Enhanced Dehydration of Synthetic Gas Using Glycol Processes

by

Muhammad Aminuddin bin Janai

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

SEPTEMBER 2013

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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SEPTEMBER 2013

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 taken or done by unspecified sources or persons.

6/1/2014

Muhammad Aminuddin bin Janai

ABSTRACT

Synthetic gas or syngas from gasification process of coal, petcoke, biomass and other carbonaceous compounds contains acidic gases that need to be removed. Being considered as state of the art process, amine absorption is widely used for this purpose. Although amine absorption eliminates almost 99% acid gas, this process however generates significant amount of water in the treated synthetic gas. Until today, no specific process was designed for removal of water from synthetic gas. This study aims to investigate the effectiveness of dehydration processes using glycol solution to remove water content in synthetic gas. Two gas dehydration processes is used in this study, which are typical gas dehydration unit and stripping gas and Stahl column gas dehydration unit to represent enhanced gas dehydration. Enhanced dehydration process is a process equipped with some modification of regeneration part to obtain higher glycol purity once it has been recycled. From the simulation run by Aspen HYSYS, the results showed that both typical gas dehydration unit and enhanced gas dehydration unit had successfully achieved the dehydration objective. These results are exhibited using phase envelope diagram of gas stream exiting the dehydration unit. Besides, gas dehydration system using ethylene glycol (MEG) also had reduced the water content of the synthetic gas down to the accepted level and meets the fuel specification.

ACKNOWLEDGEMENT

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Synthetic gas or syngas is a mixture of hydrogen, H_2 and carbon monoxide, CO in various composition ratios. Synthetic gas can be produced from gasification of carbonaceous (carbon-rich) compounds such as coal, biomass, municipal waste, plastic, petroleum coke (petcoke) or any similar materials. Variation of feedstocks for gasification results in various composition of syngas (Mondal, Dang, & Garg, 2011). Typically, raw synthetic gas produced from coal, petcoke, petroleum residue, etc. contains in volume percent, 25-30% H_2, 30-36% CO, 5-15% CO_2 and 2-3% H_2O (Gills, 2006; Gupta, 2005) and small portions of CH_4, H_2S, N_2, NH_3, HCN, Ar, Ni, and Fe carbonyls are also present (Gills, 2006). The uses of synthetic gas are diversified from the heat or power application, to a variety of synthetic fuels as shown in Figure 1.1.

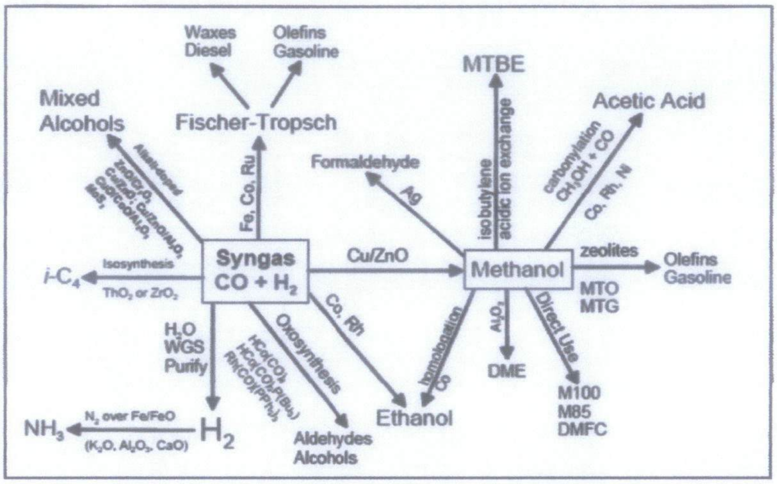

Figure 1.1: Syngas conversion technologies (Spath & Dayton, 2004)

As reported in several studies, sulfur contaminants, in form of H_2S, and carbon dioxide, CO_2, or termed as acidic gases, are found in the synthetic gas and it is important to remove the acidic gases to meet process requirement (Woolcock & Brown, 2013). Besides, these gases are also corrosive under moist conditions, because its dissolve in water to produce acidic solution (Mondal, Dang, & Garg, 2011). Table 1.1 shows the desired quality of produced synthetic gas for various downstream applications.

Table 1.1: Desired quality of treated synthetic gas for various downstream applications (Gills, 2006).

Downstream use	Power	Hydro-processing	Chemical
Sulfur (wppm)	10-15	<1	<0.01-1
CO_2 (vol %)	-	<0.1	0.05-2.0
CO	-	<50 wppm	H_2/CO control as per requirement

To acquire the minimum level of H_2S and CO_2, amine absorption is a well known and often used in industry for this purpose (Peters et al., 2011). Amine solutions such as monoethanol amine (MEA), di-ethanol amine (DEA), methyl-diethanol amine (MDEA) and hindered amines are used for chemical absorption of acid gases from synthetic gas (Caballo, Kerestecioglu, & LINDE, 2006). Being considered as state-of-the-art technology, amine absorption however gives out processed gas with significant water content (Nielsen, 1997; Blauwhoff et al., 1984; Peters et al., 2011). This phenomenon will be investigated by simulating amine process and passing synthetic gas into the process to assess the water content of the gas.

In natural gas operations, the glycol process is well known process for gas dehydration. Glycol is used as liquid desiccant to remove water vapour from the gas. This is because water and glycols show complete mutual solubility in the liquid phase due to hydrogen-oxygen bonds, and their water vapour pressures are very low (Mohamadbeigy, 2008). Several types of glycols used are ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG). Among those glycols, TEG is the most common and frequently used for gas dehydration (Isa et al., 2013).

1.2 Problem Statement

Amine absorption used for acid gas treatment has generated a significance amount of water and this amount needs to be leveled down to meet the requirement of downstream application. Removal of water is important because the presence of water will induce hydrate formation which results in blockages inside pipelines or process equipments (Ripmeester et al.,1987; Tohidi et al., 1990) and also reduces the combustion efficiency (Rohani, 2009).Simulation of amine process conducted by Lars et al. (2011) by using natural gas as feed had proven this premise. It is observed that the amount of water generated from amine process is significantly large, and if applicable to synthetic gas, the amount is exceeding the normal water content requirement of gas turbine. Table 1.2 below shows the amount of water content resulted from amine process simulated as aforementioned:

Table 1.2: Water generated from amine absorption process (Lars et al., 2011).

	Sour Gas (Before amine process)			Sweet Gas (After amine process)		
Case	1	2	3	1	2	3
Water content (ppm)	10	10	10	1,115	1,172	846

As the predicted water content of treated synthetic gas after amine process is high, it is important for the synthetic gas to undergo gas dehydration process to remove the water vapour in the gas. Until today, there is no specific process was designed to perform water removal from synthetic gas. Therefore, application of natural gas dehydration process for this purpose will be looked into to see its suitability and practicality. By using phase envelope diagram, the effects of gas dehydration will be illustrated and analyzed.

1.3 Objective of Study

Three (3) objectives have been outline for this study:

1) To simulate and validate different gas dehydration process and treatment by using Aspen HYSYS
2) To investigate triethylene glycol (TEG) and ethylene glycol (MEG) as potential solvents of synthetic gas absorption at different gas dehydration processes.
3) To evaluate the dew point of the outlet gas expressed by phase envelop diagram and to come with recommendation for process improvement.

Effects of various parameters such as type of gas dehydration processes, concentration of solvent, the number of equilibrium stages, re-boiler temperature, stripping gas flow-rate, etc. will also be analyzed to determine the practicality of synthetic gas dehydration by using this method. Also by using these data, analysis and recommendation is to be made to design an efficient synthetic gas dehydration system, and produce synthetic gas with low water content that is suitable for various purposes, i.e. heat processing, electric power generation, and liquid fuels etc.

1.4 Scope of Study

In this project, amine absorption process using DEA will be first simulated to study the effects of amine process to the gas water content. The treated gas is then fed into two gas dehydration units (GDUs); typical gas dehydration unit, and to an enhanced gas dehydration, stripping gas and Stahl column GDU. These two gas dehydration units are chosen because of their commonly used in industry, and moreover, stripping gas and Stahl column gas dehydration unit is proven to be a better process compared to typical GDU. The performance of these gas dehydration units is to be investigated in terms of water dew point and water content remaining in the gas after dehydration.

Using typical gas dehydration unit simulation, two potential absorbents will be used and investigated in this study. The two absorbents are triethylene glycol (TEG) and ethylene glycol (MEG). Technical and economic evaluation will be performed to establish the most suitable absorbent for synthetic gas dehydration unit.

1.5 Feasibility of Project

28 weeks in two semesters have been allocated to perform this study; semester May and Sept 2013. During the duration, it is possible to complete the study and to achieve all the objectives. Work-planning and Gantt chart of the project will be shown on Chapter 3: Methodology. Multiple references and sources of literatures existed and available nowadays also helped in creating understanding and built strong foundation on the theoretical parts of the projects. Research within the scope of study is to be performed before proceeding to the next phase of the project work which is simulating all processes and obtaining the results. Besides, to facilitate the simulation process, identifying related data is needed especially in pertaining parameters of all the processes. Strong raw data will produce good result after the simulation. In addition, real life data available from previous studies will be used to validate all the simulation using Aspen HYSYS software. Real life data is used to compare and modify the simulation in getting accurate results for the simulation of data for the study.

CHAPTER 2
LITERATURE REVIEW

2.1 Amine Absorption Process

Today, absorption processes with chemical solvents are the most applied technology in post-combustion CO_2 capture (Chakma, 1997; Desideri & Corbelli, 1998). By comparing to other post-combustion capture processes, it is by far the most efficient systems and have the lowest costs, besides they have reached the commercial stage for CO_2 separation from natural gas and for CO_2 production as a technical gas from coal combustion and gasification (Singh, et. al.,2003; Iijima & Takashina, 2004; Romeo, Bolea, & Escoma, 2008). Further, the heat of absorption of CO_2 is generally between 50 and 80 kJ/mole CO_2 and, in order to reuse the solvent, a regeneration stage is included in the chemical absorption systems where CO_2 is desorbed from the solvent at high temperature (100-140 °C) and at moderate pressure (approx. 1 bar). Thermal energy is required in the regeneration stage for solvent-heating purposes (Desideri, 2010). The following chemical reactions in Figure 2.1 describes the absorption of acid gases into aqueous amine solution (Nielsen, 1997; Blauwhoff et al., 1984). During the process, the water is formed physically and chemically. Water from amine solution used as absorbent is transferred into gas stream, and water is also produced chemically from reaction (2.4).

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2{}^+ \quad (2.1)$$

$$CO_2 + OH^- \leftrightarrow HCO_3 \quad (2.2)$$

$$CO_2 + H_2O \leftrightarrow HCO_3{}^- + H^+ \quad (2.3)$$

$$CO_2 + R_1R_3COHCNH + OH^- \leftrightarrow R_1R_3COCO_2CNH^- + H_2O \quad (2.4)$$

$$H_2O \leftrightarrow H^+ + OH^- \quad (2.5)$$

$$H_2S \leftrightarrow H + HS^- \quad (2.6)$$

$$HS^- + R_1R_2NH \leftrightarrow S^{2-}R_1R_2NH^{2+} \quad (2.7)$$

Figure 2.1: Series of reaction for amine absorption process.

Figure 2.2 shows a simplified flow sheet of amine absorption process for natural gas. Lean amine and natural gas will enter the absorber column and flows countercurrently. The acid gas components will react with amine and dissolve into liquid phase. From the absorber column, sweet natural gas (free from acid gas) will leave the column at top while enriched DEA solutions leaves the column at the bottom. The rich amine solutions will further proceeds to regeneration steps and becomes lean amine solution (Nielsen, 1997; Parrish & Ridnay, 2006).

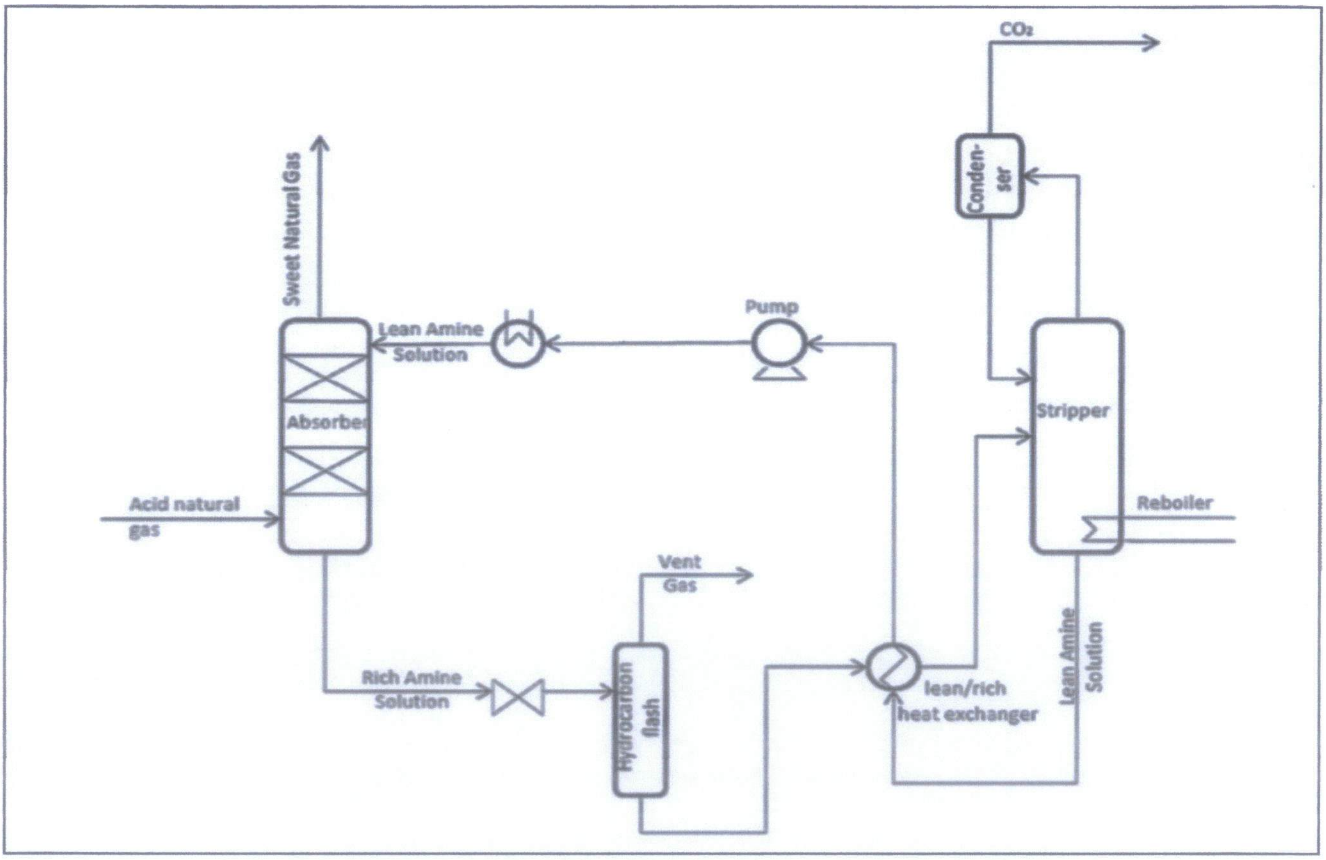

Figure 2.2: Simplified flow sheet of an amine absorption process.

2.1.1 Selection of Amine for Absorption Medium

Gas treatment by diethanolamine (DEA) solution is a state of the art technology. DEA is a secondary amine and will be less reactive with CO_2 and H_2S compared to primary amines like monoethanolamine (MEA). Due to less reactivity, DEA also requires lower energy requirement for the generation (Bhide et al., 1998) and this property is important in predicting gas processing cost. The heat of reaction for DEA with CO_2 is less, which is about 25% less than for MEA. Besides, the degradation products of DEA are much less corrosive than those of MEA. Therefore, it can be said that DEA is a suitable absorbent for amine process, and will be used in this study. Table 2.1 shows some properties for various amine solutions.

Table 2.1: Characteristic of chemical solvents for CO2 absorption (Bailey & Feron, 2005)

Solvent	**Monoethanolamine (MEA)**	**Diglycolamine (DGA)**	**Diethanolamine (DEA)**	**Diisopropanolamine (DIPA)**	**Methyldiethanolamine (MDEA)**
Concentration (% mass)	< 30	< 60	< 40	< 40	< 50
Solvent loading (mole/mole)	0.3	0.35	0.30-0.70	0.45	0.45
Heat of regeneration ($MJ/kg\ CO_2$)	2.0	2.0	1.5	1.5	1.3
Chemical formula	C_2H_7NO	$C_4H_{11}NO_2$	$C_4H_{11}NO_2$	$C_6H_{15}NO_2$	$C_5H_{13}NO_2$

2.2 Natural Gas Dehydration using Glycol Processes

Natural gas dehydration is a process of removing water vapour from the gas stream to lower the dew point of the gas. It is an important process to prevent hydrate formation which results in blockages inside pipelines or process equipments, and retards the flow of gaseous hydrocarbon stream (Ripmeester et al.,1987; Tohidi et al., 1990). Hydrates are solids formed by the physical combination of water and small molecules of hydrocarbon. Hydrates grow as crystals and can build up in orifice plates, valves, and other areas not subjected to full flow (Abdel-Aal & Aggour, 2003). Besides of hydrate formation, the presence of water also reduces the combustion efficiency (Rohani, 2009) and promotes corrosion as previously discussed.

For gaseous phase dehydration, glycol compounds are known as the best absorbent (Gilbert & Boris, 1996; Gottlib, 2003). Gas dehydration by glycol is also capable to reduce water content of natural gas less than 0.1 ppm (Carroll, 2009). In this process, glycol acts as a thermodynamic inhibitor, or 'hydrate antifreeze', where it changes the thermodynamic properties of the fluid system, therefore shifting the equilibrium conditions for hydrate formation (Speight, 2006). The most commonly used dessicants at present for this process are ethylene glycol, or known as ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG) and some other coumpounds for special circumstances, such as glycerol or methanol. Among all the glycols, triethylene glycol (TEG) is the most widely used for natural gas dehydration (Woodcock, 2004). TEG provide less losses due to lower vapour pressure (Kelland, 2009) and it can highly reduce benzene, toluene, ethyl benzene and xylene (BTEX) emissions (Braek et al., 2001; Ebeling, 1998). Table 2.3 presents the physical properties of TEG and MEG, two potential absorbents to be used and investigated in this study.

Table 2.2: Physical Properties of TEG and MEG (Isa et al., 2013; The Dow Company, 2013).

Physical Properties	Value (TEG)	Value (MEG)
MW	150	62
Specific weight (g/cm3)	1.125	1.115
Melting point (°C)	-7	-13
Boiling point (°C)	286	197.6
Vapour pressure (Pa) at 25°C	0.05	7.99
Decomposition temperature (°C)	204	163

Bahadori and Hari (2009) has described the natural gas dehydration using glycol process as follow; absorption of water takes place in a glycol contactor, whether a tray column or packed bed, with TEG and wet natural gas flowing counter currently. At the bottom part of the contactor, water-enriched TEG will flows out and continue flowing to a heat exchanger. The TEG is then flows into a flash drum, to release and separate flash gases from the stream. Afterward, TEG is cooled inside TEG/TEG heat exchanger and brought into a reboiler to boil out water from it. The reboiler temperature should not exceed 208°C based on the decomposition temperature of TEG. Next, TEG without water content or regenerated TEG will flow back to the hot side of TEG/TEG heat exchanger, and pumped back to the top of the contactor. The overall process is depicted in Figure 2.3 below:

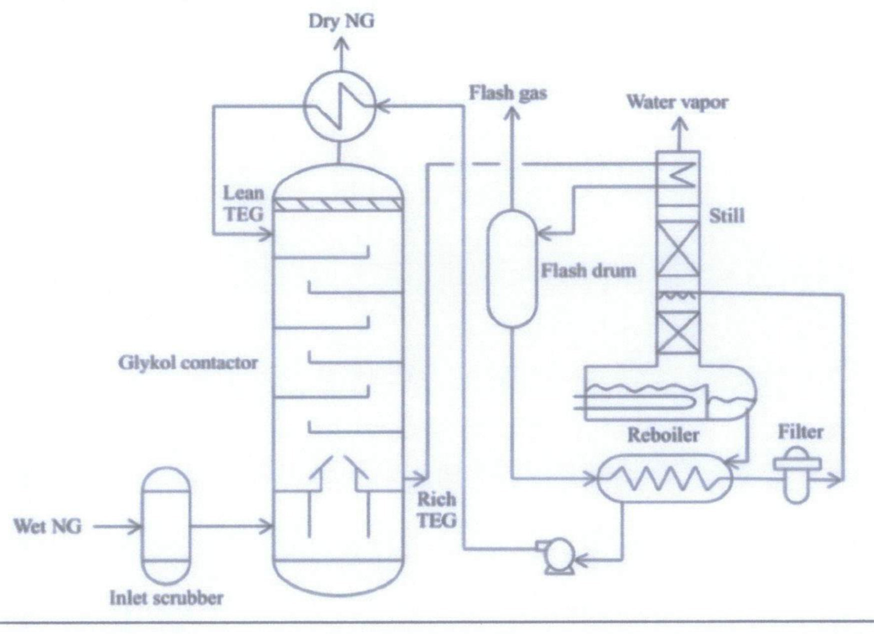

Figure 2.3: Scheme of Absorption Dehydration (Bahadori & Hari, 2009).

2.2.1 Enhanced Dehydration Process

Another focus topic in this study is the enhanced dehydration process where the regeneration of the glycol in this absorption process is upgraded to increase the purity of TEG. Many researchers have been attracted on this matter because it can greatly increase the capability of glycol dehydration process. Enhanced regeneration of glycol is defined as any system or method that improves glycol regeneration to achieve leaner or more concentrated solution once it has been recycled, to produce glycol with high purity (Ebeling, 1998).

To increase the efficiency of regeneration process, some methods need to be applied. According to Ebeling (2008), he mentioned that enhanced regeneration could be achieved by injection of stripping gas into re-boiler, azeotropic distillation for regeneration or other proprietary processes which typically the rich TEG is regenerated under low pressure and high temperature Another way of improving the regeneration is by vacuum regeneration which the process will take place in low pressure, lower than atmospheric pressure. This method however, is complicated and costly ineffective (Rahimpour et. al, 2013). Some of the methods mentioned are applied in several enhanced gas dehydration unit, for example stripping gas and Stahl column GDU is using stripping gas to increase the regeneration, and DRIZO GDU using azeotropic distillation for this purpose and Coldfinger technology.

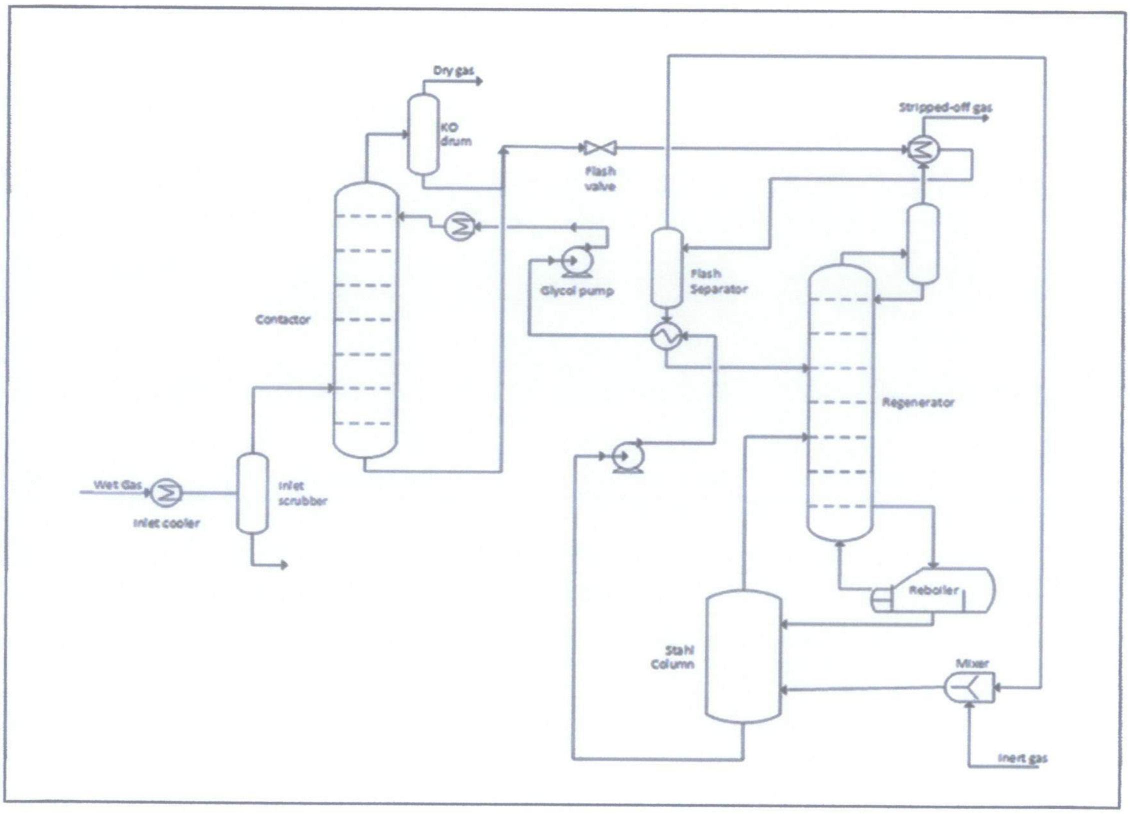

Figure 2.4: Stripping gas and Stahl column GDU (Christensen, 2009)

2.3 Dew Point Requirement

The amount of water to be removed from the gas is depending on the lowest temperature at which the gas will be exposed in the pipeline. As the temperature is reducing, the water vapour contained in the gas stream tends to condense into liquid after it reaches the dew point, in which will increase the tendency of hydrate formation (Isa *et al*, 2013). Dew point is the point of where water and the gas start to condense. To indicate the quantity of water vapour present in the gas, the dew point is often used. Lower dew point means that the gas has minimum water content, therefore the gas can operate in low temperature with formation of hydrates is unlikely.

Two major companies in producing gas turbines, General Electric (GE) and PC McKenzie have outlined the allowable water content inside the fuel gas for their turbines. General Electric Company (2002) specifies that the allowable moisture content for pipeline transportation of the gas fuel for its gas turbine is typically around 7 lbs/mmscft (152 ppm) or significantly less. The use of dew point in determining the water content is shown in the next figure. Figure 2.5 provides a guide in determining the expected moisture dew point from the moisture concentration and gas fuel pressure of typical natural gas (General Electric (GE) Company, 2002). In another related note, PC McKenzie Company (n.d) also reported that the allowable water content for gas transmission ranges from 4 – 7 lbs/mmscft (87.2 – 152 ppm).

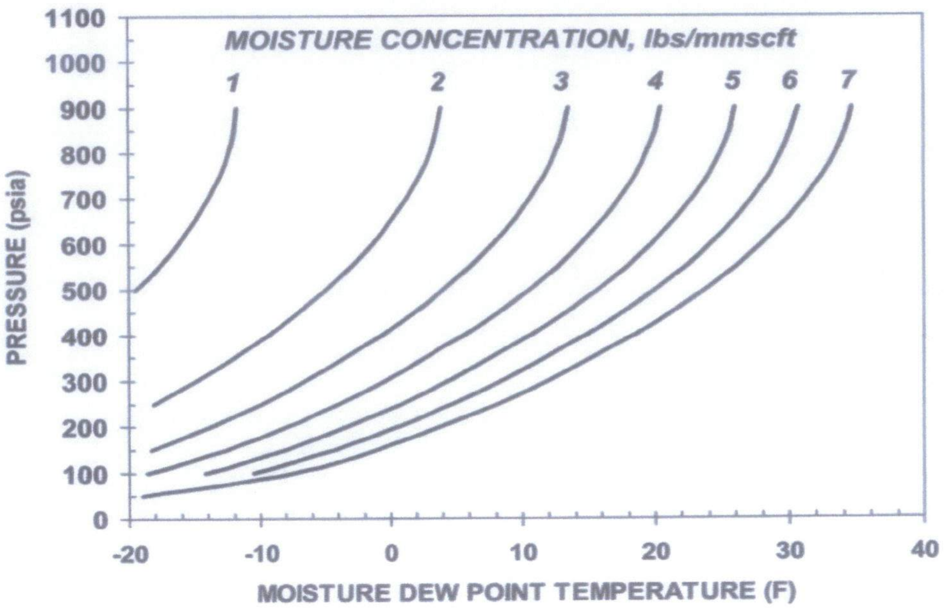

Figure 2.5: Moisture Dew Point as a function of Concentration and Gas Pressure for a typical natural gas fuel (General Electric (GE) Company, 2002).

2.4 Simulation of Gas Dehydration Unit

In gas dehydration process, association between water and TEG causes them to mix and creates a single liquid phase, and due to same reason, this mixture is difficult to be simulated (Sloan, 1990; Christensen, 2009). In order to precisely simulate the water/glycol mixture in this process, proper thermodynamic equations are necessary. Peng and Robinson (1976) explained that, some models based on cubic equations of state (EOS) guarantee a good phase equilibrium prediction over wide ranges of temperature and pressure. In a view of modelling multicomponent systems in dehydration units, this is crucial. It is necessary to take into account for the presence of gases and the high operating pressure of the absorption column (Peng & Robinson, 1976). Simulation software, Aspen HYSYS is the main platform used for this study and two thermodynamic packages will be employed; Peng and Robinson, and Twu et al. (Peng & Robinson, 1976; Twu et al., 2005). Peng-Robinson thermodynamic package alone could not calculate accurately the TEG-water system for the regeneration part, but however, it can calculate significant amount of TEG as the bottom product of the regeneration process (Bahadori et al., 2008).

In real case, the vapor pressure of TEG at the regeneration column is very low therefore reduces its tendency to vaporize and to become top product (Isa *et al.*, 2013). Since TEG regeneration process involves high temperature, Twu-Sim-Tassone (Glycol) thermodynamic package is suitable to be used. This thermodynamic package is accurate in determining the activity coefficients of the TEG-water system and it it also applicable to wide ranges of pressure and temperature (Twu et al., 2005). The performance of gas dehydration unit will be investigated in terms of water dew point and water content remaining in the dry gas after gas dehydration process. Phase envelope diagram will shows the moisture dew point of the gas. DRIZO™ GDU is proven to produce most significant changes on water dew point curve followed by conventional Stripping gas and Stahl column GDU and typical GDU (Isa *et al*, 2013).

2.5 Water Content with Respect to Hydrate Region

Since hydrate formation is a time dependent process, the rate of formation depends on several factors. Some of the factors effecting the rate are gas compositions, presence of crystal nucleation sites in the liquid phase, and degree in agitation (Moshfeghian, 2010). To understand the hydrate line and the effects of dehydration on the gas stream, phase evelope diagram is often used. Phase envelope or P-T diagram shows the correlation between temperature and pressure of a system. In phase envelope diagram, several curves are plotted to see the differences between them. The curves are; hydrocarbon dew point, water dew point, and hydrate formation curves. By observing the location and the behaviour of these curves on this plot, we can analyze the condition of the gas stream, therefore determining whether hydrate will form or not. The example of phase envelope diagram is shown below in Figure 2.6.

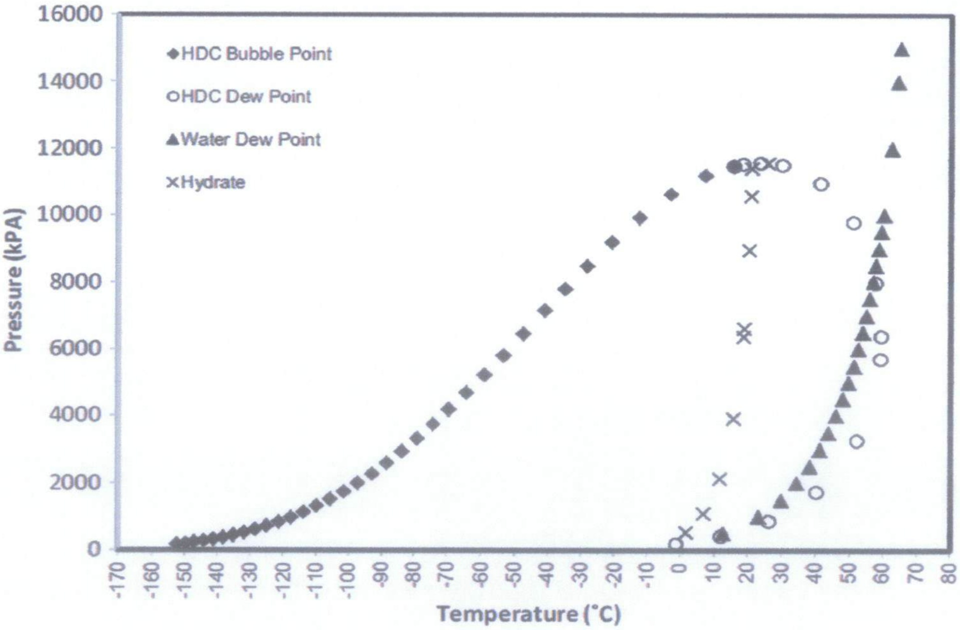

Figure 2.6: P-T Diagram of wet natural gas (Isa *et. al.*,2013)

Figure 2.6 shows the phase envelope or P-T diagram of wet natural gas (Isa et. al.,2013). In this diagram, 4 curves were plotted; hydrocarbon dew point, hydrocarbon bubble point, water dew point and lastly hydrate curve. Since the gas is saturated with water vapour, the water dew point is on the right hand-side of the graph. Besides, we can observe that the dew point temperature is quite high, which is within 10°C and 60°C. Under this condition, hydrate formation is very likely to happen if the temperature of the stream goes within the water dew point range. To have gas without free-water to form and preventing the hydrate formation, the water dew point temperature must be lowered down to the temperature of hydrate formation, or graphically, shift the water dew point line to the left side of the hydrate curve.

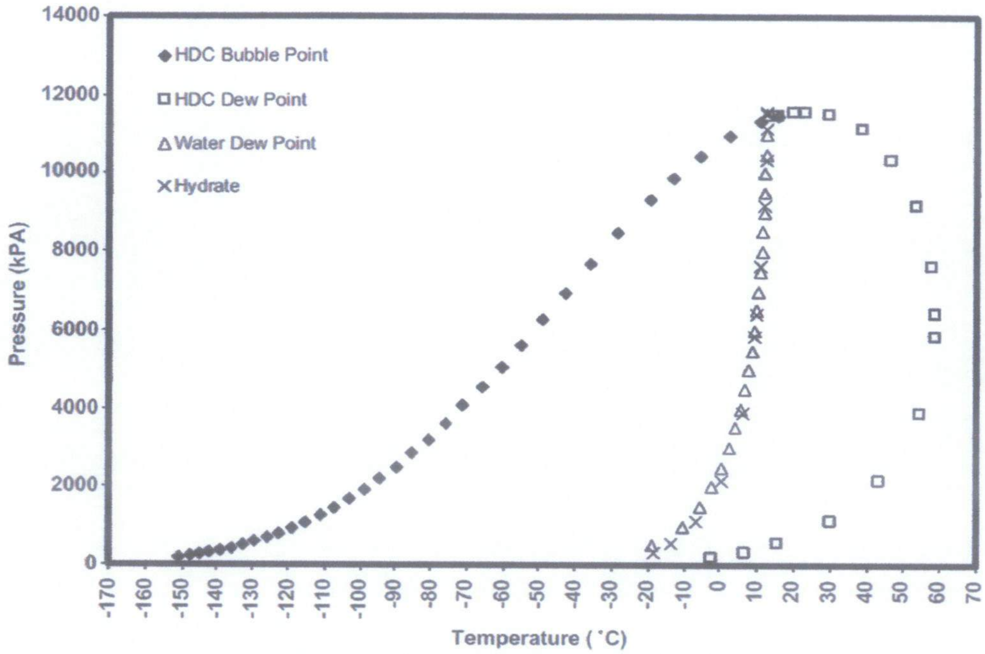

Figure 2.7: P-T diagram of dry natural gas after typical GDU (Isa *et al*, 2013)

The diagram shown above (Figure 2.7), is the phase envelope of dry natural gas after it went through gas dehydration process. The figure shows that the water dew point line is on the left side of the hydrate formation curve. This indicates that the gas is under-saturated with water, in which the condition is known as 'meta-stable' water condition. Under this condition, the gas is thermodynamically unstable and will not form a free aqueous phase. Otherwise, if the water dew point line is located on the right side of the hydrate curve, free water and hydrates may form (Ebeling, 1998). The condensed water phase will transform into solid hydrate as the temperature declining, eventhough it is higher than freezing point of water. Once the hydrate is formed, the 'meta-stable' water condition is now known as 'meta-stable' equilibrium (Isa, *et al*, 2013).

CHAPTER 3
METHODOLOGY

3.1 Procedure for The Study

Several steps needed to be taken to perform this study. Charts below will explain briefly the methodology and procedures for this project:

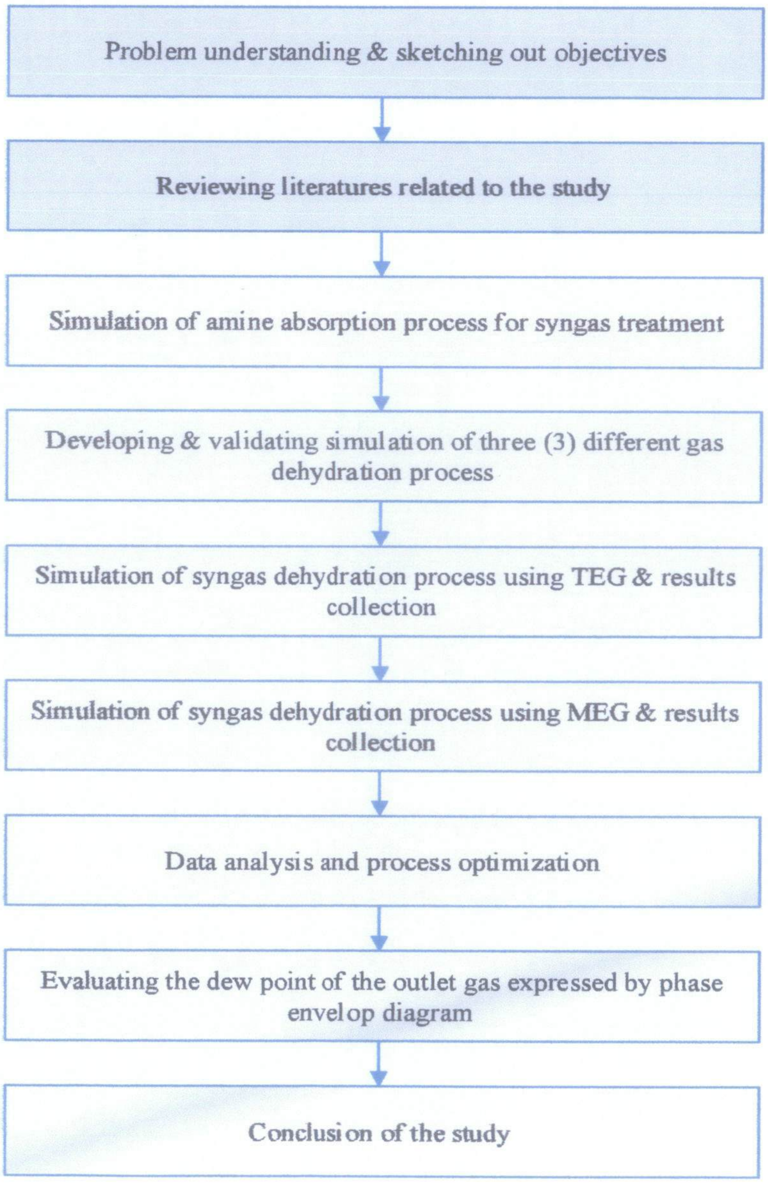

Figure 3.1: Methodology of the study

3.2 Research Methodology

After identifying the problems faced and the objectives of the study, literature research is conducted from several trusted sources, i.e books, journals, thesis, websites etc. to clearly understand the principles and theories behind the subject. By reviewing related literatures, it creates strong foundation and comprehension before proceeding with the projects, and it is also helped in creating authenticated work. The literatures available is reviewed and will be summarized in the report as references for the study.

The next step of the project is to simulate and validate amine absorption process. This step is taken to obtain accurate result on how much water content is generated by the process. Multiple simulation has been done by researchers on amine absorption process by using natural gas as feed, but up-until-today there are no study has been made in simulating amine process on synthetic gas . Accurate composition of treated synthetic gas is needed for gas dehydration process simulation in order to achieve solid results towards the end of the study. Once completed, the compostion data of the processed gas is analyzed to examine the water content of the gas. Phase envelope diagram of the processed synthetic gas is also drawn to illustrate the data.

After getting the composition of treated synthetic gas , the study will be proceeded with simulation of conventional gas dehydration unit, and enhanced gas dehydration unit which are Stripping gas Stahl Column Gas Dehydration Unit. The simulation is based on one of the onshore oil production facilities located in Abu Dhabi, and operated by ADCO (Braek *et al.*, 2001) Upon completion of these three GDUs, real data is obtained to validate all the simulation. Validated simulations will then be used to run the process with the synthetic gas feed and the results will be collected and analyzed.

To analyze the results, the dew point of the outlet gas will be evaluated by using phase envelop diagrams. Phase envelop diagrams will indicates the effectiveness of the dehydration process, therefore it is a correct tool to examine the efficiency and effectivity of the gas dehydration processes on treated synthetic gas . By observing the results taken, conclusion of the study will be drawn and final report will be prepared on this study.

3.3 Gantt Chart & Key Milestones

Table 3.1: Gantt Chart of the project

No	Details	Semester May 2013														Semester Sept 2013													
		W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14
1	Problem understanding & sketching out objectives														Study & Examination Week														Study & Examination Week
2	Reviewing literatures related to the study																												
3	Proposal submission & Proposal Defence																												
4	Simulation of amine absorption process for syngas treatment																												
5	Developing & validating three (3) different gas dehydration process																												
6	Submission of Interim Report																												
7	Simulation of syngas dehydration process																												
8	Result & data collection																												
9	Data analysis & process optimization																												
10	Evaluating the dew point of the outlet gas by using Phase Envelop Diagram																												
11	Concluding the study																												

3.4 Material & Chemical

To perform this study, list of chemicals below will be used:

- Synthetic gas from gasification of coal, petcoke and biomass
- Dimethyl amine (DEA) for amine absorption process
- Triethylene glycol (TEG)
- Ethylene glycol (MEG)
- Water for preparing glycol and amine solution

3.5 Tool Required

Aspen HYSYS will be used for the simulation of the study.

CHAPTER 4
RESULTS AND DISCUSSIONS

Throughout the project, multiple simulations were developed and ran to achieve the objectives of the study. Amine absorption process was first simulated to obtain the amount of water generated inside the treated synthetic gas. Next, three gas dehydration units covered in this project were simulated and the performance of different gas dehydration processes was investigated for the water/hydrocarbon dew point and concentration of regenerated TEG. In terms of water content remaining in the dry synthetic gas after it passes through gas dehydration units, the generated data was manipulated by several parameters; number of stages in absorption column, volume flow rate of TEG and re-boiler temperature of the TEG regenerator.

By applying the optimum parameters, the performance of gas dehydration units were then evaluated by using phase envelope diagrams. Apart from that, the effect of absorbent used was also determined by using the same method. Graphical comparison was made to investigate the efficiencies of both absorbents; TEG and MEG.

4.1 Amine Absorption Process

In the first part of this study, amine absorption process is simulated by using Aspen HYSYS to investigate amount of water generated by the process. Synthetic gas is fed to the process for acid gas removal. Acid gases, CO_2 and H_2S will be removed from the synthetic gas by contacting the gas with DEA solution in an absorber column. In order to reuse the DEA solution, a regenerator unit is introduced to remove the acidic gas component inside the solution and this will produce a lean DEA solution for the process. The configuration of amine absorption process for this project is adapted from Peters et al. (2011), Lars Erik Øi (2007), and Kucka et al. (2003) as shown in Appendix 1. After completing the simulation, it is then validated by real data obtained from a journal paper by Peters et al. (2011). In this paper, simulation is conducted by using natural gas as inlet feed data and is passed through amine absorption process.

To run the Aspen HYSYS simulation, 2 feed gas cases are employed in this study and the water generated was observered after it passes through the process. The composition of both synthetic gas cases used is shown in Table 4.1;

Table 4.1: The composition of synthetic gas employed in this study in mol fraction (Wang et al,2009)

Case I								
H_2	O_2	N_2	CO	CO_2	H_2S	C_1	C_2	Water
0.2823	$3.3x10^{-6}$	0.0287	0.4147	0.1527	0.0075	0.1124	0.0016	$1.4x10^{-4}$

Case II								
H_2	O_2	N_2	CO	CO_2	H_2S	C_1	C_2	Water
0.3238	0	0.0329	0.4760	0.0357	0	0.1289	0.0018	0.001

After amine process using DEA solution, both feed gas cases reach the specified simulation goals of reducing the CO_2 and H_2S level inside the gas. It was observed that the water content inside the sweet gas is increasing to a level exceeding the pipeline specification which typically around 150ppm. The water content inside the gas for both cases are summarized in the Table 4.2 as follows;

Table 4.2: Water generated from amine absorption process for synthetic gas

	Sour Gas (Before amine process)		Sweet Gas (After amine process)	
Case	1	2	1	2
Water content (ppm)	89	115	934.3	920.5

4.2 Effects of Operating Conditions on the Efficiency of Gas Dehydration Unit

Typical gas dehydration unit model developed using Aspen HYSYS was used to analyze the effects of the operating conditions towards the efficiency of gas dehydration process. The generated data given by the simulation in term of water content remaining in the gas after passed through the process is being manipulated by several parameters. The parameters selected; number of stages of absoption column, volume flow rate of TEG, and re-boiler temperature, do have the effects on the process efficiency. The results from this step show a parametric study of a typical gas dehydration unit in optimizing the dehydration process.

4.2.1 Effects of Number of Equilibrium Stages in Absorption Column

The effect of number of equilibrium stages of Gas-TEG contactor on residual water content exiting the dehydration unit is illustrated by Figure 4.1. The gas dehydration unit is operated under the re-boiler temperature of 204°C, with TEG flow rate kept constant at 2.72 m^3/hr. The graphical display shows that as the number of equilibrium stages in the contactor is increased, more water are allowed to be absorbed and this situation is reflected by the amount of water in the residual gas. Lowei water content inside the residual dry gas indicates that more water is absorbed by TEG. It is also observed that after stage number 6, the effects of increasing stage number on the water content of the residual gas is minimum. Therefore, we can determine that stage number 6 is the optimum number for gas dehydration unit and increasing the stage number may become unnecessary, and increasing the cost value of the process.

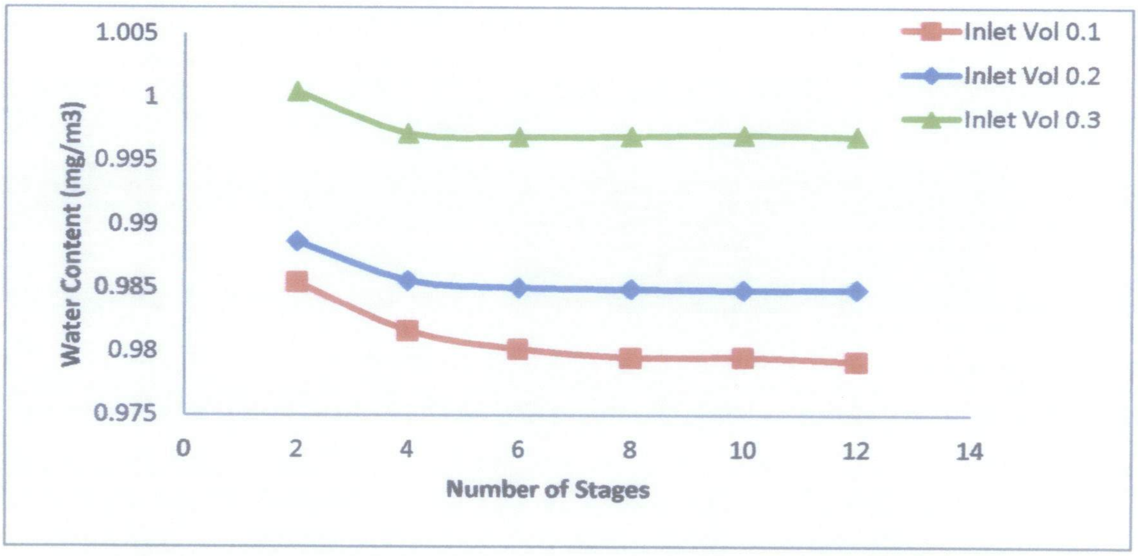

Figure 4.1: Effects of number of equilibrium stages on residual water content

4.2.2 Effects of Volume Flow Rate of TEG in Absorption Column

To increase the degree of contact between gas and TEG in which increasing the efficiency, higher TEG flow is needed. High volume flow rate of TEG will absorbed more water inside the gas, therefore lowering the residual water content. As the water content of the dry gas is falling low, the depression of water dew point will occur, and this condition meets the requirement of fuel specification of synthetic gas. Figure 4.2 visualizes the relation between the TEG flow rate and the residual water content of the gas after the process. It is expected that with more TEG flow, the lower water content inside the gas will be obtained. Comparing the effects of number of stages and the effects of TEG flow rate, TEG flow rate influenced more on the water content of the dry gas. Lowering or increasing the flow will have greater effects towards the water content on the product gas.

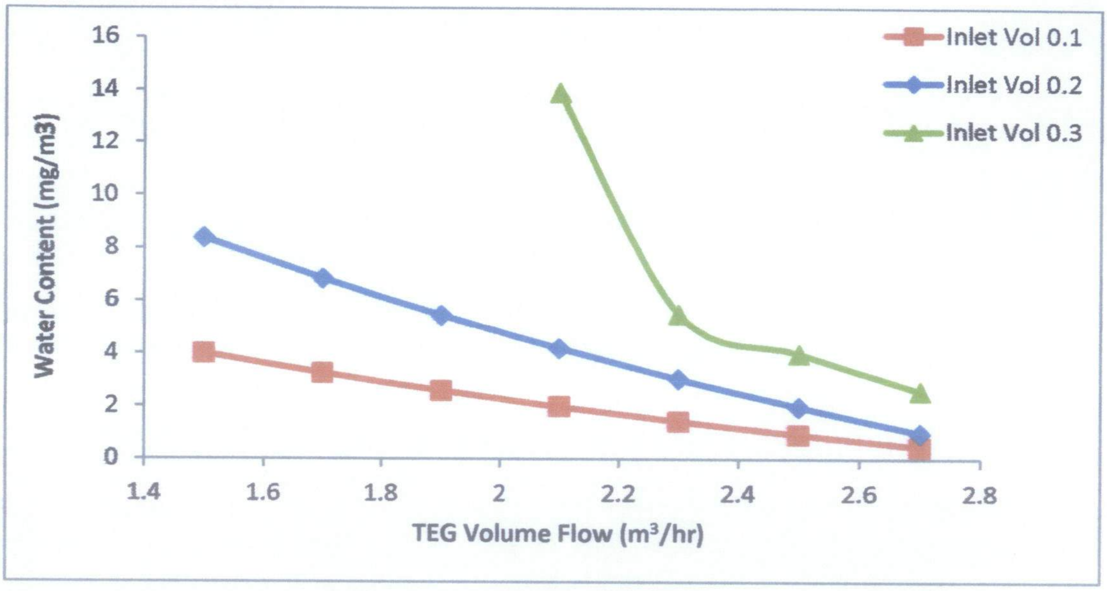

Figure 4.2: Effect of TEG flow rate on the residual water content

4.2.3 Effects of Re-boiler Temperature

Decomposition temperature is the temperature where TEG begins to reaact with water and decompose into MEG. As reported by Christensen (2009), TEG is having a decomposition temperature at 204°C, therefore the re-boiler temperature should not exceeding this value. The effects of re-boiler temperature at regeneration stage for TEG does give significant outcomes on the water content of the residual gas. As the temperature increases, the water content after the dehydration unit is decreasing. This is because having high temperature of re-boiler will regenarate TEG with high purity. Re-boiler temperature influences the purity of the regenerated TEG, hence the water absorbed as well. High purity of TEG will absorb more water vapour from the wet gas, and depressed the water dew point of the outlet gas. Figure 4.3 shows that as the temperature increases, the water content of the residual gas decreases and it will achieve lowest water dew point depression at temperature of 204°C.

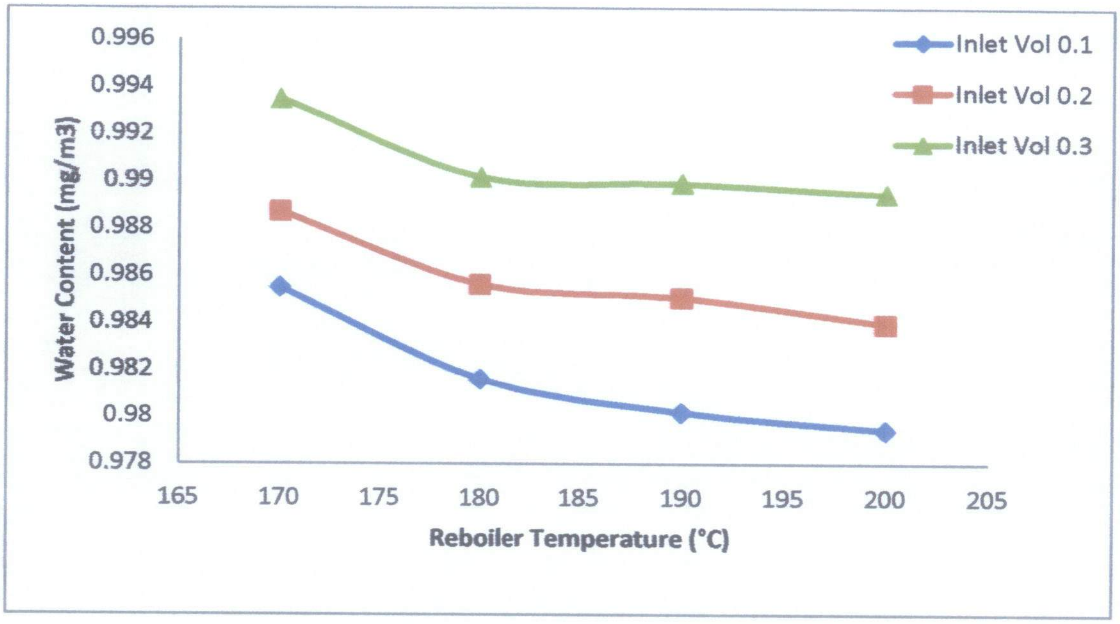

Figure 4.3: Effects of re-boiler temperature on the residual water content

4.3 Simulation of Gas Dehydration Units (GDU)

Two gas dehydration units (GDU) were simulated by using Aspen HYSYS. The data used for simulation is gatheed from a real data plant resemble one of the onshore oil production facility located in Abu Dhabi (Braek, et al., 2001) and these data were the basis of the simulations. The two gas dehydration units simulated are:

- Typical gas dehydration unit
- Enhanced gas dehydration (Stripping gas Stahl column gas dehydration unit)

To examine the performance of these gas dehydration units, the information of remaining water content in the dry gas, in term of water dew point, after it went through the process is gathered. The performance can be compared and analyzed by plotting the data in a phase envelope diagram. As previously discussed, phase envelope is used to depict the water dew point curve behaviour as well as hydrocarbon dew point and hydrate curves. Figure 4.4 exhibits the phase envelope diagram (P-T diagram) of the wet synthetic gas after the amine process using DEA solution, and before entering gas dehydation processes.

From the P-T diagram, it can be seen that water dew point curve is located on the right side of the hydrate curve. This behaviour indicates that the gas is saturated with water vapour and under this condition, hydrates may form as free water is available. If hydates are form, 'meta-stable' equilibrium is now known for this 'meta-stable' water condition (Isa, et al., 2013). The pattern of the curves also can be intepreted such a way that at low operating temperature, water will begin to condense as the water dew point of the gas is very high. The water dew point range of wet synthetic gas is within 20°C and 50°C. Graphically, the objective of dehydration is to shift the water dew point curve to the left side of the hydrate curve, as far as possible. The far left water dew point curve indicates that the water dew point has been depressed to a much lower temperature.

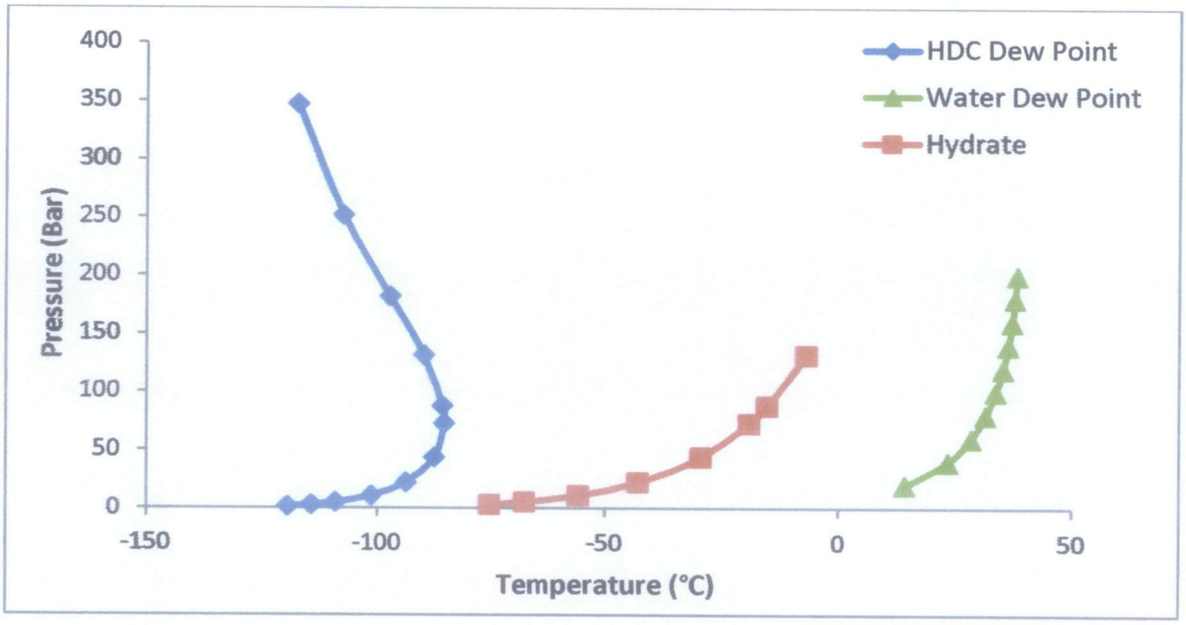

Figure 4.4: P-T Diagram of wet synthetic gas

The diagram also exhibits a very low temperature range for hydrocarbon dew point. It is observed that the hydrocarbon dew point curve is on the most-left of the graph. This situation is may be because of one of the property of synthetic gas which contains less hydrocarbon inside the gas. To compare with natural gas, the range of dew point for hydrocarbon in natural gas is between 0°C to 60°C, since the major constituents of natural gas is mainly hydrocarbon. On the other hand, the composition of hydrocarbon in synthetic gas is only around 12%. Hence, the compositions of the gas does have a huge effects on the dew point behaviour.

4.3.1 Phase Envelope of Dry Gas Stream at Typical Gas Dehydration Unit

In order to evaluate the performance of typical gas dehydration unit, phase envelope diagram is plotted. Figure 4.5 displays the P-T diagram of dry gas after is went through gas dehydration process using typical GDU. From the simulated data, three curves were plotted, the hydrocarbon dew point curve, water dew point and hydrate curves. The behaviour of these curves is observed to analyze the effects of gas dehydration process towards synthetic gas. Furthermore, the efficiency of this process on synthetic gas dehydration was also determined.

The P-T diagrams demonstrates that the water dew point has been shifted to far left of the graph, while no significant changes on hydrocarbon dew point and hydrate curves. This situation indicates that water dew point depression has occurred as the water content from the synthetic gas is reduced significantly. The results from the simulation stated that the water content was levelled down to 1.3ppm. Hence, the dry gas from the absorption process can now operates under low process and pipeline temperature since the water dew point temperature has been lowered to under than -100°C. At temperature higher that the water dew point temperature, the gas will be under-saturated with water, and free aqueous phase will not form. This condition also would not allow and free water, hence no hydrates will be formed.

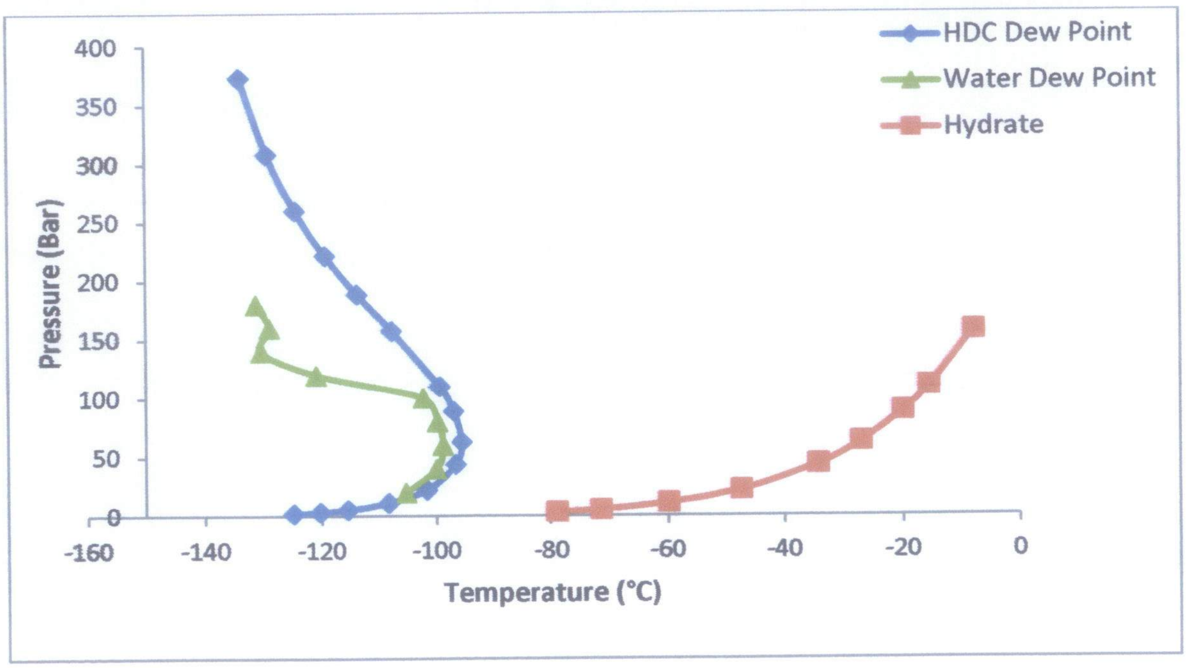

Figure 4.5: P-T Diagram of dry synthetic gas from typical GDU

4.3.2 Phase Envelope of Dry Synthetic Gas Stream from Enhanced Gas Dehydration

Typical gas dehydration unit normally produces gas with limited water dew point depression due to purity of regenerated TEG and the circulation rate limit (Netusil, et al., 2011). To solve this limitation, enhanced gas dehydration system is introduced using gas stripping to enhance TEG regeneration. One of the enhanced gas dehydration unita is the stripping gas and Stahl column GDU. Stripping gas and Stahl column GDU reduces the partial water vapour pressure in the regenerator column by introducing the use of stripping gas and additional Stahl column, or by lowering the operating pressure of regenerator column on vacuum condition. However, usage of stripping gas is more practical because to reduce the column pressure below atmospheric pressure may need complicated procedure and it is also may not be cost effective. An additional Stahl column gives an extra stage for regeneration as it takes the solvent from re-boiler and sends it to be in contact with a flow of sry stripping gas.

Data obtained from simulation of stripping gas and Stahl GDU showed that the enhanced regeration does producing lean TEG with higher purity. The concentration of lean TEG recorded was 99.89%. The simulation also showed less TEG loss throughout the process. Only 0.02% of the original is loss during the process. The stripping application are considered successful in producing TEG with high concentration. Theoretically, this will increase the capability of TEG to absorb more water from the gas into the solution. Previous study with natural gas also had support this hypothesis, where enhanced dehydration process will gives out gas with lower water content.

However, as exhibited in Figure 4.6, the phase envelope of the exiting synthetic gas from this process was showing another observation. As displayed, the behaviour of the water dew point curve is different with one from typical gas dehydration unit as it is far more on the right side, however still on the left side of the hydrate curve. The dehydration process is said to still achieve the objective of the process to remove water content, and depressing the water dew point, but it may not be as effective as typical gas dehydration. The water dew point temperature of the dry gas from this GDU is higher than from typical GDU, therefore the formation of hydrate is still unlikely. The recorded water dew point is low; ranging from -50°C to -60°C.

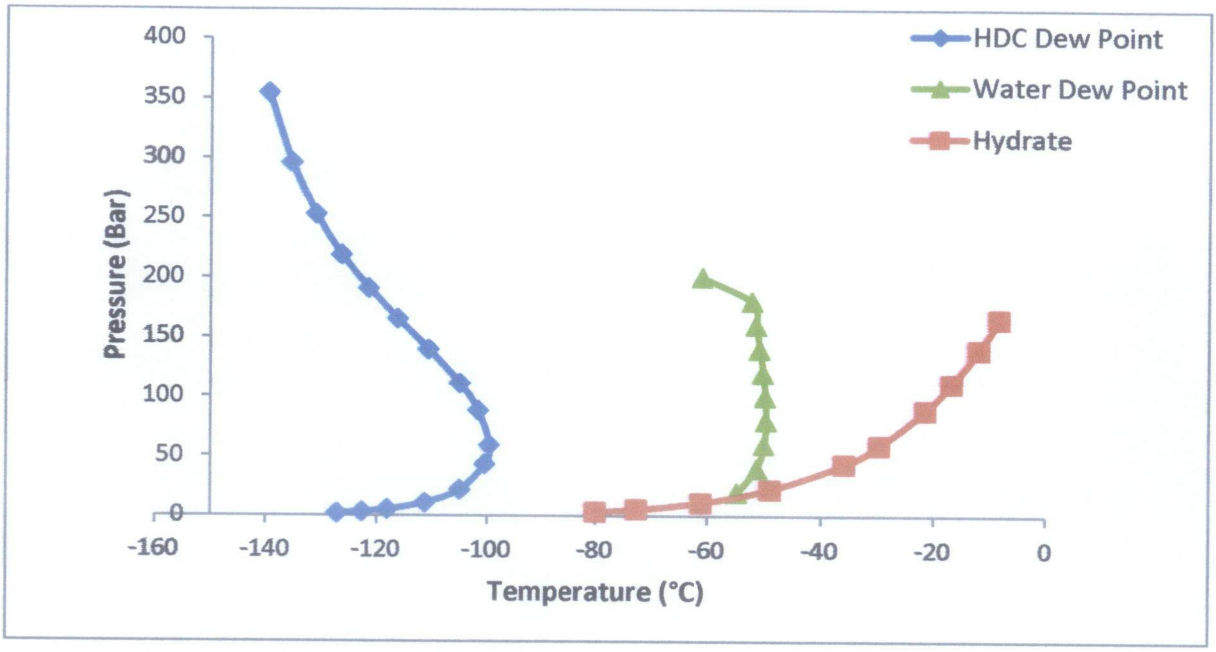

Figure 4.6: P-T Diagram of dry synthetic gas from Stripping gas and Stahl Column GDU

Although the purity of regenerated TEG is indeed higher than TEG regenerated from typical GDU, the water content of the dehydrated gas from this proccess is higher. The water content were supposed to have lower value than in TEG. This had showed an interesting difference from expected result built from previous study. The data is tabulated in Table 4.3.

Table 4.3: Water content of synthetic gas for gas dehydration units

Gas Dehydration Unit (GDU)	**Typical GDU**		**Stripping gas and Stahl column GDU**	
Water content (ppm)	Wet gas	Dry gas	Wet gas	Dry gas
	920.5	1.3	920.5	2.1

This differences may be because of the effects of synthetic gas composition. In comparison, synthetic gas contains almost 50% CO gas while in natural gas, no CO content. Besides, another major component in synthetic gas is hydrogen, which occupied around 30% of gas composition. These two compounds may have different reaction with TEG and this occurrence can be looked into to have better understanding of it.

Another point of view in analyzing the data, is that, in comparison with the effects of dehydration towards natural gas, enhanced gas dehydration did work more effective. This point is made based on the observation on how low the water dew point is depressed. In natural gas dehydration, Stahl column GDU had successfully reduced the water dew point temperature to -20°C (lowest point). On the other hand, the same process reduces the water dew point temperature of synthetic gas to a lower temperature, which is -50°C. This gap of difference is significant. We can conclude that stripping gas and Stahl column GDU works better for synthetic gas compared to natural gas.

4.4 Comparison Between Typical and Enhanced Gas Dehydration for Syngas

To summarize the finding of synthetic gas dehydration, a comparison table is made to recognize the differences between typical gas dehydration and enhanced gas dehydration (stripping gas and Stahl column gas dehydration). The table will differentiate the effects of both processes towards synthetic gas dehydration, and to see how the result is different with natural gas dehydration.

Table 4.4: Comparison between typical and enhanced dehydrations for synthetic gas

	Typical GDU	Stripping Gas and Stahl Colum GDU
Operating Condition	Contactor + Regenerator	Additional stripping column
TEG purity after regeneration	99.75%	99.89%
Water Content after dehydration	1.3 ppm	2.1 ppm
Water dew point range	-100°C to -140°C	-50°C to -60°C
Effects on HDC dew point curve	Less	Less
Effects on Hydrate curve	Less	Less
Water dew point range for NG dehydration	0°C to -20°C	0°C to -20°C
Effects on HDC dew point curve (natural gas)	Less	Less
Effects on Hydrate curve (natural gas)	Significant (-10°C)	Significant (-10°C)

In term of phase envelope diagram, the comparison is made by plotting both diagrams in one plot to see the differences. Therefore, from Figure 4.7, it is shown that for synthetic gas dehydration, typical GDU will remove more water content, and having higher efficiency compared to enhanced GDU.

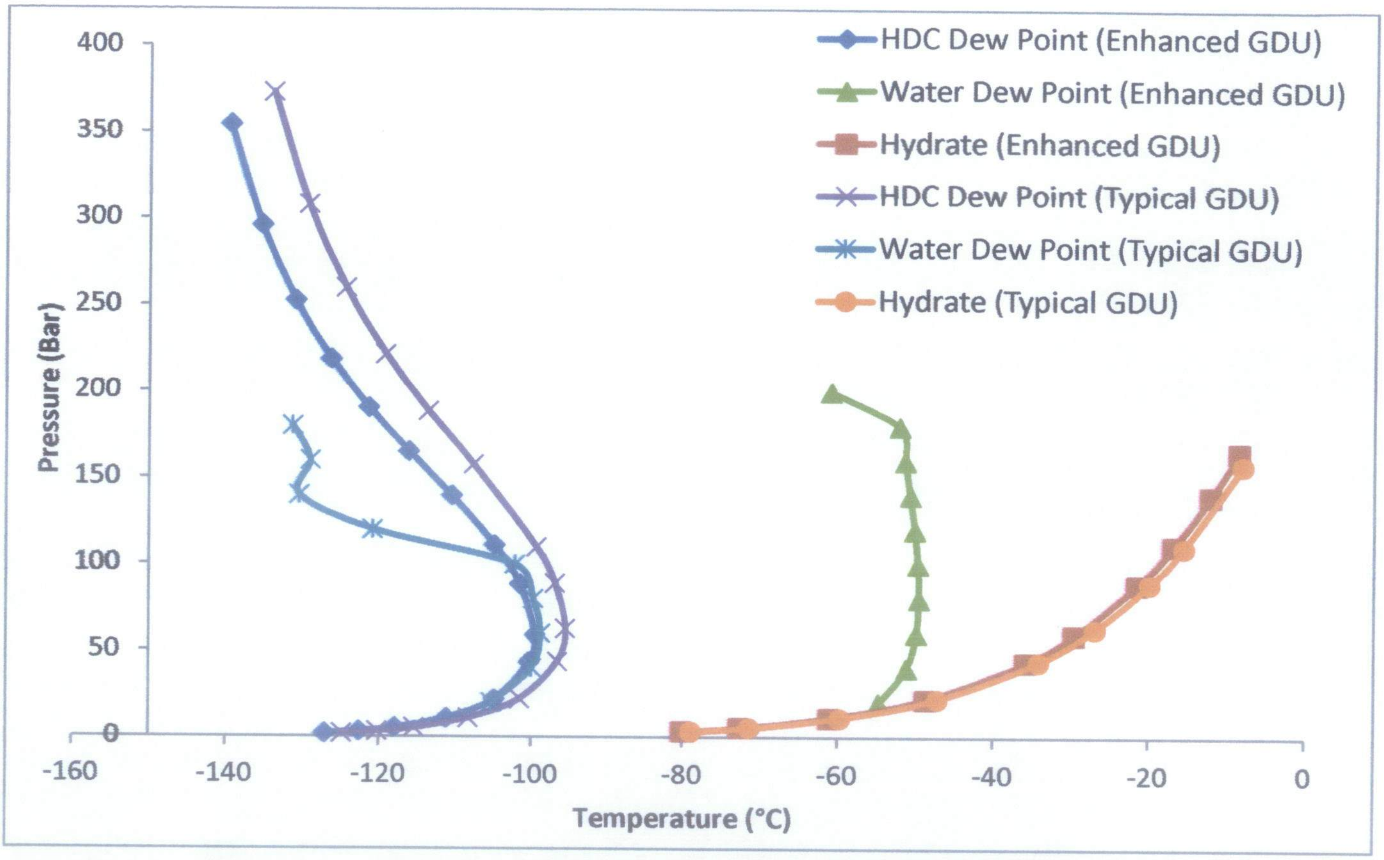

Figure 4.7: Comparison between typical and enhanced GDU performance

4.5 Effects of Ethylene Glycol (MEG) on Synthetic Gas Dehydration

The study is then proceeded to investigate the effects of ethylene glyol (MEG) for dehydration process. Physically, MEG is smallest compared to other glycols, and it also has lower boiling point but with higher vapour point. In distillation, normal boiling point and vapour pressure creates great influence because the higher the difference for these properties between the top and bottom product, the easier it is to separate the components (Christensen, 2009). TEG is well known for gas dehydration compared to MEG is because of this factor. The higher difference between normal boiling point and vapour point makes TEG in favour due to easy regeneration during the process. However, MEG is cheaper compared to TEG, and it has lower decomposition temperature. Low decomposition temperature of MEG will need a low re-boiler temperature to operate the regeneration process. This may be more cost effective compared to TEG process.

By using the simulation of typical GDU as previously developed, the absorbent was changed to MEG to study it's effects on dehydration process for synthetic gas. Other parameters such as number of stages, feed compositions and flow rate, and MEG volume flow rate are kept constant during the simulation. However, the re-boiler temperature needed changing to cater the low decomposition temperature of MEG. The re-boiler temperature was set to 163°C. Figure 4.8 shows the product of GDU operating with MEG.

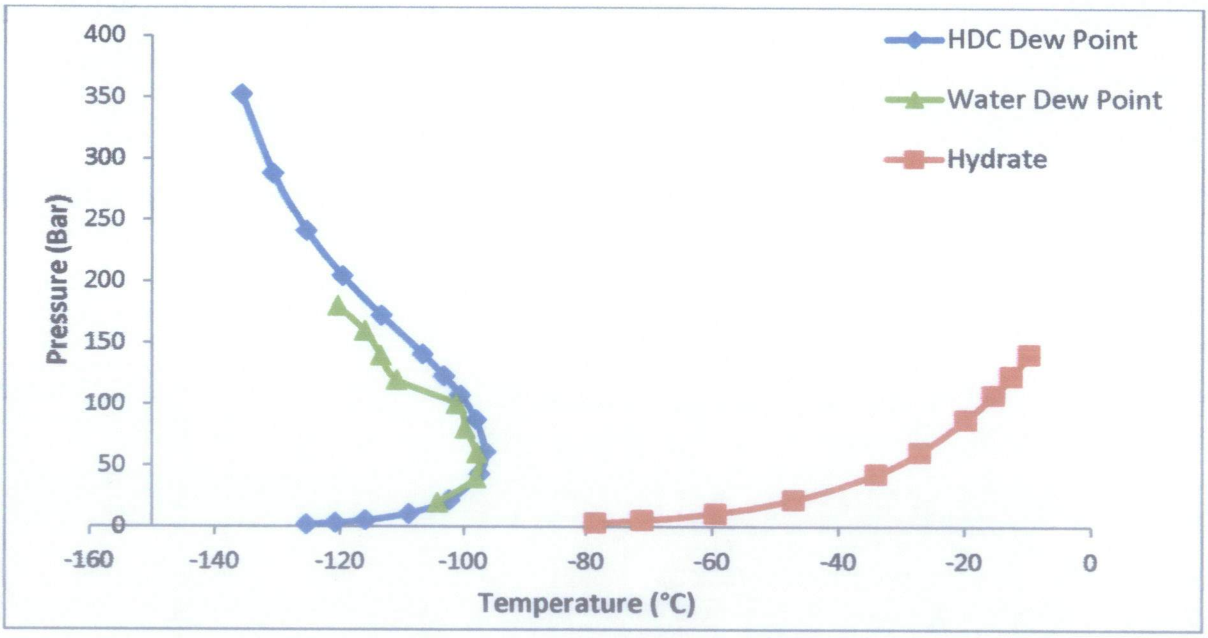

Figure 4.8: P-T Diagram of dry synthetic gas from typical GDU with MEG

From the phase envelope, it is clearly shown that the dehydration system with MEG achieved the process objective; to reduce the water content and creating water dew point depression. The water dew point curve has shifted to the far left of the graph, and this supports the premise. The condition of the gas is now under-saturated and free from water vapour, therefore preventing hydrates formation.

To compare the efficiency of both TEG and MEG system, water dew point curves are used and plotted in a same graph. Water dew point curve is chosen because it demonstrates significant change of behaviour compared to hydrocarbon dew point and hydrate curves. Figure 4.9 shows the water dew point curve behaviour after it pasees through gas dehydration process for both systems; TEG and MEG. From the graph, we can see that the water dew point temperature for the gas from TEG dehydration is slightly lower that temperature from MEG dehydration at lower pressure. However, after 100 bar, this difference becomes greater. The water dew point temperature of gas after TEG dehydration is very much lower than MEG at pressure higher than 100 bar. Therefore, to have a higher efficiency of synthetic gas dehydration, TEG should be chosen and this has been proven by comparing the water dew point temperature of the dry gas.

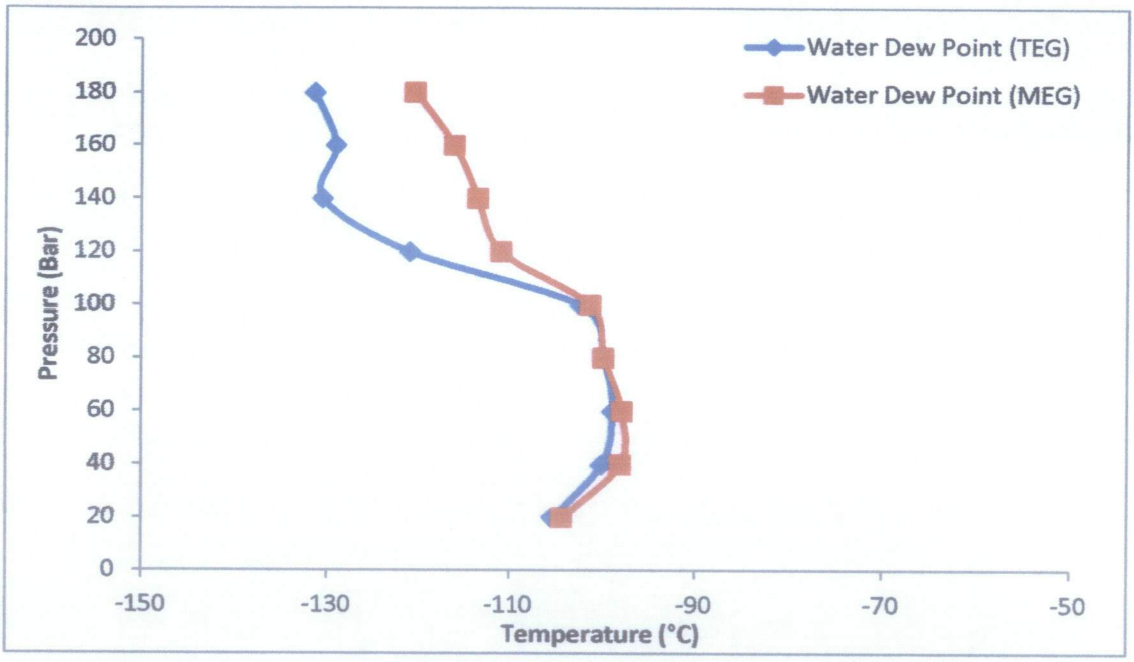

Figure 4.9: Comparison of water dew point curve for TEG and MEG dehyrations

Table 4.5 represents the clear comparison between MEG and TEG, including the performance and advantages of the two absorbents;

Table 4.5: Comparison between TEG and MEG

	TEG	MEG
Operating Condition	Re-boiler Temp: 204°C	Re-boiler Temp: 163°C
TEG purity after regeneration	99.75%	99.73%
Water Content after dehydration	1.3 ppm	1.35 ppm
Water dew point range	-100°C to -140°C	-95°C to -120°C
Effects on HDC dew point and hydrate curve	Less	Less
Advantages	• Lower losses • Reduce BTEX	• Produced locally • Low price

CHAPTER 5
CONCLUSION AND RECOMMENDATION

After completion of the project work and gathering the results, the objectives of the study are achieved. The simulation of amine absorption process using DEA solution for acid gas removal proves the hypothesis that amine process does generate significant water content inside the treated synthetic gas. It also gives an accurate data of wet synthetic gas after it went through the process, since no previous study has been made for this purpose. The data obtained is an important part of the study as this data was used for the next part of the project, which is simulating gas dehydration units for synthetic gas. From the simulation, the treated synthetic gas from amine process contains a significant amount of water vapor as the value reaches up to 900 ppm in average.

By using simulation software Aspen HYSYS, two gas dehydration units were successfully simulated. To achieve high performance dehydration, process optimization step was taken to find the optimum conditions for gas dehydration. Several factors affecting the residual water content of the dry gas were manipulated and the best condition was determined and used in this study. Afterwards, the gas dehydration processes were simulated and from the simulation run, both dehydration units met the objective of the process; to reduce the water content of the outlet gas and to depress the water dew point of the gas. Typical GDU has showed more significant changes on water dew point curve behaviours. Although the water dew point for outlet gas of stripping gas and Stahl column GDU was higher, but it regenerates higher TEG purity as gas stripping and additional column were introduced.

Next, the study of effects on type of absorbent used for this project was done. The simulation of typical GDU with MEG absorbent showed an almost similar phase envelope graph of the dry gas. However, in detailed comparison, the water dew point of gas exiting TEG system is slightly lower than one from MEG system although having almost similar hydrocarbon dew point and hydrate curves. These differences will become greater if the pressure of the system is increased, exceeding 100 bar. Justifying this factor, the usage of MEG can be considered as acceptable for industry practices if the process is operating under low pressure.

For further development of the project, several approaches can be taken to validate the conclusion made and also for improvement purposes. Several recommendations are as follows:

- Detailed study on the phase envelope of synthetic gas will produces good reasoning and understanding for any changes on curves behavior, especially the water dew point curve.
- Experimental approaches on amine absorption process and gas dehydration processes using glycol should be done to validate and verify the result obtained from this study.
- The investigation of the effects of absorbents used for synthetic gas dehydration should be conducted for more type of glycol such as di-ethylene glycol (DEG) and tetra-ethylene glycol (TREG). This will determined the most effective absorbents to be used for synthetic gas dehydration.
- More method for synthetic gas dehydration can be investigated, for example adsorption on solid desiccants method and condensation method. Furthermore, effects of other enhanced gas dehydration units; DRIZO GDU and COLDFINGER GDU, can be studied to find the best method to serve the same purpose.

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APPENDICES

APPENDIX 1 : Simulation of Amine Absorption Process

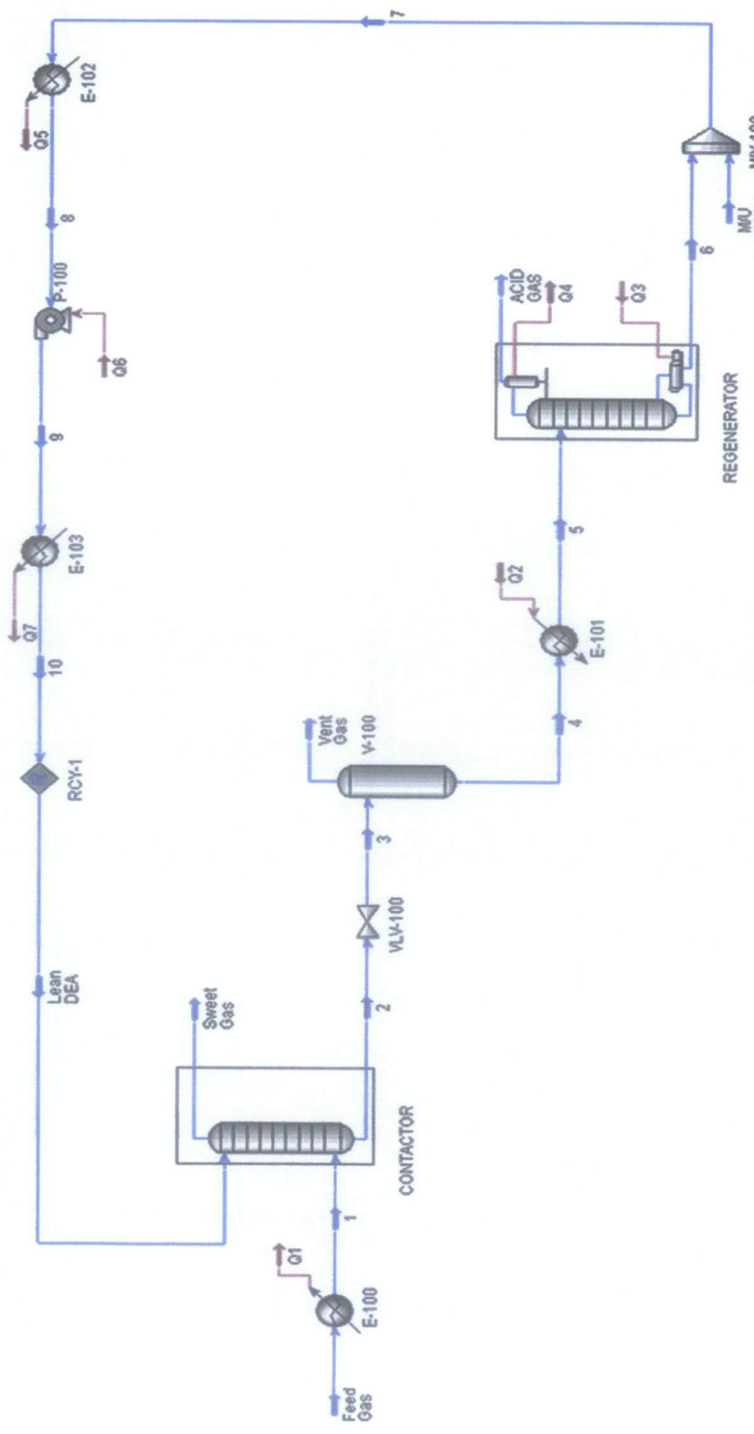

Figure 1: Amine absorption process using DEA solution

APPENDIX 2: Operating Condition of Amine Absorption Process

Table 1: Operating condition

	DEA Contactor	Regenerator
Number of Stages	18	14
Pressure (kPa)	9000	Cond: 210 Reb: 210
Gas inlet temperature (°C)	30	96.45
Gas outlet temperature (°C)	34.6	47.8
Solvent inlet temperature (°C)	33	-
Solvent outlet temperature (°C)	60.7	118.3

APPENDIX 3: Simulation of Gas Dehydration Units (GDUs)

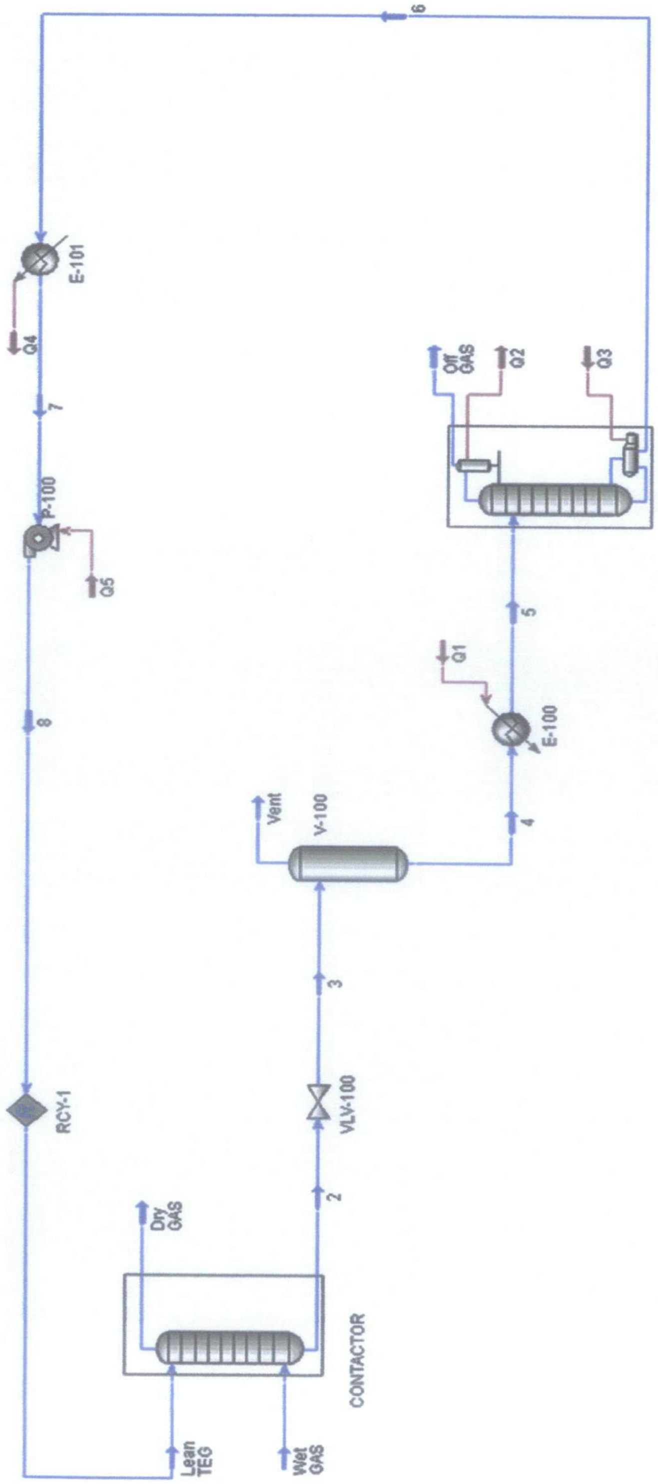

Figure 2: Typical gas dehydration unit

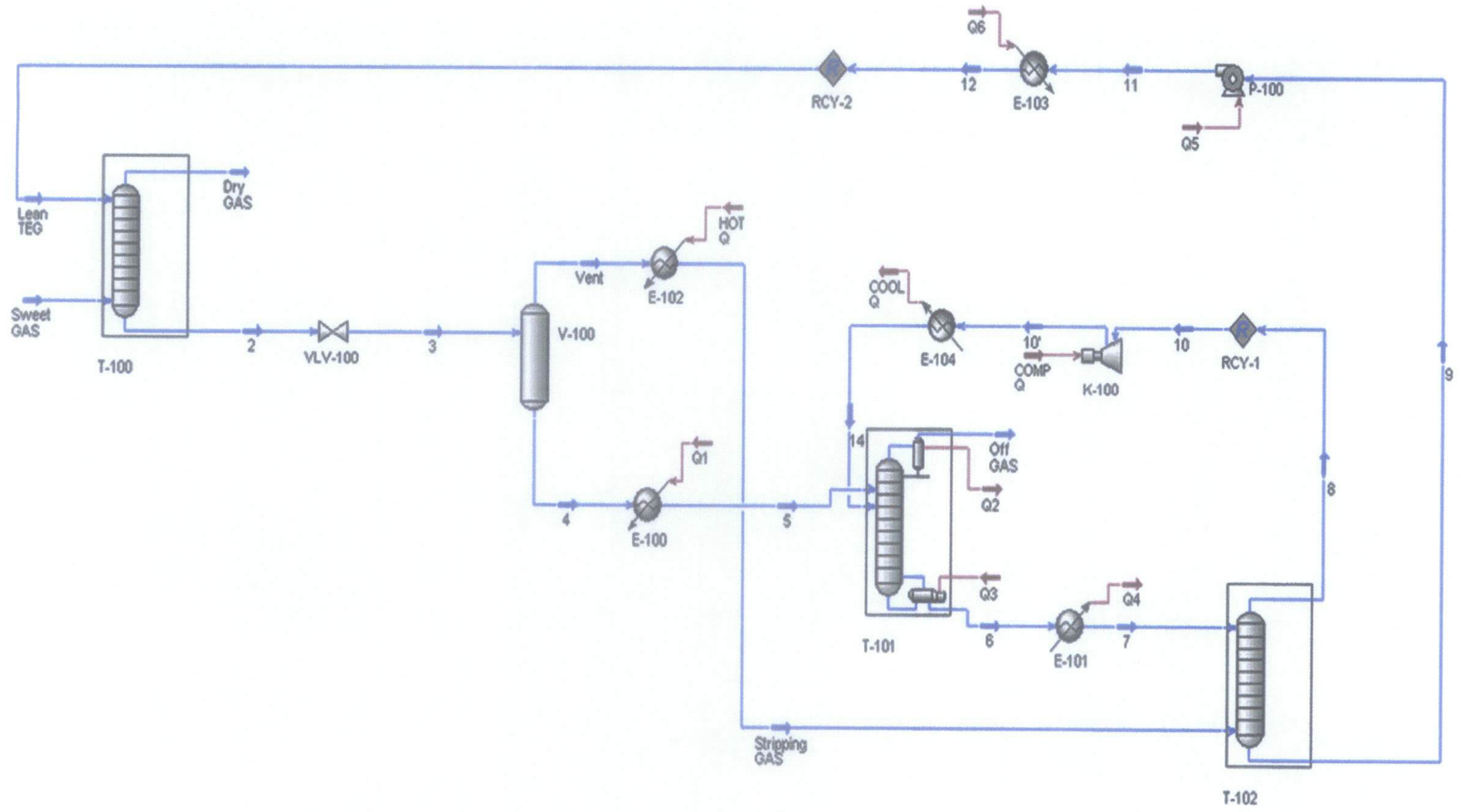

Figure 3: Stripping gas and Stahl column gas dehydration unit

APPENDIX 4: Operating Condition of Gas Dehydration Process

Table 2: Operating condition

	Operating Conditions
Wet Gas	Temperature = 53.9 °C Pressure = 3900 kPa Molar Flow = 874.4 kmole/hr
Lean TEG/MEG	Temperature = 61 °C Pressure = 4400 kPa
Absorber	Number of stages = 6 Pressure = 3900 kPa
Regeneration Column	Number of stages = 4 Pressure (Cond.) = 110 kPa Pressure (Reb.) = 120 kPa
Stripping Column	Number of stages = 3 Pressure = 130 kPa