

**Evaluation of MEG as alternative of TEG for higher performance of
natural gas dehydration**

by

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Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2012

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CERTIFICATION OF APPROVAL

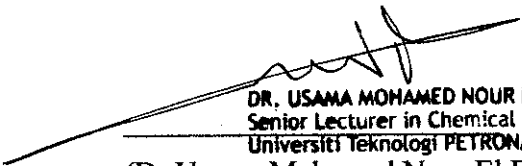
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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

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CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

Glycol dehydration is a widely used method for the removal of water from natural gas, using glycol as a solvent to absorb water from the gas stream. The presence of water will promote the occurrence of corrosion and hydrate formation along the gas pipelines. Tri-Ethylene Glycol (TEG) is commonly used as the solvent for glycol dehydration. The main environmental concern of this TEG process is the emission of benzene, toluene, ethylbenzene and xylene (BTEX) compounds to the atmosphere.

This study will be using Mono-Ethylene Glycol (MEG) as the solvent, where the objectives are to compare the performance of MEG with TEG, mainly in reducing the amount of BTEX emissions. The scopes of this study are the simulation of three glycol dehydration technologies which are basic, Stahl and Drizo. MEG will be used as the dehydrating agent in this study, and optimization of operating conditions is done in order to have an optimized process operation of MEG.

The data and results are obtained by process modeling using the Aspen Hysys simulation package. Performance of MEG is evaluated and compared with TEG. Based on our analysis we can see that the usage of MEG significantly reduced the amount of BTEX emissions without any need of equipment addition for the same glycol dehydration technology, where the amount of emission is almost zero. However, usage of MEG will result in higher amount of glycol losses. If MEG is used, it must be determined if the cost of glycol replacement is less than the cost of treating the BTEX emissions.

ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim. First and foremost, praise to Allah the Almighty, for His blessings and will that have helped and guided me in completing my Final Year Project.

I would like to express my sincere gratitude to both of my parents, for being very supportive and keeps on motivating me to complete this project. My greatest appreciation for my supervisor, Dr Usama Mohamed Nour El Demerdash for his guidance and sharing of knowledge that have helped me a lot in planning and executing the whole process throughout the completion of this project.

A huge thank you for Mr. Muhammad Aimen bin Isa for his willingness in assisting me and providing relevant information regarding this project and to Mr. Mohd Zaki bin Zainal Abidin for the time spent in guiding me especially in doing the Hysys simulations. Also, I would like to extend my appreciation to my friends and colleagues that have been a continuous source of support and strength for me throughout this final semester of my undergraduate studies.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural gas is a fossil fuel, a mixture of hydrocarbon gaseous which consists mainly of methane. Natural gas is an important energy source where it is used in many sectors, including industrial, electricity, residential and transportation sector.

Raw natural gas obtained from gas wells need to be processed to meet the specifications of markets and customers, where trace compounds such as sulfur, water vapour, hydrogen sulfide and carbon dioxide will be removed. Water vapour is an undesired impurity that has to be removed from the gas stream in order to prevent corrosion problems and the formation of hydrates. There are three major methods for natural gas dehydration which are direct cooling, adsorption and absorption method.

Glycol dehydration process is an example of absorption process, where a liquid desiccant is used to absorb water vapour from the gas stream. Glycol functions as a dehydrating agent that absorbs water vapour from the gas stream, where Tri-Ethylene Glycol (TEG) is most commonly used. TEG will come in contact with the gas stream in the absorber/contacting tower and water-free TEG will be regenerated to high glycol concentration where water is removed in a reboiler and TEG will be recirculated to the absorber. Different type of glycols can be used where the difference in properties of the glycols will affect the overall efficiency of the process. This study will investigate the usage of Mono-Ethylene Glycol (MEG), to be compared with the performance of TEG.

1.2 Problem Statement

Existence of water vapour in natural gas will lead to corrosion problems and hydrate formation. Corrosion will occur when water vapour comes in contact with hydrogen sulfide or carbon dioxide which are regularly present in natural gas stream. Hydrates formed can block pipelines, valves and other process equipments. Liquid water can also condense on the pipelines and accumulates at low points along the line and reducing its flow capacity. Natural gas dehydration is important in order to protect and ensuring smooth operation of gas transmission lines.

Glycol dehydration process is a common method to remove water from natural gas. The usage of TEG will absorb a huge amount of volatile organic compounds, mainly benzene, toluene, ethylbenzene and xylene (BTEX) compounds. Major environmental concerns of this process are the emissions of BTEX to the atmosphere, where BTEX has been listed among the Hazardous Air Pollutants (HAPs). Recent developments in environmental regulations have lead to the increase of selection of process alternatives to minimize the emissions of BTEX.

OPTIMAL Glycols (M) Sdn Bhd located in Kerteh, Terengganu is producing Mono-Ethylene Glycol (MEG) with production of 365,000 MTPA of MEG. The production of MEG locally in Malaysia is seen as an attractive alternative that can replace the usage of TEG and helps in reducing the emission of BTEX. Here in this project we are interested in evaluating the performance of MEG compared to TEG in a glycol dehydration system, mainly in reducing BTEX emissions.

1.3 Objectives

The objectives of this project are as listed below:

- i. To compare the performance of MEG and TEG in a glycol dehydration process
- ii. To minimize BTEX (benzene, toluene, ethylbenzene and xylenes) emission of the glycol dehydration process
- iii. To optimize the natural gas dew point temperature

1.4 Scope of Study

The scopes of study of this project are listed below:

- i. Simulation of three glycol dehydration technologies which are basic, Stahl and Drizo.
- ii. Usage of MEG as the dehydrating agent
- iii. Optimization of operating conditions in order to have an optimized process operation
- iv. Evaluation of MEG as alternative to TEG

1.5 Relevancy of The Project/ Project Significance

The main highlight in this project is the study of performance of MEG as a dehydrating agent. Several manipulations will be done on the operating conditions in order to obtain higher performance of the glycol dehydration process. This study is important in showing the comparison between using MEG with TEG, particularly in glycol recovery and reduction of environmental emissions. At the end of this project, it is expected to have a conclusion on the better glycol to be used for natural gas dehydration.

1.6 Feasibility of The Project

Two academic semesters has been allocated to accomplish the objectives of this project. The first semester will be used for literature analysis and deep understanding of the glycol dehydration method. Simulation of the process and optimization of the process parameters will be conducted in the second semester where the overall result will be recorded and the performance of MEG will be compared with TEG. Therefore this project is feasible within the scope of study and time frame given.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Gas Dehydration

Water vapour is an undesired impurity that contains in natural gas streams. Existence of water could lead to corrosion problems and also hydrate formation that will plug valves and gas lines. Liquid water will condense and accumulate along the gas lines, reducing the efficiency of the pipeline. Dehydration is the process of removing water from natural gas, where we are reducing the water content to an acceptable limit. According to Salamat (2009), the acceptable water content in a gas transmission line is 6-10 lb/MMscf (96-160 kg/MMm³) giving a gas dew point of 15-29 °F (-2 to -9 °C).

An important property of sales gas is the water and hydrocarbon dew point. Water dew point is the temperature where the water vapour in the gas stream will condense into liquid at a constant pressure. Hydrocarbon dew point is the temperature at which hydrocarbon components in the gas starts to condense. The dew point of the gas will decrease as the water content is reduced (Salamat, 2009). We have to keep the gas stream above both the water and hydrocarbon dew point in order to prevent condensation from occurring.

Below are the objectives of natural gas dehydration as discussed by Arubi & Duru (2008):

- i. Meet water dew point requirement of sales gas that is stipulated by buyers
- ii. Prevent hydrate formations in downstream units
- iii. Prevent pipeline corrosion, since process gas may be contaminated by acid gases (carbon dioxide and hydrogen sulfide).
- iv. Minimize free water condensing in the pipeline that reduced gas flow throughput.

Based on the issues caused by water presence in natural gas, this study will focus on solutions that can overcome these problems. There are three methods for natural gas dehydration, which are absorption, adsorption and condensation (Kohl & Nielsen, 1997).

2.2 Glycol Selection

Absorption process employs the usage of a liquid desiccant for natural gas dehydration. Below are the characteristics of liquid desiccants that are suitable to be used for commercial applications (Carroll, 2003).

1. Highly hygroscopic
2. The hydrocarbon components of the natural gas should have a low solubility in the solvent
3. Easily generated to higher concentration for reuse
4. Have a very low vapour pressure
5. Exhibit thermal stability, particularly in high temperature ranges found in the reboiler
6. Will not solidify in the temperature ranges expected in dehydration process
7. Non-corrosive to the equipments used in the process
8. Will not chemically react with any components in the natural gas

The glycols, particularly mono-ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T₄EG) come closest to satisfying these criteria. Water and the glycols show complete mutual solubility in the liquid phase due to hydrogen-oxygen bonds. The factors that have led to the widespread use of glycols for gas dehydration are their unusual hygroscopicity, their excellent stability with regard to thermal and chemical decomposition, their low vapour pressures and their ready availability at moderate cost. Tri-ethylene glycol (TEG) is the most commonly used liquid desiccant for this process. The properties of MEG and TEG can be referred in table below, as listed by Kohl & Nielsen (1997).

Table 2.1: Properties of Glycols

Property	Mono-Ethylene Glycol	Tri-Ethylene Glycol
Formula	$C_2H_6O_2$	$C_6H_{14}O_4$
Molecular weight	62.1	150.2
Boiling point @ 760 mmHg, $^{\circ}C$	197.6	288.0
Initial decomposition temperature, $^{\circ}C$	165	207
Density @ 25 $^{\circ}C$, g/ml	1.110	1.119
Vapour pressure @ 25 $^{\circ}C$ (Pa)	12.24	0.05
Viscosity, abs, cp		
@ 25 $^{\circ}C$	16.5	37.3
@ 60 $^{\circ}C$	5.08	9.6

2.3 Background on Aromatic Components in Natural Gas Stream

The aromatic series (type formula C_nH_{2n-6}) is chemically active, where it may form either addition or substitution products. It contains a benzene ring that is unsaturated but very stable and frequently behaves as a saturated compound. The BTEX compounds (benzene, toluene, ethyl benzene and xylene) are large volume aromatics used by the petrochemical industry.

The BTEX has been listed as hazardous air pollutants (HAPs) in the year 1990 under the Clean Air Act Amendments (Collie, Hlavinka, & Ashworth, 1998). The act regulates 189 HAPs from major and area sources, where a major source is defined as a stationary source (or group of sources) that emits more than 10 tons per year of any one pollutant or 25 tons per year total. Many glycol dehydration plants fall into this category (Kohl & Nielsen, 1997). The BTEX compounds are irritants and have narcotic effects; with benzene in addition is a human carcinogen. Their presence in water can create hazard to public health and the environment. Because of their polarity and soluble characteristics, BTEX will be able to enter the soil and groundwater systems and cause pollution problems. These health effects may come either through inhalation or ingestion of contaminated groundwater (Braek, 2000).

When glycol is used to remove water from natural gas stream, it will also absorb the BTEX compounds. Some of the BTEX are flashed off in the flash tank; however a significant fraction will be rejected at high temperature in the regeneration unit and appears as vapour in the stripping column offgas, where this emission is a major environmental issue for glycol dehydration plants. Table below shows the relative solubility of benzene and toluene in MEG and TEG, where lower solubility in MEG is an important factor that will reduce BTEX emissions.

Table 2.2: Solubility of Benzene and Toluene in Glycols (Ebeling, Lyddon, & Covington, 2006)

Compound	Solubility (wt% at 25 °C)	
	in MEG	in TEG
Benzene	5.7	Completely soluble
Toluene	2.9	24.8

2.4 Glycol Dehydration Technology

Figure below shows the simplified flow diagram of a basic glycol dehydration unit:

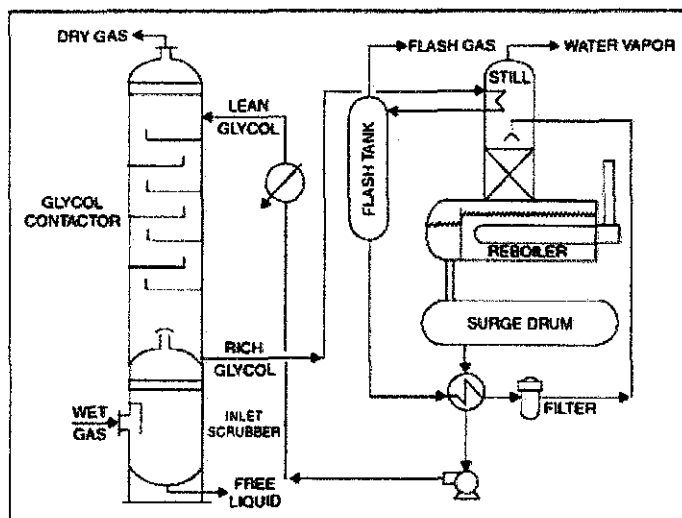


Figure 2.1: Simplified flow diagram for a glycol dehydration unit (Carroll, 2003)

The lean (dry) glycol removes the water from the gas in an absorption column known as a contactor. After the contactor the rich (wet) glycol is regenerated for reuse in the contactor by distilling the glycol thus removing the water. With glycol absorption it is possible to lower the water contents down to approximately 10 ppm_{vol}, depending on the purity of the lean glycol (Christensen, 2009).

According to Abdel-Aal, Aggour, & Fahim (2003), the absorption process improves at higher pressures because the higher-pressure gas will contain less water vapour. But a very high gas pressure will increase the column's pressure rating thus increasing cost and requires high glycol pumping power. A very low gas pressure on the other hand will require a larger column size. Most operations are designed at pressures between 1000 and 2000 psi.

Glycol regeneration is better achieved at low pressures, and usually takes place at atmospheric pressure. The glycol temperature is normally raised up to between 370-390 °F and this result in a lean glycol concentration of about 98.5-98.9%. A higher temperature will cause degradation of glycol (Abdel-Aal, Aggour, & Fahim, 2003).

2.5 Enhanced Stripping Processes

The degree of dehydration that can be attained with a glycol solution is primarily dependent on the extent to which water is removed from the solution in the glycol regenerator. A typical concentration of glycol achieved at atmospheric conditions is about 98.5 to 99.0% by weight because glycol degrades at temperatures above approximately 400 °F. When significantly higher concentrations are needed to meet stringent gas dehydration requirements, the use of an enhanced stripping technique is necessary (Kohl & Nielsen, 1997). Stripping gas injection, vacuum stripping, Drizo process and Cold-finger are some of known methods for enhanced stripping of TEG.

2.5.1 Stahl column and stripping gas

Stahl column is a separate stripping gas column between the reboiler and the surge tank. A portion of sales gas or inert gas is used as stripping gas. A Stahl column gives an extra stage of regeneration by taking the solvent from the reboiler and

contacting it with a flow of stripping gas. Reduction in water partial pressure causes much water removing from the desiccant. Stahl columns are essential when the dried gas must have a very low dew point of below -25°F . Stripping gas permits more water removal from the solvent and increases the dry TEG from 98.8 wt% to 99.8 wt%. Figure below shows the Stahl column in the regeneration section.

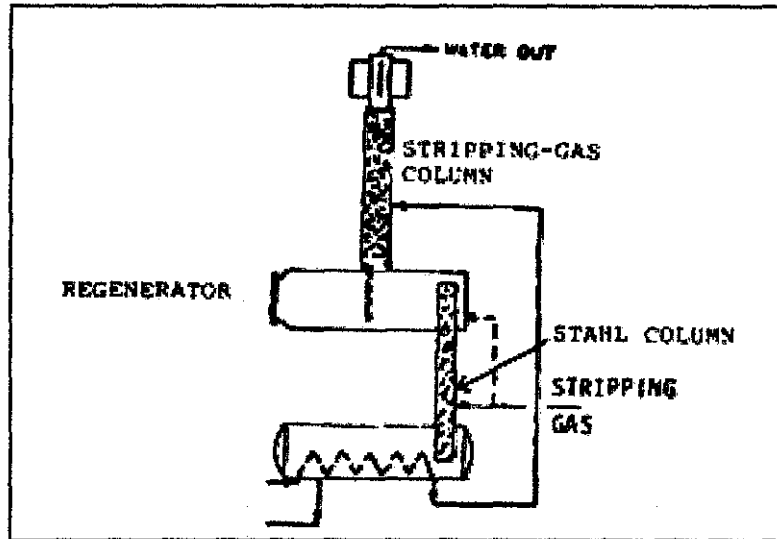


Figure 2.2: Stahl or gas stripping column (Manning & Thompson, 1991)

2.5.2 Drizo process

Drizo regenerates the glycol by solvent stripping instead of the conventional gas stripping. The solvent required by the Drizo™ process is usually obtained from the BTEX present in the natural gas itself and in most cases the process will even produce some liquid hydrocarbons. The process has the advantages over the use of noncondensable stripping gas of permitting the recovery of BTEX components and avoiding the consumption of valuable sales gas. The principle is that a stripping gas medium used in the regeneration columns is recovered as a liquid after the regeneration column. The liquid is separated from the condensed water in a three phase separator and is recycled to the regeneration columns. According to Kohl & Nielsen (1997), Drizo process can achieve concentrations of over 99.99% with TEG, resulting in potential product gas water dew points in the -100 to -140°F range. Below is the flow diagram of Drizo process.

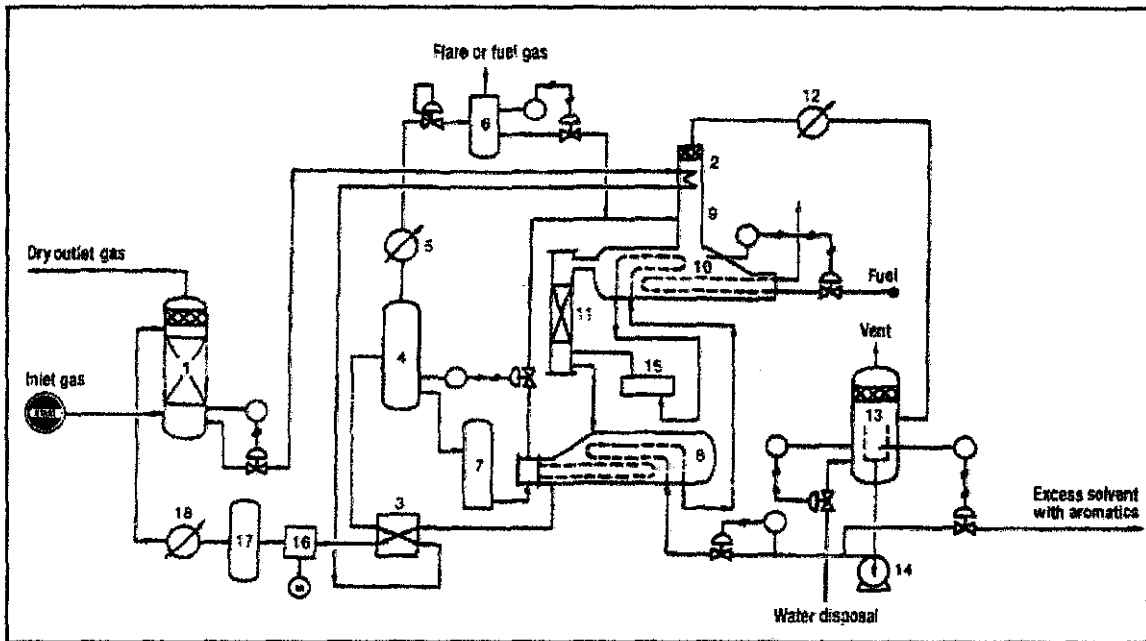


Figure 2.3: Flow diagram of Drizo process showing (1) glycol contactor, (2) reflux condenser, (3) glycol-glycol plate exchanger, (4) flash tank, (5) solvent recovery condenser, (6) recovered solvent drum, (7) glycol filter, (8) surge tank/exchanger, (9) rich stripper, (10) glycol reboiler, (11) lean stripper, (12) solvent-water condenser, (13) solvent-water separator, (14) solvent pump, (15) solvent superheater, (16) glycol pump, (17) acoustical filter, and (18) glycol cooler (Kohl & Nielsen, 1997).

2.6 Addition of Salts to Improve Absorption Capacity of Glycol

Gavlin & Goltskin (1998) has reported the usage of a dissolved salt that comprised of at least one potassium carboxylate that will improve the absorption capacity of glycols. The salt selected is potassium acetate and potassium formate. It is found by Gavlin & Goltskin (1998) that the addition of this salt will increase the absorption capacity of glycol up to three times or more. Table below shows the solubilities in glycols at 30 °C of potassium acetate and potassium formate respectively.

Table 2.3: Potassium formate and potassium acetate solubility in glycol solutions
(Gavlin & Goltskin, 1998)

Salt	Solution	Solubility (wt%)
Potassium Acetate	anhydrous ethylene glycol (EG)	40
	anhydrous diethylene glycol (DEG)	35
	anhydrous triethylene glycol (TEG)	4
Potassium Formate	anhydrous ethylene glycol (EG)	40
	anhydrous diethylene glycol (DEG)	25
	anhydrous triethylene glycol (TEG)	21

From the table we can see that the solubility of potassium acetate and potassium formate is the same in anhydrous ethylene glycol solution. The experimental work regarding glycol modification has been done on triethylene glycol (TEG) only. Table below shows the effect of adding potassium formate solution to the percent of water vapour absorbed from the natural gas stream. Here in this project we are interested in using Hysys simulation to obtain results for MEG modification by addition of salts.

Table 2.4: Percent of water vapour absorbed by weight (Hallman, 2005)

	Original wt% in solution	24 hours	48 hours	72 hours	96 hours
KOOCH	20.27	50	71	87	
70 wt%	43.44	16	28		
	35.88	25	32	59	61
	43.65	22	33	49	56
	63.22	13	22	31	
TEG 100wt%	21.06	36	46	56	
	37.44	19	26	32	
	44.37	17	23	30	

2.7 Equilibrium Correlations for Predicting Water Dew Point

Evaluation of TEG dehydration system involves the establishment of the minimum concentration of TEG required to meet the putlet gas water dew point specification (Bahadori & Vuthaluru, 2009). Bahadori & Vuthaluru (2009) has developed a

correlation that can be used to estimate the required TEG concentration for a particular application or the theoretical dew point depression for a given TEG concentration and contactor temperature.

The correlation covers for TEG–water system for contactor temperatures between 10 °C and 80 °C and TEG concentrations ranging from 90.00 to 99.999 wt%. In this project we are going to use this correlation as the point of reference to validate the results that we have generated through simulation.

Figure below shows the relation between the water dew point (T_d) of natural gas stream with respect to the concentration of TEG, with their tuned coefficients for equations (2)-(5) are reported in Table 2.5

$$T_d = a + bT + cT^2 + dT^3 \dots\dots\dots(1)$$

Where :

$$a = A_1 + B_1W + C_1W^2 + D_1W^3 \dots\dots\dots(2)$$

$$b = A_2 + B_2W + C_2W^2 + D_2W^3 \dots\dots\dots(3)$$

$$c = A_3 + B_3W + C_3W^2 + D_3W^3 \dots\dots\dots(4)$$

$$d = A_4 + B_4W + C_4W^2 + D_4W^3 \dots\dots\dots (5)$$

Figure 2.4: Equilibrium correlations between water dew point (T_d) of dry gas with respect to concentration of regenerated TEG (Bahadori & Vuthaluru, 2009)

Table 2.5: Tuned coefficients used in Equations (2)-(5) (Bahadori & Vuthaluru, 2009)

Coefficient	90%<TEG<99%	99%<TEG<99.9%	99.9%<TEG<99.999%
A1	2.73E+07	5.95E+09	-1.43E+13
B1	-8.63E+05	-1.79E+08	4.30E+11
C1	9.10E+03	1.80E+06	-4.31E+09
D1	-3.19E+01	-6.01E+03	1.44E+07
A2	-2.65E+05	-6.03E+07	1.38E+11
B2	8.39E+03	1.82E+06	-4.13E+09
C2	-8.84E+01	-1.82E+04	4.14E+07
D2	3.10E-01	6.10E+01	-1.38E+05
A3	8.62E+02	2.04E+05	-4.36E+08
B3	-2.73E+01	-6.14E+03	1.31E+07
C3	2.87E-01	6.17E+01	-1.31E+05
D3	-1.01E-03	-2.06E-01	4.37E+02
A4	-9.32E-01	-2.27E+02	4.62E+05
B4	2.95E-02	6.85E+00	-1.39E+04
C4	-3.10E-04	-6.87E-02	1.39E+02
D4	1.09E-06	2.30E-04	-4.62E-01

CHAPTER 3

METHODOLOGY

3.1 Project Activities



Figure 3.1: Research process flow chart

3.1.1 Literature Review

For the first phase of the project, literature research is conducted to obtain relevant information from trusted resources. This information is used in understanding the glycol dehydration technologies, the BTEX emission issues and the comparison of different glycols to be used. Having a strong understanding on the topic is very important in ensuring the development and completion of this project.

3.1.2 Pre-simulation Data Gathering

Data collection of MEG properties

For this project we have identified our source of MEG in Malaysia, which is OPTIMAL Glycols (M) Sdn. Bhd. (Optimal). Optimal is located in Kerteh, Terengganu with the production 365,000 MTPA of MEG. The manufacturing specification of MEG produced by Optimal as listed in EOG-Quality-MEG01000 dated 10 May 2010 is attached at Appendix I.

The MEG produced is polyester grade, supplied to customers in liquid form with the main usage as antifreeze, for electronic application, polyester-fiber (garments) and PET bottles. The current price of MEG in Malaysian market for January 2012 is USD 1099/MT.

Data collection of natural gas

The composition of the wet natural gas to be used in our study, where the composition is based on Isa (2011) is attached in Appendix II.

3.1.3 Computer Simulation

The data that has been gathered is used as input for our simulation run using Aspen Hysys software. Before doing our simulation, we have to select the appropriate fluid package to be used. Fluid packages are thermodynamic models that are used to represent the phase equilibrium behavior and energy level of pure compound and mixture systems (Guerra, 2006). The fluid package selected for our simulation is Peng-Robinson for MEG-water system and Glycol package for TEG-water system. The main operating conditions for the base case of our simulation are listed in Appendix III.

Simulation of three glycol dehydration technologies

Three simulation cases are performed using MEG which are typical gas dehydration unit (GDU), stripping gas and Stahl column and Drizo system. Appendix IV shows the Hysys simulation diagram for the three glycol dehydration technologies. Phase envelope is constructed with values of water dew point, hydrate point, bubble point and dew point of the wet and dry natural gas stream. The performance of these three technologies is evaluated based on the phase envelope diagram.

Comparison between MEG and TEG

Glycol dehydration technology that has the best performance will be used for evaluating the comparison between MEG and TEG. The performance of MEG and TEG is based on two main parameters, which are total glycol losses and total BTEX emissions. All operating parameters are set at the same condition, except for reboiler temperature at the regeneration column. The reboiler temperature is determined to be less 20 °C from the decomposition temperature of glycol. The reboiler temperature is set to 145 °C and 175 °C for MEG and TEG respectively. Simulations were performed using MEG and TEG for glycol circulation rates between 2 to 6 m³/hr with inlet gas rate of 10.98 MMSCFD.

Optimization of MEG process

Optimization is carried out later during this stage to ensure greater efficiency of MEG dehydration process in terms of water content of dry gas. The parameters that are manipulated in optimizing the water content of dry gas are number of contactor stages, volume flow rate of stripping gas and reboiler temperature of the regeneration column. Simulations were performed using MEG with glycol circulation rates from 20 to 40 m³/hr with inlet gas rate of 10.98 MMSCFD.

MEG Modification by Addition of Salts

Potassium formate (KOOCH) is selected to be added to our MEG stream to increase the absorption capacity of MEG. Potassium formate solution with concentration of 70wt% is defined by using the hypothetical manager tool in Hysys by specifying the liquid density, boiling point and solubility of the solution. Potassium formate solution is added to the lean MEG stream starting with 0.1 kg/hr and the flow rate is increased gradually, and ensuring that it does not exceed the maximum solubility of potassium formate in MEG which is at 40 wt%. The water content of dry gas leaving the contactor is observed and recorded.

Equilibrium Correlation in Predicting Water Dew Point

Validation of our simulation is done by using the equilibrium correlations stated in Chapter 2.7. The water dew point value for each TEG concentration based on our TEG process simulation calculated by Hysys is compared with the correlation and it must be ensured that the error between the two values must not exceed 10% difference.

3.1.4 Collection and Analysis of Data

The data from Hysys is collected and stored using Microsoft Excel. It is important to ensure that the data collected will represent the objectives of this project. Among the data collected are dew point temperatures of dry gas, water content of dry gas, amount of BTEX emission at regeneration column and amount of glycol losses.

3.1.5 Report Writing

The analysis and discussion of this project is stated in Chapter 4. Based on the analysis, we can have a conclusion and determine whether the objectives of this project are achieved. All the data and analysis involved in this project is documented in this dissertation.

3.2 Key Milestone

- i. Performance of MEG as a dehydrating agent is evaluated and compared with TEG
- ii. BTEX emission for glycol dehydration unit is reduced
- iii. The dehydrated natural gas stream has the optimized dew point value that will prevent condensation to occur in the downstream pipelines

3.3 Tools

In this study, Aspen Hysys simulation package will be used to simulate the glycol dehydration process. Aspen Hysys is a process modeling tool for steady state simulation, design, performance monitoring, optimization and business planning for oil and gas production, gas processing and petroleum refining industries (Aspen Tech, 2004). A Hysys modeling of the process will be developed where the process parameters will be optimized to have a better performance of gas dehydration. The result of the simulation will be collected in analyzing the performance of MEG as a dehydrating agent.

3.4 Gantt Chart

Table 3.1: Timelines for Final Year Project II (FYP II)

NO	Detail/ Week	1	2	3	4	5	6	7	MID-SEMESTER BREAK	8	9	10	11	12	13	14	15		
1	Project Work Continues	█																	
2	Submission of Progress Report										█								
3	Project Work Continues										█	█	█	█	█				
4	Pre-EDX													█					
5	Submission of Dissertation(soft bound)														█				
6	Submission of Technical Paper															█			
7	Oral Presentation																█		
8	Submission of Project Dissertation (hard bound)																	█	

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Study of Phase Behaviour of Natural Gas Stream

Based on our scope of study, simulation of three gas dehydration technologies, which are basic (typical GDU), stripping gas with Stahl column and Drizo is performed using Aspen Hysys software. Phase envelope diagram or P-T diagram is used in determining the best glycol dehydration technology. The performance of each gas dehydration unit is investigated in terms of water dew point and water content of the dry natural gas stream. Below is the P-T diagram of the wet gas before dehydration.

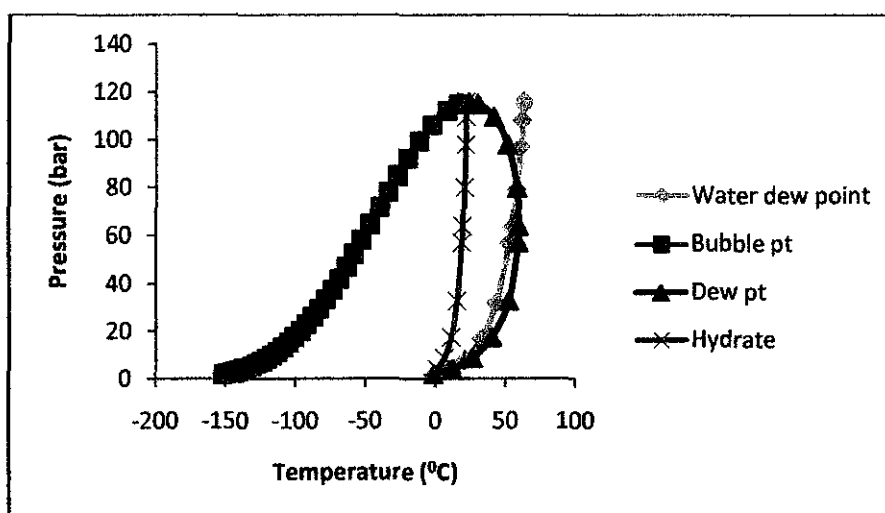


Figure 4.1: P-T diagram for wet gas

The water dew point curve (blue curve) indicates where the liquids will begin to condense and hydrate line shows the temperature and pressure where hydrate will start to form. For all three gas dehydration technologies, we can see from the phase envelope that the water dew point and hydrate line is shifted to the left; where this indicates the reduction of water content of the dry gas, and this permits the natural gas pipelines to be operated at lower temperatures. Drizo technology shows the greatest reduction of water content. This proves that Drizo has the highest capability

for natural gas dehydration, which produces dry gas with very low water dew points (typical dew point depressions to $-100\text{ }^{\circ}\text{C}$ or more).

We can see that the hydrate formation line, the variations of the line location is not much difference compared to water dew point line. This is because hydrate formation is controlled mainly by light hydrocarbons, and methane being the major constituent in the natural gas is not removed during the dehydration process. The following figures show the phase envelope for each gas dehydration unit.

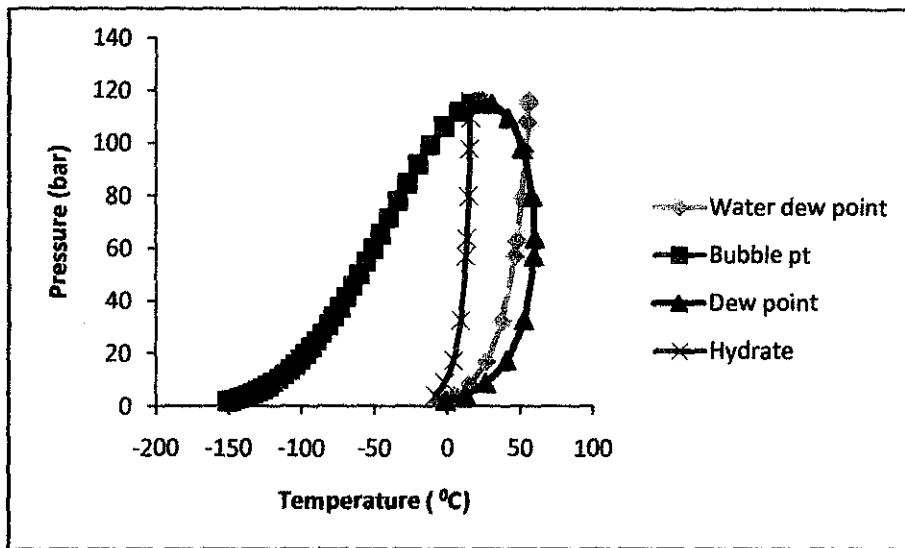


Figure 4.2: P-T diagram of dry gas- Typical GDU

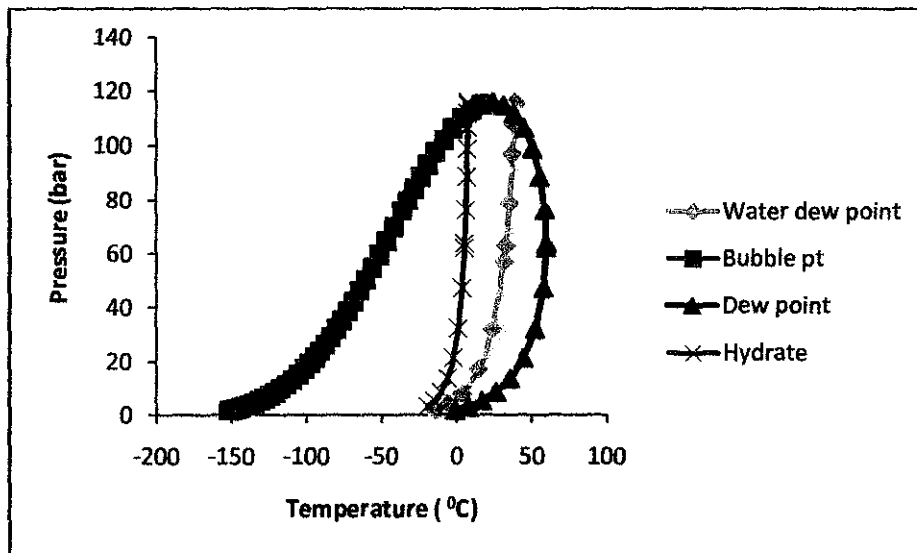


Figure 4.3: P-T diagram of dry gas- Stahl column

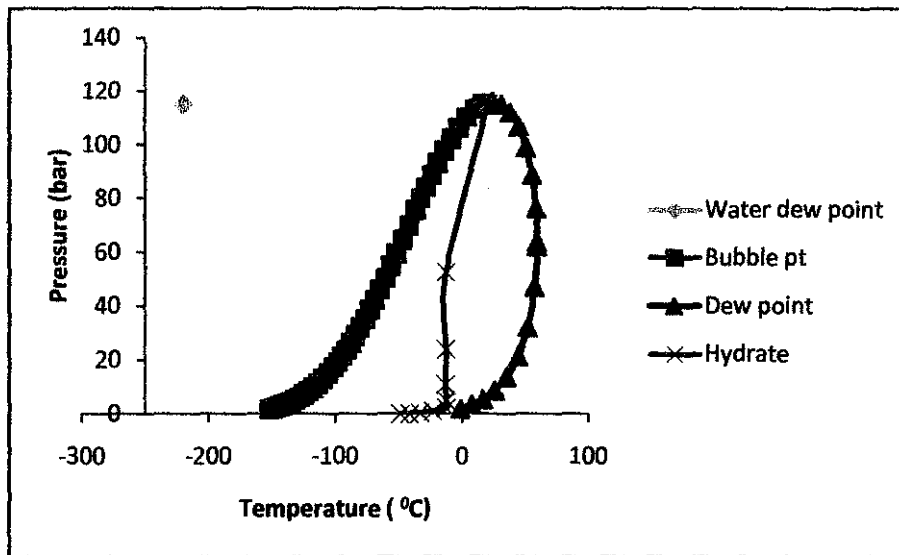


Figure 4.4: P-T diagram of dry gas- Drizo

4.2 Comparison of Performance between MEG and TEG

Based on Chapter 4.1, we selected Drizo process to be used for comparison of performance between MEG and TEG. We are comparing in terms of total BTEX emissions and total glycol losses.

4.2.1 Comparison of BTEX emission

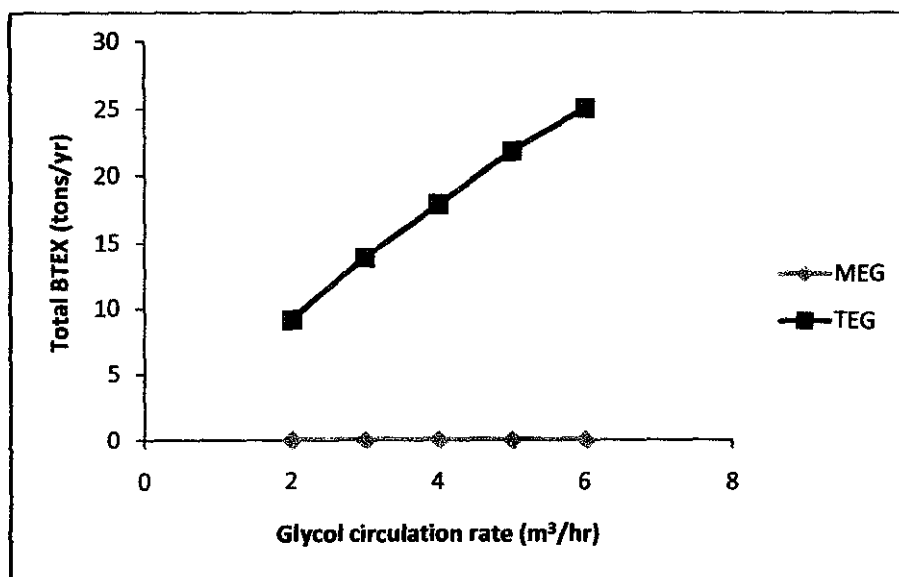


Figure 4.5: Comparison of BTEX emission

Based on the figure we can see that the usage of MEG shows significant result where the emission of BTEX is almost zero, and we have the reduction of almost 100% in BTEX emission value. This is due to lower solubility of BTEX in MEG compared to TEG. The regulatory agencies limit for BTEX emission is 25 tons/yr of total pollutants (Ebeling, Lyddon, & Covington, 2006) and the usage of MEG for all three cases complies with this limit.

4.2.2 Comparison of glycol losses

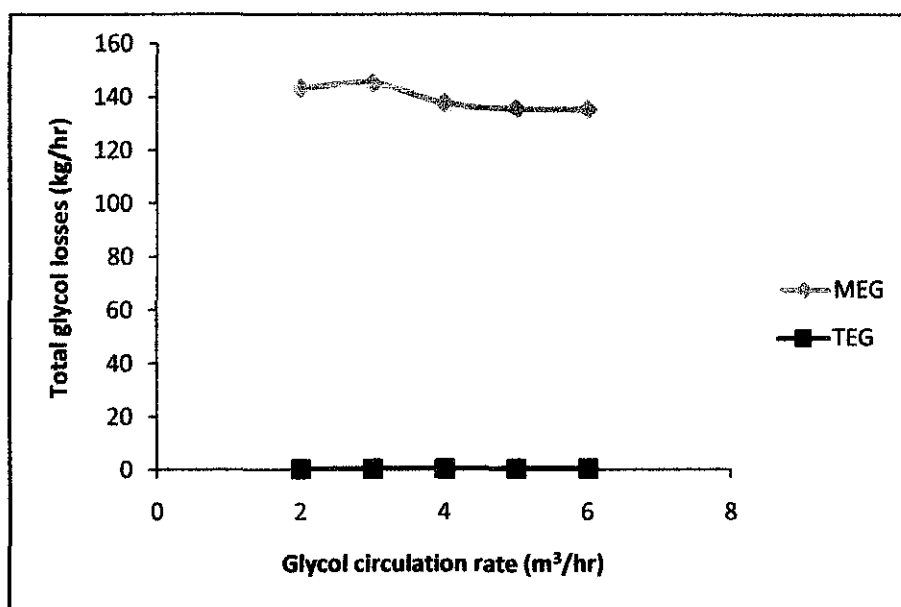


Figure 4.6: Comparison of glycol losses

Usage of MEG as a dehydrating agent result in higher losses due to higher volatility (lower boiling point) of MEG compared to TEG. Increasing reflux ratio at the regeneration column helps reducing the loss of MEG in the column. The reboiler temperature is reduced to 140 °C to prevent huge vaporization of MEG, and figure below shows the effect of increasing reflux ratio with MEG losses at regeneration column.

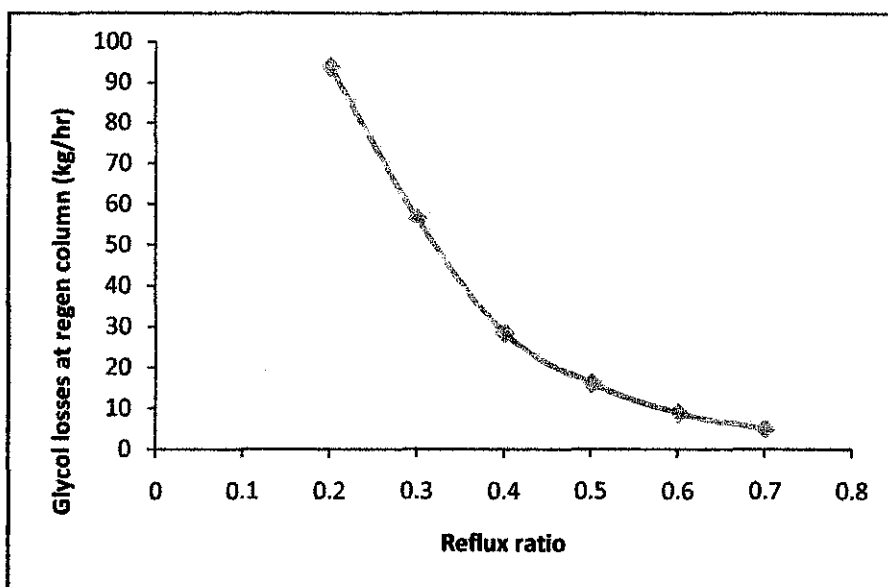


Figure 4.7: Effects of reflux ratio on MEG losses

Based on the comparisons above, the results indicate that usage of MEG is most favourable in reducing BTEX emission. For the same glycol dehydration technology, the usage of MEG requires no additional equipment where this indicates minimal addition in costs. Lower reboiler temperature used for MEG means lower energy requirement for MEG regeneration compared to TEG.

However, glycol loss for MEG is higher; hence higher glycol replacement is needed. The cost of glycol replacement must be determined if MEG is used, to evaluate whether it is less than the cost of treating the regenerator vent gases (Ebeling, Lyddon, & Covington, 2006).

4.3 Optimization of MEG Process

4.3.1 Effect of number of contactor stages

Figure below shows the effect of increasing number of contactor stages to the water content of dry natural gas with reboiler temperature at regeneration column is 140 °C. We can see that increase of number of stages will result in lower water content of dry natural gas. This is because with higher number of stages we will have higher degree of contact between MEG and natural gas stream and this allows the gas to approach equilibrium with lean glycol (Arubi & Duru, 2008).

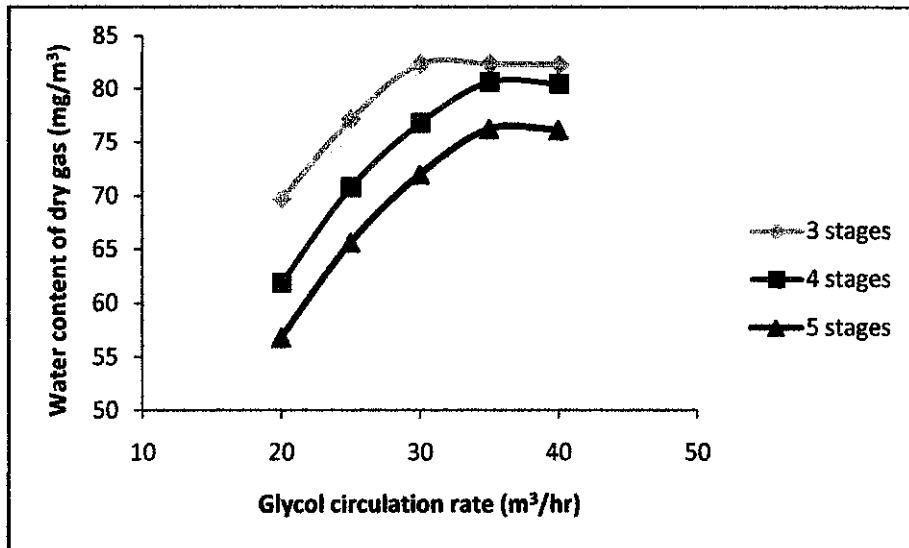


Figure 4.8: Effect of number of contactor stages to water content of dry gas

4.3.2 Effect of reboiler temperature

Higher reboiler temperature will yield higher concentration of MEG, but this value must not exceed the limitation of MEG decomposition temperature. The reboiler temperature will affect the concentration of lean MEG, and higher concentration of MEG will have higher absorption capacity thus producing low water content of dry natural gas. Figure below shows that at 145 °C we have the lowest water content in dry natural gas compared to lower temperature with the same operating conditions.

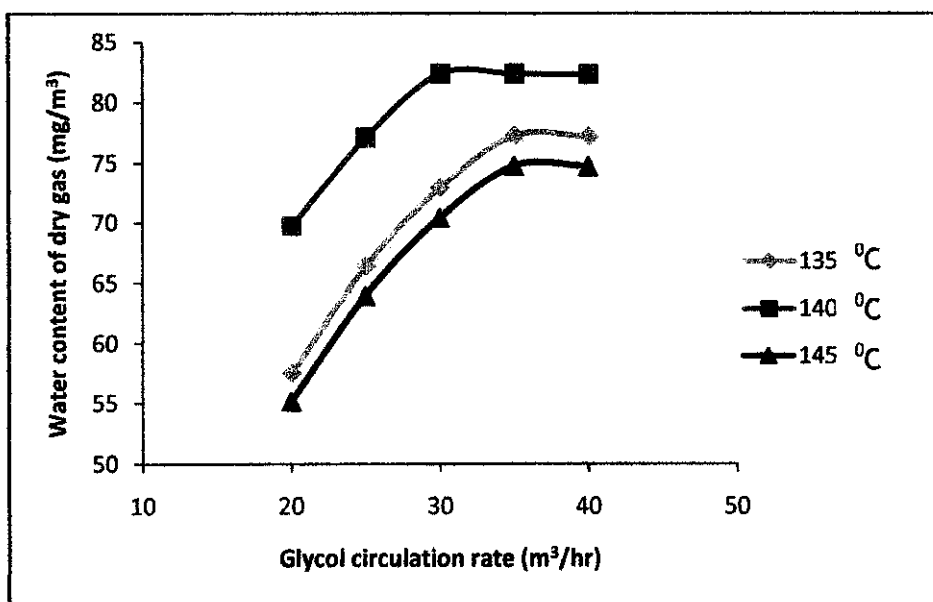


Figure 4.9: Effect of reboiler temperature on water content of dry gas

4.3.3 Effect of stripping gas flow rate

The limitation of decomposition temperature in producing higher concentration of MEG can be solved by introducing a stream of stripping gas. Low water dew points value if dry natural gas will need up to 99.9 wt% concentration of glycol. The usage of stripping gas will introduce contact of stripping gas with the MEG-water stream, and this will reduce the partial pressure of water vapour. Reduction on partial pressure will reduce the boiling point of water vapour, thus higher amount of water vapour can be separated from MEG to produce much higher concentration of lean MEG. From figure below, we can see that higher flow rate of stripping gas stream will result in much lower water content of dry natural gas.

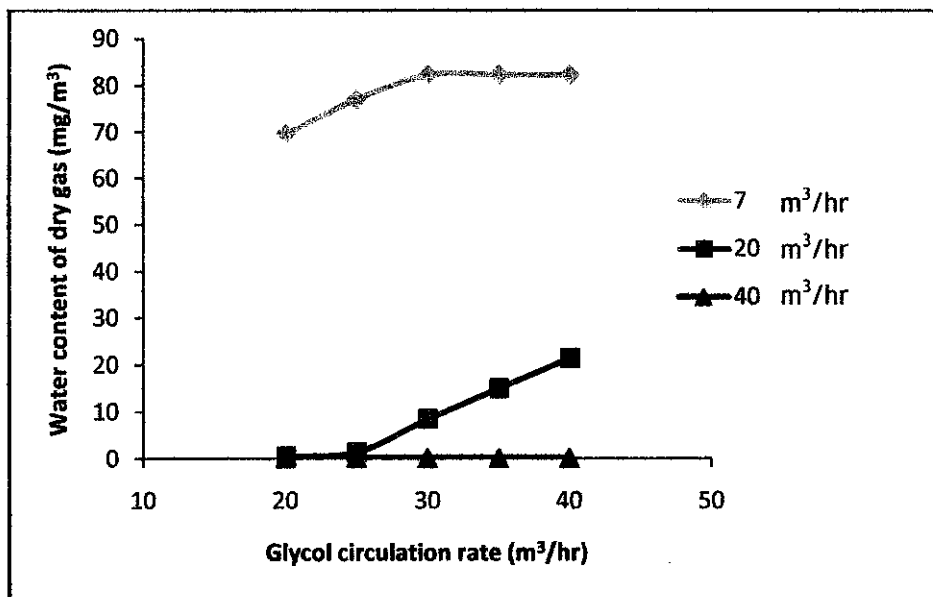


Figure 4.10: Effect of stripping gas rate on water content of dry gas

Below is the general summary of comparison between MEG and TEG by using Drizo process, after optimization of MEG with the following operating conditions:

- Number of contactor stages: 5
- Stripping gas flow rate: 20 m³/hr
- Glycol circulation rate: 20 m³/hr

Table 4.1: Summary of comparison of performance between MEG and TEG

Type of Glycol	MEG (with reflux ratio 0.1)	TEG
Reboiler temperature ($^{\circ}\text{C}$)	145	175
BTEX emission (tons/yr)	0.049	62.919
Water content of dry gas (mg/m^3)	0.7821	0.5189
Glycol losses (kg/hr)	0.3742	0.263

4.4 MEG Modification by Addition of Salts

The addition of salts (potassium formate) to the anhydrous MEG solution shows significant reduction of water content in dry natural gas. Increase of potassium formate flow rate further reduces the water content of dry gas. The potassium formate solution is at 70 wt% concentration, and added gradually to lean MEG stream with mass flow rate 7.611 kg/hr. Table below shows the effect of addition of salts in MEG.

Table 4.2: Effects of addition of potassium formate to water content of dry gas

Mass flow rate of potassium formate (kg/hr)	Water content of dry gas (mg/m^3)
0.0	7.714
0.4	1.657
0.8	0.6136
1.2	0.3433
1.6	0.2283
2.0	0.1844
2.4	0.1683

Usage of MEG has an added advantage compared to TEG in terms of salt addition due to higher solubility of potassium formate in MEG (40 wt%) compared to TEG (21 wt%). Based on Isa (2011), at maximum limit amount of potassium formate to be mixed with TEG, the water content in dry gas is found to be at 28 ppm. This result shows higher water content reduction in MEG system compared to TEG.

4.5 Equilibrium Correlation in Predicting Water Dew Point

Validation of our data is based on correlation developed by Bahadori & Vuthaluru (2009). The method states the relation between TEG concentration and water dew point value. Results shown below shows that our simulation data is satisfying, where we have consistent water dew point value for our simulation, with less than 10% difference with predicted values.

Table 4.3: Comparison of water dew point of dry natural gas between simulation and predicted values

TEG concentration (wt%)	T_d predicted (K)	T_d hysys (K)	% difference
91.99	313	310.12	0.920128
93.99	310	306.17	1.235484
95.99	303	300.4	0.858086
97.97	291	290.29	0.243986
97.99	290	290.34	0.117240
98.99	281	280.173	0.294306
99.09	277	280.173	1.145490
99.29	274	274.913	0.333210
99.49	271	269.93	0.394834
99.69	265	262.27	1.030189
99.89	252	244.91	2.813492
99.91	244	243.17	0.340164
99.93	240	238.95	0.437500
99.95	242	233.26	3.611570
99.97	239	225.02	5.849372
99.995	217	205.85	5.138249

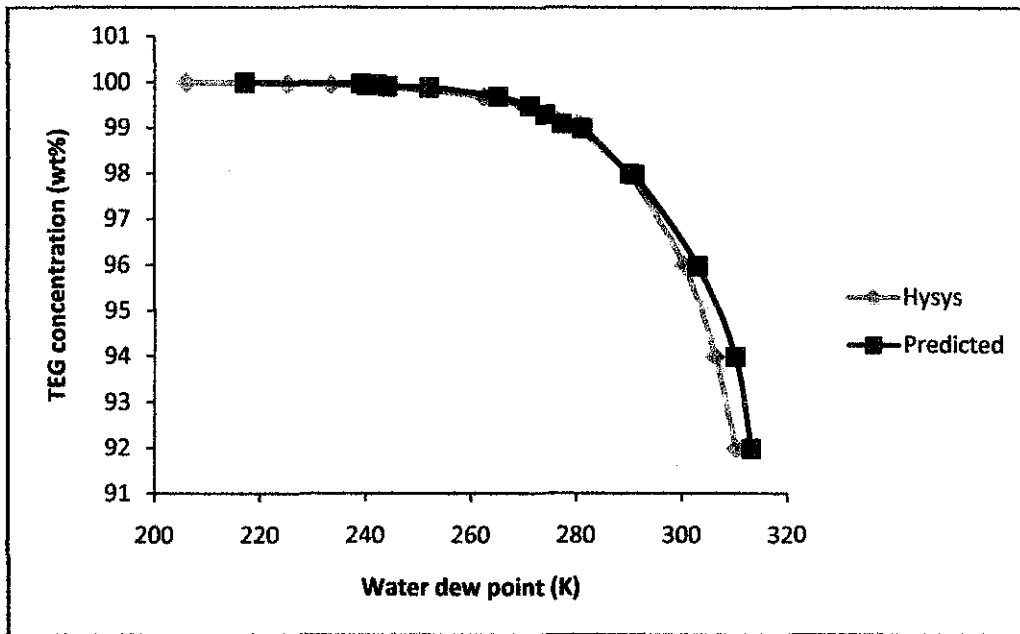


Figure 4.11: Comparison of water dew point of dry natural gas between simulation and predicted values

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The objectives targeted for this project are clear with specific scopes of study. Many journals and articles have been consulted showing the study of optimizing the glycol dehydration unit, although the usage of MEG as dehydrating agent is still very low.

BTEX emission is a very huge environmental issues for glycol plants, and reduction of this BTEX will greatly increase the plants' performance. When the emission of BTEX is the main concern, it is favourable to opt for alternative glycols other than TEG that will help reducing the emissions while still meeting the water content specifications of dry natural gas.

It is found that the usage of MEG instead of TEG when BTEX is the main concern can greatly reduce BTEX emissions, where the emission of BTEX is almost zero. This will greatly contributes in the reduction of costs in reducing/treating environmental emissions. But glycol loss for MEG is much higher; which results in higher glycol replacement. If MEG is used, it must be determined if the cost of glycol replacement is less than the cost of treating the BTEX emissions.

Validation of Hysys data for water dew point of dry natural gas at different TEG concentration shows less than 10% difference from predicted values calculated using equilibrium correlation, leads to the conclusion that Hysys results are reliable. Based on our overall analysis and discussions, we can say that the objectives of this project has been met.

5.2 Suggested Future Work

Below are the suggested future works for the expansion and continuation of this project:

1. The results obtained in this study is based on simulation output, and validation of water dew point value can only be done for TEG process. Lack of data for MEG process imposed a limitation in our validation and it is suggested to have laboratorial work for MEG dehydration process or simulation run based on a real MEG-operating dehydration plant.
2. The laboratory data on modification of glycol by addition of salts is only available for TEG. It is suggested that laboratory experiment will be conducted in obtaining the data of modification of MEG by addition of salts. This is important in order to have a set of reference value to validate our simulation results. Specifications of potassium formate by hypothetical manager in Hysys simulation is still a preliminary approach used in this study. It is suggested to perform computational fluid dynamics study in order to have a better chemical properties of the modified MEG when potassium formate is added.

REFERENCES

- Abdel-Aal, H. K., Aggour, M., & Fahim, M. A. (2003). *Petroleum and Gas Field Processing*. CRC Press.
- Arubi, I. M., & Duru, U. I. (2008). Optimizing Glycol Dehydration System for Maximum Efficiency: A Case Study of a Gas Plant in Nigeria. *CIPC/SPE Gas Technology Symposium 2008 Joint Conference*. Calgary, Alberta, Canada.
- Aspen HYSYS- AspenTech. (n.d.). Retrieved January 30, 2012, from Aspen Hysys: www.aspentech.com/hysys/
- Bahadori, A., & Vuthaluru, H. B. (2009). Rapid estimation of equilibrium water dew point of natural gas in TEG dehydration systems. *Journal of Natural Gas Science and Engineering* .
- Braek, A. M. (2000). Optimization of Process Parameters for Glycol Unit to Mitigate the Emission of BTEX/VOCs. *9th Abu Dhabi International Petroleum Exhibition & Conference*.
- BTEX Definition Page*. (2011). Retrieved April 10, 2012, from United States Geological Survey: <http://toxics.usgs.gov/definitions/btex.html>
- Carroll, J. J. (2003). *Natural gas hydrates: a guide for engineers*. Gulf Professional Publishing.
- Christensen, D. L. (2009). *Gas Dehydration- Thermodynamic simulation of the water/glycol mixture*. Aalborg University Esbjerg.
- Collie, J., Hlavinka, M., & Ashworth, A. (1998). An Analysis of BTEX emissions from Amine Sweetening and Glycol Dehydration Facilities. *Laurance Reid Gas Conditioning Conference Proceedings*. Oklahoma.
- Ebeling, H. O., Lyddon, L. G., & Covington, K. K. (2006). Reduce Emissions and Operating Costs with Appropriate Glycol Selection. *Seventy-Seventh GPA Annual Convention*. Tulsa: Bryan Research & Engineering, Inc. - Technical Papers.
- Gavlin, G., & Goltskin, B. (1998). *Patent No. 5,725,636*. Chicago.
- Guerra, M. J. (2006). *Aspen Hysys Property Packages*. Retrieved April 20, 2012, from Best Practices Optimum Simulations Hysys Property Packages: <http://www.scribd.com/doc/61296696/BestPracticesOptimumSimulationsHYSPropertyPackages>
- Hallman, J. H. (2005). *Patent No. 6,896,718 B2*. Houston, TX (US).

- Hlavinka, M. W., Hernandez-Valencia, V. N., & Bullin, J. A. (1992). Design Glycol Units for Maximum Efficiency. *Proceedings of the Seventy-First GPA Annual Convention*. Bryan Research & Engineering, Inc.
- Hlavinka, M. W., Hernandez-Valencia, V. N., & Bullin, J. A. (1993). Influence of Process Operations on VOC and BTEX Emissions from Glycol Dehydration Units. *Proceedings of the Seventy-Second GPA Annual Convention*. Bryan Research & Engineering, Inc.
- Isa, M. A. (2011). *Natural Gas Dehydration by Absorption Process: A comparative simulation study towards high effective natural gas dehydration using TEG technology*. Universiti Teknologi PETRONAS (Unpublished).
- Kohl, A. L., & Nielsen, R. B. (1997). *Gas Purification* (5th Edition ed.). Elsevier.
- Manning, F. S., & Thompson, R. E. (1991). *Oilfield Processing of Petroleum: Natural Gas* (Vol. 1). PennWell Books.
- Salamat, R. (2009). Choose the Right Gas Dehydration Method and Optimize Your Design. *International Petroleum Technology Conference* .

APPENDICES

Appendix I: MEG manufacturing specification

Component		Specification
MEG	99.91	wtp, minimum
DEG	0.035	wtp, maximum
Water	0.038	wtp, maximum
Acidity	18	ppm, maximum
Iron	0.045	ppm, maximum
Chlorides	0.1	ppm, maximum
Color	4.5	PtCo, maximum
Total carbonyl	8	ppm, maximum
UV220 nm	82.0	%T, minimum
UV250 nm	91.0	%T, minimum
UV275 nm	95.0	%T, minimum
UV350 nm	98.3	%T, minimum

Appendix II: Wet gas composition

Component	Mass fraction
H ₂ O	0.002
CO ₂	0.084
N ₂	0.005
C ₁	0.386
C ₂	0.129
C ₃	0.158
n-C ₄	0.097
i-C ₄ (isobutane)	0.052
n-C ₅	0.032
i-C ₅	0.033
n-C ₆	0.006
c-C ₆ (cyclo hexane)	0.002
i-C ₆	0.006
n-C ₇	0.001
i-C ₇	0.001
c-C ₇	0.002
i-C ₈	432PPM
c-C ₈	807PPM
C ₆ H ₆ (benzene)	857PPM
C ₇ H ₈ (toluene)	697PPM
C ₈ H ₁₀ (xylene)	402PPM
C ₈ H ₁₀ (ethyl benzene)	40PPM

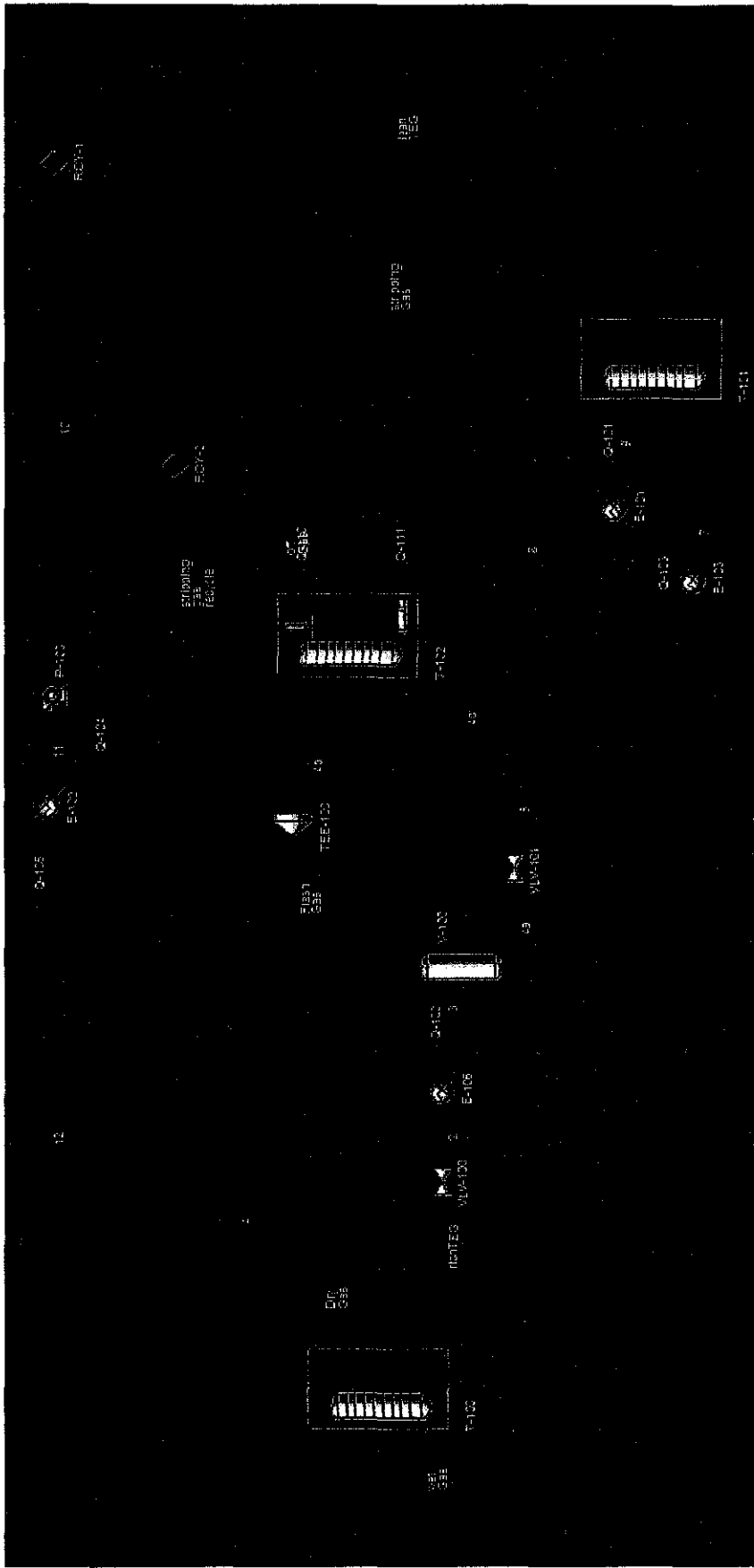
Appendix III: Operating conditions of the base case used in the simulation

Stream/Unit	Operating condition
Wet gas	Temperature = 56 °C Pressure = 4261 kPa Volume flow = 11 MMSCFD
Lean MEG/ Lean TEG	Temperature = 60 °C Pressure = 4261 kPa
Absorber (contactor tower)	Number of stages = 3 Pressure = 4261 kPa
Regeneration column	Pressure = 101.3 kPa Reboiler temperature (MEG) = 145 °C Reboiler temperature (TEG) = 175 °C
Stripping column	Number of stages = 5 Pressure = 101.3 kPa

Appendix IV-1: Hysys simulation diagram for typical gas dehydration unit (GDU)



Appendix IV-2: Hysys simulation diagram for Stripping gas and Stahl column gas dehydration unit (GDU)



Appendix IV-3: HYSYS simulation diagram for DRIZO gas dehydration unit (GDU)

