CASE STUDY AND ANALYSIS

Of THE PERFORMANCE OF INDUSTRIAL ACID GAS REMOVAL UNIT (AGRU) AT ELNG (EGYPTIAN LIQUIEFIED NATRUAL GAS) COMPANY THROUGH PROCESS SIMULATION

LINA SAMY AHMED EL-SAWY MOHAMED

Dissertation submitted in partial fulfillment

of the requirements of

Bachelor Degree of Engineering (Hons)

(Chemical Engineering)

SEPTEMBER 2011

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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

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(Dr. Usama Nour El-Dermerdash)

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September 2011

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.

Lina Samy Ahmed El-Sawy

ACKNOWLEDGEMENT

The author wishes to take the opportunity to express her utmost gratitude to the individuals that have taken the time and effort to assist the author in completing the project. Without the cooperation of these individuals, no doubt the author would have faced some minor complications throughout the course.

First and foremost, I would like to express my gratitude to Allah SWT for His Blessings and for granting me the opportunity to complete this Final Year Project (FYP). Secondly, I would like to thank my supervisor Dr. Usama Nour El-Dermerdash for his valuable guidance and advice while conducting this project. The willingness to spend his valuable time and effort to assist me has vastly contributed to the successful completion of the project.

I also acknowledge Engineer Mohamed El-Saadany, who has provided all the necessary guidance for the basic knowledge and the calculation methodology used throughout the project. It really helped my understanding on how to acquire the vital model for the project.

Last but not least, I cannot neglect the support of my family in Egypt and my friends in UTP for the continuous support, back up and strong belief in me, which has been a great motive in order to finish the project successfully.

I hope that this project will be beneficial and contribute greatly to the industry in the future.

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NOMENCLATURE

Ppm	= Part per million, volume
°C	= Temperature in deg C
Wt%	= percentage water content
Kw	= Mechanical shaft work, kilowatt
LLP steam	= Low Low Pressure Seam
DGA	= Diglycolamine
CO2	= Carbon Dioxide
H2S	= Hydrogen Sulfide

ABSTRACT

Acid gas removal process, which is also known as sweetening process, is considered a very important industrial operational process which has taken place in many works. The main idea of this process is based on absorption, and the selection of the solvent is mainly based on its capability of removing acid gases from the feed gas such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Such acid gases found in the gas can cause operational problems like corrosion and equipment plugging. The solvent used for the absorption processes to sweeten the natural gas is classified into two types which are chemical and physical absorption. The most used absorption processes for sweetening the natural gas are using the chemical solvents such as alkanolamines or "amine". In this context, diglycolamine (DGA) is used in the aqueous solution to remove the acid gases from natural gas stream.

In this research, existing process flow diagram of industrial Acid Gas Removal Unit (AGRU) will be modified in terms of solvent composition used in the absorption process. Manipulating the ratio of solvent to moisture content in the solvent solution will replace the existing solvent composition. Simulation using Aspen Hysys is then performed to parameters, which are absorption column removal efficiency, power consumption, heating duty and cooling duty. The simulation results are expected to show improvement to the existing AGRU system used at ELNG (Egyptian Liquefied Natural Gas Company).

CHAPTER 1

INTRODUCTION

1.1 NATURAL GAS AND ITS INDUSTRY.

The natural gas industry began in early 1900s in the United States of America and is currently evolving. This high quality fuel and chemicals feedstock plays a specific role in the industrial world and it's becoming an important export for other countries.

1.1.1 History and Background of Natural Gas.

The Chinese are known to be the pioneers in using natural gas commercially 2400 years ago. They used to obtain the gas from shallow wells, and transporting it in bamboo pipes where they used to produce salt form brine in gas-fired evaporators. Manufactured gas was used in the United States of America and Britain both beginning of the 18^{th} century for streetlights and house lighting. In 1821, natural gas was commercially used by a number of small, local programs involving the use of the gas, but larger scale activities began to take place in the early years of the 20^{th} century. The highest boom in gas industry occurred after World War II, when engineering technologies allowed the construction of safe, reliable, long distance pipelines for gas transportation. By the end of 2004, the United States occupied more that 479,000 kilometers of gas pipelines, both interstate and intrastate. In 2004, the U.S. was the world's second largest producer of natural gas 543 billion standard cubic meters (BSm^3) and the leading world consumer 647 BSm^3.

Even though, the main use of natural gas is fuel, it is also a source of hydrocarbons for petrochemicals feedstock and a major source of elemental sulfur, which is an important industrial chemical. Natural gas's popularity as an energy source has been enlarged substantially in the future because it presents a lot of environmental advantages over petrol and coal.

1.1.2 Natural Gas Industry In Egypt

Natural gas is amongst one of the fastest growing component of the world primary energy consumption. Consumption of natural gas worldwide of 2660 Bm^3 in 2005 is forecasted to increase by more than 90 per cent by year 2030. Globally, the industrial and electric power sectors are the largest consumers of natural gas. The total world gas reserves currently stand at 171136 Bm^3 with Russia, holding 27 per cent having the largest reserves.

Over the last two decades, the Egyptian gas industry has grown significantly with the support of government policies that are aimed at reducing dependence on oil while ensuring a cleaner environment. A large part of this success is attributed to careful planning that has facilitated the timely development of the country's abundant gas resources to meet national economic and energy objectives.

With oil in decline, Egypt is increasingly reliant on natural gas to fuel power generation, as a source of export revenue and to fuel transportation. (In 2009, Egypt had 122 thousand vehicles running on Compressed Natural Gas (CNG) according to EGAS; the Egyptian Natural Gas Holding Company. The milestone for 2015 is 300 thousand vehicles.)

- Establishing and investing in an LNG export industry that will provide export revenues over
- At least 20 years.
- Creating long term job opportunities.
- Transferring cutting-edge technology and technical know-how to Egypt's industrial sector and
- Gas business.
- Transferring international best practice in a range of management areas such as HSE, human
- Resources, performances management, corporate governance and finance.
- Ensuring that the project operates to the highest environmental protection standards.

- Supporting the local communities by establishing growth and development opportunities within the society it operates.

1.1.3 Sources of Natural Gas

Conventional natural gas usually occurs in deep reservoirs, or in reservoirs that contain little or no crude oil. Associated gas, also known as crude oil is produced with the oil and separated at the casing head or wellhead. Gas produced is also known as casing head gas, oil well gas, or dissolved gas. Non-associated gas is sometimes referred to as gas-well gas or dry gas. However; this dry gas can still contain significant amounts of natural gas liquid (NGL) components.

The differences of associated gas and non-associated gas in term of the compositions are shown in the Table 1.1 below.

Table 1.1: Differences between associated gas and non-associated gas in term of the compositions. (Valais, 1983)

Components	**Non-associated Gas Lacq (FRA) (vol %)**	**Associated Gas Uthmaniyah (SAU) (vol%)**
Methane	69.0	55.5
Ethane	3.0	18.0
Propane	0.9	9.8
Butane	0.5	4.5
Pentane plus	0.5	1.6
Nitrogen	1.5	0.2
Hydrogen Sulphate	15.3	1.5
Carbon Dioxide	9.3	8.9

1.1.4 Compositions of Natural Gas

Natural gas is a combustible mixture of hydrocarbon gases. While it is formed primarily of methane, it can also include ethane, propane, butane and pentane. The composition of natural gas can vary widely; Table 1.2 illustrates the typical makeup of natural gas before it is refined.

Table 1.2: Typical Composition of Natural Gas

Components	**Typical Analysis (mole %)**	**Range (mole %)**
Methane	94.9	87.0-96.0
Ethane	2.5	1.8-5.1
Propane	0.2	0.1-1.5
iso-Butane	0.03	0.01-0.3
normal-Butane	0.03	0.01-0.3
iso-pentane	0.01	trace-0.14
normal-pentane	0.01	trace-0.04
Hexanes plus	0.01	trace-0.06
Nitrogen	1.6	1.3-5.6
Carbon Dioxide	0.7	0.1-1.0
Hydrogen Sulphate	1.0	0.1-5.0
Oxygen	0.02	0.01-0.1
Specific Gravity	0.585	0.57-0.62
Gross Heating Value (MJ/m^3), dry basis	37.8	36.0-40.2

1.2 ACID GAS IN NATURAL GAS FLOW

Acid gas removal or gas treating involves reduction of the acid gases such as carbon dioxide and hydrogen sulphide, along with other sulphur components, to sufficiently low levels. This removal process is needed in order to meet certain specifications without causing corrosion and plugging problems.

Carbon dioxide is a colorless, odorless gas. When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. This sensation can also occur during an attempt to stifle a burp after drinking a carbonated beverage. Amounts above 5,000 ppm are considered very unhealthy, and those above about 50,000 ppm (equal to 5% by volume) are considered dangerous to animal life.

Hydrogen sulfide is highly toxic, and the presence of water it forms a weak, corrosive acid. The threshold limit value (TLV) for prolonged exposure is 10ppm and at concentrations greater than 1000 ppm, death occurs in minutes (Engineering Data Book, 2004). It is readily detectable at low concentration by its "rotten eggs" odor. Unfortunately, at toxic levels, it is odorless because it deaden nerve endings un the nose in a matter of seconds.

When H2S concentrations are well above the ppmv level, other sulfur species can be present. These compounds include carbon disulfide (CS2), mercaptans (RSH), and sulfides (RSR), in addition to elemental sulfur. If CO2 is present as well, the gas may contain trace amount of carbonyl sulfide (COS). The major source of COS typically is formation during regeneration of molecular sieve beds. Carbon dioxide is nonflammable; consequently, large quantities are undesirables in a fuel. Like H2S, it forms a weak, corrosive acid in the presence of water.

The presence of H2S in liquids is usually detected by use of the copper strip test (ASTM D1838 Standard test method for copper strip corrosion by liquefied petroleum (LP) gases). This test detects the presence of materials that could corrode copper fittings. One common method of determining ppm level in H2S in gases is to use stain tubes, which involves was sampling into a glass tubes that changes color on the basis of H2S concentration.

1.3 Acid Gas Removal Processes.

Acid gas removal unit is an important industrial operation, which has been described in various processes. The process is mainly based on absorption, and the selectivity of the suitable solvent is based on the affinity of the chemical or physical type. Adsorption is used for intensive purification.

Many factors have to be considered when selecting an acid gas removal process like acid gas content in the feed gas, natural gas composition, final specifications to be met, inlet pressure and temperature conditions, H2S removal conditions with or without sulfur recovery, acid gas disposal method and relative cost.

1.3.1 Process Based on Chemical Solvents.

1.3.1.1 Using Amine Solution:

From Figure 1.2, the sour gas enters the bottom of the absorber at pressure 1000 psi and temperature of 32 C. The gas moves upward, countercurrent with lean amine solution, which flows in the opposite direction down from the top. The lean amine should be maintained at the temperature above the vapor that exits the contactor in order to prevent condensation of heavy liquid hydrocarbon. The contact between the gas and the amine solution occurs by the existence of either trays or packing in the absorber.

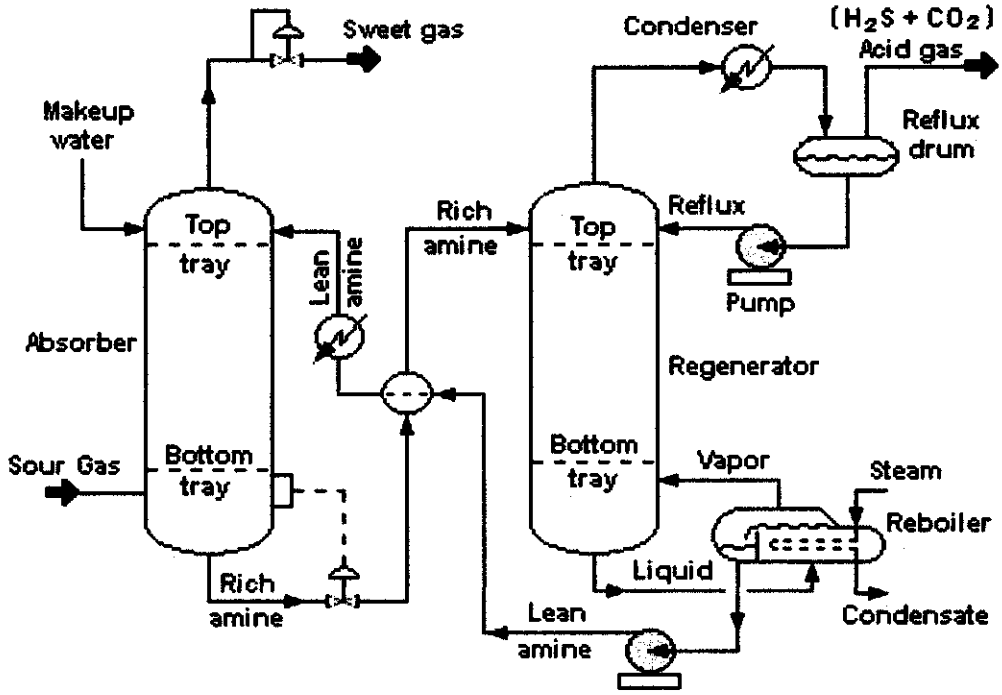

Figure 1.1: Simplified Process Flow Diagram for Acid Gas Removal Unit (AGRU)

The contactor operates above ambient temperature because of the combined exothermic of the absorption and reaction. The maximum temperature is in the lower portion of the tower because the majority of the absorption and reaction occurs near the bottom of the unit. The temperature bulge in the tower can be up to about 80°C.

The treated gas leaves the top of the tower water saturated and at a temperature controlled by the temperature of the lean amine that enters, usually around 38°C.The rich amine leaves the bottom of the contactor unit at temperatures near 60°C and enters the flash tank, where its pressure reduced to 75 to 100 psig to remove by flashing any dissolved hydrocarbons. The dissolved hydrocarbons are generally used as plant fuel. If necessary, a small stream of lean amine is contacted with the fuel gas to reduce H2S concentration. The rich amine passes through the heat exchanger and enters the solvent regenerator (stripper) at temperatures in the range of 80 to 105°C. The re-boiler on the stripper generally uses low-pressure steam. The vapor generated at the bottom flows upwards through either trays or packing, where it contacts the rich amine and strips the acid gases from the liquid that flows down. A stream of lean amine is removed from the stripper, cooled to about 45°C, and reenters the contactor at the top to cool and condense the upward flowing vapor stream. The vapor, which consists mostly of acid gases and water vapor, exits the top of the stripper and is generally processed for sulfur recovery. The lean amine exits the bottom of the stripper at about 130°C and is pumped to the contactor pressure, exchanges heat with the rich amine stream, and is further cooled before it enters the top of the contactor.

1.3.2 Processes Based on Physical Solvents.

These processes offer the advantages of requiring little or no heat to desorbs the acid gases. On the other hand, they are sensitive to the presence of the heavy hydrocarbon in the gas, which are absorbed by the solvent and then desorbed with the acid gases. The use of the process based on the physical solvent is favored by the following conditions, which are gas available at relatively high pressure, low concentration of heavy hydrocarbon in the feed, high acid gas content in the feed and desired H2S/CO2.

The absorption step is carried out in a tray or packed column. Regeneration is performed by successive expansions, stripping by neutral gas or re-boiling of the solution. A number of processes are available (Maddox, 1982).

1.3.3 Acid Gas Removal Process by Adsorption.

Adsorption is appropriate when very high gas purity is required. The use of molecular sieves helps to achieve simultaneous water and acid gas removal down to very low water contents such as 0.1-ppm vol. (Thomas and Clark, 1967; Consiver, 1965). Large pore molecular sieves, such as 13X sieves, are used more frequently than 4A and 5A sieves, because they also allowed separation for all mercaptans (Kohl and Riesenfeld, 1985; Maddox, 1982). In the presence of CO2, molecular sieves tend to catalyze the formation of COS by reaction between H2S and CO2. New molecular sieves have been developed to retard this reaction (Kumar, 1987).Traces of glycol; glycol degradation products of absorption oil can poison the molecular sieve. If precautions are taken, a lifetime of 3-5 years before renewal of the sieve is considered normal (Conviser, 1965).

1.3.4 Acid Gas Removal by Gas Permeation

Gas permeation is already applied industrially to remove carbon dioxide from natural gas (Meyer et al., 1991; Cooley, 1990).Gas permeation allows simultaneous removal of CO2 and water (H2O) from natural gas. This also offers the advantages of reducing the methane losing the permeate. The most advantageous alternative in economic terms is generally to operate with a single stage, without recompression of the low-pressure gas that passes through the membrane. Under this condition, gas permeation units can be justified economically with commercially available membranes only if the inlet carbon dioxide concentration is high and the final specification are not strict (Johnston and King. 1987).

1.3.5 Using amine as a solvent for chemical absorption

Amines are compounds formed from ammonia (NH3) by replacing one or more of the hydrogen atoms with another hydrocarbon group. Replacement of single hydrogen produces a primary amine, replacement of two hydrogen atoms produces a secondary amine, and replacement of all three of the hydrogen atoms produces a tertiary amine. Primary amines are the most reactive, followed by secondary and tertiary amines. Sterically hindered amines are compounds in which the reactive center (the nitrogen) is partially shielded by neighboring group so that larger molecules cannot easily approach and react with the nitrogen. The amines are used in water solutions in concentration ranging from approximately 10 to 65 wt% amines. Amines removed H2S and CO2 in two steps process, which are by dissolving the gas in the liquid (physical absorption) and the dissolved gas, which is weak acid, reacts with the weakly basic amines.

1.5 Problem Statement

Problem statement in this case study discusses a vivid problem which occurred at ELNG (Egyptian Liquefied Natural Gas) company and needs to be solved. The following points will describe the cause and effect of the problem and help to choose the most convenient solution in order to optimize the results.

The typical operating problem occurring in Acid Gas Removal Unit using Amine solvent are foaming, corrosion and solvent loss. Foaming is the common problem in this process which results in poor vapor-liquid contact, poor distribution, and solution holdup with resulting carryover and off spec gas. Among the causes of foaming are suspended solids, liquid hydrocarbons, and surface-active agents, such as those maintained in inhibitors and compressor oils. One obvious cure is to remove the offending materials; the other is to add antifoaming agents.

1.6 Objectives

This study case discusses two major objectives. The first objective is to:

Use a systematic approach in order to analyze and compare the performance of the AGRU of the Liquefied Natural Gas streamline facilities at ELNG at different parameters without change of the main solvent used in absorbing the acid gases which is DGAmine.

The second objective is to:

Explore the capability of HYSYS process simulator to predict the CO_2 removal process operating conditions range at which hydrocarbon and chemical loss (amine solvent) can be minimized.

1.7 Scope of the Study Case

This project will be focusing on simulation through Aspen Hysys, which will be done on the industrial Acid Gas Removal process flow sheet that use optimized specifications of the Amine solution instead of the current one.

1.8 Project Relevancy and Feasibility

In this study case, the motivation to use optimized Amine solvent for industrial AGRU system is based on overall process and economic performances. While typical AGRU has operational problems such as foaming and solvent degradation, the optimization of the solvent is therefore very crucial. Enhancing the solvent performance will offer both process and economic advantages.

CHAPTER 2

LITERATURE REVIEW

2.1 ACID GAS REMOVAL UNIT (AGRU)

In this study case we will be mainly focusing on the Acid Gas Removal Unit at ELNG.

2.1.1 ELNG (Egyptian Liquefied Natural Gas) Company Profile

Egyptian LNG is Egypt's largest LNG partnership sponsored by EGAS, EGPC, BG Group, Petronas, and Gaz de France, operating as a free zone company. We have successfully built a 7.2 mtpa capacity, two-train processing plant bringing USD 2 billion of foreign investment into the Egyptian economy.

The establishment and successful operation of Egyptian LNG has placed Egypt as a new Mediterranean LNG exporter which holds the 13th place worldwide in the LNG exporting club. Moreover, it has contributed to the country's sustainable development.

2.1.2 Overall Process Description

- Treatment of natural gas and removal of H2S, CO2, water and mercury.
- Gas cooling to −160°C in cold heat exchangers using Propane, Ethylene and Methane as refrigerants.
- Natural Gas conversion to LNG and then pumped into insulated storage tanks (140,000 m^3 each).
- Heavy Hydrocarbons are separated throughout the Process and later returned to Upstream.

LNG product is exported in pipelines utilizing Egyptian LNG port facilities –designed to accommodate ships ranging in capacity from 40,000 m3 to 165,000 m3.

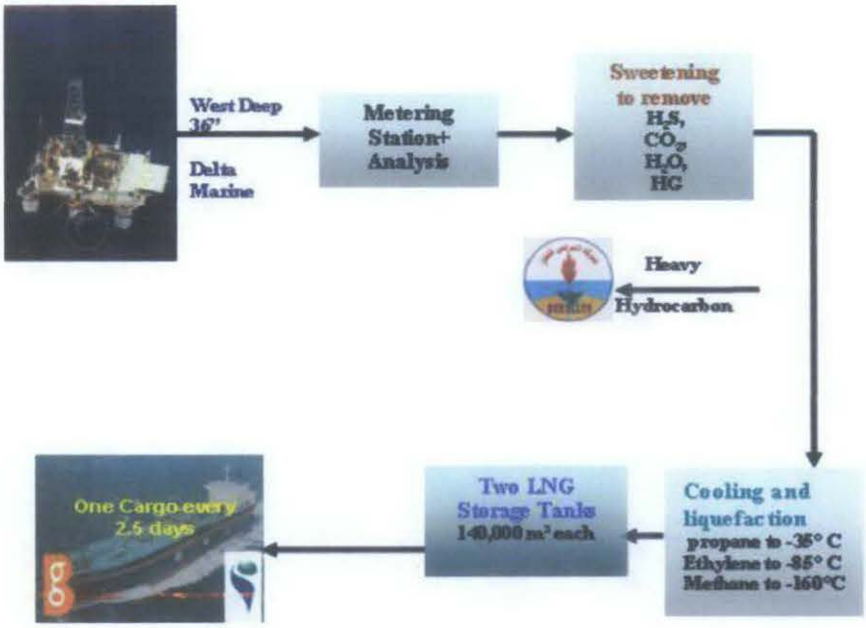

Figure 2.1 Overall Process Description

2.1.3 Unit 12 Process Description

The feed gas contains carbon dioxide (0.5 mol% maximum) and traces of hydrogen sulphide (50 PPMV maximum).

The C02 must be removed to avoid C02 freezing problems in the downstream liquefaction area. The H2S must be removed to meet LNG sulphur specifications and prevent equipment corrosion.

The removal of C02 and H2S is accomplished by passing the feed gas through a Regenerated Amine System.

Diglycol Amine was selected as the solvent for acid gas removal based on its ability to remove CO2 to less than 100 PPMV, and H2S to less than 4 PPMV.

The design of the amine system is based on the use of a 50% by weight solution and a circulation rate of 116 M3/hr, to the Absorber.

2.1.4 Acid Gas Removal

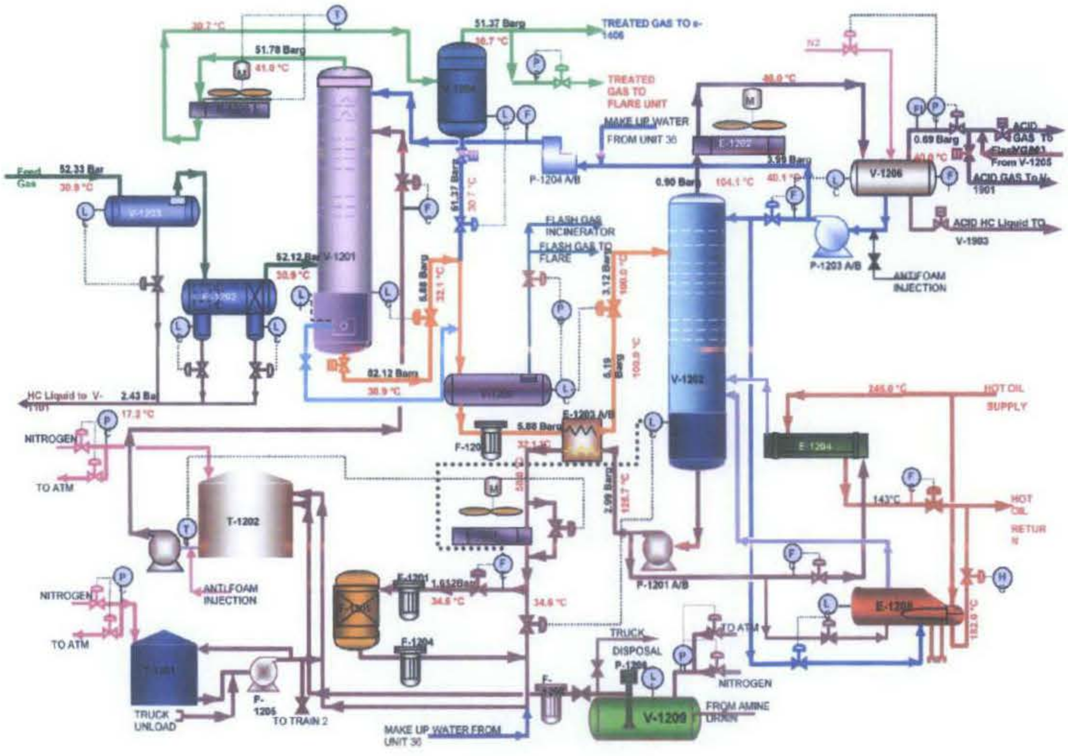

Figure 2.2 Acid Gas Removal Unit

The sour gas is normally fed at 52.3 barg and 30.9°C to the Feed Gas Separator (1V-1203) and then to the Feed Gas Filter Coalescer (1F-1202), which prevents gas-carried contaminants 1 micron and larger from getting into the circulating amine solution. The gas then enters the bottom of the Absorber (1V-1201) and counter-currently contacts with amine solution.

The Absorber is equipped with twenty (20) Amine contacting trays

Four (4) additional water wash trays (bubble-cap trays) are provided above the lean Amine feed point to remove any entrained amine solution from the gas, thus reducing Amine losses. Wash water is supplied by the de-mineralized water system and the Solvent Regenerator reflux via the Wash Water Pumps (1P-1204A/B).

In the Absorber, CO_2 in the feed gas is reduced to less than 100 PPMV, and H_2S to less than 4 PPMV. It is expected that the Diglycolamine will also remove some of the mercaptans.

The now sweetened gas is air-cooled in the Absorber Overhead Gas Cooler (1E-1206) to 30.7°C, thereby lowering the saturated water content. Condensed water is removed in the Treated Gas K.O. Drum (1V-1204).

During extreme cold weather, the temperature at the discharge of air cooler 1E-1206 should be maintained at a temperature above 18°C to avoid any hydrate formation.

CHAPTER 3

METHODOLOGY

3.1 WATER CONTENT OF NATURAL GAS

Water vapor could be present in natural gas due to its occurrence in the well production stream, the storage of the gas in the underground reservoir, distribution through moisture containing lines. The saturated water content of a gas depends on pressure, temperature and composition. The effect of the composition increase when pressure increases and it is more important when the gas contain a certain amount of carbon dioxide, which is an acid gas, since it has high affinity for water. However at pressure less than 31 bara the saturation water content of acid gas decreases with increase in pressure and independent of composition (Carroll et. al, 1999). Beyond this pressure the formation of liquid phase increases the ability of gas to hold water.

The water content of natural gas can be measured using three different methods (Rejoy et al., 1994).

1. Observation of the dew point

2. Water retention on an adsorbent

3. Absorption in liquid

It is important to determine the saturated water content of acid gas in order to estimate the operating conditions of gas treating process to maintain a non-hydrate formation.

In this study case, it's crucial to determine the saturated water content to define the compositions of the geed gas stream into the Acid Gas Removal Unit. Thus HYSYS Simulator will be used to define the saturated water content of natural gas.

3.2 WATER CONTENT DETERMINATION USING HYSYS SOFTWARE

HYSYS can calculate the water content of the saturated gas at specific temperature and pressure inserted however, the application doesn't provide the capability to estimate water content of natural gas at standard condition. In order to achieve this, excel sheet will be used to calculate the mass of water content in 1 m3 of gas (kg) which will be first prepared in HYSYS and linked with Microsoft excel to convert it to standard condition using Clapeyron equation. Detail of the calculation procedures is still in progress.

3.3 HYSYS PROCESS SIMULATION PACKAGE

Aspen HYSYS simulation software is a market-leading process modeling tool for conceptual design, optimization, business planning, asset management, and performance monitoring for oil & gas production. It is powerful software for simulation of chemical plants and oil refineries which includes tools for estimation of physical properties and liquid-vapor phase equilibria.

The program is built upon proven technologies, with more than two decades of supplying of process simulation tools to the oil and gas industry. HYSYS is an interactive and flexible process modeling software which allows the engineers to design, monitoring, troubleshooting; perform process operational improvement and asset management. Therefore enhance productivity, reliability, decision making and profitability of the plant life cycle.

In HYSYS, all necessary information pertaining to pure components flash and physical properties calculations is contained in the fluid package, choosing the right fluid package for a given component is essential. Proper selection of thermodynamic models during process simulation is also absolutely necessary as a starting point for accurate process modeling.

A process that is otherwise fully optimized in terms of equipment selection, configuration, and operation can be rendered worthless if the process simulation is based on inaccurate fluid package and thermodynamics models. For amine process simulation, amine fluid package and non-ideal vapor phase models was found to be more accurate and applicable (Aspen Tech 2003).

Once the fluid package and the thermodynamics model equation are selected, it is now possible to enter the simulation environment where the detail process flow diagram of a given plant can be constructed. In HYSYS stream to stream connection is difficult some fictitious units (such as Mixer and Splitters) to produce a satisfactory model is used, though this have little or no effect on the accuracy or optimization results of the process under investigation. Simulation of the built process flow diagram is achieved by supplying some important physical, thermodynamics and transport data of the stream and equipment involves, this is done until all the units and the streams are solved and converged.

HYSYS require minimal input data from the user, the most important input parameters needed for streams to solve are the Temperature, pressure and flow rate of the stream.

HYSYS offers an assortment of utilities which can be attached to process stream and unit operations. The tools interact with the process and provide additional information. For instance the flow sheet within the HYSYS simulation environment can be manipulated by the user to estimate desired output.

3.3 AMINE BASE PROCESS FACILITY

3.3.1 DGA Selection

Amine base solvent (DGA) was chosen in this study case to establish the operating conditions at which the CO2 removal process from the natural gas can be operated to meet the LNG specifications and to minimize the emission to the environment.

Diglycolamine (DGA) exhibits similar properties with monoethanolamine, but is less volatile, and therefore be use in much higher concentration (40 – 60%). This helps to reduce the circulation rate, thus increase the economics of the process.

3.3.2 Economic factors in operating gas treating process

The circulation rate is the single most important factor in the economics of gas treating with chemical solvents. Solvent circulation rate influenced the size of pumps, lines, heat exchangers and regeneration tower, thus has a large effect on the capital cost of gas treating plants. Circulation also influenced the energy requirement for solvent regeneration because the reboiler heat duty is associated directly with liquid rate. Other factors that play and important role in gas treating economics include solution corrositivity, which determine the material of construction particularly in the flash and regenerator because of high temperature and acidity.

Economic operation of CO2 removal process can be achieved by taken advantage of a strong correlation between the solvent working capacity and solvent circulation rate. The solvent circulation rate can be reduced by increasing the working capacity; this is done by increasing the solvent (DGA) concentration in solution and allows the acid gas loading in solution to rise above the traditional level. Though working capacity may be limited by corrosion. In most favourable case, solvent circulation rate is reduced by over 50% relative to the traditional process, leading to reduction of investment cost by nearly 50% and fuel cost by over 65%.

3.3.3 Environmental concerns

The removal of CO2 process from natural gas consists of certain operations that need to provide clean LNG feed gas and pipeline quality gas. In return, these operations cause several wastes that must be monitored according to the environmental laws and regulations to minimize the harm of the environment.

Emissions related to CO2 removal process include; carbon monoxide (CO), sulfur oxides (SOx), ammonia (NH3), hydrogen sulfide (SOx), nitrogen oxides (NOx), particulates, (volatile Organic compounds (VOCs), metals, and a wide range of toxic organic compounds. These pollutants may be discharged to the atmosphere as air emissions, waste water, or solid wastes. All of these wastes are possible to be treated except air emissions which are more complicated to treat when compared to waste water and solid wastes. Thus, we can consider air emissions the largest source of untreated wastes discharged to the atmosphere.

Air emissions consist of two sources which are point and non-point. Point sources are emissions that exist stacks and flares and are easy to monitor and treat. On the other hand, non-point sources "fugitive emissions" are difficult to locate and treat. They take part in valves, pumps, tanks, pressure relief valves, flanges, etc. Generally, Identification and characterization wastes generated can be organized into 3 major categories (Myerski et al, 1993);

- **Intrinsic**: wastes that are derived from the natural gas stream and are generated at facilities receiving and handling natural gas from production to storage field.
- **Treatment/Processing**: wastes that are generated from equipment or unit operations required to treat process and transport natural gas.
- **Maintenance**: wastes resulting from maintaining facility equipment in clean working order.

Table 3.1 Summary of wastes generated from different CO2 removal process units.

	Types of Contaminants/Chemical released to the Environment		
	Intrinsic	**Treatments/Processing**	**Maintenance**
Physical Absorption Processes			
Selexol	CO2, COS,VOC, H2S	Organic peroxide, CO2, NOX, VOC	Sludges, Waste Solvents / Degreasers
Rectisol		Mercury Amalgam, CO2, NOX, VOC	
Fluor		CO2, NOX, VOC.	
Chemical Absorption Processes			
Amine Base	CO2, NOx, SOx, VOC.	BTEX, HEI, HEED,OX, Carbamate.	Sludges, Waste Solvents / Degreasers, corrosion

			Inhibitors wastes
Carbonate Base	COS , CS2, NOx, VOC,	Ammonium Oxalate, NOX, VOC, BTEX	Sludges, Waste Solvents / Degreasers, corrosion Inhibitors wastes
Hybrid Processes			
Sulfinol	Mercaptans,CS2, COS	BTEX, VOC	Waste Hazardous DIPA
Cryogenic Processes			
Cooling/Distillation	CO2, CS2, COS, SOX	Acetylene, absorbed C2	Waste water, Toxic Cryogenic fluids (acetylene)
Adsorption Processes			
Molecular Sieve	CO2, CS2, COS, SOX	CO2, CS2, COS, SOX	Degraded/Spent Zeolite
Membrane Separation	CO2, CS2, COS, SOX	CO2, CS2, COS, SOX	Degraded/Spent Fibers

*Information used in the above table is derived from (Sorensen et al, 1999), (Mustard et al, 2000), (John et al, 1995).

However, in this study case the wastes identified above can be eliminated by establishing optimum operating conditions which will enhance the process environmental performance. This involves modifications of current process parameters (Temperature, Pressure, and Solvent circulation rate) to minimize the toxicity rate of wastes that are produced.

For instance, if we take the absorber as an example, it operates under low temperature and high pressure in order to increase the acid gas loading by the solvent, and regeneration of the solvent is carried out in the stripper at low pressure and high temperature (within solvent stability temperature to avoid solvent degradation and loss as a vapour with the acid gas).

Operating and optimum conditions ensure low hydrocarbon and chemical losses, thus reducing wastes accumulating in the process units and emission of toxics to the environment.

The details of Analysis are shown in chapter 4.

3.4 HYSYS SIMULATION OF AMINE PROCESS

3.4.1 Description of process equipment

Most often, amine unit operating problems can be traced to contaminants brought in with the gas from the pipeline. Pipeline contaminants can be in the form of "down-hole" corrosion inhibitors or other "treating" chemicals, liquid slugs caused by pipeline volume surges or line pigging, well "workover" fluids sent to the pipeline, and compressor lubricating oils. These contaminants are prevented from getting into the units by slug catcher. For the CO2 removal units the following is a brief description of the major equipment necessary for successful simulation of amine unit to meet the LNG specifications and to operate environmental acceptable units.
Here, we will be discussing only the major equipments in the unit.

Hp inlet separator: The function of the inlet separator is to remove the entrained liquid amine carried over with the gas from the pipeline/slug catcher before getting to the absorber. Vertical separator is used to handle some anticipated liquid slugs. It also limits liquid re-vaporization (Ikoku, 1980).

DGA contactor: The contactor allows counter-current flow of lean amine from the top and sour gas from the bottom. Here, the amine solvent absorbs CO2 and rich amine flows to the bottom while the sweet gas is collected at the top for further processing.

Lean/rich Amine heat exchanger: The lean/rich amine heat exchanger is a heat conservation device where hot lean solvent preheats cooler rich solvent. In this study case, Shell-and-tube type E exchanger is used in the simulation. The shell and tube side pressure drop is set to 3.4 barg and heat loss is assumed zero. The heat exchanger helps to raise the rich amine solvent temperature before entering the stripper. Thus reducing re-boiler work load.

Amine stripping tower: Depends mainly on the solvent type, it is normally a 20-tray packed tower which strips the CO2 from the rich solvent. Physical solvents can require fewer trays. It is assumed that the trays in the upper rectifying sector are made out of stainless steel to avoid corrosion.

Amine cooler, reflux condenser: Air-cooled, forced draft with automatic louvers for temperature control. Col climate service may require air-recirculation or preheat media on fans/coils. Condenser tubes should be made of stainless steel.

Regenerator reflux pumps: The reflux pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber. The main circulation pump depends on the contactor pressure and solvent flow rates.

Cooler: The lean amine solvent from the re-boiler through lean/rich amine heat exchanger is cooled down before entering the absorber again, since absorbers operate better at relatively low temperature.

Solvent reboiler: This is either a direct-fired fire tube type or cabin heater, or indirect hot oil or steam heated unit. Typically heat flux rate should be kept in the 7500 to 10,000 Btu/hr/ft2 range; to assure no surface burning of the solvent. This exchanger provides the steam necessary to heat and strip the solvent back to a "lean" condition.

3.4.2 Hysys simulation procedures

A base case has been established using the following steps; the first step is to select the appropriate fluid package; here Peng-Robinson package is selected as in figure1 below:

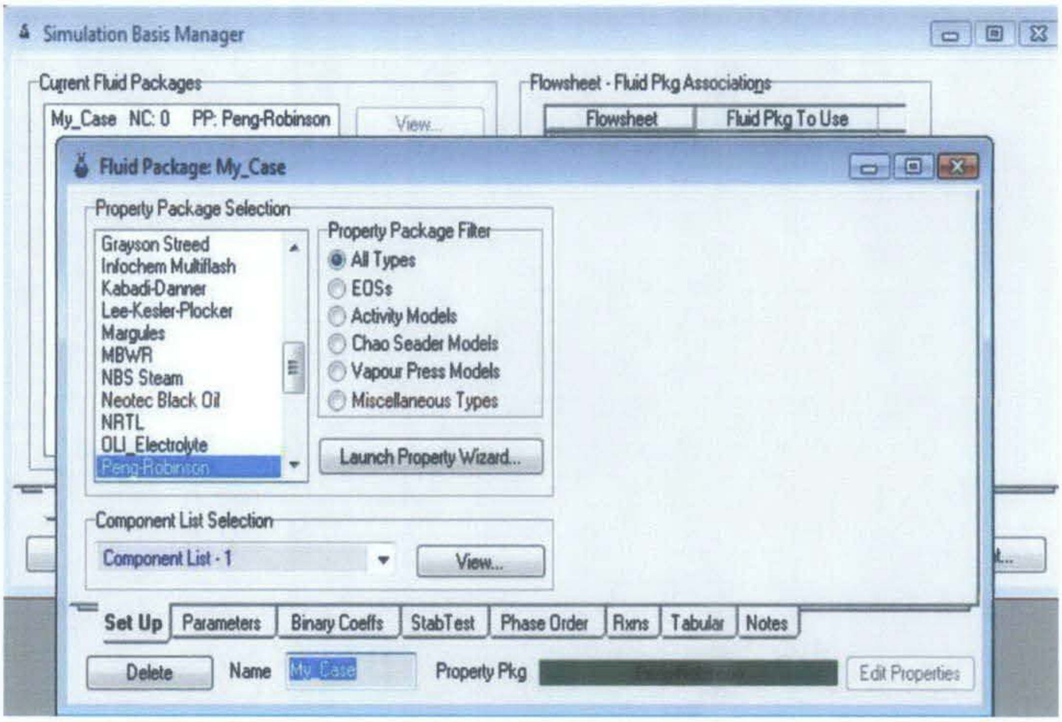

Figure 3.1: Fluid Package Basis (Peng-Robinson Package)

The component selection window is open by selecting view in the component-list show in fig 1. Figure 2 shows dialog window is use for components selection

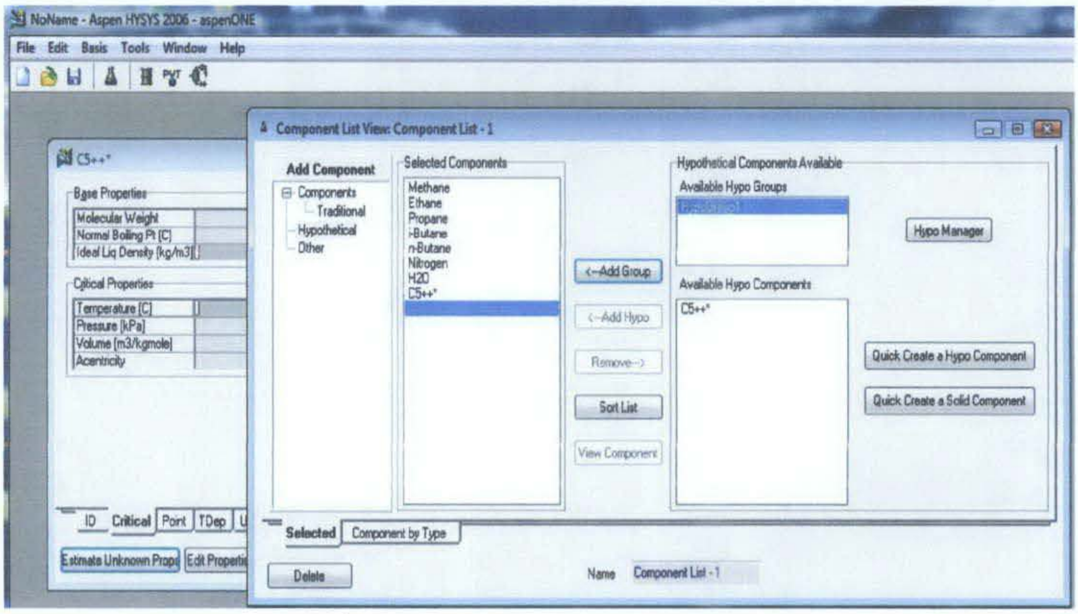

Figure 3.2: Component selection windows.

After selecting the component of the fluid, one can enter the simulation environment where the process flow diagram (PFD) is built. Amine PFD simulation environment is shown in figure 3 below:

Figure 3.3: Un-simulated Amine Process Flow Diagram

The simulation of the process begins with the simulation of the feed sour gas stream by specifying the gas temperature, pressure and flow rate (Blue color) and HYSYS calculate the remaining parameters (**Black color**) as shown in figure 4 below;

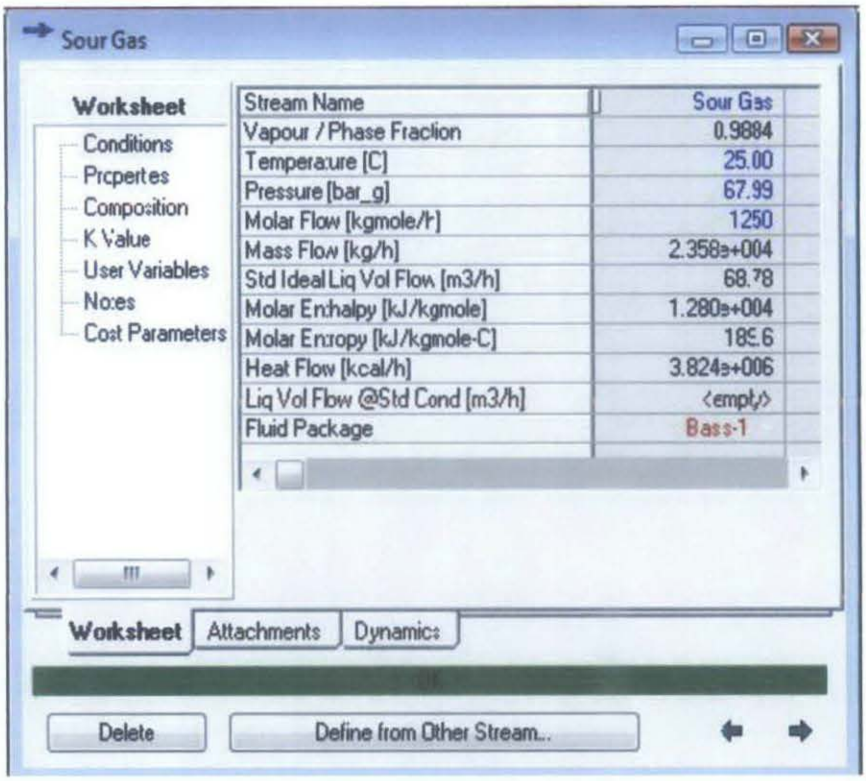

Figure 3.4: Sour Gas Specification window

Other streams specifications made are; the regenerated feed out of the L/R amine heat exchanger temperature in order to monitor the exchanger factor, DGA to contactor temperature and flow rate, make up water and DGA to recycle temperature. With entering these specifications into HYSYS, it calculates forward and backward to completely simulate the process.

One of the hard tasks is the convergence of the absorber and the regenerator, to converge the absorber, top and bottom temperature and pressure must be specified and run, figure 5.

While the regenerator is converged by specifying the condenser and re-boiler pressure, and the reflux ratio rate, then column is run, figure 6.

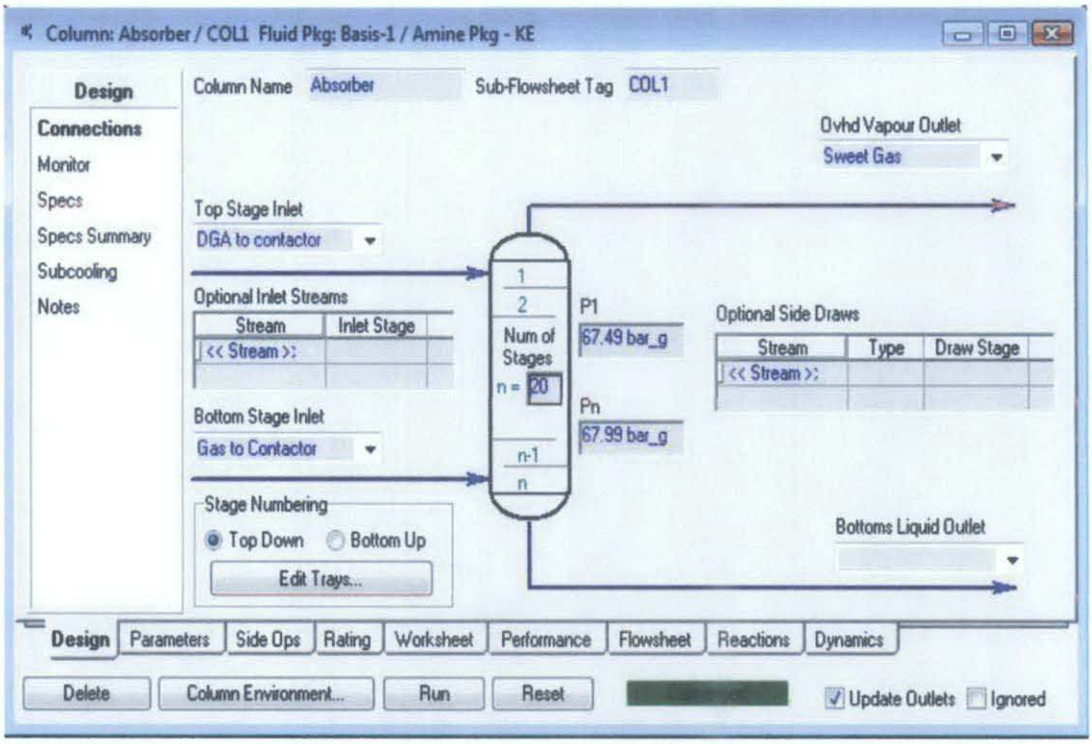

Figure 3.5: Convergence of the Absorber

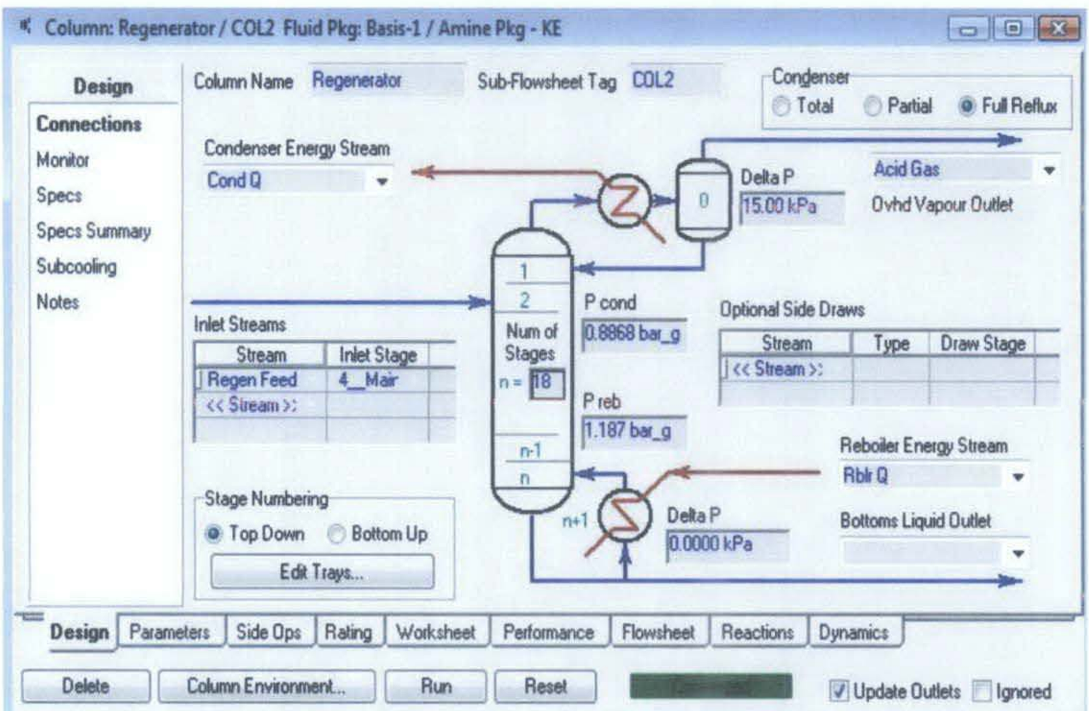

Figure 3.6: Convergence of the regenerator

With the convergence of the absorber and the regenerator units, a complete amine simulation for the study case has been established as shown in figure 7. Next step is to carry out the optimization of the process by modification of some parameters to meet the study case aims.

Detail parameters of the study case are still in progress.

Figure 3.7: Complete Simulations Unit.

CHAPTER 4

RESULTS AND DISCUSSION OF RESULTS

4.1 SIMULATION RESULTS

Detail simulation results are shown in the lists of tables and chart below.

4.2 DISCUSSION OF RESULTS

The Simulation objectives are to analyze, manipulate and compare results at different parameters in order to optimize the current AGRU without exceeding the typical LNG product specifications, as well as establish optimum conditions to reduce CO2 emission & chemical loss.

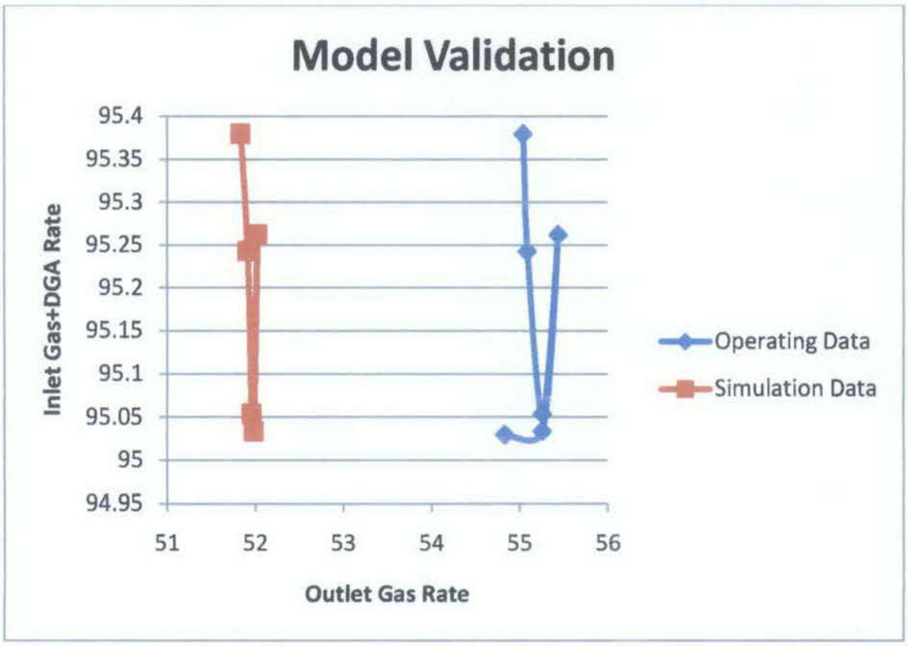

Figure 4.1: Model validation of the simulation

From Figure 4.1 we can observe the plotted graph of the operating values taken from 5 consecutive day analysis from the industrial unit, and the simulation values of both inlets (DGA and sour feed gas) to the contactor versus the outlet stream of sweet gas.

The resulted data are used in order to validate the simulation work of the AGRU.

The percentage error obtained from the graph above was calculated for 5 consecutive data between (5.761298-6.2541307) % which makes the simulation valid for further data generation and analysis.

Percentage of Error Calculation:

{Simulation top gas -Operating top gas /Simulation top gas}*100%

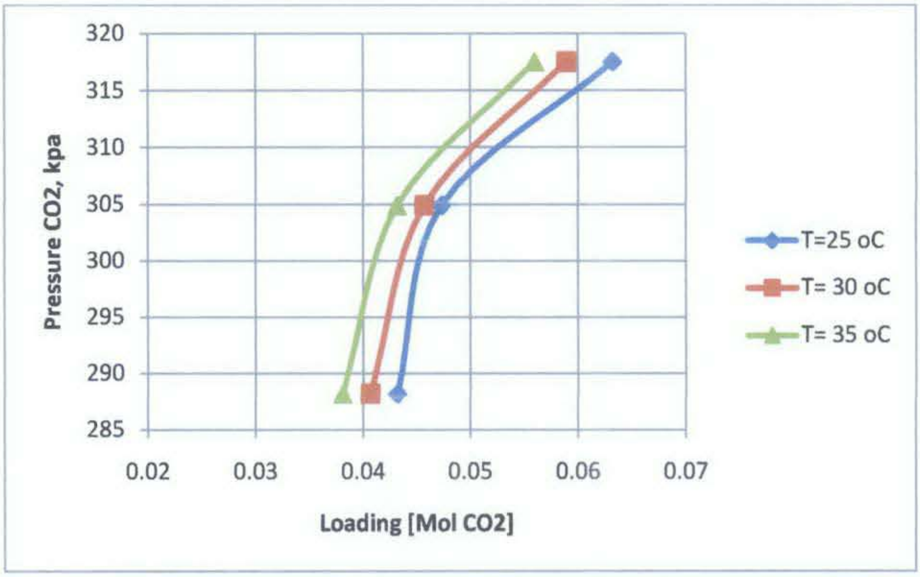

Figure 4.2 Partial Pressure of CO2 in Solution as Function of CO2 Loading of 35wt% DGA

Partial Pressure of CO2 in Solution as Function of CO2 Loading of 35wt% DGA; with 35 wt% DGAmine the loading [molCO2/molDGA] ranges from (0.0432 – 0.05597).

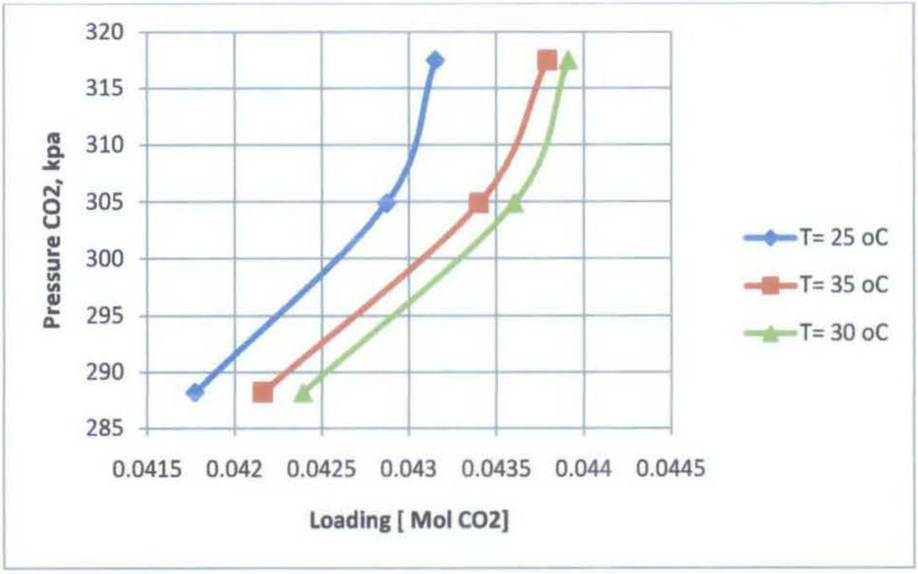

Figure 4.3 Partial Pressure of CO2 in Solution as Function of CO2 Loading of 40wt% DGA

With 40 wt% the increase loading ranges from (0.04177 – 0.04379).

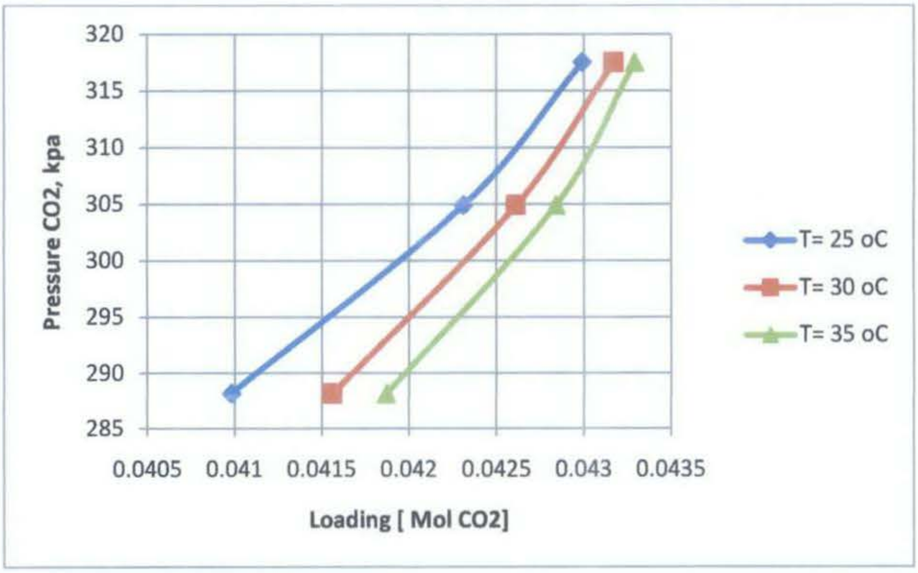

Figure 4.4 Partial Pressure of CO2 in Solution as Function of CO2 Loading at 45wt% DGA.

With 45 wt% the increase loading capacity ranges from (0.0409-0.04329) The loading was observed to increase with increase of temperature at a given CO2 partial pressure.

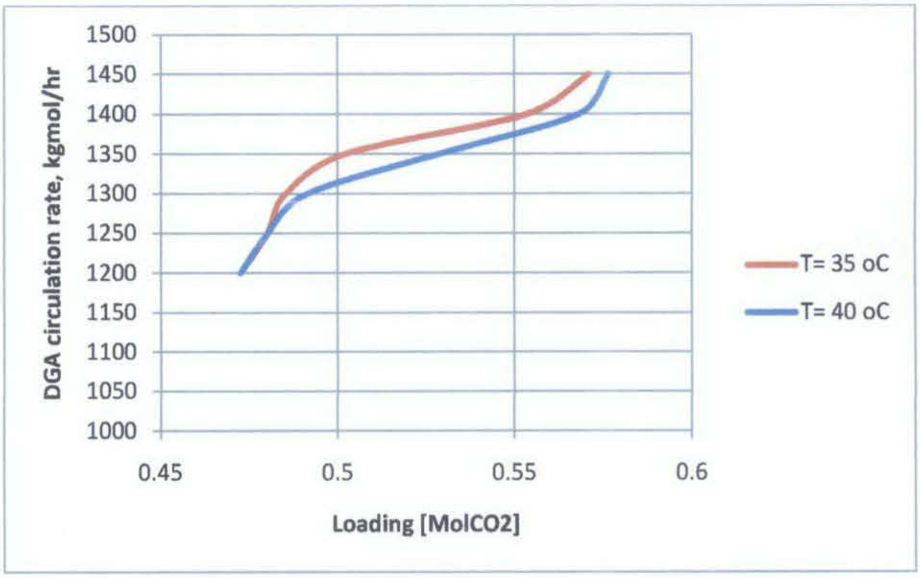

Figure 4.5 Lean DGAmine Circulation rate vs. CO2 loading in 45wt% DGAmine.

This figure illustrates the effect of Lean Amine circulation rate on Amine loading capacity; the loading capacity increases with increase circulation rate and decrease in temperature.

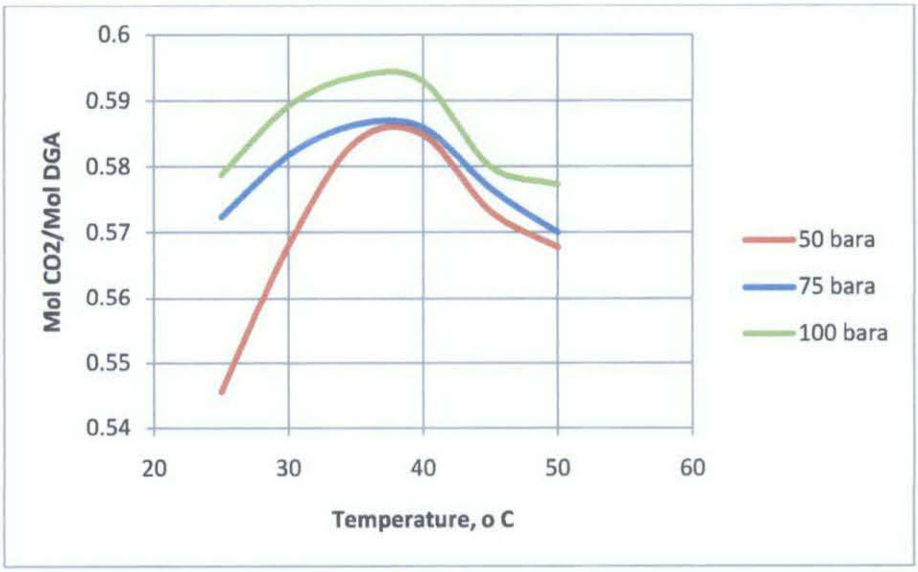

Figure 4.6 Effects of CO2 Loading in DGA with Pressure and Temperature

Figure 4.6 shows the effect of CO2 loading in DGA solvent with change of pressure and temperature. The figure shows the results at pressure 50, 75 and 100 bara, where we can conclude that CO2 loading in DGA is directly proportional with pressure.

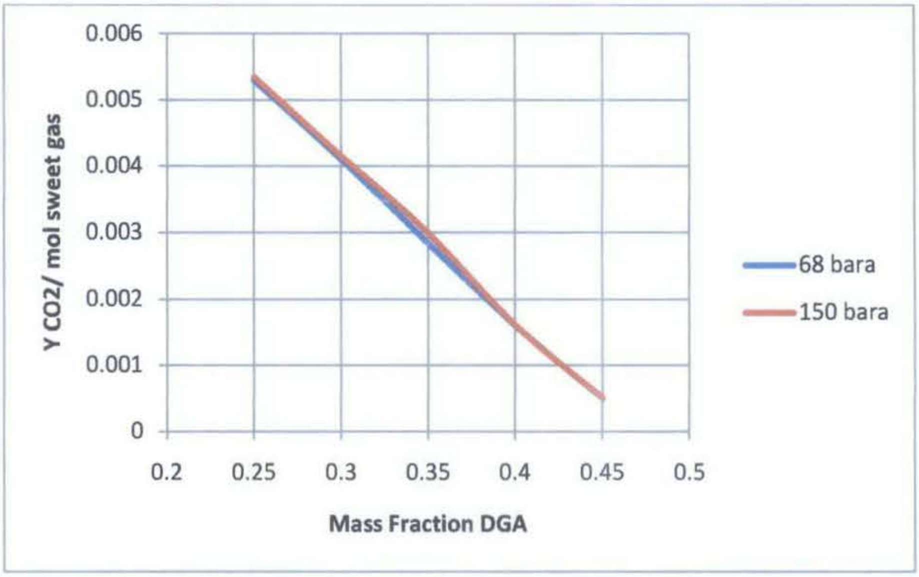

Figure 4.7 % of CO2 in the sweet gas as a function of amine concentration with changes in absorber pressure.

It was shown in the figure above where the percentage of CO2 in the sweet gas is plotted against the concentration of the amine solvent that as the concentration of amine increases, the % mole concentration of CO2 in the sweet gas decreases. This is attributed to the increase in the Amine solvent capacity with increase in concentration of Amine in the solution. The specifications ranges were met at 45 wt% DGA and above.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION AND RECOMMENDATIONS

Based on the literature reviewed and the results taken from the simulation case the following conclusion can be made:

The loading of the amine solvent (DGA) should be increased appropriately to increase acid gas (CO2) loading in the solvent.

The CO2 emission and chemical loss is directly proportional to the amine circulation rate. Thus the lean amine circulation rate should be decreased and at minimum possible temperature to lower solvent evaporation rate and therefore increase its loading capacity.

Absorber should operate at high possible pressure and low Temperature to enhance amine loading capacity; and increase the rate of solubility of CO2 in the amine solvent, therefore minimize CO2 emission and chemical loss.

Additionally, for enhancing the performance of acid gas removal, several points are considered:

Several software could be considered to use as an alternative for HYSYS such as ICON, Pro MAX.

We can consider using Aspen plus program instead of Aspen HYSYS for adding new chemical additives such as NaOH or NH3 and compare their effect on the solvent efficiency with previous data shown.

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APPENDICES

APPENDIX A: KEY MILSTONES FOR FYP II

No	Action	Date
1	Project work commences	3/10/2011
2	Briefing & update on students' progress	5/10/2011
3	Submission of Progress Report	14/11/2011
4	Poster Presentation	14/12/2011
5	Submission of Draft Dissertation	14/12/2011
6	Submission of (CD & Softbound)	19/12/2011
7	Final Oral Presentation/Viva	28/12/2011
8	Submission of Technical Paper	6/01/2012
9	Submission of hardbound Dissertation	13/01/2012

APPENDIX B: GANTT CHART FOR FYP II

No	Detail/ Week														
1	Study case data extraction	√	√												
1	Utilization of HYSYS 3.2 software to conduct the Simulation			√	√	√	√	√							
2	Submission of Progress Report I			√											
3	Simulation Validation and Data extraction						√	√	√	√	√				
4	Submission of Progress Report II								√						
5	Generation of Graphs										√	√			
6	Submission of Dissertation Final Draft												√		
7	Submission of Dissertation													√	
8	Oral presentation														√

APPENDIX C: Basic Raw Data and Base Case Simulation Data

Table 1-Typical LNG Product Specification, (David Coyle et al 2003)

Component	**Limit (Maximum)**
Hydrogen Sulfide	3 – 4 ppmv
Total Sulfur	30 milligrams per normal cubic meter
Carbon Dioxide	**50 – 100 ppmv , 2- 3 mol%**
Mercury	0.01 micrograms per normal cubic meter
Nitrogen	1 mol %
Water Vapor	1 ppmv
Benzene	1 ppmv
Ethane	6-8 mol %
Propane	3 mol %
Butane and heavier	2 mol %
Pentane and heavier	1 mol %
High Heating Value	1050 Btu/Scf (Europe and USA) > 1100 Btu/Scf (East Asia)

Table2 -Tabulated Generated Data from Simulation

DGAmine Inlet V-1201	Gas Inlet V-1201	Combined Gas+DGA INLET	Top Gas (Sweet Gas) V-1201	Simulation Combined Gas+DGA INLET	Simulation Top Gas (Sweet Gas)	Percentage Error (%)
73.00327	22.37616	95.37942886	55.034241	95.38	51.83	5.82226752
72.98037	22.26264	95.24301338	55.083527	95.24	51.91	5.7612989
72.95149	22.10234	95.0538311	55.252445	95.05	51.96	5.95891314
73.05054	22.21174	95.26228714	55.433456	95.26	52.02	6.15775498
72.95448	22.07937	95.03385544	55.253082	95.03	51.98	5.92380034
72.98278	22.04715	95.02993011	54.829082	95.03	51.4	6.25413072

Table 3- Data Generation from Simulation Model

35 wt% DGA				
P feed gas, (KPA)	P Co2 (kpa)	T (°C)	Mol CO2 / MOL DGA	Mol Co2 / sweet gas
6900	288,2	25	0.04216	0.002813
		30	0.04071	0.002974
		35	0.03812	0.003011
7200	304,9	25	0.04405	0.002313
		30	0.04396	0.002348
		35	0.04317	0.002391
7500	317,5	25	0.05782	0.002156
		30	0.05604	0.002203
		35	0.05597	0.002216

Table 4- Data Generation from Simulation Model

40% wt DGA				
P feed gas (KPA)	P CO2 (kpa)	T (°C)	Mol CO2 /Mol DGA	Mol CO2 / sweet gas
6900	288,2	25	0.041771	0.001230
		30	0.04216	0.001276
		35	0.04239	0.001292
7200	304,9	25	0.04287	0.001172
		30	0.04182	0.001235
		35	0.04176	0.001243
7500	317,5	25	0.04315	0.001201
		30	0.04379	0.001229
		35	0.04342	0.001238

Table 5-Data Generation from Simulation Model

45% wt DGA				
P feed gas (KPA)	P CO2 (kpa)	T (°C)	Mol CO2 /Mol DGA	Mol CO2 / sweet gas
6900	288,2	25	0.04098	0.001010
		30	0.04156	0.001330
		35	0.04187	0.001752
7200	304,9	25	0.04212	0.000998
		30	0.04199	0.001245
		35	0.04273	0.001304
7500	317,5	25	0.04299	0.001002
		30	0.04317	0.001247
		35	0.04329	0.001465

Table 6 (a & b) - Effect of Lean Amine Circulation Rate on Amine Loading:

Table 6a-

45 wt% DGA, T= 35 oC, P= 100 bara			
CirDGAmine	Mol Co2/ Mol DGA	Mol C1/mol DGA	Mol Co2/sweet gas
1200	0.4724	0.00951	0.002268
1250	0.4801	0.00977	0.002764
1300	0.4851	0.00991	0.002979
1350	0.5239	0.01015	0.003023
1400	0.5534	0.01097	0.003125
1450	0.5672	0.01138	0.003179

Table 6b-

45 wt% DGA, T= 40 oC, P= 100 bara			
CirDGAmine	Mol Co2/ Mol DGA	Mol C1/mol DGA	Mol Co2/sweet gas
1200	0.4791	0.00951	0.002856
1250	0.4878	0.00977	0.002937
1300	0.4912	0.00991	0.003051
1350	0.5286	0.01015	0.003178
1400	0.5681	0.01097	0.003199
1450	0.5764	0.01138	0.003212