

**THE CHARACTERIZATION AND REMOVAL OF FOAM PROMOTING  
IMPURITIES FROM THE BLENDED METHYLDIETHANOLAMINE-  
PIPERAZINE SOLUTION USING MEMBRANE**

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PIPERAZINE SOLUTION USING MEMBRANE

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## **DEDICATIONS**

For my beloved Mother & Father  
My wife Wiriasti Ramadani  
My Children Nadilla, Devira and Valdano

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## ABSTRACT

The removal of acid gases from natural gas stream is an important process in many gas processing plants and for environmental protection. The most widely used acid gas removal technology nowadays is the absorption process using amine-based solvent. Foaming is the major cause that leads operational problems, resulting in excessive solvent losses, failure to meet treated gas specification and a reduction in gas treating capacity. Therefore, the main objectives of this research were to study the foam characteristics and the surface tension phenomenon of alkanolamines solution and to reduce their foaming promoters. The effect of natural gas impurities (foam promoters) in the blended methyldiethanolamine (MDEA)-piperazine solution such as hydrocarbon liquids, iron sulfide (dissolved solid), sodium chloride (salt), acetic acid (organic acid), methanol (hydrate inhibitor) and glycol (dehydrating agent) were investigated. The concentration of MDEA was found to significantly influence the foam activity in the solution. Iron sulfide, hydrocarbon and sodium chloride present in the solution had been identified as the impurities which apparently contributed to the high foaming tendency. At 5000 ppm concentration of impurities, the foam height achieved was 425 ml. Iron sulfide appeared to be the major foam promoter in the range of concentration solutions studied. Response surface methodology and central composite design had been applied to optimize the three factors that affected the foaming phenomenon. These factors were then correlated to the surface tension and foaming tendency. Asymmetric mixed matrix membrane (MMM) was applied to remove foam promoters in the amine solvent in order to reduce its foaming tendency. The MMM characteristics and performance were tested using scanning electron microscope, differential scanning calorimetry, Fourier transform infrared and membrane filtration tests. The contents of iron sulfide, hydrocarbon and sodium chloride as the main foam promoters had been successfully reduced as indicated by reduction of surface tension values by 12 %, 6.3% and 16 % respectively. These results indicated that membrane is a promising and viable technology to enhance the effectiveness of gas treatment system through the reduction of foam formation.

## ABSTRAK

Penyingkiran gas berasid daripada aliran gas asli adalah proses yang penting dalam kebanyakan loji pemrosesan gas dan untuk perlindungan alam sekitar. Penggunaan yang paling luas bagi teknologi penyingkiran gas berasid pada masa kini adalah proses serapan menggunakan pelarut berasaskan pelarut amina. Pembuihan adalah punca utama yang menyebabkan masalah operasi, yang juga mengakibatkan kehilangan besar pelarut, gagal mematuhi spesifikasi bagi gas terawat dan penurunan dalam keupayaan merawat gas. Oleh kerana itu, objektif utama penyelidikan ini adalah mengkaji ciri-ciri pembuihan dan fenomena tegangan permukaan larutan alkanolamina dan strategi untuk mengurangkan agen pembuihan. Kesan bendasing gas asli (agen pembuih) dalam larutan campuran metildiethanolamina (MDEA)-piperazina seperti cecair hidrokarbon, ferum sulfida (pepejal terlarut), natrium klorida (garam), asid asetik (asid organik), metanol (perencat hidrat) dan glikol (agen penghidratan) telah dikaji. Kepekatan MDEA didapati amat mempengaruhi aktiviti buih dalam larutan. Ferum sulfida, hidrokarbon dan natrium klorida adalah bendasing yang telah menyumbang kepada kecenderungan pembuihan yang tinggi. Pada kepekatan bendasing 5000 ppm, ketinggian buih yang dicapai adalah 425 ml. Ferum sulfida merupakan agen pembuih utama dalam julat kepekatan larutan yang dikaji. Metodologi permukaan respon dan rekabentuk eksperimen pusat telah diguna bagi mengoptimum tiga faktor yang mempengaruhi fenomena pembuihan. Faktor ini telah diguna untuk menghubungkaitkan kepada tegangan permukaan dan kecenderungan pembentukan buih. Membran tak simetrik campuran matrik telah diguna untuk menyingkir agen pembuihan di dalam larutan amina untuk mengurang kecenderungan pembentukan buih. Ciri-ciri dan prestasi membran campuran matrik telah diuji menggunakan mikroskopi imbasan elektron, pembezaan imbasan kalorimeter, Fourier pengubahan sinar infra merah dan ujian penurasan membran. Kandungan ferum sulfida, hidrokarbon dan natrium klorida sebagai agen pembuih utama telah berjaya dikurangkan seperti yang ditunjukkan dengan pengurangan nilai tegangan permukaan sebanyak 12 %, 6.3 % dan 16 % dengan menggunakan teknologi membran. Keputusan ini menunjukkan bahawa membran merupakan teknologi yang berdaya saing untuk meningkatkan keberkesanan sistem rawatan gas melalui pengurangan pembentukan buih.

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## LIST OF SYMBOLS

PI	:	Polyimide
PES	:	Polyethersulfone
NMP	:	1-methyl-2pyrrolidinone
CNTs	:	Carbon nanotubes
MMM	:	mixed matrix membrane
$T_g$	:	Glass transition temperature
FESEM	:	Field emission scanning electron microscopy
DSC	:	Differential scanning calorimetry
RSM	:	Response surface methodology
CCD	:	Central composite design
ANOVA	:	Analysis of variant
$\gamma$	:	Surface tension
$W_{adh}$	:	Weight adhesion
$W_{coh}$	:	Weight cohesion
L	:	Length
P	:	Pressure
F	:	Force
$f_v$	:	Force vertical
$f_s$	:	Force surface
$\alpha$	:	Contact angle
A	:	Area
T	:	Temperature
Å	:	Angstrom
$X_i$	:	Independent variable
n	:	Number of independent variables
$\alpha$	:	Star Point
$N_o$	:	Number of experiment at center point

$Y_p$	:	Predicted response
$Y_o$	:	Response variable
$\beta_0$	;	Offset term/constant
$\beta_1$	:	Linear term
$\beta_{11}$	:	Squared term
$\beta_{1j}$	:	Interaction term
$\beta_1$	:	Linear coefficient
$\beta_2$	:	Linear coefficient
$\beta_3$	:	Linear coefficient
$\beta_{11}$	:	Quadratic coefficient
$\beta_{22}$	:	Quadratic coefficient
$\beta_{33}$	:	Quadratic coefficient
$\beta_{12}$	:	Cross product coefficient
$\beta_{13}$	:	Cross product coefficient
$\beta_{23}$	:	Cross product coefficient
$R^2$	:	Coefficient of determination

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Introduction

Natural gas, whether produced from a condensate field or as associated gas from an oil reservoir, usually contains water vapor and frequently contains Hydrogen Sulfide ( $H_2S$ ) and Carbon Dioxide ( $CO_2$ ). The separation of gas impurities such as  $CO_2$  and  $H_2S$  from the gas mixtures is an important operation in natural gas treating, petroleum refining, coal gasification and ammonia manufacturing industries. The level of acid gas concentration in the feed gas is an important consideration for selecting the proper sweetening process. Some processes are applicable for removal of large quantities of acid gas but these processes might not sweeten to product specifications. Other processes have the capacity for removing acid gas constituents to the parts per million (ppm) ranges, which are only applicable to low concentrations of acid gas constituents in the feed gas to be treated. This process is called deep acid gas removal.

Carbon dioxide present in the natural gas needs to be removed in order to; increase the heating value of the gas, prevent corrosion of pipeline and gas processing equipment and prevent crystallization of  $CO_2$  during cryogenic processing. It is also found to be the major cause of the catalyst poisoning in ammonia synthesis (Astarita *et al.*, 1983). Natural gas pipe lines usually permit from 1% to 2% of  $CO_2$  and sometimes as high as 5% (Buckingham, 1964). In the past decades,  $CO_2$  removal from flue gas streams started as a potentially economic source of  $CO_2$ , mainly for the enhanced oil recovery (EOR) operations.

Organo-sulfur compounds and hydrogen sulfide are common contaminants in natural gas stream, which must be removed prior to most applications. The removal is not only aimed for the environmental protection but also to avoid problems such as corrosion and process blockage (Astarita *et al.*, 1983). Gas with a significant amount of sulfur impurities, such as hydrogen sulfide, is termed as sour gas; gas with sulfur or carbon dioxide impurities is called acid gas. The removal of these main impurities is called acid gas removal process.

## 1.2. Acid Gas Removal Technology

Acid gas removal is the absorption of acid gases such as carbon dioxide and hydrogen sulfide from natural gas, synthesis gas, refinery tail gas, and flue gas. There are many methods that can be employed to remove acid components from gas streams. The available methods can be categorized as those depending on chemical reaction, absorption, adsorption or permeation through a membrane. Process selection of gas separation depends on the raw gas conditions and treated gas specification. The most important raw gas condition is the partial pressure of the acid gas (mole fraction of acid gas times the total pressure, usually expressed in mm Hg). The alkanolamines are the most generally accepted and widely used of many available solvents for the removal of carbon dioxide and hydrogen sulfide in the natural and refinery gas treating unit. The alkanolamines use was patented since 1930 and is mainly used for the gas sweetening process (Maddox and Morgan, 1998). The alkanolamines, which are usually considered in the acid gas removal, are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA). However, triethanolamine is rarely used. All of these materials may be classified as “chemically reactive” substances and this is what accounts for their popularity for the sweetening natural gas.

The absorption of CO<sub>2</sub> by solutions of alkanolamines is mainly through chemical reactions where both kinetic and thermodynamic equilibrium play

important roles in determining the ultimate gas loading that can be achieved (Huntington, 1950). Alkanolamines are weak basic compounds that react with certain acid gases, forming weak chemical bonds. These bonds are easily broken upon mild heating. The strength of the alkanolamine's bond and the corresponding heat needed to break it depends on the number of organic hydrocarbon groups attached to the nitrogen atom. Depending on the number of such groups, alkanolamines are classified into three types, namely primary, secondary and tertiary. Alkanolamines are used primarily to absorb carbon dioxide and hydrogen sulfide (Koh and Riesenfeld, 1960). Carbon monoxide and nitrous oxides are very weak and do not chemically react with alkanolamines. Sulfur dioxide and nitrogen dioxide form very strong chemical bonds with alkanolamines. The heat required to break these bonds would decompose the alkanolamines themselves. They must be removed before treatment. Carbonyl sulfide and carbon disulfide react with primary amines, forming non-regenerative decomposition products, except in the case of diglycolamine (DGA).

Primary and secondary amines such as MEA and DEA respectively are very reactive and therefore exhibit high rates of absorption. MEA and DGA are primary amines (Libreros *et al.*, 2004a). However, MEA was the most widely used solvent compared to DGA. MEA with one ethanol group attached to the basic nitrogen atom is the strongest amine. It reacts quickly with both hydrogen sulfide and carbon dioxide, forming strong but thermally regenerative chemical bonds. MEA is virtually effective in removing all hydrogen sulfide and carbon dioxide, but requires a large quantity of heat to regenerate in order to break the chemical bonds formed. 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. DGA is similar to MEA in term of their performance, but DGA has a lower vapor pressure, which results in less solvent vaporization losses. DGA forms regenerable reaction products with carbonyl sulfide and carbon disulfide. Typically, this regeneration is carried out in the reclaimer at elevated temperature, as opposed to the reboiler where carbon dioxide and hydrogen sulfide are removed. DGA was specifically developed to replace MEA in low-pressure applications as a means of reducing vaporization losses.

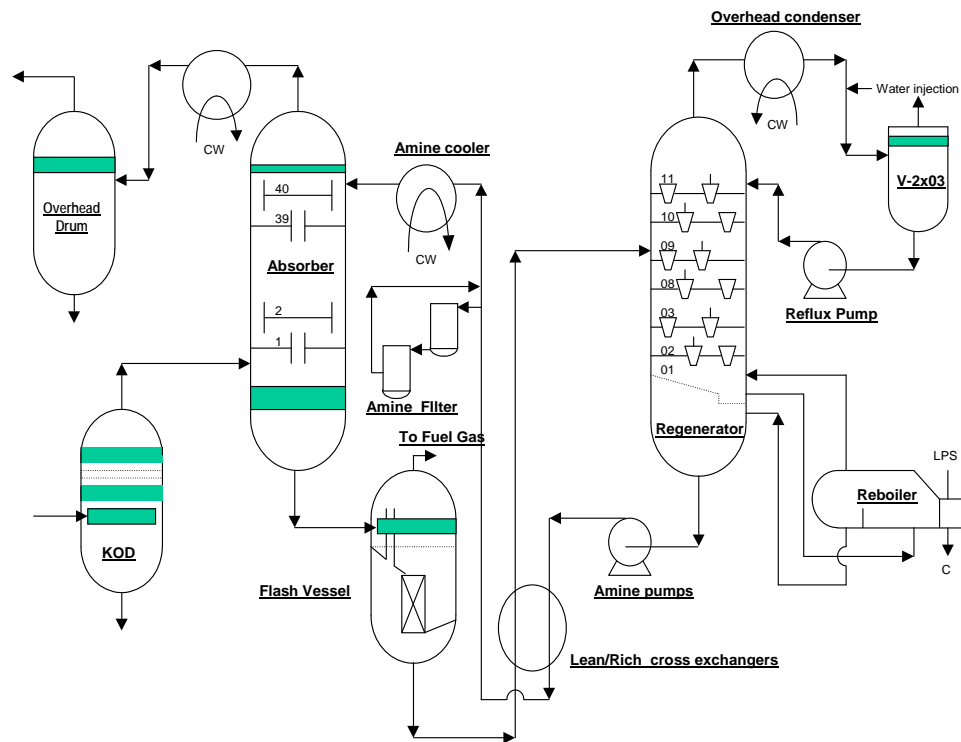
DEA came into use in refineries as a replacement for MEA. DEA and DIPA are included as secondary amines with two ethanol groups or two isopropanol groups, respectively, attached to the nitrogen atom. The additional alcohol groups draw most of the free electron characters away from the nitrogen atom, which in turn makes the secondary amines somewhat weaker bases. Secondary amines are suited for gas streams with less stringent product specifications. DEA was resistant to COS degradation which caused high corrosion rate. DEA is used when the specification allows for some carbon dioxide to be left in the treated gas. DEA does not form non-regenerative degradation products with carbonyl sulfide, which makes it a suitable choice for treating refinery gases. DIPA is used almost exclusively in refinery operations to remove carbonyl sulfide and hydrogen sulfide. DIPA is used with the presence of additives in both the Adip process and Sulfinol process. Secondary amines are less corrosive, require less heat to regenerate and can be used to treat the gas streams that contain carbonyl sulfide and carbon disulfide. However, secondary amines are not effective at deep carbon dioxide removal.

MDEA and triethanolamine (TEA) are tertiary amines (Libreros *et al.*, 2004a). MDEA has two ethanol groups attached to the nitrogen atom, along with a methyl group. 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 (Maddox and Morgan, 1998). MDEA's general acceptance followed after DEA. MDEA is a relative newcomer to the group of ethanolamines used for natural gas sweetening. It received a great deal of attention during the 1980's due to the lower energy costs for regeneration, its degradation resistance, lower corrosion and because of its capability for "selective" reaction with hydrogen sulphide in the presence of carbon dioxide. TEA is also a tertiary amine. TEA has three ethanol groups attached to the nitrogen atom. It is the weakest amine and requires the least heat to regenerate. TEA is only applicable on high-pressure gas streams when even moderate acid gas removal is not essential. Tertiary amines are less inherently corrosive and can be used in higher concentrations, but tertiary amines are not a good choice when the raw gas pressure is low or the specification calls for deep carbon



dioxide removal. However, tertiary amines, particularly MDEA, are well suited for selective absorption on high-pressure gas streams.

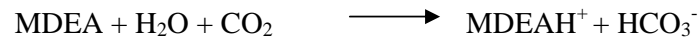
The general process flow for an amine sweetening unit is shown in Figure 1.1:



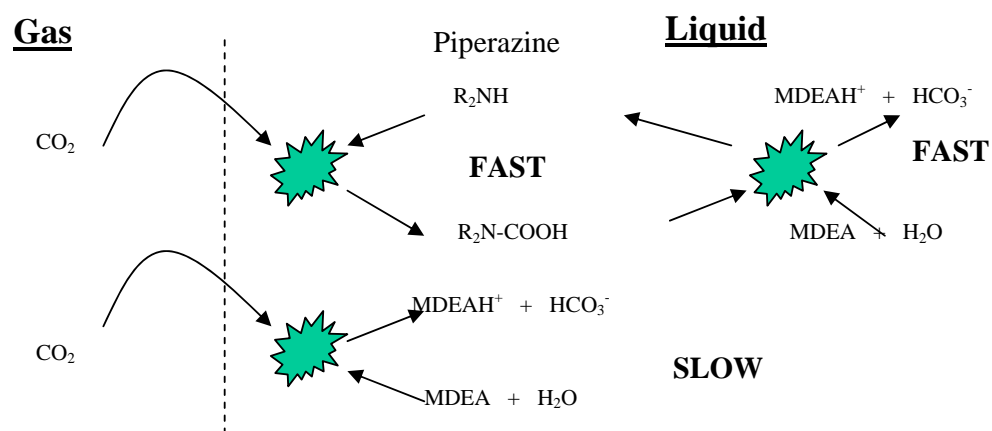
**Figure 1.1:** Typical amine-based process (Ratman, 2002)

The recent technology for CO<sub>2</sub> removal uses activator like piperazine (PZ) to enhance the rate of absorption especially when it is added to conventional alkanolamines. When added to conventional amines, PZ accelerates the carbon dioxide absorption due to the formation of di-carbamate which can be attributed to the unique six-sided ring structure of the molecule (Bishnoi and Rochelle, 2000). They observed that at low solution loading, the dominant reaction products are piperazine carbamate and protonated piperazine. However, at higher loading, the dominant reaction product obtained was protonated piperazine carbamate. From the kinetic mechanism of PZ, they also concluded that piperazine (PZ) can be an

effective promoter for carbon dioxide removal from gas streams. The carbon dioxide absorption follows the following reaction:



This reaction is slow and an activator (additive) is required to speed up the kinetics of the reaction. Piperazine (secondary amine) is added as an activator, which serves as both liquid catalyst and chemical corrosion inhibitor. In addition, some proprietary ingredients are added to enhance the solvent capability. The mechanism of absorption is illustrated in Figure 1.2.



**Figure 1.2:** General absorption mechanism in the reaction of MDEA-piperazine (Hasanah and Ratman, 2003)

The main advantage of activated MDEA is its high pick-up ratio of carbon dioxide compared to other solvents. This will result in a lower solvent circulation rate. It is claimed that there are no degradation products and very low hydrocarbon co-absorption. General important advantages of amine-based processes include low operating costs, as the chemical solvent is regenerated continuously. Another advantage are the capability to handle important turndowns and selective removal of hydrogen sulphide (Loo *et al.*, 2007). They are acceptably suited for low operating pressure applications where the acid gas partial pressure is low and low level of acid

gas is desired in the residue gas since their acid gas removal capacity is relatively high and insensitive to acid gas partial pressure, as compared to physical solvents. Alkanolamines are widely used in both natural gas and refinery gas processing industries. The process involved has an important acceptance in the industry.

### **1.3. Problem Statement**

In the acid gas removal plant, there are several common problems may be encountered during operations, such as failure to meet treated gas specifications, corrosion, excessive solvent losses and foaming (Blauwhoff *et al.*, 1985 and Aquila *et al.*, 2004). A failure to meet the treated gas specifications during operations are normally contributed by many factors, which can not be easily detected in the short time (Maddox and Morgan, 1998). The causes could be coming from the feed gas operating conditions, poor regeneration, mechanical failure of equipment, contaminated solvent and etc. The operator should investigate at the soonest and find the solution to sustain the production. If it could not be solved, a long term solution should be taken, such as repairing the mechanical failure and reclamation of contaminated solvent

Corrosion is another problem that can be detected in the long term period (Veldman, 2000). For all the types of alkanolamines, the presence of oxygen, a high content of acid gas, high temperature and also thermal degradation of the amine in the regenerator increase the likelihood of product degradation and corrosion problems. Corrosion management and monitoring the causes are normally applied for its mitigation. Like corrosion, the excessive solvent loss is known during long term period. It may be caused by the poor separation of demister pad and the solvent loss via acid gas venting. In the normal operation, it is very rare to loose huge amount of solvent, except when there is a big leak of the solvent inventory equipment, such as flash drum leaks, which isa due to the severe stress corrosion cracking which is commonly happened in the amine units.

Foaming is the most common cause of an upset of acid gas removal unit, resulting in excessive solvent losses, off specification treated gas and a reduction of treating capacity, which subsequently may affect the operating costs, revenues and

reputations (Bullin and Donnelly, 2006). Generally, when the amine solvents become contaminated, they can show a tendency to foam. In order for foaming to occur in gas liquid systems, the gas/liquid interface must be stabilized. This may comprise resistance of the surface against changes in the surface area as well as prevention of drainage of liquid from the boundary layer between foam cells. When the foaming appears, some actions and efforts are usually taken to control it, in order to avoid situation to be worsen that may give further significant impact to the plant operation. Therefore, the present study is devoted to studying the foaming phenomenon in the amine unit and to find the solutions in curing the basic foaming problems.

#### **1.4. Objectives of Study**

The aims of this study are to find the main foaming promoter in the amine solvent and to control the foaming tendency down to non-foamability level. The objectives are:

- a) To characterize the foaming phenomenon in the amine solvent.
- b) To identify the root causes that give major contribution to foaming.
- c) To find the most influential foaming promoter by using the amine foamability and surface tension data.
- d) To study the possibility of applying membrane-based technology to further reduces foaming promoter concentration.

#### **1.5. Scope of Study**

In order to achieve all of the objectives set above, several scopes have been outlined, which are:

- a) Preparing of blending MDEA-piperazine at various of concentration.
- b) Preparing the natural gas stream impurities such as hydrocarbon, iron sulfide, sodium chloride, methanol, organic acid and ethylene glycol at various concentrations.
- c) Preparing the solution of blending MDEA-piperazine with the several of impurities and concentration.

- d) Testing the MDEA-piperazine with natural gas stream impurities on foaming tendency and surface tension.
- e) Optimization of the effect of natural gas stream impurities on the surface tension using response surface methodology.
- f) Analyzing the possibility of the application of asymmetric mixed matrix membrane to reduce the foam promoter concentration into the level of non foamability solvent.

### **1.6. Significance of the Study**

In the recent gas and LNG industry, gas-treating unit stability is very important to achieve treated gas specification to the downstream units. Foaming is the most common cause of upset in the unit. In normal operation, the symptoms of foaming can be detected by fluctuating pressure drops in absorber and/or regenerator, amine carry over from absorber and/or regenerator, swinging liquid levels in any vessels/ columns, off-specification of treated gas and poorly stripped gas. In addition, the foam test results are the indication of increasing foam activity. When the foaming occurs, it may result in a number of different problems. Plant gas throughput may be severely reduced and treating efficiency may decrease to the point that treated gas cannot be met. In addition, amine losses may be significantly increased. Therefore, managing foam activity is crucial to maintain plant stability and to avoid significant financial and opportunity losses

In the case of uncontrolled foaming problem, amine circulation rate may be decreased to allow for the liquid bubbling to drop rapidly thus avoiding, more amine to be carried over to downstream equipment. As a result, gas throughput may be reduced as order to anticipate any acid gas breakthrough which will cause serious impact to the whole plant operation. The worst case, that may happen, is to trip amine pumps as a result of uncontrolled regenerator level drop. If this occurs, the whole plant will be shutdown to stop acid gas breakthrough to the unanimous number. The shutdown will result a loss of million dollars since the plant can not produce as expected. In addition, restarting up the plant takes time and efforts in

order to recover the plant back to the stable operation. Further impacts to the above problem are company reputation (and images), which may cause not to fulfill the commitment, environmental protection due to amine carry over and public complaint, which resulted in a shutdown with smoky flares.

## **1.5. Organization of the Thesis**

The thesis consists of six chapters. Chapter 1 presents the background, research problem, objectives and the significance of the study. Chapter 2 describes the background and discusses the theory of natural gas and carbon dioxide removal from natural gas. In addition, a review of previous experimental studies of foaming problem in carbon dioxide removal from natural gas using conventional process is also covered. Chapter 3 discusses the results of foam behavior of pure blended MDEA-piperazine solution as well as the effect of natural gas impurities against its foam behavior.

Chapter 4 extends the study to investigate the influences of natural gas impurities (as foam promoters) against surface tension parameter of the MDEA-piperazine solution. From the result obtained, the most influential impurities that produce high surface tension can be determined. Since some of the identified main foam promoters can be presented altogether in the MDEA solution during operation, in this chapter, the effect of these combined impurities in the solution is also investigated as well as to predict the maximum surface tension that can be achieved. The prediction of maximum surface tension is obtained by using statistical analysis, which is performed by a Statistica software version 6, in order to develop its mathematical model. In the final stage of this research (Chapter 5), the possible application of asymmetric mixed matrix membrane-carbon nanotube to reduce the concentrations of the main foam promoters that have been identified in the chapter 4 is discussed. This means to control the foam formation and to reduce the surface tension of the blended MDEA-piperazine solution. The general conclusions drawn from this research are provided in Chapter 6. Some recommendations for future research are also listed in this chapter.

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