

In general, this result is in accordance with a study done by Lunsford.K.M and Bullin.J.A on Optimization of Amine Sweetening Acid. In achieving higher acid gas removal, higher amine solvent concentration is required. But in most particular case, this is not a viable option as high primary and secondary amine concentrations may cause severe corrosive problems in rich-lean amine heat exchanger and reboiler.

A study is also done to see the performance of different type of amine holding the amine concentration and carbon dioxide at constant as shown in figure 4.7. MEA is leading with the highest acid gas loading followed by DEA and MDEA. As the secondary amine, a less reactive DEA and selective MDEA, shows a lower acid gas loading compared to the primary amine, MEA.

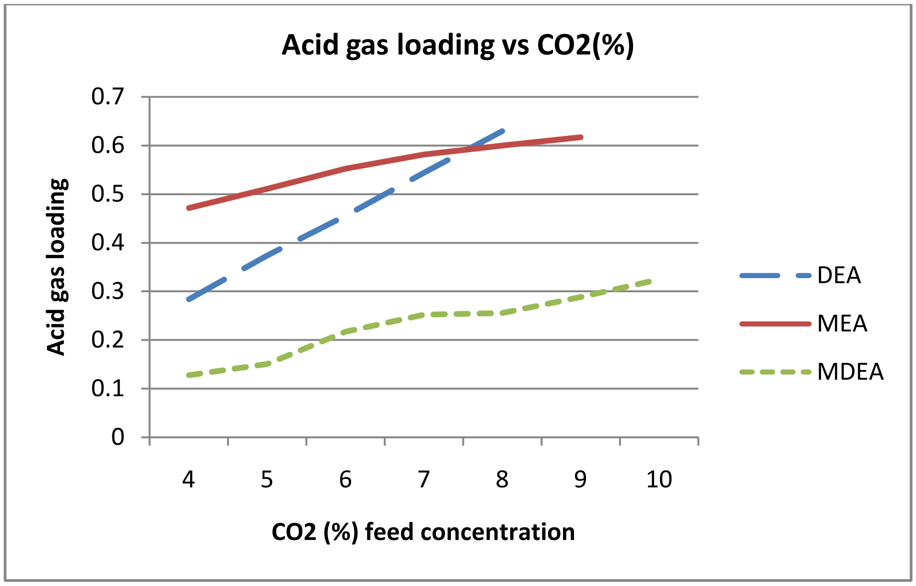


Figure 4.7 Performance of different type of amine solution in removing acid gases.

4.4 Effect of increasing pressure

Several assumed operation pressures are identified and the whole simulated results are shown as followed :

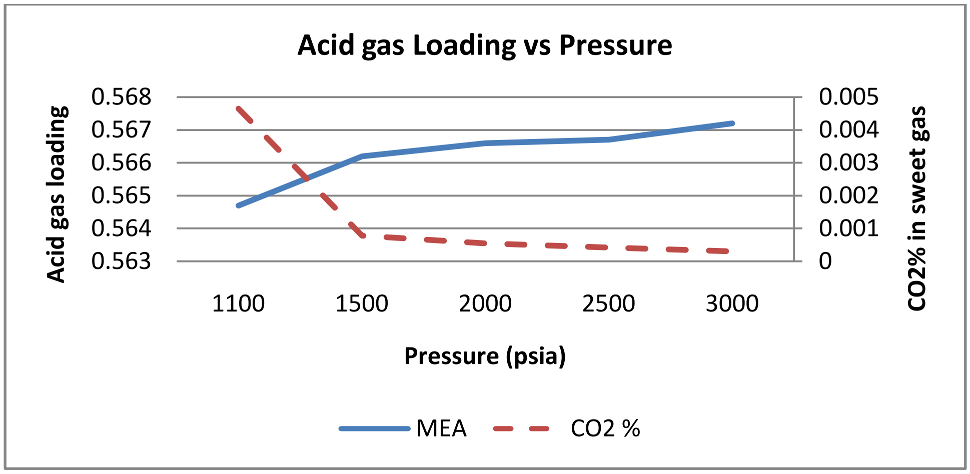


Figure 4.8.1 Effect of increasing pressure on MEA sweetening unit (20 plates absorber)

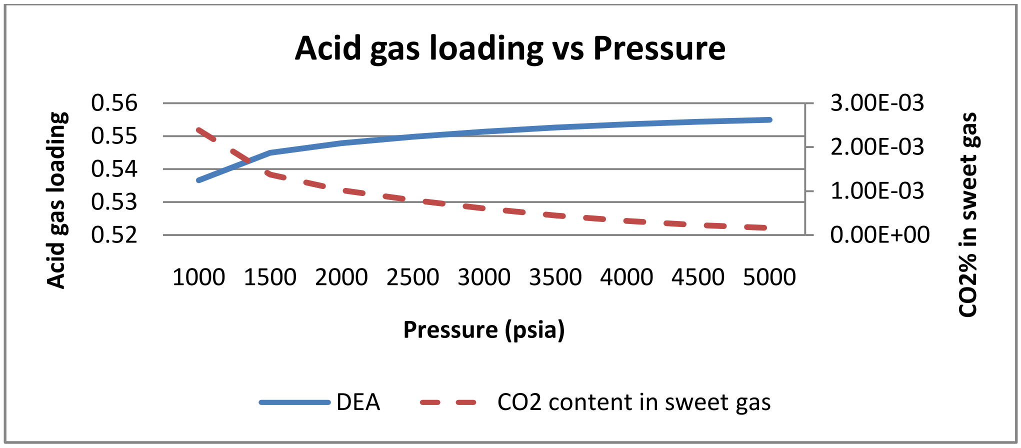


Figure 4.8.2 Effect of increasing pressure on DEA sweetening unit (20 plates absorber)

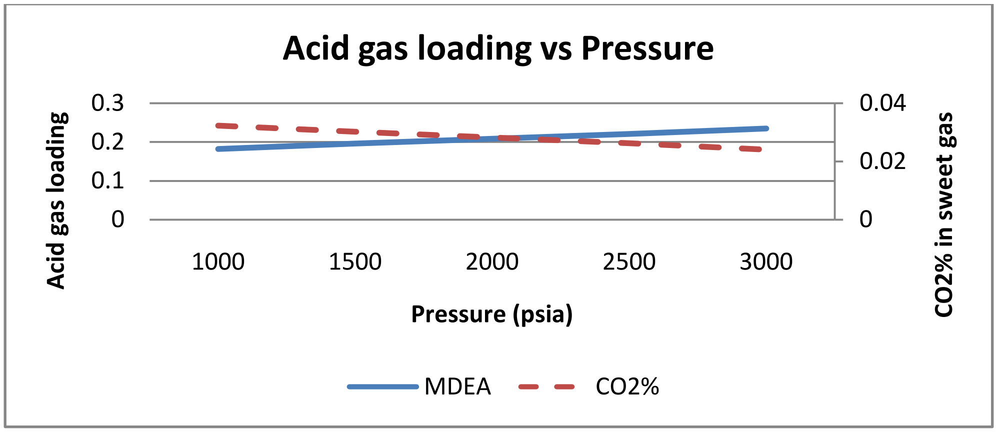


Figure 4.8.2 Effect of increasing pressure on MDEA sweetening unit (20 plates absorber)

From the above trends, it can be seen that an increase in pressure result in the increase in rich amine loading (moles of acid gases/moles of amine) thus effecting the sweetening process performance. Suitable operating pressure is important for removing significant amount of carbon dioxide, CO_2 from the feed natural gas apart from leading to a decrease in lean amine circulation rate and energy consumption by process.

4.5 Amine mixture

The increase in concentration for a single amine especially MDEA cannot easily achieved the CO_2 specification. Mixed amine is explored by using mixture of 40% MDEA 10% DEA, with all the other process variables in constant.

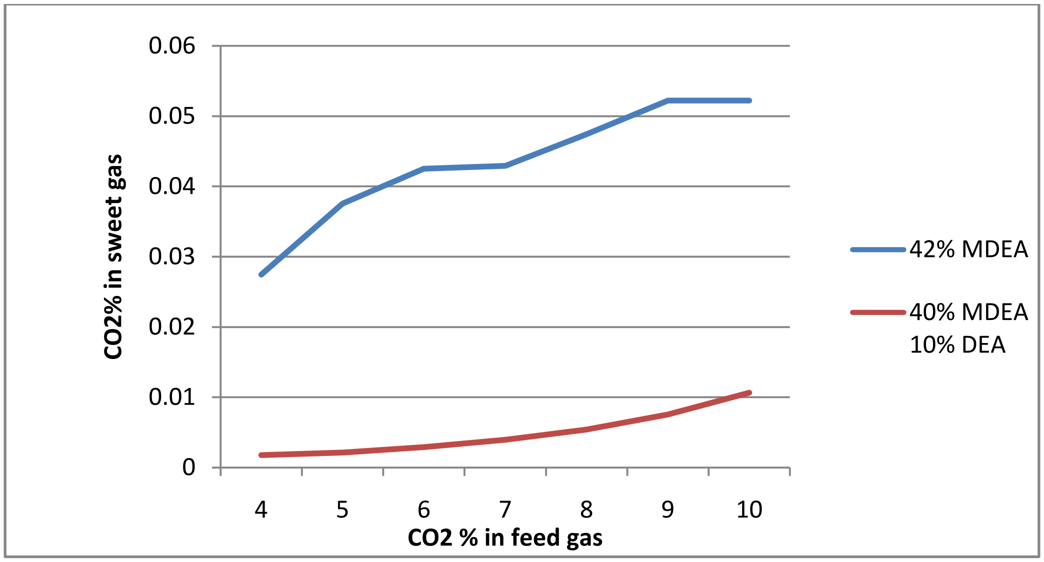


Figure 4.9 Mixed amine performance

Based on figure 4.9, the use of MDEA solvent alone shows a significant different in acid gas removal compared to the used of amine mixture. The CO_2 specification is successfully achieved in the sweet gas by using 40% MDEA 10% DEA with only 0-1 % CO_2 concentration in the sweet gas. The use of MDEA alone shown to be incapable to meet the specifications while the increase in DEA amine concentration will increase CO_2 pickup but together with the probability of exceeding corrosions limits.

Thus in improving the plant performance, the use of amine mixture is found to be one of the best alternative. By using MDEA as the based solvent, the only amine mixture to be considered is secondary amine (DEA). This amine increase the CO_2 absorption and have higher heat of absorption apart from having less tendency of corrosive when mixed.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In natural gas processing, the ultimate aim is to produce quality product which meet the product specification and as economically as possible. HYSY process simulator is used in analyzing the conventional amine treating unit with regard to amine concentration, contactor pressure and the used of amine mixture.

The performance of acid gas removal can be increased and advantageous by increasing the amine concentration if and only if the concentration does not exceed the corrosion limits. MEA shows the best performance in acid gas removal followed by DEA and MDEA solvent. For all the amine solvent especially the selective amines such as DEA and MDEA, the contactor pressure can be increased accordingly to result in further decrease of CO_2 concentration in sweet gas.

In improving the single amine performance, mixtures of amines is identified to be one of the best alternatives in increasing CO_2 absorption for DEA and MDEA as the based solution. Apart from meeting the CO_2 and H_2S specification, the use of DEA/MDEA amine mixture lead to lower reboiler sizes, circulation rates, and duties which is economically more efficient.

From this study it can be concluded that , the use of conventional amine treatment unit is considered practical for high content acid gas considering the feed composition of the acid gas to meet the gas processing plant maximum allowable concentration in consideration of process optimization and used of mixed amine.

5.2 Recommendations

In achieving higher acid gas removal, the used of higher amine concentration , contactor pressure and mixture of amine with different consideration is proved. However, the performance of the amine mixture by different mixture concentration is recommended to be further studied and monitored. With an assumed CO_2 feed concentration, 10% at maximum, which is in line with the maximum allowable acid gas concentration in gas processing plant and considered as high content acid gas, this process should be studied more considering higher concentration of CO_2.

The used of conventional amine treatment units is practical for certain limit of acid gas concentration to be economically efficient. As an alternative in achieving product specification, various other method can also be further studied in finding the most efficient treatment process.

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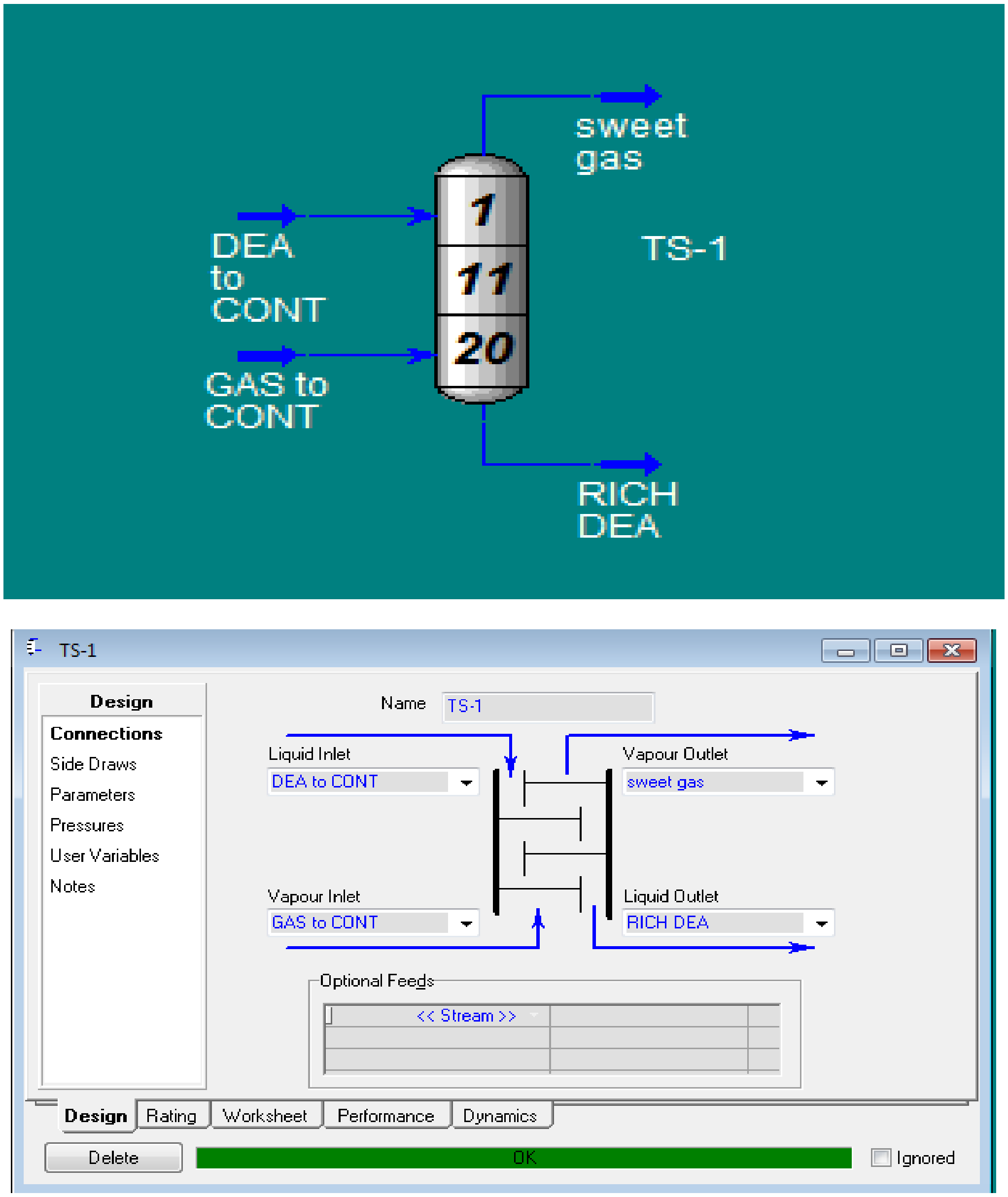
APPANDICES

APPANDIX A



TS-1

Name: TS-1

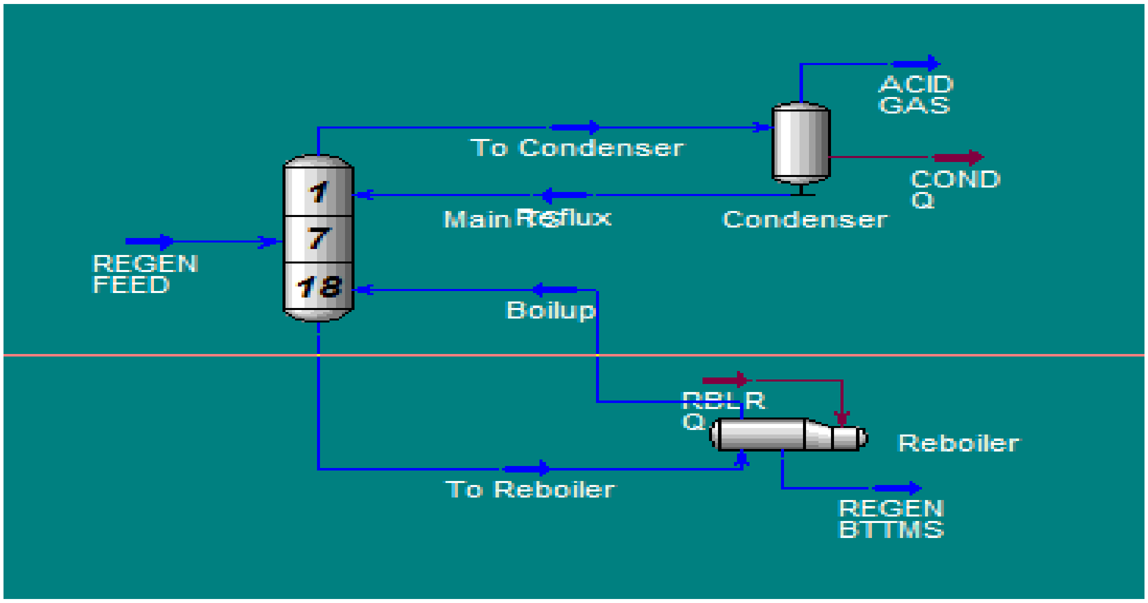
Liquid Inlet: DEA to CONT

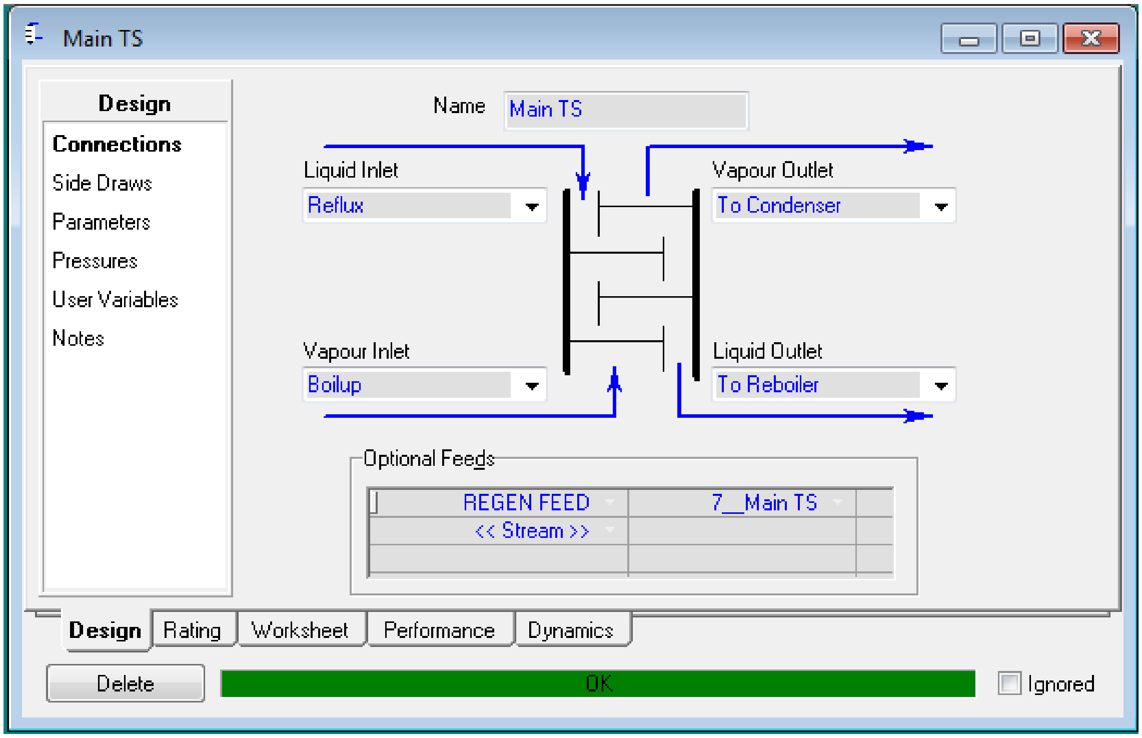
Vapour Outlet: sweet gas

Vapour Inlet: GAS to CONT

Liquid Outlet: RICH DEA

Figure A.1 The contactor column environment





Name: Main TS

Liquid Inlet: Reflux

Vapour Outlet: To Condenser

Vapour Inlet: Boilup

Liquid Outlet: To Reboiler

Optional Feeds

REGEN FEED	7__Main TS
<< Stream >>	

☐ Ignored

OK

Figure A.2 Distillation column environment

APPENDIX B (Sample of Datasheet)

Table B.1 Material streams datasheet for DEA 30%, 4% CO_2

STREAM	DEA to CONT	SOUR GAS	GAS to CONT	FWKO	sweet gas	RICH DEA	DEA to FLASH TANK	FLASH VAP	RICH TO L/R
Vapor fraction	0	0.99053727	1	0	0.999869345	0	9.44E-04	1	0
Temperature (C)	34.39623296	30	30	30	34.61868244	61.74096511	61.69612436	61.69612436	61.69612436
Pressure (bar)	68.60285291	68.9475909	68.9475909	68.9475909	68.60285291	68.94759087	6.205283178	6.205283178	6.205283178
Molar Flow (kgmole/h)	1723.668693	1245.17706	1233.39428	11.7827774	1159.974183	1797.088788	1797.088788	1.697174676	1795.391613
Mass flow (kg/h)	43146.09401	24212.5977	23685.0542	527.543504	20703.96212	46127.18611	46127.18611	30.66239148	46096.52372
Liquid Volume (m3/h)	41.95770178	69.6988519	68.8974234	0.80142849	65.18394179	45.67118342	45.67118342	9.05E-02	45.58065337
Heat flow (kcal/h)	-10784349.9	4084711.39	4058960.63	25750.7568	3937793.193	-10664200	-10664199.96	5784.797073	-10669984.76

STREAM	REGEN FEED	REGEN BTTMS	LEAN FROM L/R	ACID GAS	MAKEUP H2O	DEA TO COOL	DEA TO PUMP	DEA TO RECY
Vapor fraction	1.11E-04	0	0	0.99997328	0	0	0	0
Temperature (C)	93.33333333	124.968608	93.5683791	82.0297983	25	92.69367237	32	34.39622307
Pressure (bar)	5.515807269	2.17184911	1.4823732	1.89605875	1.482373204	1.482373204	1.137635249	68.60285291
Molar Flow (kgmole/h)	1795.391613	1696.01624	1696.01624	99.3753756	27.65245496	1723.668693	1723.668693	1723.668693
Mass flow (kg/h)	46096.52372	42647.9288	42647.9288	3448.59489	498.1617546	43146.09058	43146.09058	43146.09058
Liquid Volume (m3/h)	45.58065337	41.4585316	41.4585316	4.12212176	0.499167066	41.95769867	41.95769867	41.95769867
Heat flow (kcal/h)	-9396280.6	-7019031.7	-8292735.9	278303.753	-225410.623	-8518146.52	-10873881.03	-10784351.05

Table B.2 Composition datasheet for DEA 30%, 4% CO$_2$

STREAMS	**DEA to CONT**	**SOUR GAS**	**GAS to CONT**	**FWKO**	**sweet gas**	**RICH DEA**	**DEA to FLASH TANK**	**FLASH VAP**	**RICH TO L/R**
C1	3.46E-52	0.870592949	0.877452978	0.152500673	0.931574254	9.14E-04	9.14E-04	0.874992966	8.82E-05
C2	5.19E-54	3.94E-02	3.95E-02	2.50E-02	4.20E-02	3.15E-05	3.15E-05	3.03E-02	2.90E-06
C3	1.17E-56	9.31E-03	9.26E-03	1.51E-02	9.84E-03	5.07E-06	5.07E-06	4.96E-03	3.90E-07
i-C4	2.99E-67	2.60E-03	2.55E-03	8.17E-03	2.71E-03	9.52E-08	9.52E-08	1.00E-04	6.16E-10
n-C4	3.15E-67	2.90E-03	2.82E-03	1.18E-02	3.00E-03	1.01E-07	1.01E-07	1.06E-04	6.53E-10
i-C5	2.52E-65	1.40E-03	1.31E-03	1.07E-02	1.40E-03	5.75E-08	5.75E-08	6.03E-05	5.21E-10
n-C5	2.04E-65	1.20E-03	1.11E-03	1.13E-02	1.18E-03	4.68E-08	4.68E-08	4.91E-05	4.23E-10
n-C6	2.71E-51	1.80E-03	1.48E-03	3.54E-02	1.57E-03	4.54E-07	4.54E-07	4.46E-04	3.31E-08
n-C7	8.51E-63	7.21E-03	4.80E-03	0.259530714	5.10E-03	1.95E-07	1.95E-07	2.04E-04	2.38E-09
CO2	9.59E-04	4.14E-02	4.16E-02	1.52E-02	5.12E-04	2.92E-02	2.92E-02	3.17E-02	2.91E-02
H2S	1.93E-05	1.72E-02	1.73E-02	1.44E-02	4.45E-08	1.19E-02	1.19E-02	2.47E-02	1.18E-02
H20	0.918776512	5.01E-03	8.45E-04	0.440820082	1.16E-03	0.881068982	0.881068982	3.24E-02	0.881871253
DEA	8.02E-02	0	0	0	3.27E-08	7.70E-02	7.70E-02	4.04E-07	7.70E-02

STREAMS	**REGEN FEED**	**REGEN BTTMS**	**LEAN FROM L/R**	**ACID GAS**	**MAKEUP H2O**	**DEA TO COOL**	**DEA TO PUMP**	**DEA TO RECY**
C1	8.82E-05	3.52E-52	3.52E-52	1.59E-03	0	3.46E-52	3.46E-52	3.46E-52
C2	2.90E-06	5.28E-54	5.28E-54	5.24E-05	0	5.19E-54	5.19E-54	5.19E-54
C3	3.90E-07	1.19E-56	1.19E-56	7.04E-06	0	1.17E-56	1.17E-56	1.17E-56
i-C4	6.16E-10	3.04E-67	3.04E-67	1.11E-08	0	2.99E-67	2.99E-67	2.99E-67
n-C4	6.53E-10	3.20E-67	3.20E-67	1.18E-08	0	3.15E-67	3.15E-67	3.15E-67
i-C5	5.21E-10	2.56E-65	2.56E-65	9.41E-09	0	2.52E-65	2.52E-65	2.52E-65
n-C5	4.23E-10	2.07E-65	2.07E-65	7.64E-09	0	2.04E-65	2.04E-65	2.04E-65
n-C6	3.31E-08	2.76E-51	2.76E-51	5.97E-07	0	2.71E-51	2.71E-51	2.71E-51
n-C7	2.38E-09	8.65E-63	8.65E-63	4.30E-08	0	8.51E-63	8.51E-63	8.51E-63
CO2	2.91E-02	9.74E-04	9.74E-04	0.509999449	0	9.59E-04	9.59E-04	9.59E-04
H2S	1.18E-02	1.96E-05	1.96E-05	0.213727759	0	1.93E-05	1.93E-05	1.93E-05
H20	0.881871253	0.91745224	0.91745224	0.274618894	1	0.918776536	0.918776536	0.918776536
DEA	7.70E-02	8.16E-02	8.16E-02	9.12E-27	0	8.02E-02	8.02E-02	8.02E-02