## PROCESS MODELING AND COMPARISON STUDY OF ACID GAS REMOVAL UNIT BY USING DIFFERENT AQUEOUS AMINES

FLORENCE WEDNNA SANGGIE

UNIVERSITI MALAYSIA PAHANG

## UNIVERSITI MALAYSIA PAHANG

UNIVERSITI WALATSIA I AHANO				
BORANG PENGESAHAN STATUS TESIS				
JUDUL: <u>PROCESS MODEL</u> <u>UNI</u>	JUDUL: <u>PROCESS MODELLING AND COMPARISON STUDY OF ACID GAS REMOVAL</u> <u>UNIT BY USING DIFFERENT AQUEOUS AMINES</u>			
SESI PENGAJ	IAN: <u>2009/2010</u>			
Saya <u>FLORENCE W</u>	EDNNA SANGGIE			
mengaku membenarkan kertas projek ini disimpan di Perpustakaan Universiti Malaysia Pahang dengan syarat-syarat kegunaan seperti berikut :				
<ol> <li>Hakmilik kertas projek adalah di bawah nama penulis melainkan penulisan sebagai projek bersama dan dibiayai oleh UMP, hakmiliknya adalah kepunyaan UMP.</li> <li>Naskah salinan di dalam bentuk kertas atau mikro hanya boleh dibuat dengan kebenaran bertulis daripada penulis.</li> <li>Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian mereka.</li> </ol>				
<ul> <li>kadar yang dipersetujui kelak.</li> <li>*Saya membenarkan/tidak membenarkan Perpustakaan membuat salinan kertas projek ini sebagai bahan pertukaran di antara institusi pengajian tinggi.</li> <li>*Sila tandakan (✓)</li> </ul>				
SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)			
TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan).			
✓ TIDAK TERHAD				
	Disahkan oleh			
(TANDATANGAN PENULI	(S) (TANDATANGAN PENYELIA)			
Alamat Tetap: No 2, Lane 1, Rejang Park, 96000 Sibu, Sarawak	<u>ABDUL HALIM BIN ABDUL RAZIK</u> Nama Penyelia			
Tarikh: 1 April 2011Tarikh: 1 April 2011				

CATATAN: \* Potong yang tidak berkenaan.

- \*\* Jika Kertas Projek ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali tempoh tesis ini perlu dikelaskan sebagai SULIT atau TERHAD.
- Tesis ini dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (PSM)

"I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of degree of Bachelor of Chemical Engineering (Gas Technology)"

Signature	:
Supervisor	: Abdul Halim bin Abdul Razik
Date	:

## PROCESS MODELING AND COMPARISON STUDY OF ACID GAS REMOVAL UNIT BY USING DIFFERENT AQUEOUS AMINES

FLORENCE WEDNNA SANGGIE

A thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering Universiti Malaysia Pahang

April 2011

I declare that this thesis entitled "Process Modeling and Comparison Study of Acid Gas Removal Unit by Using Different Aqueous Amines" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:
Name	: Florence Wednna Sanggie
Date	: 1 <sup>st</sup> April 2011

To my beloved parents

who taught me the value of a good education

who always stood behind me and have personally sacrificed for me

so I can pursue my dreams.

You are amazing!

#### ACKNOWLEGMENT

Thanks to Almighty God for the completion of this Undergraduate Research Project. Only due to His blessings by giving me wisdoms and strengths, finally I have completed this thesis.

I would like to thank my beloved parents, Sanggie Lian and Bibiana Sebastian, for everything they have done, for loving me unconditionally, and taught me that the value of an education is priceless. I would also like to thank the rest of my family especially to my beloved Aunt Cecelia, for which without the supports given, I would not arrived at this moment. Looking at them, it really makes me realized how very lucky I am. I fully appreciate what I have been given and I am blessed to have them; who truly care about me and constantly keeping me on track.

My most sincere thanks goes to my supervisor, Abdul Halim bin Abdul Razik. I thank him for his patience, invaluable insights and suggestions. Thank you for the guidance all the way from beginnings.

Also, thanks to my loved one for the supports and tremendous assistants during the process of completing this thesis. Not to forget, to all my dearest friends, thanks for the support, and for always being there for me and help me get through the difficult times. Last but not least, I offer my regards and blessings to everyone who has supported me in any way during the completion of this thesis.

Thanks!

#### ABSTRACT

Natural gas need to be purified to meet the quality standards since it contains impurities such as carbon dioxide  $(CO_2)$  and hydrogen sulfide  $(H_2S)$ , which are they are the main acid gases that as its can cause corrosion, reduce the heating and sales value of gas. Aqueous amine solutions are proven to be practical solvents for the treatment of natural gas. By simply changing their amine solutions, many inefficient acid gas removal units can be optimized. Acid gas removal unit (AGRU) simulation is an essential tool for control and operations in gas processing plant because it can be used to stimulate and analyses the under different operating conditions. In this study, Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) will be use to model the acid gas removal unit process by using Aspen Hysys. MEA is effective at removing almost all hydrogen sulfide and carbon dioxide among the other amines. Meanwhile, DEA and MDEA allows for some carbon dioxide to be left in the sweet gas that are suit for gas steams with less stringent product specifications. Accordingly, the heat consumption at the regenerator was in the following order MEA >DEA > MDEA. Improvement studies were extended to the effect of increasing the circulation rate, amines concentration and reboiler heat consumption. By increasing the circulation rate, MEA causes the CO<sub>2</sub> to be almost completely absorbed in the column even at the lowest low circulation rate followed by DEA and. MDEA. By increasing concentration of amine, MEA and MDEA showed at 15 wt % or greater is required to achieve the specified acid gas removal and 25 wt % for DEA. One also can reduce heat of reaction by changing from a primary to secondary amine which both gives almost the same acid gas removal efficiency. This research can broaden by using different simulation tools available model the AGRU and also perform the comparison on the cost estimating for MEA, DEA and MDEA.

#### ABSTRAK

Gas Asli perlu diproses atau ditapis untuk memenuhi standard kerana ia mengandungi benda asing seperti karbon dioksida (CO2) dan hidrogen sulfida (H2S), yang merupakan gas-gas asid utama yang boleh menyebabkan hakisan, mengurangkan nilai pemanasan dan nilai jualan gas. Amina terbukti sebagai penyelesaian pratikal untuk menapis gas asli. Dengan menukar penyelesaian jenis pengunaan amina, banyak acid removal unit (AGRU) dapat dioptimumkan. AGRU simulasi adalah alat yang penting untuk kawalan dan operasi di pusat pemprosesan gas kerana ia boleh digunakan untuk menganalisis pada operasi yang berbeza. Dalam kajian ini, Monoethanolamine (MEA), Dietanolamine (DEA) dan Methyldiethanolamine (MDEA) akan digunakan untuk model AGRU dengan menggunakan Aspen Hysys. MEA berkesan menyingkirkan hampir semua hidrogen sulfida, dan karbon dioksida berbanding dengan amina lain. Sementara itu, DEA dan MDEA membenarkan beberapa karbon dioksida dibiarkan dalam gas manis yang sesuai untuk stim gas dengan spesifikasi produk yang rendah.Dengan demikian, pengunaan tenaga di Regenerator adalah mengikut urutan MEA berikut> DEA> MDEA. Kajian diteruskan dengan kesan meningkatkan tahap sirkulasi, kepekatan amina dan pengambilan reboiler panas. MEA adalah yang terbaik kerana CO<sub>2</sub> yang akan hampir sepenuhnya terserap bahkan pada peredaran rendah terendah. Dengan meningkatkan kepekatan amina, MEA dan MDEA menunjukkan sebanyak 15% wt atau lebih besar diperlukan bagi mencapai jumlah penyingkiran gas asid dan 25% wt untuk DEA. Dengan meningkatkan. Untuk mengurangkan pengunaan tenaga, menukar dari amina primer ke sekunder yang baik memberikan hampir gas asid kecekapan penyerapan yang sama. Penyelidikan ini dapat diperluaskan lagi dengan menggunakan alat simulasi pelbagai model dan juga melakukan perbandingan terhadap kos untuk MEA, DEA dan MDEA.

### **TABLE OF CONTENT**

CHAPTER	TITLES	PAGE
	DECLARATION	V
	DEDICATION	vi
	ACKNOWLEDGEMENTS	vii
	ABSTRACT	viii
	ABSTRAK	ix
	TABLE OF CONTENTS	Х
	LIST OF TABLES	vii
	LIST OF FIGURE	viii
	LIST OF ABBREVIATIONS	xiv
	LIST OF SYMBOLS	XV
1	INTRODUCTION	
	1.1Natural Gas and Impurities	1-3
	Removal	
	1.2 Problem Statement	4
	1.3 Objectives	5
	1.4 Scope of Study	5
	1.5 Rationale & Significance of Study	5
2	<b>LITERATURE REVIEW</b> 2.1 Introduction	6
	2.2Amines	
	2.2.1Monoethanolamine (MEA)	7-8
	2.2.2Diethanolamine (DEA)	8
	2.2.3Methyldiethanolamine(MDEA)	9-11

2.3 Comparative study of MEA, DEA	11-13
and MDEA as chemical solvent	
2.4 Acid Gas	14-15
2.5 Acid Gas Removal Processes	16-17
2.6 Process Chemistry	18-20
2.7 Hysys Process Simulation Package	21
METHDOLOGY	
3.1 Introduction	22-23
3.2 Obtain the flow sheet and design	24
data of AGRU	
3.3 Select the suitable package for	25
AGRU simulation process	
3.4 Simulate AGRU process using	
MEA, DEA and MDEA as a chemical	26-30
solvent	
3.5 Compare the process performance	31
3.6 Suggestion for improvement	31
<b>RESULT &amp; DISCUSSION</b>	
4.1 Introduction	32-34
4.2 Absorption efficiency of amines	34-37
4.3 The effect of Circulation rate	37-38

57-38
38-41
41-43
44
45
46-48
49

## LIST OF TABLE

FIGURE NO.	TITLE	PAGE
2.1	The physical properties of MEA, DEA and	10
	MDEA	
2.2	Typical operating conditions and data for amines	11
2.3	Typical composition of natural gas mixture	15
4.1	Simulation Results of Amine Acid Gas	33
	Absorber	
4.2	Simulation Result of mole component of	39
	H <sub>2</sub> S and CO <sub>2</sub> in sweet gas with different	
	amine concentration	
4.3	Simulation Result of Reboiler Duty at	41
	Regenerator with different concentration of	
	MEA	
4.4	Simulation Result of Reboiler Duty at	42
	Regenerator with different concentration of	
	DEA	

#### LIST OF FIGURES

### FIGURE NO.

TITLE

## PAGE

2.1	Schematic of simple acid gas removal unit	16
3.1	Flowchart of methodology	23
3.2	Process Flow Diagram of AGRU	24
3.3	Fluid Package Basis (Amine fluid Package)	25
3.4	Component selection windows	26
3.5	Simulation approach for the absorber and	27
	regenerator	
3.6	Simulation Environment	28
3.7	Converged window of the Absorber	29
3.8	Converged window for regenerator unit	30
4.1	The absorption performance by the number of	35
	stage (height of column)	
4.2	CO <sub>2</sub> Absorption efficiency with increasing	35
	CO <sub>2</sub> loading	
4.3	CO <sub>2</sub> Absorption efficiency with increasing	36
	liquid load	
4.4	Effect of Circulation Rate on CO <sub>2</sub>	37
	composition in Sweet Gas	
4.5	Effect of increasing the concentration of	39
	amines to the $CO_2$ in the Sweet Gas	
4.6	Effect of increasing amine concentration to	40
	the CH <sub>4</sub> losses in Sweet Gas	
4.7	Effect of increasing MEA concentration to the	42
	reboiler duty	
4.8	Effect of increasing DEA concentration to the	43
	Reboiler duty	

## LIST OF ABBREVIATION

CH <sub>4</sub>	-	Methane
$C_2H_6$	-	Ethane
$C_3H_8$	-	Propane
$C_{4}H_{10}$	-	Butane
$C_{5}H_{12}$	-	Pentane
CO <sub>2</sub>	-	Carbon Dioxide
COS	-	Carbonyl Sulfide
$CS_2$	-	Carbon disulfide
MDEA	-	Methyldiethanolamine
MEA	-	Monoethanolamine
DEA	-	Diethanolamine
$H_2S$	-	Hydrogen sulfide
AGRU	-	Acid Gas Removal Unit
Ppm	-	Part Per Million
TEA	-	Triethanolamine (TEA)
TSCF	-	Trillion standard cubic feet

## LIST OF SYMBOLS

°C : Celsius % : Percent

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 NATURAL GAS AND IMPURITIES REMOVAL

Natural gas has now become a crucial component of world's supply energy. The demand for natural gas has risen drastically over the past few years due to its importance in various industries and also for the domestic purposes. Malaysia is ranked 14th in the world in terms of its gas reserves and as of 1st January 2008, the natural gas reserves in Malaysia stood at 88.0 trillion standard cubic feet (tscf) or 14.67 billion barrels of oil equivalent, approximately three times the size of crude oil reserves of 5.46 billion barrel (Gas Malaysia, 2008).

The production of Natural Gas started millions of years ago. It is combustible mixture hydrocarbon gases with colorless, shapeless, and odorless characteristics. It is a subcategory of petroleum that is a naturally occurring, complex mixture of hydrocarbons, with a minor amount of inorganic compounds. It is formed from the remains of ancient microorganisms as well as plant and animal matter that have undergone conditions of extreme heat and pressure over very long periods of time. Intense compression and high temperature conditions cause carbon bonds in the organic matter to break down, a chemical transformation resulting in the formation of natural gas and other fossil fuels.

Natural gas has to be purified to meet the quality standards specified by the major pipeline transmission and distribution companies since the natural gas contains others impurities such as liquids (water, heavier hydrocarbons), sand, mercury and other gasses like nitrogen, helium and acid gases (carbon dioxide, hydrogen sulfide

and mercaptans such as methanethiol and ethanethiol). Carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and other sulfide compound are the main acid gases that may require complete or partial removal as they can cause corrosion, reduce the heating and sales value of the gas to meet gas purchaser's acceptance in distribution specification, safety and transport requirement. Those quality standards vary from pipeline to pipeline and are usually a function of a pipeline system's design and the markets that it serves. Generally, one of the standards specifies that natural gas contain no more than trace amounts of components such as acid gases. In general, an acid gas pipeline specification is 4.0 ppm H<sub>2</sub>S and 1.0% CO<sub>2</sub> (Arnold et.al, 2007). At 0.13 ppm by volume, H<sub>2</sub>S can be sensed by smell. At 4.6 ppm the smell is quite noticeable (Fahim et.al, 2003).

However, one of the challenges of operating the gas processing plant is how the operational procedures can be adjusted to meet the dynamic and future demands of customers. Thus, acid gas removal simulation is an essential tool for control and operations in gas processing plant because it can be used to stimulate and analyses the acid gas removal unit (AGRU) under different operating conditions. Analyses of chemical and phase equilibrium are needed whenever significant changes in patterns and magnitudes of demand or supplies occur (Alfadala, 2009). In the absence of such analyses, the operational procedures may not be optimal, resulting in unnecessarily high operating cost.

The main removal processes are based on absorption and selectivity of the solvent with respect to acid gases is based on an affinity of the chemical or physical type. Removal of  $H_2S$  and  $CO_2$  from natural gases by using alkanolamines technology has been around for decades. By simply changing their amine solutions, many inefficient acid gas removal units can be optimized. Suitable amine selection can drastically reduce the regeneration energy requirement and solution circulation rate. Hence, the process conditions can have a dramatic impact on the overall costs associated with AGRU.

Industrially important alkanolamines for this AGRU are monoethanol amine (MEA), diethanol amine (DEA) and methyldiethanol amine (MDEA). Monoethanolamine (MEA), a primary amine, has been used extensively because of its high reactivity and low solvent cost. MEA is used in solution in concentration of 10% to 15% by weight. MEA on the other hand, reacts irreversibly with COS, CS<sub>2</sub> and mercaptans. It is very reactive, it absorbs H<sub>2</sub>S and CO<sub>2</sub> at once and no selectively. Its relatively high vapor pressure causes larger losses compared with the other amines and for this reason, it is mainly used for intensive purification. Dietanolamine (DEA) helps to overcome the limitation of MEA, and can be used in the presence of COS and CS<sub>2</sub>. Methyldiethanolamine (MDEA) are commonly used as chemical solvent for the removal of CO<sub>2</sub> from gas mixtures or in gas sweetening processes for the extraction of CO<sub>2</sub> and H<sub>2</sub>S (Furhacker, Pressl& Allabashi, 2003). It has become the industry's standard for selective treating application which do not require removal significant quantities of COS, mercaptans and other trace of sulphurcontaining contaminant (Okimoto, 1993). Process modelling, simulation and optimisation are practiced to reduce production cost, shorten research and development period, increasing the process effectiveness, improving product quality, handle the sophisticated problem in industry (Turton et. al, 1998). Process simulator, such as Aspen Hysys simulator, plays an important role to accomplish these objectives. Simulator can also be used to design and scale up a new plant, or optimise an existing plant.

#### **1.2 PROBLEM STATEMENT**

Since the 1960s and 1970s, several amines have come into general use, but there is little information available on which amine is best suited to a particular service. Many inefficient amine gas sweetening units can be optimized by simply changing the amines.

Between 50–70% of the initial investment for an amine-sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10–20% of the initial investment depend on the regeneration energy requirement. Between 50–70% of the initial investment for an amine-sweetening unit is directly associated with the magnitude of the solvent circulation rate and another 10–20% of

the initial investment depend on the regeneration energy requirement. Approximately 70% of gas sweetening plants operating costs, excluding labour expenses, is due to the energy required for solvent regeneration (Khakdaman et. al, 2008). Each amine has a unique set of properties which make it desirable under certain conditions and undesirable under other conditions. The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either  $H_2S$  alone or  $CO_2$  alone if desired. The selection of amines best suited to the process conditions can have a dramatic impact on the overall costs associated with a sweetening unit.

Therefore, it is important to know the performance of MEA, DEA and MDEA as a chemical solvent in acid gas removal unit and the using of Aspen Hysys for simulated this process. The removal of acid gas impurities such as  $CO_2$  and  $H_2S$  from natural, refinery and synthesis gas streams is a significant operation in gas processing. The specifications on acid gas contents are essential by safety requirement (very high toxicity of  $H_2S$ ), transport requirements (need to avoid corrosion in pipeline and crystallization in case of liquefaction) and distribution specification (commercial gas).

#### **1.3 OBJECTIVES**

The main objective of this study is to model the acid gas removal unit (AGRU) using Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) as the solvent by using Aspen Hysys as computer simulator.

In addition, the other objective of this study is to compare the performance of Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) and develop processes with some improvement in term of the efficiency of the AGRU.

#### **1.4 SCOPE OF STUDY**

In this study, software for acid gases removal unit will be needed, that is Aspen Hysys. This software can be used to simulate the acid gas removal plant. One reactive absorption and desorption columns will be used to perform this simulation program.

Next, studies on Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) as the chemical solvent in the absorption column for the simulated acid gas removal process.

#### 1.5 RATIONALE AND SIGNIFICANCE OF STUDY

The study is essential, to model and improve the process of acid gas removal based on Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) by using Aspen Hysys.

Additionally, this study also significant, to identified the best chemical solvent for AGRU process by comparing MEA, DEA and MDEA.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 INTRODUCTION

Removal of acid gas components such as  $H_2S$ ,  $CO_2$  and other sulfur species (COS,  $CS_2$  and mercaptans) from natural gas, refinery gas or natural gas liquids by aqueous amines is a regularly encountered operation in the process industry. The removal of acid gases from natural gas is important either to meet certain process specifications or to keep emission limits. The major approach towards acid gas removal is absorption into solution of alkanolamines or potassium carbonate. In the practical application, such absorption plants consist of two gas-liquid reactors operated at different temperatures and pressures: absorber and regenerator. The choice of the type of amine will affect the required circulation rate of amine solution, the energy consumption for the regeneration and the ability to selectively remove either  $H_2S$  alone or  $CO_2$  alone if desired. Because of the large scale testing is expensive; it is more practical to use simulation to evaluate each process with different amines.

#### 2.2 AMINES

#### 2.2.1 Monoethanolamine (MEA)

Ethanolamine, also called 2-aminoethanol or monoethanolamine (often abbreviated as MEA), is an organic chemical compound which is both a primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group).

Like other amines, MEA acts as a weak base. Ethanolamine is a toxic flammable corrosive colorless viscous liquid with an odor similar to ammonia. Ethanolamine is commonly called monoethanolamine or MEA to differentiate it from diethanolamine (DEA) and trietanolamine (TEA). Monoethanolamine is produced by reacting ethylene oxide with ammonia. Further treatment with ethylene oxide can yield DEA or TEA or both DEA and TEA. (ICON Group International, 2008).

MEA should commonly be used as a 10 to 20% solution in water. The acid gas loading should usually be limited to 0.3 to 0.4 moles acid gas per mole of amine for carbon steel equipment. MEA itself is not considered to be particularly corrosive. However, its degradation products are very corrosive.  $CO_S$ ,  $CS_2$ ,  $SO_2$  and  $SO_3$  can partially deactivate MEA, which may essentially require to be recovered with a reclaimer.

Since MEA is primary amine, it has a high pH. This enables MEA solutions to produce gas containing less than 6 mg/Sm<sup>3</sup> ( $\frac{1}{4}$  grains H<sub>2</sub>S per 100 Scu.ft) of acid gas at very low H<sub>2</sub>S partial pressures. The heat of reaction for CO<sub>2</sub> in MEA is about 1930 kJ/kg of CO<sub>2</sub> (460 kcal/kg of CO<sub>2</sub>). The heat of reaction for all amines is a function of loading and other conditions. It varies by only 117 to 138 kJ/kg (28 to 33 kcal/kg) up to about 0.5 mole/mole of total acid gas loadings. Above this loading, the heat of reaction varies considerably and should be calculated as a function of loading. MEA will easily reduce acid gas concentrations to Pipeline Specifications (generally less than 6 mg H<sub>2</sub>S/Sm<sup>3</sup> gas (0.25 grains per 100 Scu.ft). By proper design

and operation, the acid gas content can be reduced as low as  $1.2 \text{ mg H}_2\text{S}/\text{Sm}^3$  gas (0.05 grains per 100 Scu.ft). (Engineering Standard, 1994)

#### 2.2.2 Diethanolamine (DEA)

Diethanolamine, often abbreviated as DEA, is an organic compound which is both a secondary amine and a dialcohol. A dialcohol has two hydroxyl groups in its molecule. Like other amines, diethanolamine acts as a weak base. Other names or synonyms are bis (hydroxyethyl) amine, diethylolamine, hydroxydiethylamine, diolamine and 2,2'-iminodiethanol.

DEA is commonly used in the 25 to 35 mass percent ranges. The loading for DEA is also limited to 0.3 to 0.4 mole/mole of acid gas for carbon steel equipment. When using stainless steel equipment, DEA can safely be loaded to equilibrium. This condition can be considered for carbon steel equipment by adding inhibitors.

The degradation products of DEA are much less corrosive than those of MEA. COS and CS<sub>2</sub> may irreversibly react with DEA to some extent. Since DEA is a secondary alkanolamine, it has a reduced affinity for H<sub>2</sub>S and CO<sub>2</sub>. As a result, for some low pressure gas streams, DEA cannot produce Pipeline Specification gas. However, certain design arrangement such as split flow may be considered to fulfill the specified requirement. Under some conditions, such as low pressure and liquid residence time on the tray (of about 2 seconds), DEA will be selective toward H<sub>2</sub>S and will permit a significant fraction of CO<sub>2</sub> to remain in the product gas. The heat of reaction for DEA and CO<sub>2</sub> is 151 kJ/kg of CO<sub>2</sub> (360 kcal/kg of CO<sub>2</sub>) which is about 22% less than for MEA. (Engineering Standard, 1994)

#### 2.2.3 Methyldiethanolamine, MDEA

MDEA which stands for methyldiethanolamine is a psychedelic hallucinogenic drug and empathogen-entactogen of the phenethylamine family. It has a larger capacity to react with acid gases because it can be used in higher concentrations. This advantage is enhanced by the fact that it is reacting with all of the  $H_2S$  and only part of  $CO_2$ .

MDEA also delivers energy savings by reducing reboiler duties and lowering overhead condenser duties. MDEA as an absorption solvent of removing acid gases is widely used today in natural gas processing because it possesses the characteristics such as higher H<sub>2</sub>S selectivity, bigger absorption capacity, lower regeneration energy, smaller hot degradation and lesser corrosive.

MDEA is most commonly used in the 30 to 50 mass percent ranges. Due to considerably reduced corrosion problems, acid gas loadings as high as 0.7 to 0.8 mole/mole are practical in carbon steel equipment. Since MDEA is a tertiary amine, it has less affinity for  $H_2S$  and  $CO_2$  than DEA. Thus, as in the case for DEA, MDEA cannot produce Pipeline Specification gas for some low pressure streams. MDEA has several distinct advantages over primary and secondary amines. These include lower vapor pressure, lower heats of reaction, higher resistance to degradation, fewer corrosion problems and selectivity toward  $H_2S$  in the presence of  $CO_2$ .

\*The physical properties and the operating condition of MEA, DEA and MDEA are shown in Table 2.1 and Table 2.2

# **Table 2.1** The physical properties of MEA, DEA and MDEA(Kohl and Riesenfield, 1985)

PROPERTIES	MEA	DEA	MDEA
Overall chemical	C <sub>2</sub> H <sub>7</sub> NO	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>	C <sub>5</sub> H <sub>13</sub> NO <sub>2</sub>
formula			
Molecular weight			
(kg/kgmol)	61.08	105.14	119.17
Melting point (°C)	10.5	28.0	-23.0
Boiling point at 101 325 Pa (°C)	170.6	269.2	247.4
Specific gravity	1.0179	1.0919	1.0418
(20°C/20°C)		(30°C/20°C)	
Absolute viscosity at	0.0241	0.3800	0.1010
20°C (Pa.s)		(30°C)	
Specific heat at	2546	2512	2238
15.6°C (J/kg.K)			
Flash point (°C)	93.3	137.8	129.4

Amine type	MEA	DEA	MDEA
Solution strength, wt%	15-20	25-35	20-50
Acid gas loading, mole/mole	0.30-0.35	0.30-0.35	Unlimited
Ability for selective absorption of H <sub>2</sub> S	No	Under Limited Conditions	Under Most Condition

**Table 2.2** Typical operating conditions and data for amines(Polasek & Bullin, 1994)

#### 2.3 COMPARATIVE STUDY OF MEA, DEA AND MDEA AS CHEMICAL SOLVENT

A rate-based model has been developed for the design of acid gas absorbers using aqueous alkanolamine solutions. The model adopts the film theory and assumes that thermodynamic equilibrium among the reacting species exists in the bulk liquid. The program was developed to handle either monoethanolamine (MEA) or diethanolamine (DEA) as chemical solvents. As showed in the result, the number of stages required to meet the H<sub>2</sub>S specification is less for MEA as compared with DEA. This is primarily due to the higher reactivity of MEA with the acid gases. The concentration of H<sub>2</sub>S drops down to almost zero at about stage 16 for MEA as compared to stage 18 for DEA (Nadhir A. Al-Baghli et.al, 2001). Additionally, as the pressure is lowered, MDEA becomes less capable of picking up sufficient  $CO_2$  to meet pipeline specification. When large amounts of  $CO_2$  are being passed through to the sweet gas at relatively low pressures, it becomes difficult for MDEA to reach pipeline specification for H<sub>2</sub>S if the inlet gas contains more than about 1000 ppm H<sub>2</sub>S. At these lower pressures, the addition of a more reactive amine clearly enhances the solution ability to remove  $CO_2$ . Thus, in areas where MDEA cannot meet the residual gas requirements. Usually, to improve the plant performance the mixed amines will be used (Zare Aliabadi et.al, 2009).

From the previous study of John Polasekjerry and A. Bullin on selecting best amines for ARGU, they have compared the few amines such as MEA, DEA, Diglycolamine (DGA) and mixed amines (MEA, DEA and MDEA). The main selection is based on the pressure and acid gas content of the sour gas as well as the purity specification of the sales gas. As the result, MEA is usually not the first amine considered due to its high heat of reaction and lower acid gas carrying capacity per gallon of solution.

However, MEA is still used for plants where the inlet gas pressure is low and pipeline specification gas or total removal of the acid gases is desired. DEA is known as "workhorse" of the industry in late 1960and early 1970, due to its lower heats of reaction, higher acid gas carrying capacity and resultant lower energy requirements. DEA have potential for selective H<sub>2</sub>S removal from streams containing CO<sub>2</sub> under certain conditions.

Depending on the application, MDEA has some outstanding capabilities. Due to its low heat of reaction, it can be used in pressure swing plants for bulk acid gas removal. MDEA is currently best known for its ability to preferentially absorb  $H_2S$  and is used in tail gas cleanup units since it is desirable to slip as much  $CO_2$  as possible while absorbing the maximum amount of  $H_2S$  to be recycled back to the Claus unit. Mixed amines are typically mixtures of MDEA and DEA or MEA which enhance  $CO_2$  removal while retaining desirable characteristics of MDEA such as reduced corrosion problems and low heats of reaction (Polasekjerry and Bullin, 1994).

MEA is effective at removing almost all hydrogen sulfide and carbon dioxide, but requires a large quantity of heat to regenerate. MEA is used when the specification requires maximum hydrogen sulfide and carbon dioxide removal, particularly at low pressure. MEA reacts with carbonyl sulfide and carbon disulfide, forming non-regenerative degradation products. DEA is used when the specification allows for some carbon dioxide to be left in the treated gas and suit for gas steams with less stringent product specifications. DEA does not form non-regenerative degradation products with carbonyl sulfide, which makes it a suitable choice for treating refinery gases.

MDEA is a weak base that reacts much faster with hydrogen sulfide than with carbon dioxide, making it particularly selective under the proper design conditions. MDEA is used selectively on higher-pressure gas steams (20.6 Bar G. and above) for deep hydrogen sulfide removal with only moderate carbon dioxide removal. MDEA can also be used non-selectively for bulk removal of carbon dioxide from gas streams, but bulk removal requires the aid of absorption enhancing additives. MDEA is well suited for selective absorption on high-pressure gas streams (Wittenemann, 2008).

#### 2.4 ACID GASES

Acid gas is component of natural gas that contains significant amounts of hydrogen sulfide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), or similar contaminants. Small amounts of hydrogen sulfide occur in crude petroleum, but natural gas can contain up to 90%. Natural gas is usually considered sour if there are more than 5.7 milligrams of H<sub>2</sub>S per cubic meter of natural gas, which is equivalent to approximately 4 ppm by volume (Gas Malaysia). Table 2.3 shown the typical composition of natural gas mixture from Qatar which contain quite large amount of sour gas.

 $H_2S$  is a colorless, flammable, extremely hazardous gas with a "rotten egg" smell. Some other names for  $H_2S$  are sewer gas, stink damp, swamp gas and manure gas. It occurred naturally in natural gas and produced by bacterial breakdown of organic materials and human and animal wastes.  $H_2S$  not only has an unpleasant odour, but also is highly poisonous, being almost as toxic as hydrogen cyanide and five to six times toxic as carbon monoxide.  $H_2S$  is slightly heavier than air; a mixture of  $H_2S$  and air is explosive.  $H_2S$  is soluble in water and acts as a weak acid. A solution of  $H_2S$  in water is initially clear but over time turns cloudy. This is due to the slow reaction of  $H_2S$  with the oxygen dissolved in water, yielding elemental sulfur which precipitates out. When burned it produces sulphur dioxide (SO<sub>2</sub>), which is also obnoxious and corrosive. Its presence in synthesis gases may result in catalyst poisoning and product contamination (M. Reeid & C. Updegraff, 1950).

 $CO_2$  is a chemical compound composed of two oxygen atoms covalently bonded and one single carbon atom that exist in gas phase at standard temperature and pressure.  $CO_2$  is colorless and non-flammable. At low concentrations, the gas is odorless. At higher concentrations it has a sharp, acidic odor. $CO_2$  present in the natural gas need to be removed in other to increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and crystallization of  $CO_2$ during cryogenic process (liquefaction process).

Component	Mole Fraction
Nitrogen	3.97
$H_2S$	0.96
CO <sub>2</sub>	2.45
Methane	82.62
Ethane	4.84
Propane	1.78
i-Butane	0.39
n-Butane	0.67
i-pentane	0.29
n-pentane	0.27
n-hexane	0.34
H <sub>2</sub> O	1.42
Total	100

**Table 2.3** Typical composition of natural gas mixture. A sample was takenfrom Qatar's North Field (Qatargas, 2002)

#### 2.5 ACID REMOVAL PROCESS

Varieties of processes and improvement have been developed over the years to treat certain types of gas with the aim of optimizing capital cost and operating cost, meet gas specifications and for environmental purpose. There are many type of treating the acid gas from natural gas. These processes are including chemical solvents, physical solvents, and adsorption processes hybrid solvent and physical separation (membrane). The main processes are based on absorption, and selectivity of the solvent with respect to acid gases is based on an affinity of the chemical or physical type.



Figure 2.1 Schematic of simple acid gas removal unit (Nordenkampf, 2003)

From figure 2.1, the sour gas is entered in the absorber where it contacts with amine solution flowing down the column. The acid gas components,  $H_2S$  and  $CO_2$  are absorbed by the amine solution and sweet gas leaves the absorber for advance processing. The absorber allows counter-current flow of lean amine from the top and sour gas from the bottom. The rich amine is flow to the bottom while the sweet gas is collected at the top for further processing.

The throttling valve is used to expand the rich amine coming from the high pressure contactor; this is done by lowering gas pressure before entering the flash tank. The rich amine that contains the acid gases is sent to a stripper or regenerator. The rich amine is stripped at low pressure to remove the absorbed acid gases, dissolved hydrocarbon, and water.

Finally, a heat exchanger cools the lean solution before completing the loop back to the absorber and entering the absorber. The rich/lean exchanger is a heat conservation device where hot lean solvent preheats cooler rich solvent. The lean amine solvent from the re-boiler through heat exchanger is further cooling before entering the absorber again. The reflux and pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber.

In solvent absorption, the two main cost factors are the solvent circulation rate, which affects both equipment size and operating costs, and the energy requirement for regenerating the solvent. The advantages of using amines technology are ability to reduce the concentration of  $H_2S$  and  $CO_2$  to ppm levels and relatively insensitive to  $H_2S$  and  $CO_2$  partial pressure.

#### 2.6 PROCESS CHEMISTRY

One of the most usually used processes for the removal of acid components is absorption in alkanolamine based solvents. In this process, the acidic components react with an alkanolamine absorption liquid via an exothermic, reversible reaction in a gas or liquid contactor. In a next process step, the acidic components are removed from the solvent in a regenerator, usually at low pressure or high temperature. (Huttenhuis et. al, 2007)

The various reactions between amines and acid gases have been described on numerous occasions. In general, the  $H_2S$  is thought to react almost instantaneously with the amines by proton transfer.

$$H_2S + Amine \leftrightarrow [Amine] H^+ + HS^-$$
(i)

$$CO_2 + H_2O + Amine \leftrightarrow [Amine] COOH^+ + OH^-$$
 (ii)

$$CO_2 + H_2O + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO_3^-$$
(iii)

In reaction (i), the reaction of  $H_2S$  is thought to react almost instantaneously with the amines by proton transfer. In reaction (ii),  $CO_2$  is thought to react with primary and secondary amines to form a carbamate.

Since MDEA is a tertiary amine and does not have hydrogen attached to the nitrogen, the  $CO_2$  reaction can only occur after the  $CO_2$  dissolves in the water to form a bicarbonate ion. The bicarbonate ion then undergoes an acid-base reaction with the amine to yield the overall  $CO_2$  reaction.

$$CO_2 + H_2O + R_2NCH_3 \leftrightarrow R_2NCH_4^+ + HCO3^-$$
 (iv)

Since the  $CO_2$  reaction with the amines is relatively slow and the  $H_2S$  reaction is fast, the  $H_2S$  absorption is generally assumed to be gas phase limited while the  $CO_2$  absorption is liquid phase limited. Since the  $CO_2$  reaction rate with the primary and secondary amines is much faster than with MDEA, the addition of small

amounts of primary or secondary amines to an MDEA based solution should greatly improve the overall reaction rate of  $CO_2$  with the amine solution.

MDEA allows the selective absorption of  $H_2S$  in the presence of  $CO_2$ , but can be use effectively to remove  $CO_2$  from natural gas in present of additives. If R denotes the functional group HOCH<sub>2</sub>CH<sub>2</sub>-, between  $CO_2$  and MDEA solution is presented as follow:

$$2RNH_2 + H_2S \leftrightarrow (RNH_3)_2S \tag{v}$$

$$(RNH_3)_2S + H_2S \leftrightarrow 2RNH_3HS$$
(vi)

These reactions happened very fast and direct. The first amine was used is triethanolamine, RNH<sub>3</sub>.

The absorption of hydrogen sulphide gas follows these equilibria:

$$H_2S (vap) = H_2S (aq)$$
(vii)

 $H_2S (aq) = H^+ + HS^-$  (viii)

$$HS^{-}(aq) = H^{+} + HS^{-}$$
(ix)

Adding a basic reagent such amines will increase the pH of the solution. pH is defined as:

$$pH = -\log aH^+$$
(x)

where  $aH^+$  is the activity of the hydrogen ion.

The activity of the hydrogen ion is defined as:

$$aH + = \gamma H + [H +] \tag{xi}$$

where  $\gamma$ H+ is the activity coefficient for hydrogen ion and [H+] is the concentration of hydrogen ion.

As pH increases, the concentration of hydrogen ion decreases. As hydrogen ion decreases, the equilibria above shift to restore the equilibrium. As hydrogen ion concentration decreases, this equilibrium will dissociate more bisulfide ion (HS-) to replace the hydrogen ion. The bisulfide ion concentration will also decrease as the hydrogen ion decreases. This equilibrium will also shift to the right (decreasing the H<sub>2</sub>S concentration) as the hydrogen ion concentration decreases. A double effect occurs since the bisulfide ion is also decreasing. As the aqueous hydrogen sulfide concentration decreases, the amount of hydrogen sulfide remaining in the vapor phase will also decrease. This is why scrubbing of an acid gas using a basic solution works.

Carbon dioxide follows a similar equation path:

$$CO_2 (vap) = CO_2 (aq)$$
 (xii)

$$CO_2 (aq) + H_2O = H + HCO_3 -$$
(xiii)

$$HCO_3 = H + CO_3^{2}$$
 (xiv)

For similar reasons as with hydrogen sulfide, increasing the solution pH will cause more carbon dioxide to be absorbed.

#### 2.7 HYSYS PROCESS SIMULATION PACKAGE

AspenTech bought the program HYSYS from Hypro-Tech in 2002, and in 2006 the program name was changed to Aspen HYSYS. Aspen HYSYS has an Amines Property Package. Within this Package, one of the two models, Kent Eisenberg or Li-Mather that can be selected. The simulation program developed is used to adjust the physical, thermodynamics and transport properties of the gas and the process units involves to improve process environmental performance. The simulation program Aspen HYSYS is mainly based on equilibrium calculations.

In Aspen HYSYS, gas/liquid equilibrium for a component is normally calculated using K-values defined by the equation,

where yi, xi are the mole fractions of component in the gas and liquid phase, thermodynamic K-value.

Vapour phase composition is not at phase equilibrium. For general purpose use, equation of state models like SRK (Soave Redlich Kwong) and PR (Peng Robinson) are often used. Aspen HYSYS recommends Peng Robinson. Peng Robinson is suitable to handle systems containing hydrocarbons, water, air and combustion gases, the typical components in a natural gas based power plant.

#### **CHAPTER 3**

#### METHODOLOGY

#### **3.1 INTRODUCTION**

Simulator can also be used to design and scale up a new plant, or optimise an existing plant. Simulation of an Acid Gas Removal process makes use of the unit in gas processing plants that have been developed based on the physical laws controlling the process. The simulation allows us to predict the amount of acid gases in processed natural gas under different condition.

An important advantage with using a process simulation program for such calculations is that the available for model thermodynamic properties can be used. Aspen HYSYS has an Amine Property Package. Within the Amines Property Package, one of the two models, Kent Eisenberg or Li-Mather, can be selected.

Major challenges in the simulation of  $CO_2$  absorption and desorption processes, are the description of thermodynamics and absorption, efficiency, convergence and total energy or cost optimization. Generally, the processes can be simulated using two methods; equilibrium stage method and rate based method. The rate method is known for capability of handling actual trays and height of packing without the use of stage efficiencies, which is important for the equilibrium stage method. Equilibrium stage method is not practical due difficulties that might be associated with finding efficiencies.

Therefore, this research will give an effective way to predict such efficiencies sufficiently. In this simulation, aqueous concentration used for DEA, MEA and



Figure 3.1 Flowchart of methodology

#### 3.2 OBTAIN THE FLOW SHEET AND DESIGN DATA OF AGRU

Flow sheet is a schematic diagram showing the equipments that makes up a process plant and the information on flow rates and quantities of material. Flow sheet of AGRU as shown in figure 3.2 is important to indicate the general flow of AGRU and. Its display the relationship between major equipment of a plant facility and does not show minor details such as reactor details and designations. After carefully assessment of existing literature about the selection of an efficient and reliable alternative flow sheet were found very few references. One of the reasons can be companies' secrets.



Figure 3.2 Process Flow Diagram of AGRU

# 3.3 SELECT THE SUITABLE PACKAGE FOR AGRU SIMULATION PROCESS

🖕 Fluid Package: Basis-1				
<ul> <li>HYSYS C Aspen Properties C</li> <li>Property Package Selection</li> <li>Anone&gt;</li> <li>Antoine</li> <li>ASME Steam</li> <li>Braun K10</li> <li>BWRS</li> <li>Chao Seader</li> <li>Chao Seader</li></ul>	COMThermo Package Filter ypes s rity Models o Seader Models ur Press Models ur Press Models ch <u>Property Wizard Property Wizard Package Filter Package Filt</u>			
Component List Selection         Component List - 1         View         Set Up       Parameters         Binary Coeffs       StabTest         Phase Order       Rxns         Tabular       Notes         Delete       Name         Basis-1       Property Pkg         Amine Pkg - KE       Edit Properties				

Figure 3.3 Fluid Package Basis (Amine fluid Package)

First step is to select the appropriate fluid package. In this simulation, the amine fluid package is selected as shown in figure 3.3. Kent-Eisenberg is selected for thermodyanamic models for aqueous amine solutions and non-ideal for vapour phase model.

## 3.4 SIMULATE AGRU PROCESS USING MEA, DEA AND MDEA AS A CHEMICAL SOLVENT

Add Component List View: Component List - 1	[	-Components Avail	able in the Compone	nt Library	
□:- Components       Nitrogen         □:- Traditional       H2S         □:- Traditional       CO2         Methane       Ethane         Propane       iButane         n:Butane       n:Pentane         n:Pentane       n:Hexane         H2O       DEAmme	< <u>A</u> dd Pure <-Substitute-> <u>B</u> emove> Sort List <u>V</u> iew Component	Match C Sim Name n-Octane n-Octane n-Octane n-Octane n-C11 n-C12 n-C13 n-C14 n-C15 n-C16 n-C17 n-C18 n-C19 n-C20 n-C21 n-C22 n-C23 n-C24 n-C25 n-C26 n-C27 	Full Name / C8 C9 C10 C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C21 C22 C21 C22 C23 C24 C25 C26 C27 C27 C27 C27 C27 C27 C27 C27 C27 C27	View Filt Synonym C Fo C8H1 C9H2 C10F C11F C13F C13F C13F C14F C15F C15F C15F C15F C15F C15F C15F C15	ers mula 16 A 18 A 10 122 122 124 124 126 122 124 128 130 132 134 136 138 140 142 144 144 1450 1552 154 155 <b>•</b>
Selected Component by Type					

Figure 3.4 Component selection windows

Then, components is selected. Figure 3.4 show dialog window for components selected.



Figure 3.5 Simulation approach for the absorber and regenerator

Figure 3.5 sum up the simulation approach for the absorber and regenarator. After selecting the component of the fluid, the simulation environment is entered as shown in figure 3.6, where the process flow diagram is built.



Figure 3.6 Simulation Environment

The number of stages, column pressure profile, raw natural gas and lean amine conditions, and modelling approach (equilibrium or rate) need all to be specified for the simulator. Since the unit into consideration is an absorber, the specification for reboiler and condenser needs to remove. In addition, supplying the absorber with a temperature profile as an estimate for a new run was found to be adequate.

The Amines property package require that real trays be used in the absorber and regenerator operations. Component specific efficiencies are required to model this in Aspen Hysys for  $H_2S$  and  $CO_2$  on tray by tray basis. These proprietary efficiency calculations are provided in the column as part of Amines package.

Tray dimension must be suppled to enable component specific efficiences to be calculate by estimating height of liquid on the tray and residence time of vapor in the liquid. After that, the column is run and converged as shown in figure 3.7 and figure 3.8.

Column: Absorb	er / COL1 Fluid Pkg: Basis-1 /	Amine Pkg - KE	_
Design	Column <u>N</u> ame Absorber	Sub-Flowsheet Tag COL1	
Connections			Ovhd Vapour Outlet
Monitor			Sweet Gas 📃 💌
Specs	Top Stage Injet		
Specs Summary	DEA to Absorber	$\frown$	
Subcooling		→ 1	
Notes	Uptional Inlet Streams Stream Inlet Stage	P1	Optional Side Dr <u>a</u> ws
	<pre>Stream &gt;&gt; *</pre>	Num of 6850 kPa Stages	Stream Type Draw Stage
		n = 25	< Stream >>
	Bottom Stage Inlet	Pn 6900 kPa	) I I I
	Gas to Absorber 📃	<u>n-1</u>	
	-Stage Numbering		
		Ť	Bottoms Liguid Outlet
	Edit Trays		Rich DEA
Design Param	eters Side Ops Rating Workshe	eet Performance Flowsheet	Reactions Dynamics
Delete	Column Environment Ryn	Reset	rerged 🔽 Update Outlets 🗆 Ignored

Figure 3.7 Converged window of the Absorber

Moving to the regenerator, the column specification such as number stages, feed stage, column pressure profile, reflux ratio, calculation mode and type of condenser were all must define to Aspen Hysys. After inserting the other physical unit operation such as valve, flash tank and heat exchanger, lean amines needs to be recycled back to the absorber.



Figure 3.8 Converged window for regenerator unit

After inserting the heat exchanger, mixer, cooler and pump needs to be recycled back to the absorber. The calculation for recycle stream start with the absorber and each complete cycle is one one iteration.

Aspen hysys will be iterating and updating the stream lean amine from previous lean amine till meets stream covergence tolerance. As the number of iteration increases, the more water looses from the absorber, flash tank and regenerator.

#### 3.5 COMPARE THE PROCESS PERFORMANCE

The data from the result will be analyzed and compare to make a conclusion of the study. It is important to know whether the hypothesis or the expected result based on literature review is correct or not.

The comparison will be based on solvent absorption capacity and efficiency in removing acid gas with different amines concentration,  $CO_2$  loading and circulation rate of amines.

#### 3.6 SUGGESTION FOR IMPROVEMENT

The modification will be done if there are any mistakes in the design and start from the beginning. Improvement is done from the parameters evaluated previously in determine the performance of amines.

#### **CHAPTER 4**

#### **RESULT AND DISCUSSION**

#### 4.1 INTRODUCTION

A simplified AGRU is selected for this study. The AGRU facility has identical amine trains for  $H_2S$  and  $CO_2$  removal by using DEA, MEA or MDEA. The train was composed of one absorber and one stripper columns, which operated in parallel in the unit. The HYSYS plant simulator was used to simulate the process. The simulation use Amines property package, Kent- Eisenberg and Non-ideal Models. Simulation results of amine – acid absorber are given in the Table 4.1.

	MEA	DEA	MDEA
Lean amine concentration,	15	25	50
wt%			
Gas flow:			
H <sub>2</sub> S Inlet (mol %)	0.009721	0.009721	0.009721
CO <sub>2</sub> Inlet (mol %)	0.024827	0.024827	0.024827
Sweet Gas stream:			
$H_2S \text{ comp (mol \%)}$	0	0	0
$CO_2 \text{ comp (mol \%)}$	0.000003	0.000304	0.015089
Outlet gas temperature,			
$T_{out}$ (°C)	35.15	35.19	35.20
Outlet liquid temperature,			
$T_{out}(^{\circ}C)$	46.95	46.18	38.77
No. of stages	25	25	25
Total rich loading,	0.44	0.34	0.11
(mole/mole)			
Reboiler duty,kJ/h	1.412e+007	1.391e+007	1.312e+007
Condenser duty,kJ/h	4.669e+006	4.665e+006	4.576e+006
Total Heat of	18.789e+006	18.575e+006	17.696e+006
Regeneration,kJ/h			

**Table 4.1** Simulation Results of Amine Acid Gas Absorber

With 1000 kgmole/hr of sour gas feed, it shows that, MEA removed almost  $CO_2$  with 0.000003 mol% left in sweet gas, followed by DEA 0.000304 mol%  $CO_2$  and MDEA 0.015089 mol%  $CO_2$ .

However, MEA presents some important disadvantages, such as higher amount of heat of regeneration and low absorption capacity limited at 0.4 kg of  $CO_2$ per kg of absorbent (Williams, 2006). Accordingly, the heat consumption at the regenerator by using different amines was in the following order MEA >DEA > MDEA.

MEA, DEA and MDEA show that it can totally remove the  $H_2S$  in the sweet gas since  $H_2S$  percent in the feed natural gas is so small which is only 0.009721 mol %.  $H_2S$ .

#### 4.2 ABSORPTION EFFICIENCY OF AMINES

The absorption efficiency is an important factor since it measures the masstransfer rate of acid gas into the absorption solvent that is required to achieve a removal target (Veawab et. al, 2002).

MEA and DEA were found to have a better  $CO_2$  absorption performance over MDEA. As shown in Figure 4.1, quite large amount of  $CO_2$  at the lowest stage was absorbed by the aqueous solutions of MEA and DEA within while certain amounts of  $CO_2$  in the treated gas (at the column top) were detected in cases of MDEA. Stage number 1 is referring to the top of the column while stage number 25 is the lower of the column.

Although both MEA and DEA were able to provide a complete removal of  $CO_2$ , their absorption performance can be distinguished by considering the column height required for the absorption. The  $CO_2$  absorption into the MEA solution took stage number 7 while the DEA at stage number 2 to complete the same task. This illustrated the better performance of MEA over the DEA solution.





Consequently, the absorption performance of the test solutions was in the following order MEA >DEA > MDEA.



Figure 4.2 CO<sub>2</sub> Absorption efficiency with increasing CO<sub>2</sub> loading

The absorption simulation was further conducted under different  $CO_2$  loadings of the solution and different liquid loads in order to broaden the performance comparison.

However, the performance of the  $CO_2$  absorption had an opposite relationship with the  $CO_2$  loading of the feed solution as shown in figure 4.2, it decreases with the increasing  $CO_2$  loading of the solution. The decline of the absorption efficiency as was caused by a reduction of the available reactive amine concentration that provided a driving force during the mass transfer. (Dibenedetto, 2002).



Figure 4.3 CO<sub>2</sub> Absorption efficiency with increasing liquid load

The result also shows that increasing the liquid load caused a reduction in the  $CO_2$  concentration of gas phase, representing greater absorption efficiency as shown in figure 4.3.

The liquid solutions at a higher flow rate experienced a smaller change in its concentration, while maintaining the absorption capacity throughout the column and sustain the mass transfer driving force. The absorption efficiency increased in the order of MEA > DEA > MDEA.

#### 4.3 THE EFFECT OF CIRCULATION RATE



Figure 4.4 Effect of Circulation Rate on CO<sub>2</sub> composition in Sweet Gas

The effect of increased circulation rate is that the removal grade increases. When the circulation rate is increased for any given column, the  $CO_2$  pickup will increase (Aliabad & Mirzaei, 2009). This usually holds true for each amine in a column of fixed diameter even through the liquid residence time on a tray will decrease with increased circulation. Since the solution circulation rate dictates, to a large degree, the plant size and duty, the results are presented in the form of residual acid gas concentrations as a function of circulation rate for amines.

A larger circulation rate of amine is also required to carry the  $CO_2$  in addition to the H<sub>2</sub>S. If the H<sub>2</sub>S to  $CO_2$  ratio is 0.1, 90% of the amine circulation is being used to transport  $CO_2$ , necessitating oversized pumps, columns, and exchangers (Polasek & Bullin, 1990).

From the simulaton result shown in table 4.1, it shows again the three amines successfully removed the  $H_2S$  in the sour gas. In the figure 4.4, MEA causes the  $CO_2$  to be almost completely absorbed in the column even at the lowest low circulation rate followed by DEA and MDEA since the  $CO_2$  reaction rate with the primary and

secondary amines (MEA and DEA) is much faster than with MDEA. (Abedini et. al, 2010).

A larger circulation rate of amine is also required to carry the  $CO_2$  in addition to the H<sub>2</sub>S. If the H<sub>2</sub>S to  $CO_2$  ratio is 0.1, 90% of the amine circulation is being used to transport  $CO_2$ , necessitating oversized pumps, columns, and exchangers (Polasek & Bullin, 1990).

#### 4.4 THE EFFECT OF AMINE CONCENTRATION

The process was simulated using different concentration of amines with constant circulation rate at 43 m<sup>3</sup>/hr, duty of the reboiler was considered constant at kJ/h and condenser temperature equals 50°C. From simulation result showed in table 4.2, MEA gives the best result of removing  $H_2S$  and  $CO_2$  compare to DEA and MDEA

Amines	<b>Amines</b> (10 <sup>-3</sup> )					
	MEA		DEA		MDEA	
Concentration,	$H_2S$	C02	$H_2S$	CO <sub>2</sub>	H <sub>2</sub> S	CO <sub>2</sub>
wt%						
10	0.000	0.0040	0.0120	11.961	0.8720	0.2320
15	0.000	0.0010	0.0010	0.4270	0.0000	0.1770
25	0.000	0.0010	0.0010	0.2740	0.0000	0.1860
35	0.000	0.0001	0.0010	0.2720	0.0000	0.1920
45	0.000	0.0010	0.0010	0.3010	0.0000	0.1990
55	0.000	0.0010	0.0010	0.3740	0.0000	0.2060

**Table 4.2** Simulation Result of mole component of H<sub>2</sub>S and CO<sub>2</sub> in

 sweet gas with different amine concentration



Figure 4.5 Effect of increasing the concentration of amines to the CO<sub>2</sub> in the Sweet Gas

Increasing the amine concentration is not always feasible because of corrosion. High primary and secondary amine concentration result in rich acid gas loadings are high enough to cause severe corrosion problems in the lean/rich exchanger and reboiler (Lunsford & Bullin, 1996). Figure 4.5 shows the CO<sub>2</sub> concentration in sweet gas as function of wt % amine. DEA, MEA and MDEA were studied while holding the other process variable constant.

For DEA,  $CO_2$  concentration decreased with increasing amine concentration. Based on Figure 4.5, MEA and MDEA at 15 wt % or greater is required to achieve the specified acid gas removal and 25 wt % for DEA. At certain concentration for each amine tends to pick up a large amount of acid gases and may cause corrosive conditions. DEA is a secondary amine, attempts on increase the amine concentration should be made since it increases  $CO_2$  pickup. However, it must not exceed the corrosion limits.



Figure 4.6 Effect of increasing amine concentration to the CH<sub>4</sub> losses in Sweet Gas

The effect of methane losses by increasing the concentration also been studied. From Figure 4.5, it shows that by increasing the concentration, it will increase the methane losses. The solubility of hydrocarbons in natural gas treating solvents represents lost product (kg/hr). In all amine plants, increasing the active ingredient concentration, amine, will increase hydrocarbon picked up by solution, because the less aqueous a solution becomes the greater its affinity becomes for hydrocarbon (Refinery Details Notebook, 1998)

#### 4.5 IMPROVEMENT ON HEATING REQUIREMENT

From previous study, MEA showed excellent performance in acid gas absorption efficiency compare to DEA and MDEA. Yet, it requires the most high consume heat to regenerate. Therefore, the simulation was extend to study on the improvement by minimize the reboiler duty on MEA and DEA since they required high of heat regeneration compare to MDEA. This can be done by increasing the concentration of amines.

## **Table 4.3** Simulation Result of Reboiler Duty at Regenerator with different concentration of MEA

MEA Concentration wt%	Reboiler Duty, kJ/h
15	1.411e+007
20	1.410e+007
25	1.408e+007



Figure 4.7 Effect of increasing MEA concentration to the reboiler duty

**Table 4.4** Simulation Result of Reboiler Duty at Regenerator with different concentration of DEA

DEA Concentration wt%	Reboiler Duty, kJ/h
25	1.393e+007
30	1.392e+007
35	1.391e+007



Figure 4.8 Effect of increasing DEA concentration to the Reboiler duty

The reboiler duty decrease by increasing the concentration of amines as showed in Table 4.3 and 4.4 along with Figure 4.7 and 4.8. One also can reduce heat of reaction by changing from a primary to secondary amine which both gives almost the same acid gas removal efficiency.

Regenerator reboiler duty requires sensible heat to raise the rich amine solution temperature to reboiler temperature, heat of reaction and heat of vaporization to vaporize enough water for adequate acid gas dilution throughout the regenerator column. (Amstrong & Gardner, 1998).

#### **CHAPTER 5**

#### **CONCLUSION AND RECOMMENDATION**

#### 5.1 CONCLUSION

This research is a direct study the effect of using Monoethanolamine (MEA), Dietanolamine (DEA) and Methyldiethanolamine (MDEA) as solvent on the gas treatment process using the software Aspen Hysys.

MEA remove almost of the acid gas in the feed natural gas but on the other hand it use high amount of heat to regenerate. By comparing the absorption efficiency with increasing CO<sub>2</sub> loading and liquid load, it showed that the performance was in the following order MEA >DEA > MDEA. However, MEA presents some important disadvantages, such as higher amount of heat of regeneration and low absorption capacity limit. Accordingly, the heat consumption at the regenerator by using different amines was in the following order MEA >DEA > MDEA.

Then improvement studies were extending to the effect of increasing the circulation rate, amines circulation and reboiler heat consumption. It showed that MEA is the best because the  $CO_2$  to be almost completely absorbed in the column even at the lowest low circulation. By increasing concentration of amine, MEA and MDEA showed at 15 wt % or greater is required to achieve the specified acid gas removal and 25 wt % for DEA Increasing the amine concentration increase the  $CO_2$  pickup. In addition, by increasing the concentration of MEA & DEA, it shows that the reboiler duty decrease.

#### 5.2 **RECOMMENDATION**

This research can be further demonstrated so that the proper selection of amine can have a major impact on the performance of AGRU. The research can broaden by using different simulation tools available to model the AGRU. The simulation also can be optimized on the utility cost and equipment size requirement of absorber or regenerator.

The study could be extend to improve or advanced by doing the comparison on the cost estimating for MEA, DEA and MDEA. Approximation comparing of the probable total cost of an acid gas removal unit by using differences amines evaluate the suitable and the best amine used in the unit. Therefore, the cost estimation can significantly reduce both capital and operating costs for amine plants.

As well, there are difference parameters such total energy requirement or study on the energy losses, product losses could be done in detail.

#### REFERENCES

Armstrong Tim & Gardner. (1998). *Refining Details Notebook Amine Selection*. Hoboken, NJ: Wiley.

Arnold & Stewart (1999). *Design of gas-handling systems and facilities*. (pp: 151-194). Elsevier. Inc. doi:10.1016/B978-088415822-6/50008-8

- B. Sohbi, M. Meakaff, M. Emtir & M. Elgarni. (2007). *The Using of Mixing Amines in an Industrial Gas Sweetening Plant*. World Academy of Science, Engineering and Technology, 1-5.
- Chow A. W, Foo C. Y.2, R. M. Yunus, R. A. Aziz & Z. A. Manan. Pilot Scale Rectification Column Modeling and Design for The Separation of Fatty Acid Mixture.Chemical Engineering Department, Universiti Teknologi Malaysia, 1-8.
- Engineering Standard for Process Design of Gas Treating Units Part 1:Process Design of Sweetening Units, 1994

- Hassan E. Alfadala and Al-Musleh. Simulation of an Acid Gas Removal Process Using Methyldiethanolamine; an Equilibrium Approach. Department of Chemical Engineering, Qatar University, Elsevier B.V,doi:10.1016/B978-0-444-53292-3.50033-X
- Inc Icon Group International (2002). *Formulating: Webster's Quatation, Facts and Phrases.* [Google books Reader version]. Retrieved from Google Books database.
- Jerry A.Bullin & John Polasek. (2006). *Selective Absorption Using Amines*. Bryan Research and Engineering, Inc., 1-8.
- Lars Erik Oi. (2007) Aspen HYSYS Simulation of CO2 Removal by Amine Absorption from a Gas Based Power Plant. Telemark University College, Norway.
- Lars Kuckaa, Ivo M-ullerb, Eugeny Y. Kenigb & Andrzej Gorakb.(2003). On the modelling and simulation of sour gas absorption by aqueous amine solution. Chemical Engineering Science, 58 (1), 3571 3578.
- M.Lunsford & A. Bullin (1996). *Optimization of Amine Sweetening Units*. Bryan Research and Engineering, Inc, 1-14.

Malaysia Energy Commission, power utilities, IPPs and self-generation plants. (2007). *Natural Gas Consumption by Sectors 1990 – 2007*. Retrieved 2007 from http://www.gasmalaysia.com/about\_gas/malaysian\_ng\_demand.htm Markus Bolhar, Nordenkampf, Anton Friedl &Ulrich Koss, Thomas Tork. (2000). Modelling selective H2S absorption and desorption in an aqueous MDEAsolution using a rate-based non-equilibrium approach. Chemical Engineering and Processing 43 (2004) 701–715

Moussa Dickoa, Christophe Coqueleta, Carmen Jarnea, Scott Northropb, Dominique Richona,( 2001).*Removal ofcarbon dioxide by absorption in mixed amines modelling of absorption in aqueous MDEA=MEA and AMP=MEA solutions*. Chemical Engineering Science 56 (2001) 6217–6224

Zare Aliabad, H., and Mirzaei, S. (2009). Removal of CO2 and H2S using Aqueous Alkanolamine Solutions. World Academy of Science, Engineering and Technology 49(1), 1-8



## APPENDICES

Appendix A Acid Gas Removal Unit Simulation Environment in Aspen Hysys