

# REMOVAL OF CARBON DIOXIDE FROM NATURAL GAS FOR LNG PRODUCTION

*Semester Project Work*

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## Abstract

Removal of CO<sub>2</sub> from natural gas is currently a global issue, apart from meeting the customer's contract specifications and for successful liquefaction process in LNG project, it is also a measure for reducing the global CO<sub>2</sub> emission.

The aims of this project is to present a comprehensive review of different processes available and suitable for removal of CO<sub>2</sub> from natural gas to meet LNG production specifications and explore the capability of HYSYS process simulator to predict the CO<sub>2</sub> removal process operating conditions range at which hydrocarbon and chemical loss (amine solvent) can be minimized.

A base case of amine base CO<sub>2</sub> removal process from a text (GPSA, 1998) is used to create a steady-state simulation using Hyprotech HYSYS 3.2 process simulator. The simulation program developed is used to modify the physical, thermodynamics and transport properties of the gas and the process units involves to improve process environmental performance.

Water content of the natural gas is computed by HYSYS program to fully define the process feed stream composition and the agreement between the water content of the natural gas estimated using HYSYS at selected temperature and pressure range with the estimate from GPSA correlation chart is used as a criteria to establish the accuracy of the HYSYS model developed.

The simulation results shows that increasing amine CO<sub>2</sub> capturing capacity at low temperature and lowering the amine residence time in the stripper, reduces the tendency for CO<sub>2</sub> emission and chemical (solvent) loss.

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**List of Contents**

Abstract	ii
Acknowledgements	iii
<b>List of Tables</b>	vi
<b>List of Figures</b>	vii
<b>1 INTRODUCTION</b>	<b>1</b>
<b>2 LIQUEFIED NATURAL GAS (LNG) PRODUCTION</b>	<b>3</b>
2.1 Gas Production and Field Development	3
2.2 Onshore Gas Treatment	3
2.3 Liquefaction Process	4
2.4 LNG Shipping	5
2.5 Receiving and Re-gasification Terminal	5
2.6 End use as Fuel	5
<b>3 CARBON DIOXIDE REMOVAL PROCESSES</b>	<b>6</b>
3.1 Process selection factors	6
3.2 Physical absorption processes	7
3.2.1 Selexol process	8
3.2.1.1 Process description	8
3.2.2 Rectisol process	10
3.2.2.1 Process description of rectisol process	10
3.2.3 Fluor process	11
3.2.3.1 Process description for low –medium CO <sub>2</sub> content	11
3.2.3.2 High CO <sub>2</sub> content fluor solvent application	12
3.3 Chemical absorption process	13
3.3.1 Potassium carbonate process	14
3.3.2 Process description of carbonate process	14
3.4 Membrane process	15
3.4.1 Process description	17
3.5 Adsorption process	18
3.6 Cryogenic process	19
3.7 Hybrid separation processes	19
<b>4 WATER CONTENT OF NATURAL GAS</b>	<b>21</b>
4.1 Water content determination using GPSA chart	22
4.2 Water content determination using hysys program	22
4.3 Comparison of water content results	23
<b>5 HYSYS PROCESS SIMULATION PACKAGE</b>	<b>24</b>
<b>6 AMINE BASE PROCESS FACILITIES</b>	<b>26</b>
6.1 Process description	28
6.2 Justification of amine process	29
6.3 Economic factors in operating gas treating process	30
6.4 Process cost analysis.	30

7	<b>ENVIRONMENTAL IMPACT</b> -----	33
8	<b>HYSYS SIMULATION OF AMINE PROCESS</b> -----	36
	<i>8.1 Description of process equipment</i> -----	36
	<i>8.2 Hysys simulation procedures</i> -----	38
9	<b>SIMULATION RESULTS/DISCUSSION OF RESULTS</b> -----	42
	<i>9.1 Simulation results</i> -----	42
	<i>9.2 Discussion of results</i> -----	42
10	<b>CONCLUSIONS</b> -----	44
	<b>NOMENCLATURE</b> -----	45
	<b>REFERENCES</b> -----	46
	<b>APPENDIX A: Basic Raw Data and Base Case Simulation Data</b> -----	64
	<b>APPENDICES B: Water Content Determination Procedures</b> -----	65

**List of Tables**

Table 1: Wastes Types Generated in Different CO<sub>2</sub> Removal Process units ..... 34

Table 2: Data Generated from the Simulation Model..... 47

Table 3 Effect of Lean Amine Circulation Rate on Amine Loading at 35 °C..... 49

Table 4. Effect of Lean Amine Circulation Rate on Amine Loading at 40°C ..... 49

Table 5 Natural Sour Feed Gas Composition ..... 49

Table 6 Gas Product Stream composition after absorption process ..... 50

Table 7 Typical LNG Product Specification, (David Coyle et al)..... 50

Table 8 Water Content from HYSYS Simulator in [mg/Sm<sup>3</sup>]..... 58

Table 9 Water Content from GPSA Chart in [mg/Sm<sup>3</sup>] ..... 58

Table 10 Water Content Comparison in [mg/Sm<sup>3</sup>] for 100 and 500 kpa..... 59

Table 11 Water Content Comparison in [mg/Sm<sup>3</sup>] for 1000 and 1500 kpa..... 59

Table 12 Approximate Guideline for amine Processes (Kensell, 1979)..... 61

Table 13 Physical Properties of Amines (Source from GPSA) ..... 61

Table 14 Water Content Evaluated ..... 67

**List of Figures**

Figure 1 Fluid Package Basis (Amine fluid Package) ..... 38

Figure 2 Component selection windows..... 38

Figure 3 Un-simulated Amine Process Flow Diagrams ..... 39

Figure 4 Sour Gas specification windows ..... 39

Figure 5 Converged window of the Absorber..... 40

Figure 6 Converged windows for regenerator unit..... 41

Figure 7 Complete Simulations Unit. .... 41

Figure 8 % of CO<sub>2</sub> in the Sweet Gas as a Function of Amine Concentration..... 51

Figure 9 Effects of Pressure and Temperature on % C<sub>O2</sub> in the Sweet Gas ..... 51

Figure 10 Effects of C<sub>O2</sub> Loading in DEAmine with pressure and Temperature ..... 52

Figure 11 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 25wt%  
DEA ..... 52

Figure 12 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 30wt%  
DEA ..... 53

Figure 13 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 35wt%  
DEA ..... 53

Figure 14 Lean DEA Circulation rate vs. CO<sub>2</sub> loading in 35wt% DEA..... 54

Figure 15 Lean DEA Circulation rate vs. molCO<sub>2</sub> in the acid gas with 35wt% DEA.... 54

Figure 16A Typical Amine Base process Diagram ..... 55

Figure 17 A Typical Fluor Solvent Process unit..... 55

Figure 18 A typical Selexol Process Unit..... 56

Figure 19 Process Capabilities for gas treating process ..... 56

Figure 20 Cooling Curve of Natural Gas and Evaporating temperature in ..... 57

Figure 21 Typical LNG liquefaction Cascade arrangements..... 57

Figure 22 Typical LNG Liquefaction Mixed refrigerant arrangements (Statoil/Linde)  
..... 58

Figure 23 Comparison of Fluor solvent and Promoted MDEA process relative cost . 60

Figure 24 Comparison of Fluor Solvent and Promoted MDEA process Parameters. .... 60

Figure 25 Flow Process for Determination of Water Content ..... 62

Figure 26 Water Content of Hydrocarbon Gas from GPSA ..... 63

## 1 INTRODUCTION

The increase in demand for energy worldwide has aid the search for alternative sources of primary energy even to the remote part of the globe. The major alternative source with less environmental impact discovered some decade ago is energy from natural gas. Natural gas at its geological conditions in some deposits contain some complex contaminants such as CO<sub>2</sub>, H<sub>2</sub>S, CO, Mercaptan ( Acid Gas), which constitute great environmental hazards when get to the atmosphere and also hindered natural gas processes.

Natural gas is of little value unless it can be brought from the wellhead to the customers, who may be several thousand of kilometer from the source. Natural gas is relatively low in energy content per unit volume, it is expensive to transport. The most popular way to move gas from the source to the consumer is through pipelines. However as transportation distance increases, pipelines become uneconomical, Liquefied Natural Gas (LNG), Gas to liquid and chemicals are more viable options.

Liquefaction process which is the transformation of natural gas to liquid form involve operation at a very low Temperature (-161°C) and as low as atmospheric pressure. At these conditions CO<sub>2</sub> can freeze out on exchanger surface, plugging lines and reduce plant efficiency. Therefore there is need for removal of CO<sub>2</sub> before liquefaction process, this is done not to overcome the process bottle necks but also to meet the LNG product specifications, prevent corrosion of process equipment and environmental performance.

There are many acid gas treating processes available for removal of CO<sub>2</sub> from natural gas. These processes include Chemical solvents, Physical solvents, Adsorption Processes Hybrid solvents and Physical separation (Membrane) (Kohl and Nielsen, 1997); The chemical solvents and physical solvents or combination of these two have been used extensively in existing base load LNG facilities (David Coyle et. al 2003).

Today, computer-aided process simulation is nearly universally recognized as an essential tool in the process industries. Indeed, simulation software play a key role in: process development – to study process alternatives, assess feasibility and preliminary economics, and interpret pilot-plant data; process design to optimize hardware and flow-sheets, estimate equipment and operating cost and investigate feedstock flexibility; and plant operation to reduce energy use, increase yield and improve pollution control.

The ability of the LNG option to continue to compete with existing and emerging gas monetization, option will depend on the industry's success in reducing cost throughout the LNG value chain and maintaining exceptional safety, reliable and less environmental impact operations.

This project therefore summarizes the various processes available and suitable for removal of CO<sub>2</sub> from natural gas to meet the LNG stringent specification of about 50-100 ppmv or 2-3% CO<sub>2</sub> concentration in the product stream. Different processes scalability, advantages and disadvantages will be highlighted. Simulation of a typical amine solvent based CO<sub>2</sub> removal plant using HYSYS process simulator to establish optimum operating conditions that will improve process environmental performance will be considered in detail.

## 2 LIQUEFIED NATURAL GAS (LNG) PRODUCTION

Liquefied Natural Gas (LNG) Production is one of the fastest growing process nowadays, LNG trade is said to account for about 24.2% of international natural gas trade (Cornot-Gandolphe and chabrelie, 1995).

LNG production value chains include the following steps;

- Gas Production and Field Processing
- Onshore gas treatment
- Gas Conversion Via Liquefaction
- LNG Shipping
- Receiving Terminal
- End use as Fuel (Power Generation, Fertilizer Industry, gas Distribution, etc.)

### *2.1 Gas Production and Field Development*

The exploration and production of gas is the starting point for all gas utilization options. The source of natural gas feed to the LNG plant could be either associated gas or non-associated gas. Natural gas is naturally occurring gaseous mixture or hydrocarbon components and consists mainly of methane. Other constituents include ethane, propane and butane which is refers to as liquefied petroleum gas (LPG) and condensate which are heavier hydrocarbons. The compositions of the gas differ from one gas reservoir to another. The gas production step includes some field processing depending on the nature of the gas source and the requirement for pipeline transport to liquefaction site. Typically, field processing is needed to prevent hydrocarbon drop-out, hydrate formation or corrosion in the pipeline to the liquefaction site.

### *2.2 Onshore Gas Treatment*

The gas from the reservoir may also contain components such as nitrogen, carbon dioxide and sulfur compounds. The feed gas has to be treated for removal of impurities before it can be liquefied. Hence onshore gas treatment is required to meet the specification set by the LNG buyers as well as requirements for the LNG liquefaction process. Typical LNG product specifications are listed in table 7.

The onshore gas treatment typically comprises of gas reception facilities, Acid gas removal and disposal section, gas dehydration, mercury removal and particle filtration.

The gas reception facilities section provided for the removal of liquid entrainment gather in the system due to condensation and pressure reduction of the fluid (Joule Thomson effect). At this section the pressure of the LNG feed is adjusted to meet the requirement of the liquefaction facilities. If the pressure is lower than that of the liquefaction facilities a compressor may be installed to beef up the pressure difference.

Acid gas removal and disposal section is provided to remove acid gases (CO<sub>2</sub>, H<sub>2</sub>S and other sulfur components) from the feed gas. The extent of removal is influenced by the LNG specification and the requirement of the liquefaction process. Detail is discussed in chapter 3 of this paper.

The dehydration section removes water from the fees gas. Water vapor must be removed to prevent corrosion, and freezing in the liquefaction process of the plant that operate at cryogenic condition.

Trace of mercury in the feed gas, which attacks piping, and equipment made from aluminum and aluminum compounds is removed in the mercury removal section. Aluminum is universally used for the construction of cryogenic equipment. Filtration of the gas stream following the mercury removal unit is essential to prevent particle into the liquefaction section of the plant, thus prevent equipment plugging.

### ***2.3 Liquefaction Process***

The liquefaction section is the heart of LNG value chain. The process involved cooling the clean feed gas in succession (Pre-cooling, Liquefaction and Sub-cooling) to -161 °C using mechanical refrigeration. A typical successive cooling process curve is shown in figure 20. The refrigerants for LNG process must have high evaporating temperature to reduce power needed for heat pumping. For effective cooling there should be a close

match between the natural gas and refrigerants temperature curves and this could be achieved by the following;

- Using many stages of evaporating temperature ( Cascade Process)
- Using refrigerant that evaporate at gliding temperature ( Mixed refrigerants)

Figure 21 and 22 show typical Cascade process arrangement with three Different refrigerants combined together (Propane, Ethylene and Methane) and mixed refrigerant arrangement respectively.

### ***2.4 LNG Shipping***

After the liquefaction process and subsequent Storage, the LNG is pumped from the storage tank to a LNG ship via a loading jetty; LNG vapor return from the ship to the storage tank is always provided to avoid pressure build up in the ship. The LNG is then shipped commercially in a fully refrigerated liquid state. The ship cargo is kept cool by evaporating a fraction of the cargo which is referred to as “boiloff”. The carriers either consume boiloff or re-liquefy the gas and use diesel as fuel.

### ***2.5 Receiving and Re-gasification Terminal***

The LNG from the ship is received in this section, stored and re-vapourize for sales on demand. The amount of reserve capacity depends on expected shipping delays, seasonal variation of supply and consumption

### ***2.6 End use as Fuel***

LNG can be applied in a wide range of energy needs as follow;

- As a feedstock for manufacturing of chemicals ( Fertilizer, ammonia)
- An excellent fuel for powering boilers.
- For electrical power generation.
- As fuel for transportation ( Train, Buses and LNG ships)

### 3 CARBON DIOXIDE REMOVAL PROCESSES

The removal of acid gases (CO<sub>2</sub>, H<sub>2</sub>S and other sulfur components) from natural gas is often referred to as gas sweetening process. Carbon dioxide present in the natural gas need to be removed in other to; increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and crystallization of CO<sub>2</sub> during cryogenic process (liquefaction process). The removal of carbon dioxide can be accomplished in a numbers of ways. Varieties of processes and (improvement of each) have been developed over the years to treat certain types of gas with the aim of optimizing capital cost and operating cost, meet Gas specifications and for environmental purpose (Tennyson et .al 1977).

The major processes available can be grouped as follows (Maddox, 1982);

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)
- Physical Separation (Membrane, Cryogenic Separation)
- Hybrid Solution (Mixed Physical and Chemical Solvent)

#### *3.1 Process selection factors*

Today, the field of acid gas removal process is so wide and available processes are so numerous, thus selection of an optimum process becomes an issue. Each of the processes has advantages relatives to others for certain applications; therefore in selection of the appropriate process, the following factors should be put into consideration:

- Type and concentration of impurities in the feed gas
- The concentration of each contaminants and degree of removal required.
- Hydrocarbon composition of the gas
- Final specification
- Capital and operating cost
- Volume of gas to be processed
- Selectivity required for acid gas removal
- Conditions at which the feed gas is available for processing.

Decision in selecting a CO<sub>2</sub> removal process can be simplified by gas composition and operating conditions. High CO<sub>2</sub> partial pressure in the feed gas (345 kpa) enhances the possibilities of employing physical solvent, while the presence of significant amount of heavy hydrocarbon discourages the use of physical solvent. Low CO<sub>2</sub> partial pressures and low outlet pressure of the product stream may favour application of chemical solvents (Tennyson et al 1977). Process selection could prove difficult; a numbers of variables must be weighed prior to making final process selection. Figure 19 can be used as screening tools to make an initial selection of potential process choices.

### ***3.2 Physical absorption processes***

Physical solvent processes use organic solvents to physically absorb acid gas components rather than react chemically. Removal of CO<sub>2</sub> by physical absorption processes are base on the solubility of CO<sub>2</sub> within the solvents. The solubility of CO<sub>2</sub> depends on the partial pressure and on the temperature of the feed gas. Higher CO<sub>2</sub> partial pressure and lower temperature favors the solubility of CO<sub>2</sub> in the solvents (Absorbent), at these conditions complete removal of acid gas from natural gas is possible. Regeneration of the spent solvent can be achieved by flashing to lower pressure or by stripping with vapour or inert gas, while some is regenerated by flashing only and require no heat (Dimethyl ether of Polyethylene Glycol). Selection of physical processes for the removal of CO<sub>2</sub> from natural gas for LNG project is favoured on the following conditions;

- i. The partial pressure of the CO<sub>2</sub> in the feed should be 50 psi or higher
- ii. The concentration of heavy hydrocarbon in the feed should be low. That is the gas feed is lean in C<sub>3</sub>+
- iii. Only bulk removal of acid gas is required.
- iv. Selective removal of CO<sub>2</sub> is required.

There are various physical processes for the removal of CO<sub>2</sub> from natural gas but not all the processes available are capable of removing CO<sub>2</sub> to meet LNG specification of 50-100 ppmv of 2.5% of CO<sub>2</sub> in the product stream. The following physical processes will be discussed base on their suitability/modification to treat acid gas with high or low

concentration of CO<sub>2</sub> in the feed gas and small – large scale processes will also be considered.

The processes are as follows;

- Selexol process
- Rectisol process
- Fluor process

### ***3.2.1 Selexol process***

The selexol process uses union Carbide selexol solvent, a physical solvent made of dimethyl ether of polyethylene glycol [CH<sub>3</sub> (CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub>]. Where n is between 3 to 9 (Johnson and Homme, 1984). The solvent can be used to selectively or simultaneously remove sulfur compounds, carbon dioxide, water as well as aromatic compound (BTEX) Dehydration of the feed gas is required before entering the Selexol unit.

(Greene and Kutsher, 1965) report that initial runs on the dimethyl ether of tetra ethylene glycol (DMTEG); shows that less expensive mixture of the dimethyl ether of polyethylene glycol (DMPEG) ranging from diethylene glycol to hepta glycol was just as effective as pure DMPEG in absorption of CO<sub>2</sub>.

#### ***3.2.1.1 Process description***

A typical selexol flow unit is shown in figure 18. The dehydrated sour gas enters the absorber and flow upward counter-currently to the lean solvent which is introduced at the top of the absorber. The solvent enter the absorber slightly below ambient temperature through the use of heat exchangers on flashed solvent and lean solvent streams. Because of the high CO<sub>2</sub> content in the feed gas, a bottom- pump- around of solvent is used on the absorber and a two stage solvent introduction is employed. The leanest solvent is introduced at the top of the absorber and the semi-lean or partially stripped solvent is introduced in the mid-way of the absorber. The rich solvent leave the bottom of the absorber and flashed in a high pressure separator the vapour stream is recycled back to the absorber to reduce hydrocarbon losses.

The rich solvent from the high pressure separator is flashed in an intermediate pressure separator to release a major portion of CO<sub>2</sub> after passing through the rich solvent – sour gas exchanger. The low pressure flash stage which is at atmospheric pressure release the major portion of the remaining dissolved CO<sub>2</sub>, a portion of semi-lean solvent stream from the flash is pumped back to the intermediate point in the absorber for contacting the richest part of the sour gas stream, while the other portion is flow to the stripper column where it is air/N<sub>2</sub> stripped to remove the last traces of acid gas present and then pumped through semi-lean-lean solvent heat exchanger to the top of the absorber. The sweet gas leaving the unit contain  $\leq 2.5\%$  CO<sub>2</sub> per 100 Scf.

#### **ADVANTAGE OF SELEXOL PROCESS**

- i. The heat rise of the solvent in the absorber is low since there is no heat of chemical reaction.
- ii. The sweet gas from the absorber comes out dry because of the high affinity of selexol solvent with water.
- iii. The initial plant and operating costs are minimal.
- iv. Regeneration of the solvent is by air stripping, it's required no re-boiler's heat.
- v. Selexol process allows for construction of mostly carbon steel due to its non-aqueous and inert chemical characteristics.
- vi. The process could be operated at low pressure.

#### **DISADVANTAGES OF SELEXOL PROCESS**

- i. The solvent have high affinity to heavy hydrocarbon which will be removed with CO<sub>2</sub> and essentially result to hydrocarbon losses.
- ii. The process is more efficient at high operating pressure.

### **3.2.2 Rectisol process**

Rectisol process uses chilled methanol as a solvent, because of high vapour pressure of methanol the process is normally operated at temperature range of -30 to -100°F. The process is best suited where there are limited quantities of ethane and heavier components (Weiss, 1988). There are many possible processes configurations for Rectisol process depending on process requirement/specifications and scalability. Rectisol process is now extensively used in natural gas industry to remove CO<sub>2</sub> (Knapp, 1968).

#### **3.2.2.1 Process description of rectisol process**

In this process the methanol solvent contacting the feed gas in the first stage of the absorber is stripped in two stages of flashing via pressure reduction. The regenerated solvent is virtually free of sulfur compounds but contains some CO<sub>2</sub>.

The acid gas leaving the first stage solvent regenerator is suitable for Claus plant. The second stage of absorption then removes the remaining CO<sub>2</sub> present.

The rich solvent from the bottom of the second stage of the absorber is stripped deeply in a steam-heated regenerator and return to the top of the absorption column after cooling and refrigeration.

#### **ADVANTAGES OF RECTISOL PROCESS**

- i.** The solvent (**methanol**) does not foam and completely miscible with water thus reduces losses
- ii.** The have high thermal and chemical stability.
- iii.** It's non-corrosive.
- iv.** There are no degradation problems
- v.** The carbon steel can be widely used for the equipment.
- vi.** The rich solvent can be easily regenerated by flashing at low pressure therefore eliminate the need for re-boiler's heat.

**DISADVANTAGES OF RECTISOL PROCESS**

- i. Chilled methanol solvent used is capable of absorbing metallic trace components such as mercury (Hg) to form amalgams in the low temperature of the process.
- ii. Rectisol complex scheme and the need to refrigerate the solvent result in high capital and operating cost of the plant.

**3.2.3 Fluor process**

The Fluor solvent process is one of the most attractive processes for gas treating when the feed gas CO<sub>2</sub> partial pressure is high (> 60 psia), or where the sour feed gas is primarily CO<sub>2</sub>. The process is based on the physical solvent propylene carbonate (FLUOR™) for the removal of CO<sub>2</sub>. Propylene carbonate (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>), is a polar solvent with high affinity for CO<sub>2</sub> and  $\alpha_{ij}$  values of C<sub>1</sub> or C<sub>2</sub> to CO<sub>2</sub> are high, therefore hydrocarbon pickup in the rich solvent and subsequent hydrocarbon losses in the CO<sub>2</sub> vent stream are minimal.

The early FLUOR solvent process configurations were limited to treating a narrow range of feed gas compositions, which is application, were limited to feed gas stream with low C<sub>5</sub>+ hydrocarbon. Recently new configurations have been developed for treating; A low to medium and high CO<sub>2</sub> content sour gas

**3.2.3.1 Process description for low –medium CO<sub>2</sub> content**

For gas with CO<sub>2</sub> partial pressure of about 60-120 psia and the feed gas is at 1000psig and ambient temperature. The feed gas is first dried in a TEG contactor to remove almost all the water, this prevent water buildup in the solvent. The dehydrated feed gas is then cooled by cold treated gas from the absorber and further cooled by external refrigeration. The cooling process minimizes the temperature rise in the bottom of the absorber caused by heat of solution of CO<sub>2</sub>, which results in a close isothermal absorber temperature profile. Also it aids the removal of heavy hydrocarbon, thus minimized co-absorption of heavy hydrocarbon by solvent and reduces the recycle gas flow and hydrocarbon losses in the CO<sub>2</sub> vent. The near isothermal temperature profile of FLUOR process improves both mass transfer and rich solvent CO<sub>2</sub> loading. The rich solvent is regenerated by series of

flashes. The flash drums are stacked one on top of the other. The flash gases from the high-pressure, medium and low-pressure flash drums are recycled back to the front end of the plant via a recycle gas compressor. Flash gas recycle typically reduces hydrocarbon losses to less than 0.5% of the feed gas. Losses can be reduced further with an increase in recycle compression horsepower. Over 90% of the CO<sub>2</sub> desorbed in the atmospheric flash and residual CO<sub>2</sub> is desorbed in a vacuum flash.

The lean solvent pump directs the lean solvent back to the absorber. In this scheme no additional refrigeration is required other than that in the feed gas chilling section. The balance of the cooling duty comes from desorption of CO<sub>2</sub> from the rich solvent.

### ***3.2.3.2 High CO<sub>2</sub> content fluor solvent application***

A FLUOR solvent process configuration for a high CO<sub>2</sub> content feed gas is depicted in figure 17. The feed gas pressure in this case varies from 400 – 1200 psig with the CO<sub>2</sub> content varying from 30-70 % and more. High CO<sub>2</sub> content in the feed gas increases the amount of refrigeration produced by the flash regeneration of the rich solvent. At very high CO<sub>2</sub> partial pressures, the cooling effect from flash regeneration will exceed the cooling required for CO<sub>2</sub> absorption. Also the viscosity and surface tension of propylene carbonate increases dramatically and the absorber mass transfer rate drops drastically. This negatively impact the process, therefore overcooling of the solvent should be avoided.

The excess refrigeration is harness in this application by lower the absorption column temperature with refrigeration generated from flashing the rich solvent from high to medium pressure. This allows the absorber to operate at a lower temperature and increases the solvent loading. The flashed gasses are compressed and recycled to reduce hydrocarbon losses in the CO<sub>2</sub> vent. Excess refrigeration generated by flashing of the rich solvent flowing to the first stage flash drum is used to cool and condense the CO<sub>2</sub> vent stream from the atmospheric and vacuum flashes. The condensed CO<sub>2</sub> can be used for EOR or disposed of by injecting the liquid into an underground formation.

**ADVANTAGES OF FLUOR PROCESS**

- i. FLOUR process required no fired duty for solvent regeneration.
- ii. The FLUOR solvent has high CO<sub>2</sub> solubility and enhance CO<sub>2</sub> loading.
- iii. It's required no make up water.
- iv. The operation is simple and a dry gas as out put product.
- v. Since propylene carbonate freezes at -57 °F, winterization modification is minimal.
- vi. Modification for increasing CO<sub>2</sub> in the feed is low.

**DISADVANTAGES OF FLUOR PROCESS**

- i. Solvent circulation for the FLUOR solvent process is high.
- ii. The FLUOR solvent is very expensive ( SPE 14057)
- iii. The solvent have high affinity to heavy hydrocarbon which will be removed with CO<sub>2</sub> and essentially results to hydrocarbon losses.

**3.3 Chemical absorption process**

Chemical absorption processes are based on exothermic reaction of the solvent with the gas stream to remove the CO<sub>2</sub> present. Most chemical reaction are reversible, in this case reactive material (solvent) removes CO<sub>2</sub> in the contactor at high pressure and preferably at low temperature. The reaction is then reversed by endothermic stripping process at high temperature and low pressure. Chemical absorption processes are particularly applicable where acid gas (CO<sub>2</sub>) partial pressure are low and for low level of acid gas requirement in the residue gas. The water content of the solution minimizes heavy hydrocarbon absorption, thus making the solvent more suitable for feed sour gas rich in heavy hydrocarbon. Majorities of chemical solvent processes use either an amine or carbonate solution.

**3.3.1 Potassium carbonate process**

Carbonate process uses potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) to remove CO<sub>2</sub> from natural gas. It works best in a gas with CO<sub>2</sub> partial pressure ranges between 30 – 90 psi.

The high pressure of natural gas transmission lines yields relatively high acid gas partial pressure. As a results the hot potassium carbonate is now frequently use for the economical sweetening of natural gases having medium to high acid gas contents.

The main reactions in this process are;



(Ruziska, 1973) proposed that the equation 3.1 above actually proceed in two stages. The first step is the hydrolysis of potassium carbonate



The second stage of the reaction involves the reaction of potassium hydroxide formed during the hydrolysis process with CO<sub>2</sub> to form potassium bicarbonate.



The reaction with carbon dioxide gives two parts of potassium bicarbonate for each part of potassium carbonate reacted. Therefore the concentration of the solution of the solvent use (K<sub>2</sub>CO<sub>3</sub>) for CO<sub>2</sub> removal is controlled by potassium bicarbonate solubility rather than by potassium carbonate solubility.

**3.3.2 Process description of carbonate process**

For carbonate process the sour gas flows through a separator and to sour gas - sweet gas heat exchanger. The heated sour gas enters the bottom of the absorber and flow counter-currently with the descending lean hot potassium carbonate stream. The sweet gas exits the top of the absorber and through a gas-gas exchanger. Typically the absorber is operated at about 230 °F. The sour gas-sweet gas exchanger is use to recover sensible heat and decrease the heat requirement for the system. The acid rich potassium carbonate from the bottom of the absorber is flashed to remove some part of acid gas absorbed while the remaining is stripped at low pressure (P<sub>atm</sub>) and high temperature at the stripper which operate at approximately 245 °F.

The regenerated solvent from the bottom of the stripper is pumped back to the absorber for re-use. The entire system is operated at high temperature to increase potassium carbonate solubility, therefore a dead spot where the solution is likely to cool and precipitate should be avoided, hence the system suffer from plugging, erosion or foaming.

#### **ADVANTAGES OF THE PROCESS**

- Steam requirement for the system is low since absorber and stripper are operated at nearly the same temperature (isothermal system)
- Low cost of operation
- Degradation of the solvent is minimal
- It is a continuous circulating system employing an inexpensive chemical.

#### **DISADVANTAGES OF THE PROCESS**

- Potassium carbonate causes general stress corrosion of the units
- The solvent react with some corrosion inhibitors and cause erosion of the unit
- Tendency for foaming and solid suspension is high thus reduce CO<sub>2</sub> solvent loading
- The regenerated solution leaving the stripper is at its saturated temperature and partially vapourize in the pump suction, resulting in vibration and excessive wear of the pump impellers

#### ***3.4 Membrane process***

Polymer membranes systems are a commercially proven technology for natural gas treating application. Membranes are being used more frequently in gas field operations in removing carbon dioxide and water vapour to meet pipeline and LNG project specification. For a gas to permeate through a membrane surface the gas must first dissolve in the high-pressure side of the membrane, diffuse across the membrane wall, and evaporate from the low-pressure side. Gas separation therefore works on the principle

that some gases are more soluble in, and pass more readily through polymeric membrane than other gases.

Each particular gas species encounters a unique resistance to gas transport exhibit by a specific membrane. This resistance is dependent on two factors; first, the size and shape of the gas molecules, this control the diffusivity of the gas through the membrane and secondly, the extent of the molecular interaction between membrane and the gas characterizes the solubility of the gas molecule in the membrane.

The overall selectivity of the membrane process is dependent on the resistance in series of the boundary layer, selective film and porous substructure. A gas encountering low resistance to transport is called “fast” gas which selectively permeates through the membrane, while gas with high resistance is called “slow” gas. In natural gas carbon dioxide (CO<sub>2</sub>) species is said to be fast gas because of it linear molecular orientation and high solubility in some polymeric membrane especially “polysulfone membrane”.

Membrane permeation is pressure driven process. The partial pressure difference between the feed side and the permeate side has by far the greatest impact on the performance of a membrane separator. The driving force for transportation through a membrane is the difference in the partial pressure of the feed gas across the membrane. The greater the partial pressure, the greater the driven force. This pressure difference influences the membrane area required to achieve the desired separation at a given feed conditions. Another important process criteria is the ratio of feed pressure over permeate pressure, this has to be established in accordance to the membrane selectivity in order to achieve an efficient separation. The permeance through a gas separation membrane is given by the equation below;

$$v = kA_M (P_{i,H} - P_{i,L}) \dots\dots\dots 3.4.1$$

Where;

V = volume of permeate gas, [std m<sup>3</sup>/h]

In case of high-pressure application the difference in partial pressure of the compound have to be substituted by the fugacity

$$v = kA_M (\varphi_{i,H} y_{i,H} P_H - \varphi_{i,L} y_{i,L} P_L) \dots\dots\dots 3.4.2$$

### 3.4.1 Process description

In membrane process feed gas is normally pre-treated/conditioned before entering the membrane system to ensure efficient operation. The pre-treatment equipment varies depending on the feed gas composition and conditions. Generally for natural gas the feed gas is filtered through a high coalescing filter for removal of entrained particulates or aerosols including sand, pipe scale. The feed gas is cooled in a cooler. Any condensed liquids are removed in the gas/liquid separator and flashed back to the inlet compressor third stage discharge scrubber. After liquid removal, the feed gas enters the feed pre-heater; triethylene glycol is sometime used as a heat medium to increase the gas temperature. The temperature control is provided to maintain the gas at the desired operating temperature of the membrane fibres. The heated gas then enters the membrane gas separators where it is separated into two streams; the permeate or CO<sub>2</sub> product a-low pressure, CO<sub>2</sub>-rich stream and the non-permeate or residue, a high pressure hydrocarbon-rich stream.

#### ADVANTAGES OF THE PROCESS

- Membrane has good weight and space efficiency, which make it more applicable off shore environment
- Its has high adaptability to variation of CO<sub>2</sub> content in the feed gas
- Periodical removal and handling of spent solvent or adsorbent make the system more environmental friendly
- Membrane has limited / No moving parts thus make the process more risky to operate.

#### DISADVANTAGES OF THE PROCESS

- Separated CO<sub>2</sub> is at low pressure and requires additional compression to meet pipeline pressure requirement
- Compression of the feed gas is necessary to provide the driving force for permeation, the energy required for compression is high especially is high pressure is require thus contributing to the cost of operation.
- The hydrocarbon loss is high.

### 3.5 Adsorption process

Adsorption process involves the absorption of acid gas components by solid adsorbent. The removal processes is either by chemical reaction or by ionic bonding of solid particles with the acid gas. Commonly use adsorption processes are; the iron oxide, Zinc oxide and molecular sieve (Zeolite) process. The adsorbent is generally characterized by a micro-porous structure which selectively retains the components to be separated, once the bed is saturated with the acid gas the vessel is removed from the system for regeneration by flowing hot sweet gas through the bed. Among the adsorption processes mention above only the molecular sieve is more suitable for removal of small concentration of CO<sub>2</sub> from natural gas.

The sieve makes use of the synthetically solid crystalline Zeolite to remove the gas impurities. The crystal structure creates a large number of localized polar charges called active site. The polar gas molecule such as H<sub>2</sub>S and H<sub>2</sub>O form weak ionic bond at the active site. Non-polar molecules such as hydrocarbon will not bond at the active site. Though carbon dioxide molecules are non-polar and will not bond to the active site, but due to CO<sub>2</sub> linear structure, small concentration of CO<sub>2</sub> will be trapped in the pores. The process is therefore more applicable for feed gas with low concentration of CO<sub>2</sub>.

#### **ADVANTAGES OF ADSORPTION PROCESS**

- Molecular sieve bed does not suffer any mechanical degradation
- The operation of the process is simple.
- Simultaneous dehydration of the gas and acid removal is possible.

#### **DISADVANTAGES**

- The process is limited to small gas stream operating at moderate pressure.
- Its is unsuitable for continuous circulation due to attrition
- The design of the process is complex

### 3.6 Cryogenic process

Low temperature distillation (Cryogenic separation) is a commercial process commonly used to liquefy and purify carbon dioxide from relatively high purity (>90%) sources. It involves cooling the gases to a very low temperature (lower than -73.3 °C) so that the carbon dioxide can freeze-out / liquefy and be separated.

#### ADVANTAGES

- Suitable for feed gas with high concentration of CO<sub>2</sub>
- It produces a liquid CO<sub>2</sub> ready for transportation by pipeline.

#### DISADVANTAGES

- The energy for regeneration is very high which increases the operating cost.
- Tendency for blockage of process equipment is high.
- Some cryogenic fluids are flammable and toxic such as (acetylene, ethane)

### 3.7 Hybrid separation processes

The hybrid separation processes combine the properties of physical and chemical solvents for effective and selective removal of acid gas from natural gas. One of the well-acclaimed successful hybrid separation processes used in the oil and gas industry is the Sulfinol process, licensed by Shell E&P. Sulfinol is a mixture of sulfolane (tetrahydrothiophene-1,1-dioxide, a physical solvent), water, and either diisopropanolamine (DIPA) or methyldiethanolamine (MDEA) (both chemical solvents). The dual functionality and capacity of the physical and chemical solvents in the mixture of sulfinol make the solvent more efficient. The physical solvent, for instance, provides the system for bulk removal of acid gas and also allows much greater solution loading of acid gas than most pure base solvents. Typically, a sulfinol solution of 40% sulfolane, 40% DIPA, and 20% water can remove 1.5 moles of acid gas per mole of sulfinol solution (Ken Arnold, 1999). The technology can be used to remove H<sub>2</sub>S, CO<sub>2</sub>, COS, CS<sub>2</sub>, mercaptans, etc. For complete removal of CO<sub>2</sub> from natural gas, sulfinol-M (a combination of sulfinol with MDEA) is used.

**ADVANTAGES**

- Low energy requirement
- Low foaming and non-corrosive nature of the solvent
- High acid gas loading

**DISADVANTAGES**

- Higher co-absorption of heavy hydrocarbon
- A reclaimer is required to remove the oxazolidones produced in a side reaction of DIPA with CO<sub>2</sub>

## 4 WATER CONTENT OF NATURAL GAS

Water vapour may be present in natural gas due to natural occurrence in the well production stream, the storage of the gas in the underground reservoir, transmission or distribution through moisture containing lines. The saturated water content of a gas depends on pressure, temperature, and composition. The effect of composition increases with pressure and is particularly more important when the gas contain appreciable amount of carbon dioxide (acid gas), since carbon dioxide have 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 increase the ability of gas to hold water.

Correction can be made to account for the composition of the gas and the salinity of the water. Figure 26 shows the water content at saturation point of nitrogen-free natural gases as a function of pressure and temperature. Dissolved salts reduce the partial pressure of water in the vapour phase, thus reduce the water content of the gas. Figure 26 provide means for salinity correction (After Katz, 1962). The water content of natural gas can be measured using three different methods (Rejoy et al., 1994).

1. by observation of the dew point
2. by water retention on an adsorbent
3. by absorption in liquid

Determination of saturated water content of acid gas is essential to estimate the operating conditions of gas treating process in order to stay within non-hydrate formation zone. In this the project it is essential to estimate the saturate water content in order to fully define the compositions of the feed gas stream into the CO<sub>2</sub> removal plant. There are many correlations to define saturated water content of natural gas; the following correlations are use in this project;

- By using GPSA Correlation Chart
- By using HYSYS Simulator

#### ***4.1 Water content determination using GPSA chart***

(Mcketta et al., 1958), proposed a correlation to estimate the water content of natural gas base on some experimental data available. Figure 26 shows a chart of water content in mg per standard m<sup>3</sup> of gas at standard condition [15 °C & 101.325 kpa] and temperature at different pressure range with salinity and density correction. Once the natural gas pressure and temperature is known the corresponding water content of the gas can be read off from the chart. Determination of water content at different pressure range (100 – 1500 kpa) and temperature range of -40°C – 80°C is estimated and shown in table 4.

#### ***4.2 Water content determination using hysys program***

A simple flow sheet was made with the use of HYSYS program. The sheet shows a stream of gas with no water content going into the mixer along with pure water stream. The amount of water is high enough to saturate the gas, and to be still present as liquid in the pipe (figure 25). Therefore a stream of saturated gas with significant amount of free water above the saturation point is created in the mixer and flows to a two – phase separator the water content above the saturation level is taken away as liquid from the bottom part of the separator. The sat gas which is saturated with water is taken from the top of the separator as vapour. The temperature and pressure of saturated gas are inserted and on this basis HYSYS calculates the water content of the saturated gas. Hence the water content in [mg/m<sup>3</sup>] of gas at the set condition can be checked.

HYSYS application does not provide possibility to estimate water content of natural gas at standard condition. Therefore to achieve this, excel sheet to calculate the mass of water content in 1 m<sup>3</sup> of gas (kg) was prepared within HYSYS environment and link with MS excel to convert it to standard condition using Clapeyron equation. Correction for acid gas content of the natural gas was also taken care of using Wichert and Aziz (1992) correlation, and the compressibility factor using Hall and Yarborough correlation. Detail of the calculation procedure is shown in appendix B.

### *4.3 Comparison of water content results*

Tables 10 and 11 shows the water content estimated from GPSA chart and HYSYS program at different pressure and temperature. A statistical correlation analysis was estimated to ascertain the degree of match between the two methods. The Results from GPSA chart was considered to be the standard values. From the statistical correlation it was observed that there is a strong correlation between the two methods. Correlation of **0.999976** and **0.999807** was estimated at pressure of 100 and 500 kpa respectively. However at temperature of -40 oC and pressure of 100 and 1500 kpa, the percentage difference estimated was about 25% and 31% respectively, these differences may be due to difference in gas composition use to estimate water content in HYSYS and that from GPSA chart.

## 5 HYSYS PROCESS SIMULATION PACKAGE

HyproTech HYSYS 3.2 is powerful software for steady and dynamics state simulation processes. It includes tools for estimation of physical properties and liquid-vapour phase equilibrium, heat and material balances, design, optimization of oil and gas processes and process equipment. 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 Kent-Eisenberg thermodynamics and non-ideal vapour 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 flowsheet within the HYSYS simulation environment can be manipulated by the user to estimate desired out put.

## 6 AMINE BASE PROCESS FACILITIES

The alkanolamines are the most generally accepted and widely used of the various available solvents for removal of CO<sub>2</sub> from natural gas stream (Bottom, 1930) Their reactivity and availability at low cost especially Monoethanolamine (MDEA), and Diethanolamone (DEA), have made the solvent achieved a pinnacle position in the gas processing industry. The principle of absorption of CO<sub>2</sub> by amine solvents is governed by the following equations;

For instance the reaction of MEA with CO<sub>2</sub> is;

### Formation of carbonate bicarbonate:



### Formation of carbamate:



The reactions shown above proceed to the right at low temperature and to the left at a higher temperature, thus making CO<sub>2</sub> to be absorbed at ambient temperature. At elevated temperature (as obtained in the stripper column) the reaction is reversed that is backward reaction is favoured where the carbonate salt formed is decomposed to released the acid gas absorbed, therefore stringent control of stripper column temperature should be adopted to reduce the release of carbonate salt. Reaction (6.1) and (6.2) are slow reaction because carbon dioxide must form carbonic acid with water (slow reaction) before reacting with amine. Reaction 6.3 which predominate when MEA is involved is relatively fast, and that is why elimination of selectivity of hydrogen sulfide is impossible. Methyldiethanolamine (MDEA) and diethanolamine (DEA) are today the most tertiary amines for acid gas removal (Rejoy et.al., 1997). Other amine solutions that can be used are diglycoamine, diisopropanoamine and methyldiethanolamine

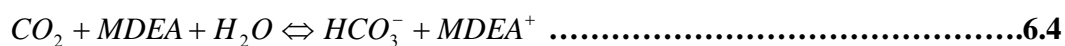
**Monoethanolamine (MEA)**; the concentration of MEA in solution is usually about 10-15% by weight. MEA is very reactive and can absorb CO<sub>2</sub> and H<sub>2</sub>S simultaneously. MEA however reacts with COS, CS<sub>2</sub> and mercaptans. Its relatively high vapour pressure causes greater losses compared with other amines. For this reason it is used for intensive purification, with fairly low H<sub>2</sub>S concentrations for a gas containing no COS or CS<sub>2</sub>.

**Diethanolamine (DEA)** helps to overcome the limitation of MEA, and can be used in the presence of COS and CS<sub>2</sub>. The application of DEA to natural gas processing was described by Berthier in 1959 (Kohl and Riesenfeld, 1985). Operating with solutions containing 25-30% by weight of DEA can be used to process natural gas with even high acid gas contents.

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

**Diisopropanolamine (DIPA)** is used, in relatively high concentrations from (30 – 40%) by the “Adip Process (Shell International Petroleum Company) (Klein, 1970). This solution is mostly used in the processing of refinery gas or liquid with high COS.

**Methylethanolamine (MDEA)** allows the selective absorption of H<sub>2</sub>S in the presence of CO<sub>2</sub>, but can be used effectively to remove CO<sub>2</sub> from natural gas in the presence of additives (Meisner and Wager, 1983). The reaction between CO<sub>2</sub> and MDEA solution is presented as follows;



The normal range of acid gas pickup, mol/ mol of amine (MDEA) is from 0.2 – 0.55 (Perry, 1974).

Amine solutions are basic, and hence non-corrosive. They are sometimes used as corrosion inhibitors. In the presence of acid gases, significant corrosion may occur at points where the concentration and temperature of acid gas is high. The primary amines are the most

corrosive. Therefore the application of primary solution requires the use of corrosion inhibitors and the unit may be made of special steels (DuPart et al., 1993). Foaming is a frequent problem in these installations due the following;

- Suspended solids
- Condensed hydrocarbon
- Amine-degradation products.
- Foreign matter from corrosion inhibitors.

The foaming tendency in these installations can be prevented by good design and operation; also anti-foaming agents can be used (Kohl and Riesenfeld, 1985). Filtration of the solvent recycled to the absorber step is essentially important. Filter that retain particle sizes larger than 10 $\mu$ m is recommended (Pauley et al., 1989). Degradation of amine solvents occur when get in contact with the air or oxygen, and the oxidation products often cause corrosion. Oxidation can be reduced by placing the amine solutions under an inert gas blanket in the storage tanks.

### ***6.1 Process description***

The general process flow diagram of an amine CO<sub>2</sub> removal process is shown in figure 16. The sour gas enters the plant through a separator to remove any free liquid or entrainment solids. The sour gas leaves the top of the scrubber and enters the bottom of the absorber in countercurrent contact with aqueous lean amine solution. Sweet gas leaves the top of the absorber and flow to a dehydration unit before being considered ready for liquefaction. Lean amine flow downward counter currently to the sour gas and absorbed the CO<sub>2</sub> constituent and become rich solution. The rich solvent from the bottom of the absorber is flashed in a separator to recover some absorbed hydrocarbon in the rich solvent and then pass through amine-amine heat exchanger to the stripper where the acid gas absorbed is stripped off at a very high temperature and low pressure. The acid gas then leaves the top of the stripper column. The lean amine from the bottom of the reboiler attached to the stripper flow through amine-amine heat exchanger and through a water air cooler before being introduced back to the top of the absorber.

The amine-amine heat exchanger serves as a heat conservation device. A part of absorbed acid gas is flashed from the heated rich solution on the top tray of the stripper. The remainder of the rich solution flows downward through the stripper in countercurrent contact with vapour generated in the reboiler; which strips the acid gas from the rich solution. The stripper overhead products (acid gas and steam) pass through a condenser where the steam is condensed and cooled and returned to the top of the stripper as a reflux, while the acid gas is separated in a separator and sent to the flare or compressed for sequestration process.

### ***6.2 Justification of amine process***

Amine base solvent (DEA) was chosen in this project to establish the operating conditions at which the CO<sub>2</sub> removal process from the natural gas can be operated to meet the LNG specifications and to minimized emission to the environment. The process justification was based on the following conditions;

- The CO<sub>2</sub> concentration of the feed gas to be treated is relatively low (5.23%) with high hydrocarbon contents, the amine process is considered more suitable (Tennyson et al, 1977).
- The solvent apply (DEA) is considered to be chemically stable; DEA can be heated to its normal boiling point (269 °C at 760mmHg) before decomposition. Therefore reduce the solvent degradation during stripping and reduce solvent loss and accumulation in the units.
- The heat of reaction of DEA with CO<sub>2</sub> is low compared to other amines as shown in table 12 (Kensell, 1979) the heat generated in the absorber is low which increase the solvent loading capacity in the absorber. Since solubility/loading of CO<sub>2</sub> increases at low temperature.
- The CO<sub>2</sub> recovery rates from amine base solvent can be as high as 98% and purity can be in excess of 99%. Amine base solvent process is more efficient for acid gas available at high or low partial pressure and with low or relatively high partial pressure acid gas product figure 19

### ***6.3 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 an important role in gas treating economics include solution corrosivity, which determine the material of construction particularly in the flash and regenerator because of high temperature and acidity.

Economic operation of CO<sub>2</sub> 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 (DEA) 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%.

### ***6.4 Process cost analysis.***

Estimates of the cost of equipment and other cost related to the capital investment play a crucial role in selecting among the design alternatives. Capital cost estimates, combined with process operating cost and other expenses are vital factors that need to be given full consideration since the profitability of a proposed venture or existing units depend on these factors. The detail cost analysis of different processes available will not be discussed in this project. However, comparison of two CO<sub>2</sub> process in terms of total install cost and operating cost will be highlighted briefly. The processes under consideration are the Amine base chemical absorption process using promoted MDEA and a physical base absorption process using fluor solvent ( Fluor process).

Comparison between these two processes will be based on how feed gas composition, pressure, temperature, flow and the sales gas specification affect the total installation capital, and the operating costs.

The capital cost comprises of investment in fixed facilities or equipment. For promoted MDEA process the units includes an absorber, a flash drum, a lean/rich exchanger, an amine regenerator, a reboiler, an amine regenerator overhead condenser a lean solvent cooler and pump. See figure 16. While the Fluor solvent process unit configuration shown in figure 17 Shows the units to comprise of a TEG dehydration unit, an inlet exchanger, refrigeration cooler, a absorber, and several flash regenerations stages, with the last flash stage operating under vacuum. The relative cost of Fluor solvent and promoted MDEA process is shown in figure 23 taken MDEA process to have a base value of 100 (Mak et al, 2003). The total installation cost for Fluor solvent have about 21% less than that of promoted MDEA process.

The operating cost for the two processes can be analyzed by considering the following factors;

- Solvent circulation; the MDEA solvent is assumed to have higher acid gas pick up per gallon of rich solvent than the Fluor solvent. The solvent circulation rate in promoted MDEA is therefore lower; hence reduce the cost on solvent circulation. Fluor solvent is assumed to have solvent circulation cost of about 9% higher than that of promoted MDEA process.
- Heat duty; the Flour solvent process does not require an external heat source for solvent regeneration. However, the process uses a small amount of waste heat energy from power generation to regenerate the TEG use to dry the feed gas. The TEG regeneration duty is about 1% of the promoted MDEA process heat duty.
- Air cooler; the process cooling required by the Fluor solvent process is for the refrigeration condenser and the recycle compressor after cooler. The cooling required by the amine process is for the amine regenerator overhead condenser and the lean amine cooler. The required cooling duty for the Fluor solvent process is about 11% of the amine process cooling duty.

- Power; the primary power consumers in the Fluor solvent process is the solvent circulation pumps, the refrigeration units, the recycle gas compressor, the vacuum pump and the air coolers. In the amine process unit the power consumption of lean amine air cooler, the amine regenerator overhead condenser, and the lean amine pumps is slightly higher than the power demand of Fluor solvent process. The Fluor solvent requires about 3% less than promoted MDEA process. See figure 24.

For a given economic analysis, chosen a process with low initial installation cost might not be the best option, since the operating cost for such process may be high thus making breaking even unattainable. Therefore careful cost analysis using all the available data and figures is essential when making any proposal.

## 7 ENVIRONMENTAL IMPACT

The removal of CO<sub>2</sub> from natural gas process is comprised of operations required to provide clean, pipeline quality gas and, LNG feed gas. These operations in return produce some wastes that must be managed in accordance with the applicable environmental regulatory agency, to ensure operations with less impact to the environment.

Emissions associated with CO<sub>2</sub> removal process includes; VOCs (volatile Organic compounds), carbon monoxide (CO), sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), particulates, ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), metals, spent solvents, and numerous toxic organic compounds. These pollutants may be discharged as air emissions, waste water, or solid waste. All of these wastes are treated. However, air emissions are more difficult to capture than waste water or solid waste. Thus, air emissions are the largest source of untreated wastes released to the environment.

Air emissions include point and non-point sources. Point sources are emissions that exit stacks and flares which can be monitored and treated. Non-point Sources are "fugitive emissions" which are difficult to locate and capture. Fugitive emissions occur through valves, pumps, tanks, pressure relief valves, flanges, etc. Generally, Identification and characterization wastes generated can be organized into three major categories (Myerski et al, 1993);

- **Intrinsic** – wastes that are derived from the natural gas stream and are generated at facilities that receive and handle natural gas from production well head 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 1 below shows the summary of wastes generated from different CO<sub>2</sub> removal process units.

**Table 1:** Wastes Types Generated in Different CO<sub>2</sub> Removal Process units

	Types of Contaminants/Chemical released to the Environment		
	Intrinsic	Treatments/Processing	Maintenance
<b>Physical Absorption Processes</b>			
Selexol	CO <sub>2</sub> , COS, VOC, H <sub>2</sub> S	Organic peroxide, CO <sub>2</sub> , NOX, VOC	Sludges, Waste Solvents / Degreasers <sup>c</sup>
Rectisol		Mercury Amalgam, CO <sub>2</sub> , NOX, VOC	
Fluor		CO <sub>2</sub> , NOX, VOC.	
<b>Chemical Absorption Processes</b>			
Amine Base	CO <sub>2</sub> , NO <sub>x</sub> , SO <sub>x</sub> , VOC.	BTEX, HEI, HEED, OX, Carbamate. <sup>a</sup>	Sludges, Waste Solvents / Degreasers, corrosion Inhibitors wastes
Carbonate Base	COS, CS <sub>2</sub> , NO <sub>x</sub> , VOC,	Ammonium Oxalate, NOX, VOC, BTEX	Sludges, Waste Solvents / Degreasers, corrosion Inhibitors wastes
<b>Hybrid Processes</b>			
Sulfinol	Mercaptans, CS <sub>2</sub> , COS	BTEX, VOC <sup>b</sup>	Waste Hazardous DIPA
<b>Cryogenic Processes</b>			
Cooling/Distillation	CO <sub>2</sub> , CS <sub>2</sub> , COS, SO <sub>x</sub>	Acetylene, absorbed C <sub>2</sub>	Waste water, Toxic Cryogenic fluids (acetylene)
<b>Adsorption Processes</b>			
Molecular sieve	CO <sub>2</sub> , CS <sub>2</sub> , COS, SO <sub>x</sub>	CO <sub>2</sub> , CS <sub>2</sub> , COS, SO <sub>x</sub>	Degraded/Spent Zeolite
<b>Membrane Separation</b>	CO <sub>2</sub> , CS <sub>2</sub> , COS, SO <sub>x</sub>	CO <sub>2</sub> , CS <sub>2</sub> , COS, SO <sub>x</sub>	Degraded/Spent Fibers

(a) Information derived from (Sorensen et al, 1999).

(b) Information derived from (Mustard et al, 2000).

(c) Information derived from (John et al, 1995).

However, in this project the wastes/emissions identified above can be eliminated by establishing optimum operating conditions that will improve process environmental performance. This involves modification of process operating parameters (Temperature, Pressure and Solvent circulation rate) to reduce the amount or toxicity of wastes that are generated. For instance the absorber is set to operate at low Temperature and high pressure to increase acid gas loading by the solvent and regeneration of the solvent was

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 at optimum conditions ensure low hydrocarbon and chemical (Solvents) losses, thus reduces waste accumulated in the process units and emission to the environment. Detail of the analysis is presented in chapter 8.

## 8 HYSYS SIMULATION OF AMINE PROCESS

### 8.1 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 CO<sub>2</sub> 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 fictitious units such as mixer will not be discussed.

**a. 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 effectively handle some anticipated liquid slugs. It also limits liquid re-vaporization (Ikoku, 1980).

**b. DEA CONTACTOR;** The contactor allows counter-current flow of lean amine from the top and sour gas from the bottom. Here the amine solvent absorbed CO<sub>2</sub> and rich amine is flow to the bottom while the sweet gas is collected at the top for further processing.

**c. THROTTLING VALVE;** The valve is used to expand the rich amine coming from the high pressure contactor. This is done by lowering gas the pressure before entering the flash tank.

**d. FLASH TANK;** The gas from the throttling valve is flashed to remove the hydrocarbons components carried along with the rich amine, this unit serves as a recovery unit for hydrocarbons. Horizontal flash tank is used to prevent foaming. (Ikoku, 1980) The flashed overhead product can be used as fuel gas.

**e. AMINE-AMINE HEAT EXCHANGER;** The rich/lean exchanger is a heat conservation device where hot lean solvent preheats cooler rich solvent. In this project

Shell-and-tube TEMA type E exchanger is used in the simulation. The shell and tube side pressure drop is set to 70 kpa and heat loss/leak is assumed zero. The heat exchanger helps to raise the rich amine solvent temperature before entering the stripper. Thus reduce re-boiler work load.

**f. AMINE STILL;** Depending upon the solvent type, this is normally a 20-tray or equivalent packed tower. Here 18- trays were sufficient to strip the CO<sub>2</sub> from the rich solvent. Physical solvents can require fewer trays. Trays diameter is about 4m with 0.5 spacing. Liquid and jet floods in the 65-75% range with a 75% foam factor. It is assumed that the trays in the upper third, be stainless steel due to the corrosivity of the environment.

**g. AMINE COOLER, REFLUX CONDENSER;** Air-cooled, forced draft with automatic louvers for temperature control. Cold climate service may require air-recirculation and/or preheat media on fans/coils. Condenser tubes should be made of stainless steel, as this is a wet, acid gas environment and sloped to the outlet side.

**h. REFLUX ACCUMULATOR:** This vessel separates the reflux water and water-saturated acid gases. The water is pumped back to the still and the acid gases are directed to vent, incinerator, or sulfur recovery unit. A reflux accumulator with a 4” to 8” thick mist pad is used.

**i. 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/ft<sup>2</sup> 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.

**j. COOLER;** The lean amine solvent from the re-boiler through amine-amine heat exchanger is further cool here before entering the absorber again, since absorbers operate more efficiently at relatively low temperature. The pressure drop across the cooler is about 35 kpa with corresponding duty of 1.097 E+7 kJ/h.

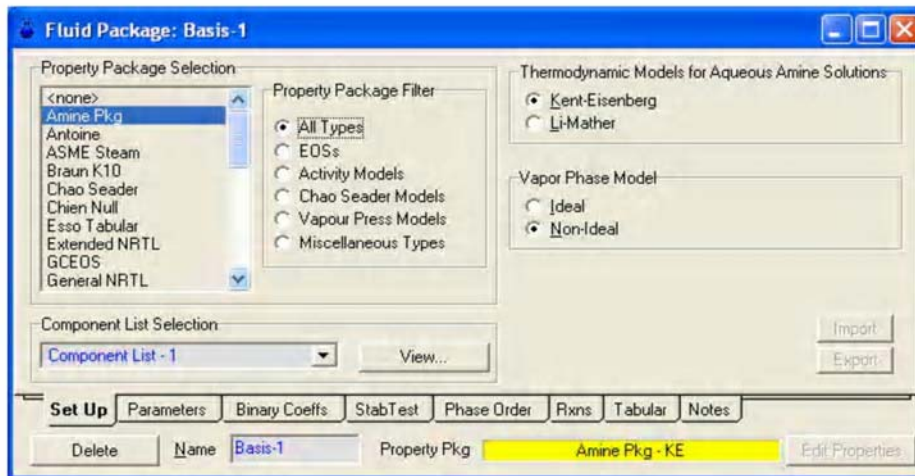
**k. PUMPS:** The reflux and booster centrifugal pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber. The main circulation pump choice depends upon contactor operating pressure and solvent flow rates. Centrifugal pump considered in this project is set to 75% adiabatic efficiency for low head cases and

large volume, high head cases which is specifically design for amine service and have non-lubricated packing/system seal with ceramic or hard coated fluid parts.

**8.2 Hysys simulation procedures**

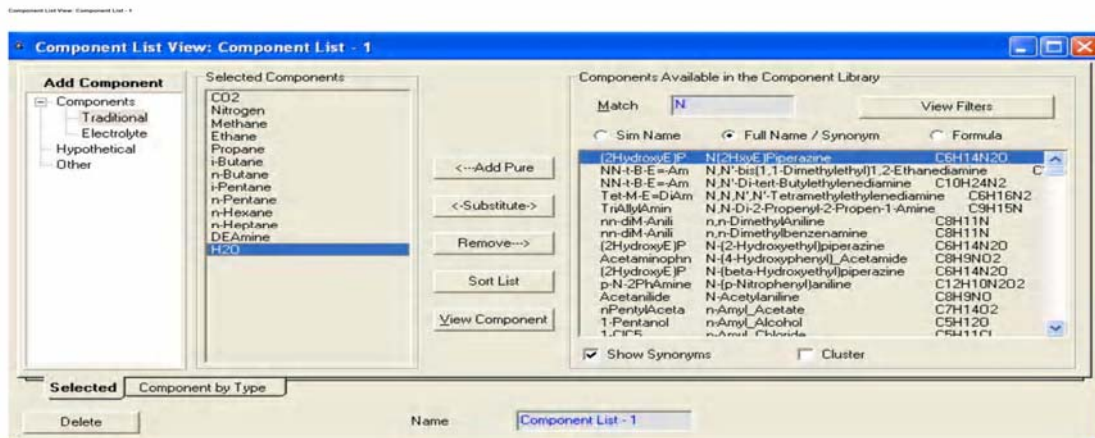
A base case was established using the following steps; the first step is to select the appropriate fluid package; here amine fluid package and Kent-Eisenberg model is selected as in figure1 below;

**Figure 1 Fluid Package Basis (Amine fluid Package)**



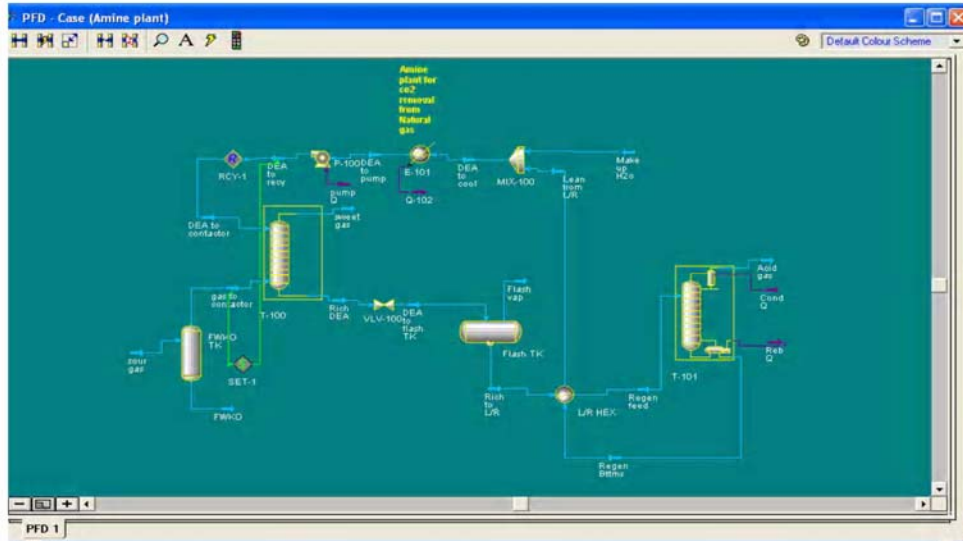
The component selection window is open by selecting view in the **component-list** show in fig 1. Figure 2 shows dialog window is use for components selection

**Figure 2 Component selection windows.**



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

**Figure 3 Un-simulated Amine Process Flow Diagrams**



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 colour**) and HYSYS calculate the remaining parameters (**Black colour**) as shown in figure 4 below;

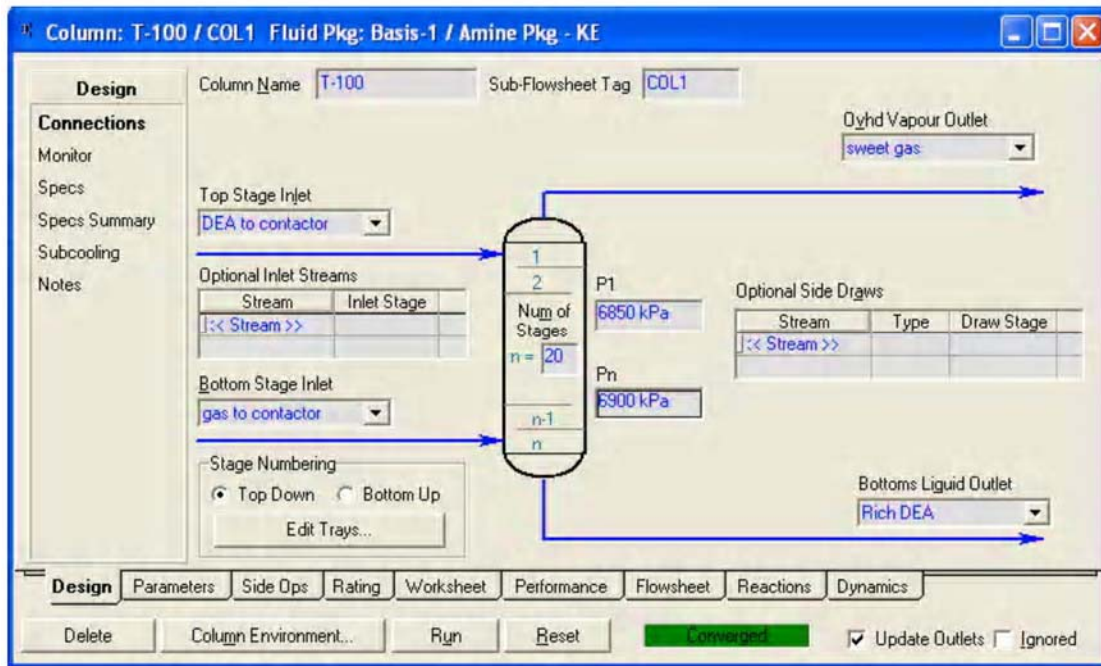
**Figure 4 Sour Gas specification windows**

sour gas	
<b>Worksheet</b>	Stream Name: sour gas
<b>Conditions</b>	Vapour / Phase Fraction: 0.9931
Properties	Temperature [C]: 35.00
Composition	Pressure [kPa]: 6900
K Value	Molar Flow [kgmole/h]: 1250
User Variables	Mass Flow [kg/h]: 2.290e+004
Notes	Std Ideal Liq Vol Flow [m3/h]: 68.00
Cost Parameters	Molar Enthalpy [kJ/kgmole]: 1.297e+004
	Molar Entropy [kJ/kgmole-C]: 190.0
	Heat Flow [kJ/h]: 1.621e+007
	Liq Vol Flow @Std Cond [m3/h]: <empty>
	Fluid Package: Basis-1

Other streams specifications made are; the regenerated feed out of the amine-amine heat exchanger temperature to control the exchanger fit factor, DEA to Contactor temperature pressure and flow rate, make up water temperature and DEA to recycle temperature. With these specifications made, HYSYS make use of its flexibility of calculating forward and backward to completely simulate the process. One of the rigorous tasks is the convergence of the absorber and the regenerator, to converge the absorber the absorber top and bottom temperature and pressure was specified and run, figure 5.

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

**Figure 5 Converged window of the Absorber**





## 9 SIMULATION RESULTS/DISCUSSION OF RESULTS

### 9.1 Simulation results

Detail simulation results are shown in the lists of tables and chart in page 48

### 9.2 Discussion of results

The simulation objectives are to meet the LNG specifications of about 50 – 100 ppmv or 2- 3 % CO<sub>2</sub> concentration in the product stream, and then establish optimum conditions to reduce CO<sub>2</sub> emission and chemical loss. From table 5 the % composition of CO<sub>2</sub> of the feed gas is about 5.6% which is above LNG CO<sub>2</sub> specifications of 2 – 3 % as shown in table 7

Figure 8 shows the treatment of feed sour gas with different amine concentrations and the observed % mole concentration of CO<sub>2</sub> in the sweet gas. It was observed that as the concentration of amine increases, the % mole concentration of CO<sub>2</sub> in the sweet gas decreases. This is attributed to the increase in Amine solvent capacity with increase in concentration of amine in the solution. The specifications ranges were reached at 20 wt% DEAmine and above.

Table 2 shows that for a given partial pressure of CO<sub>2</sub> in the feed gas the amine loading increase with increasing amine wt% in the solution. With 25 wt% DEAmine the loading [mol<sub>CO<sub>2</sub></sub>/mol<sub>DEA</sub>] ranges from 0.6 – 0.64 figure 11, for 30 wt% the loading ranges from 0.535 – 0.56 figure 12, with 35 wt% the increase loading capacity ranges from 0.465 – 0.49 figure 13, and the loading was observed to decrease with increase temperature at a given CO<sub>2</sub> partial pressure. The % mole of CO<sub>2</sub> in the sweet gas increases with contactor (Absorber) operating temperature and decrease with pressure figure 9. While the hydrocarbon (C<sub>1</sub>) co-absorbed with the CO<sub>2</sub> in the solvent increases with pressure and decrease with increase in temperature. This is due to decrease in amine loading capacity as its viscosity decrease with temperature

Figure 14 illustrates the effect of lean amine circulation rate on amine loading capacity. The loading capacity decreases with increase in circulation rate, figure 15 and tables 3 and 4 shows that the CO<sub>2</sub> emission/present in the sweet gas and amine loss with the acid gas increases with solvent circulation rate.

## 10 CONCLUSIONS

Based on the literature reviewed and the results from the simulation model the following conclusions can be made:

- The loading capacity of the amine solvent should be increased appropriately to increase acid gas (CO<sub>2</sub>) loading in the solvent.
- The CO<sub>2</sub> emission and chemical loss is directly proportional to the amine circulation rate. Therefore the lean amine circulation rate should be minimized and at minimum possible temperature to minimize solvent evaporation rate and thus increase its loading capacity.
- Absorber should be operated at High possible pressure and low Temperature to enhance amine loading capacity; therefore minimize CO<sub>2</sub> emission and chemical loss.
- The amine solvent residence time in the stripper should be minimized to reduce its degradation tendency.
- The stripper operating pressure should be nearly or at atmospheric pressure, while the reboiler temperature should be within the solvent stability conditions, for DEAmine the reboiler temperature range of about 110 – 121 °C is appropriate.

## NOMENCLATURE

BTEX: Benzene, Toluene, Ethyl benzene, Xylene

DEA: Diethanolamine

DGA: Diglycolamine

DIPPA: Diisopropanolamine

EOR: Enhanced Oil Recovery

GPSA: Gas Processors Suppliers Association

HEED: N-hydroxyethyl-1, 2-ethylenediamine

HEI: N-hydroxyethyl imidazolidone

LNG: Liquefied Natural Gas

MDEA: Methyldiethanolamine

MEA: Monoethanolamine

NO<sub>x</sub>: Nitrogen Dioxide

OX: 2-oxazolidinone

Ppmv: Part Per Million Volume

Sox: Sulfur Dioxide

TEA: Triethanolamine

TEG: Triethylene Glycol

TEMA: Tubular Exchanger Manufacturer Association.

VOC: Volatile Organic Components

$P_{iL}$ : Low Pressure

$P_{iH}$ : High Pressure

$\alpha_{ij}$ : Activity Series

$\phi$ : Fugacity

k: Permeance Constant

Hg: Mercury

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**Table 2: Data Generated from the Simulation Model**

<b>25 wt%DEA, Circulation rate 1400kgmol/hr</b>					
<b>P<sub>feed gas</sub></b> <b>(kpa)</b>	<b>P<sub>CO2</sub> ( kpa)</b>	<b>Temp °C</b>	<b>mol<sub>CO2</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>C1</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>CO2</sub>/sweet gas</b>
5000	286,2	30	0,6117	0,01401	0,2438
		35	0,6074	0,01366	0,2693
		40	0,6021	0,01348	0,3039
10000	572,6	30	0,6314	0,02625	0,1014
		35	0,6309	0,02563	0,1052
		40	0,6284	0,02531	0,1143
15000	858,9	30	0,6401	0,03739	0,0481
		35	0,6405	0,03659	0,0496
		40	0,6419	0,03618	0,0538
<b>30 wt%DEA</b>					
<b>P<sub>feed gas</sub></b> <b>(kpa)</b>	<b>P<sub>CO2</sub> ( kpa)</b>	<b>Temp °C</b>	<b>mol<sub>CO2</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>C1</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>CO2</sub>/sweet gas</b>
5000	286,2	30	0,5366	0,01084	0,1227
		35	0,5402	0,01056	0,1236
		40	0,5427	0,01036	0,1264
10000	572,6	30	0,5484	0,0237	0,0514
		35	0,5527	0,01991	0,0615
		40	0,5495	0,02037	0,0623
15000	858,9	30	0,5541	0,02908	0,0192
		35	0,5579	0,02848	0,0246
		40	0,55482	0,02817	0,0271
<b>35 wt%DEA</b>					
<b>P<sub>feed gas</sub></b> <b>(kpa)</b>	<b>P<sub>CO2</sub> ( kpa)</b>	<b>Temp °C</b>	<b>mol<sub>CO2</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>C1</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>CO2</sub>/sweet gas</b>
5000	286,2	30	0,4688	0,008668	0,1225
		35	0,4743	0,008451	0,1927
		40	0,4773	0,008302	0,2786
10000	572,6	30	0,4767	0,01634	0,0456
		35	0,4815	0,01598	0,0478
		40	0,4843	0,01573	0,0492
15000	858,9	30	0,481	0,02336	0,0155
		35	0,4851	0,0229	0,0196
		40	0,4873	0,02259	0,0269

**Table 3 Effect of Lean Amine Circulation Rate on Amine Loading at 35 °C**

<b>35 wt%DEA , T = 35°C ,P = 100 bara</b>				
<b>CirDEAmine</b>	<b>mol<sub>CO2</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>C1</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>CO2</sub>/sweet gas</b>	<b>mol<sub>DEA</sub>/Acid gas [10<sup>-8</sup>]</b>
1400	0,4851	0,01832	0,0457	3,268
1500	0,5534	0,01843	0,0523	4,013
1600	0,5672	0,01876	0,0634	5,243
1800	0,6012	0,01923	0,0702	6,093
1900	0,6423	0,02034	0,0832	6,352
2000	0,6537	0,02175	0,0905	7,277

**Table 4. Effect of Lean Amine Circulation Rate on Amine Loading at 40°C**

<b>35 wt%DEA , T = 40°C ,P = 100 bara</b>				
<b>CirDEAmine</b>	<b>mol<sub>CO2</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>C1</sub>/Mol<sub>DEA</sub></b>	<b>mol<sub>CO2</sub>/sweet gas</b>	<b>mol<sub>DEA</sub>/Acid gas [10<sup>-8</sup>]</b>
1400	0,4951	0,01832	0,0557	3,468
1500	0,5574	0,01843	0,0623	4,053
1600	0,5872	0,01876	0,0684	5,243
1800	0,6312	0,01923	0,0782	6,193
1900	0,6473	0,02034	0,0872	6,532
2000	0,6637	0,02175	0,0945	7,287

**Table 5 Natural Sour Feed Gas Composition**

<b>Components</b>	<b>Mole Fraction</b>
<b>Nitrogen</b>	<b>0.001372</b>
<b>Hydrogen sulfide</b>	<b>0.000</b>
<b>Carbon dioxide</b>	<b>0.0568</b>
<b>Methane</b>	<b>0.8991</b>
<b>Ethane</b>	<b>0.0257</b>
<b>Propane</b>	<b>0.0061</b>
<b>n-Butane</b>	<b>0.001902</b>
<b>n-Pentane</b>	<b>0.00078</b>
<b>Water</b>	<b>0.000</b>

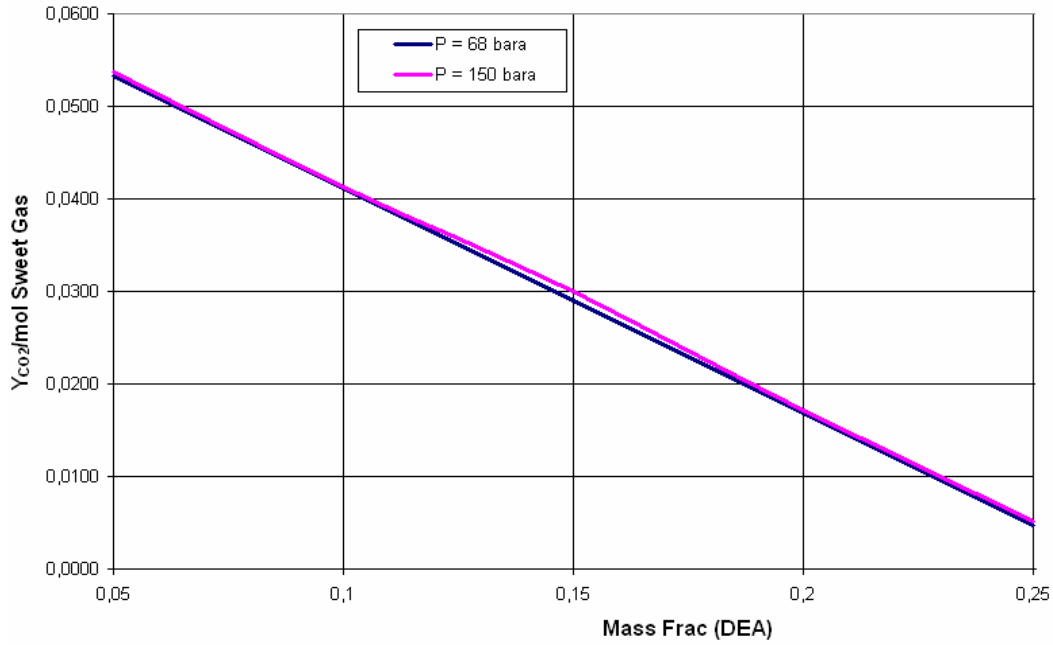
**Table 6 Gas Product Stream composition after absorption process**

<b>Components</b>	<b>Mole Fraction</b>
Nitrogen	0.001359
Hydrogen sulfide	0.000
<b>Carbon dioxide</b>	<b>0.004629</b>
Methane	0.956
Ethane	0.0273
Propane	0.006490
n-Butane	0.002025
n-Pentane	0.000838
Water	0.001288
DEAmine	2.0*10 <sup>-8</sup>

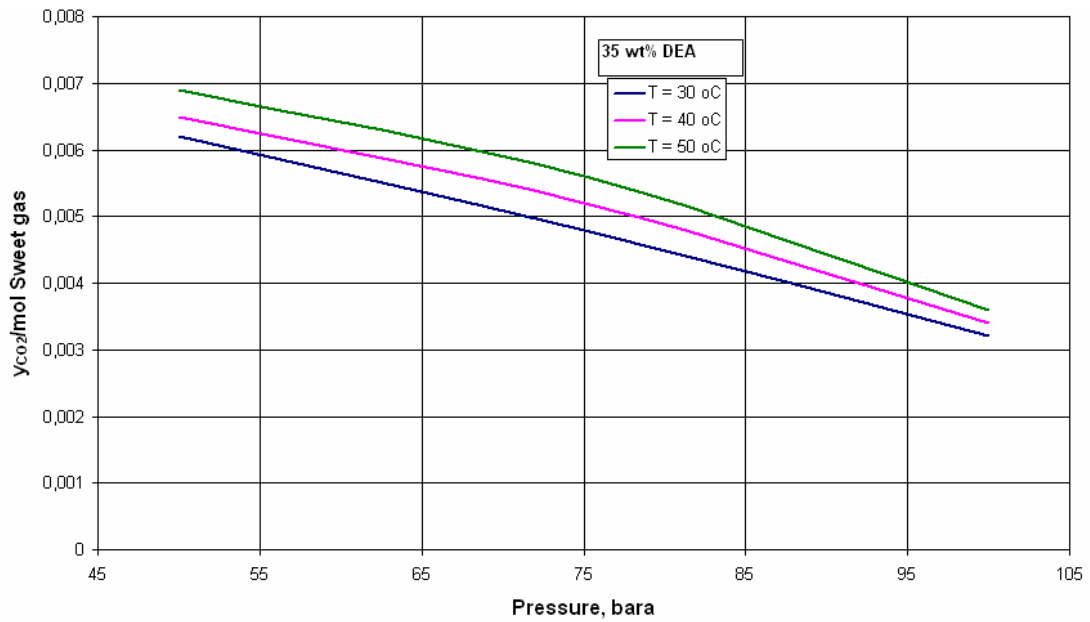
**Table 7 Typical LNG Product Specification, (David Coyle et al 2003)**

<b>Component</b>	<b>Limit ( Maximum)</b>
Hydrogen Sulfide	3 – 4 ppmv
Total Sulfur	30 milligrams per normal cubic meter
<b>Carbon Dioxide</b>	<b>50 – 100 ppmv , 2- 3 mol%</b>
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)

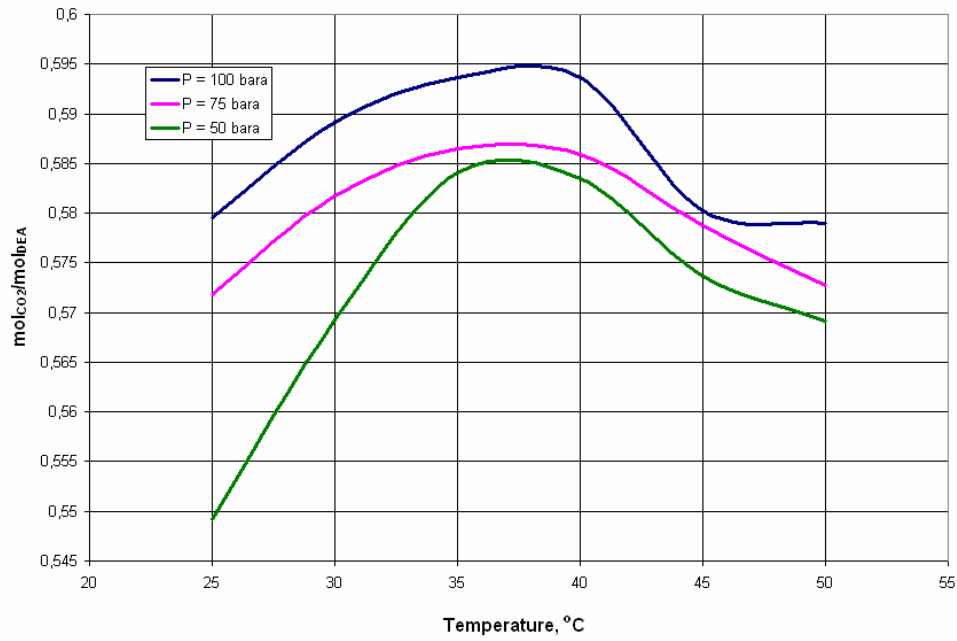
**Figure 8 % of CO<sub>2</sub> in the Sweet Gas as a Function of Amine Concentration With Changes in Absorber Pressure**



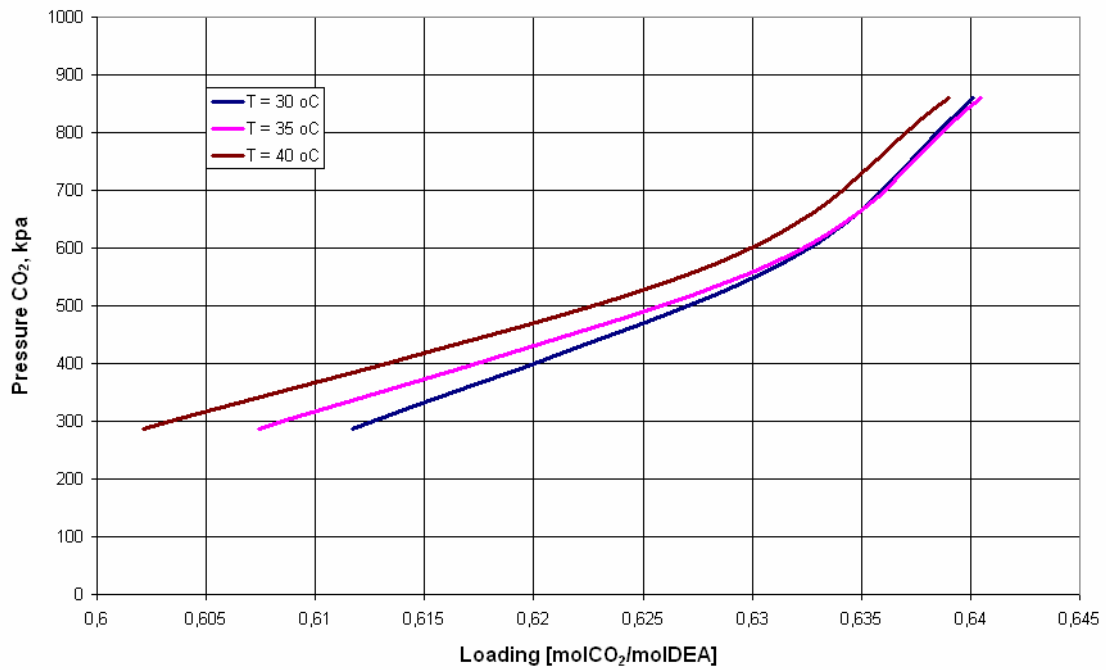
**Figure 9 Effects of Pressure and Temperature on % CO<sub>2</sub> in the Sweet Gas With DEAmine Concentration of 35 wt%**



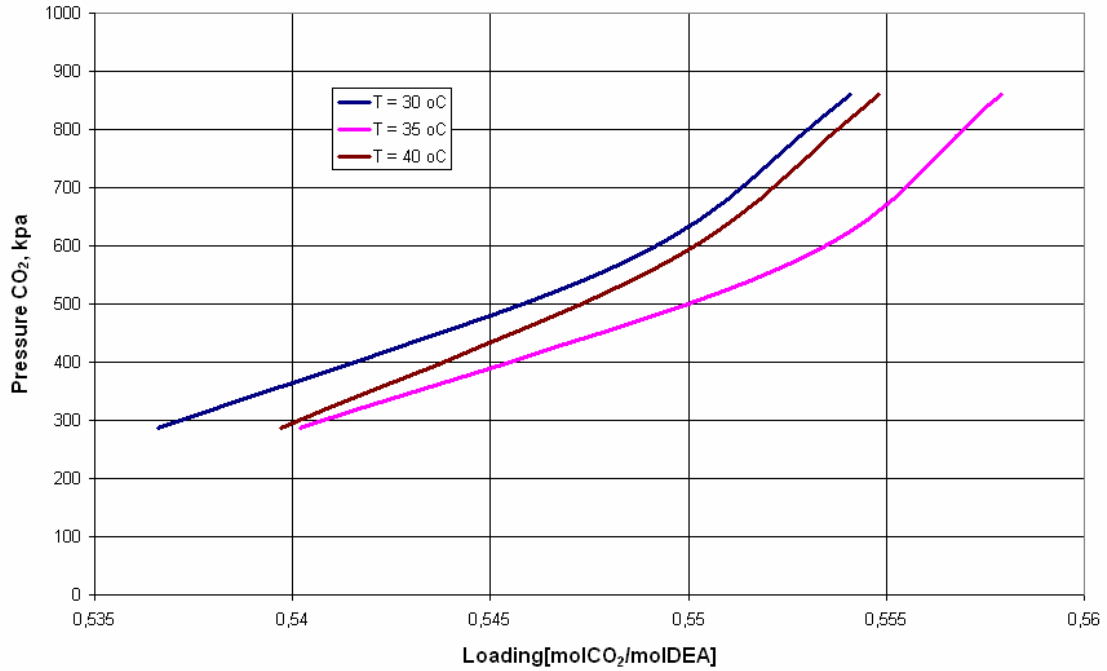
**Figure 10 Effects of CO<sub>2</sub> Loading in DEAmine with pressure and Temperature**



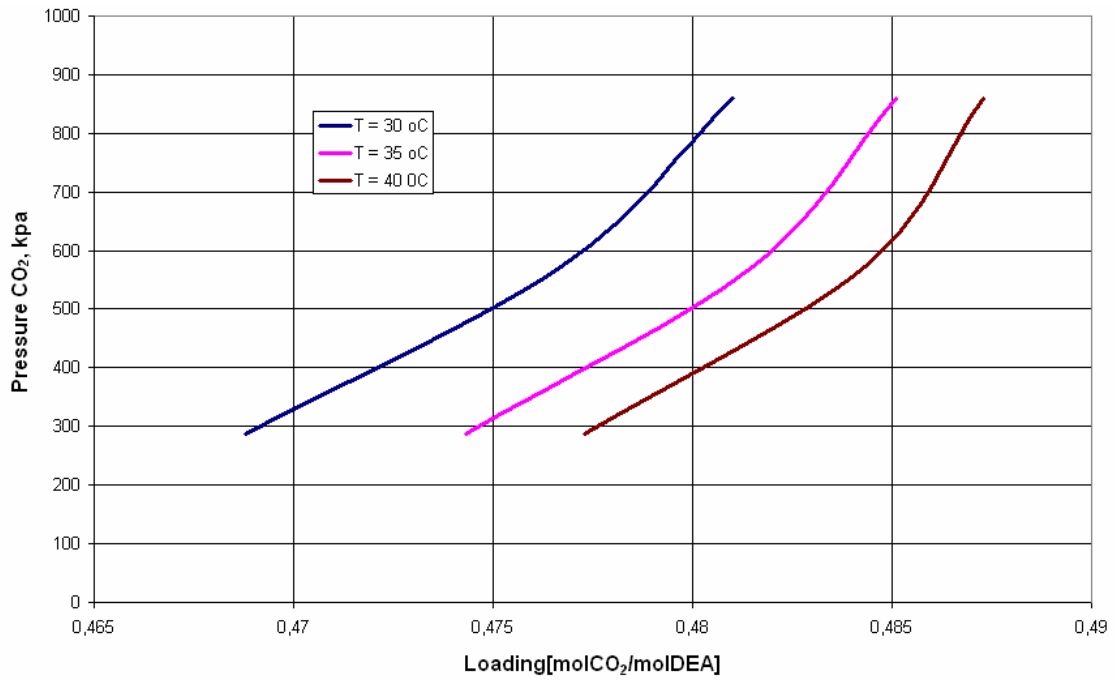
**Figure 11 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 25wt% DEA**



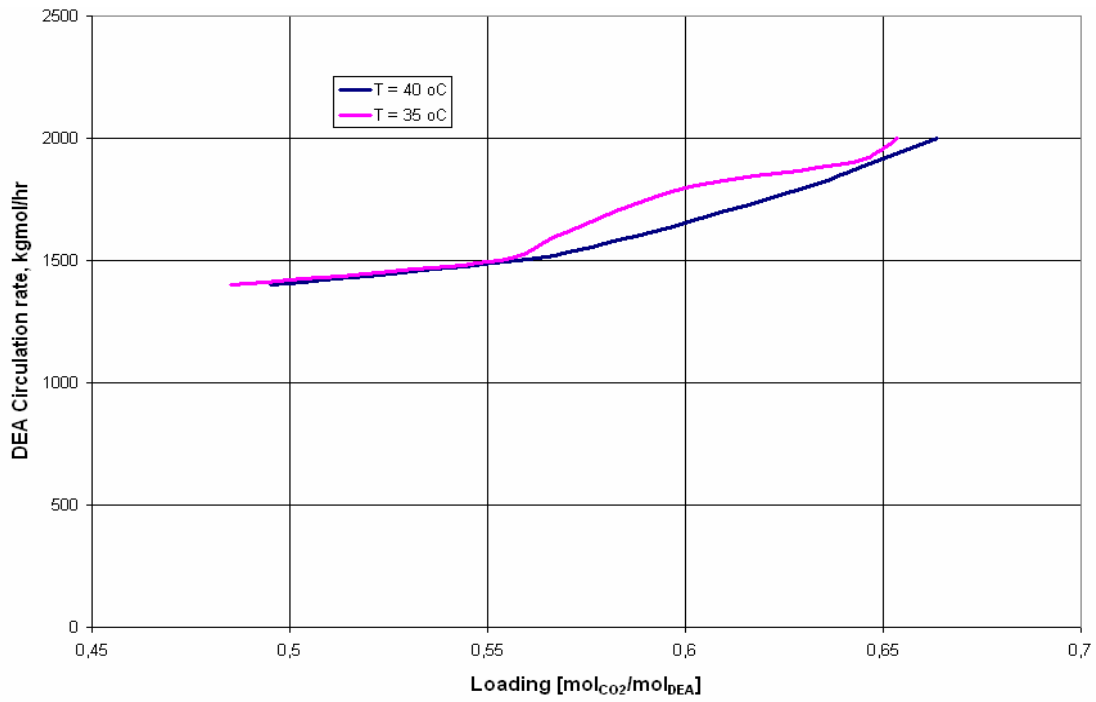
**Figure 12 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 30wt% DEA**



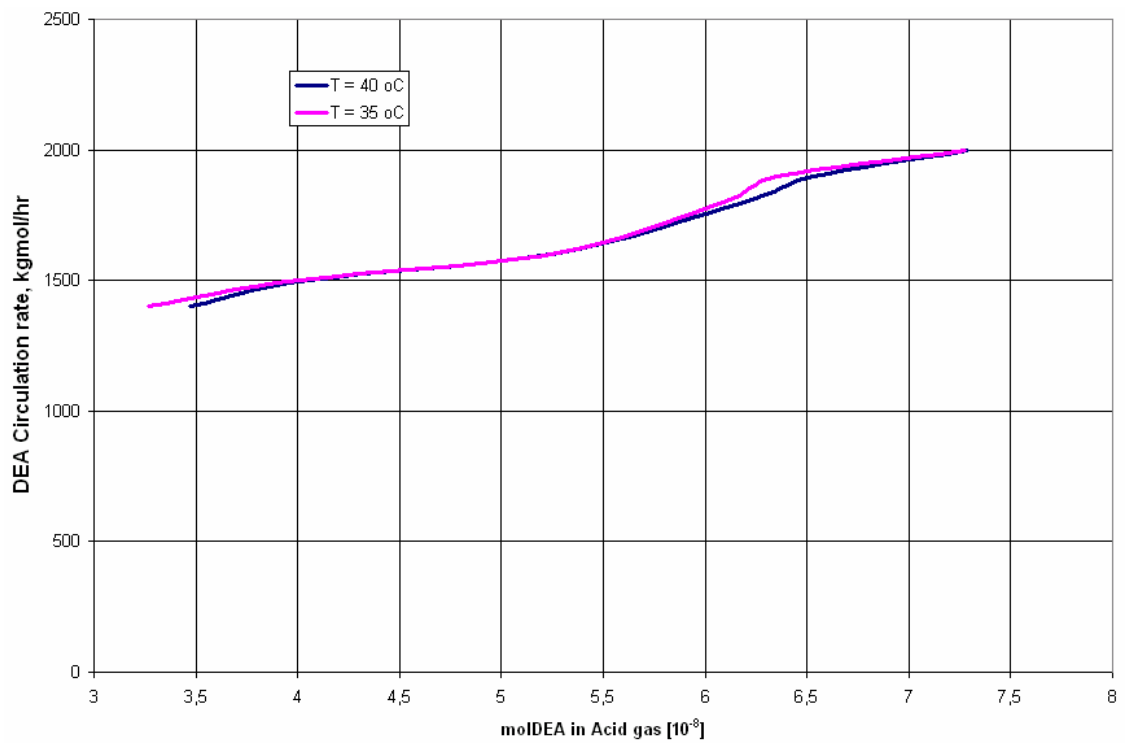
**Figure 13 Partial Pressure of CO<sub>2</sub> in Solution as Function of CO<sub>2</sub> Loading of 35wt% DEA**



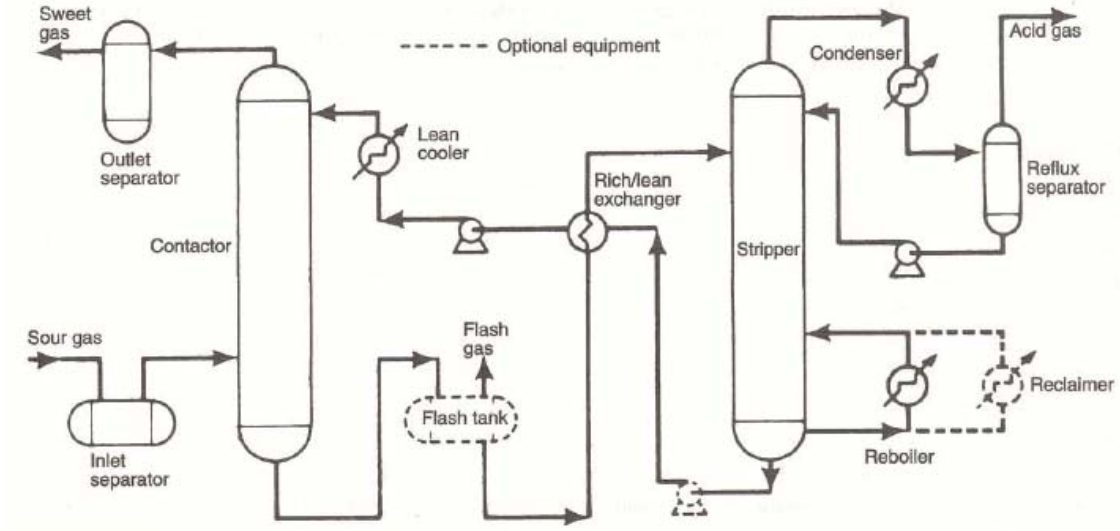
**Figure 14 Lean DEA Circulation rate vs. CO<sub>2</sub> loading in 35wt% DEA**



**Figure 15 Lean DEA Circulation rate vs. molCO<sub>2</sub> in the acid gas with 35wt% DEA**



**Figure 16** A Typical Amine Base process Diagram



**Figure 17** A Typical Fluor Solvent Process unit

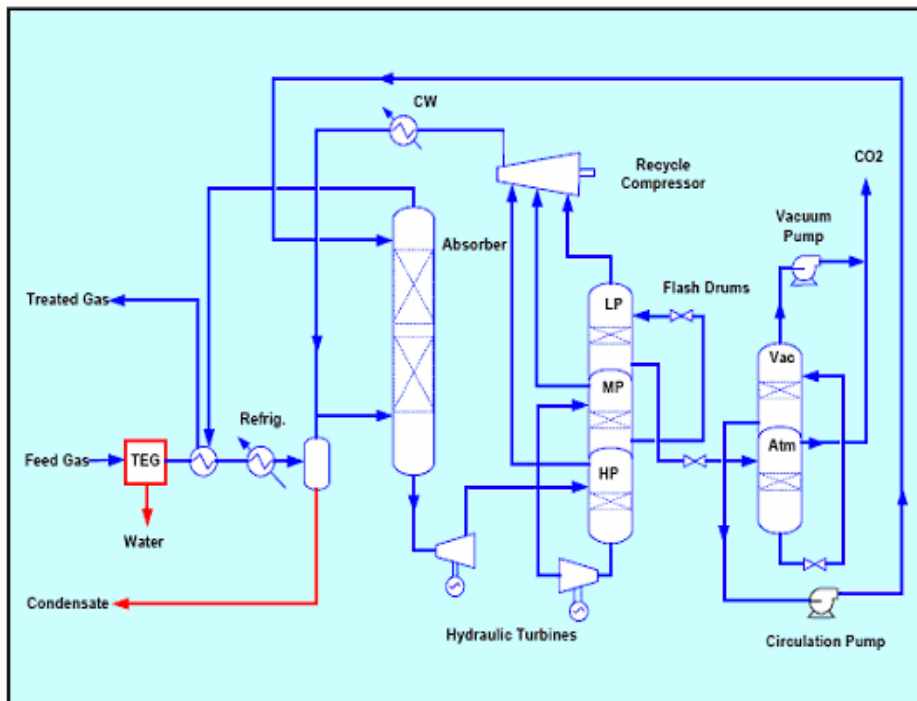


Figure 18 A typical Selexol Process Unit

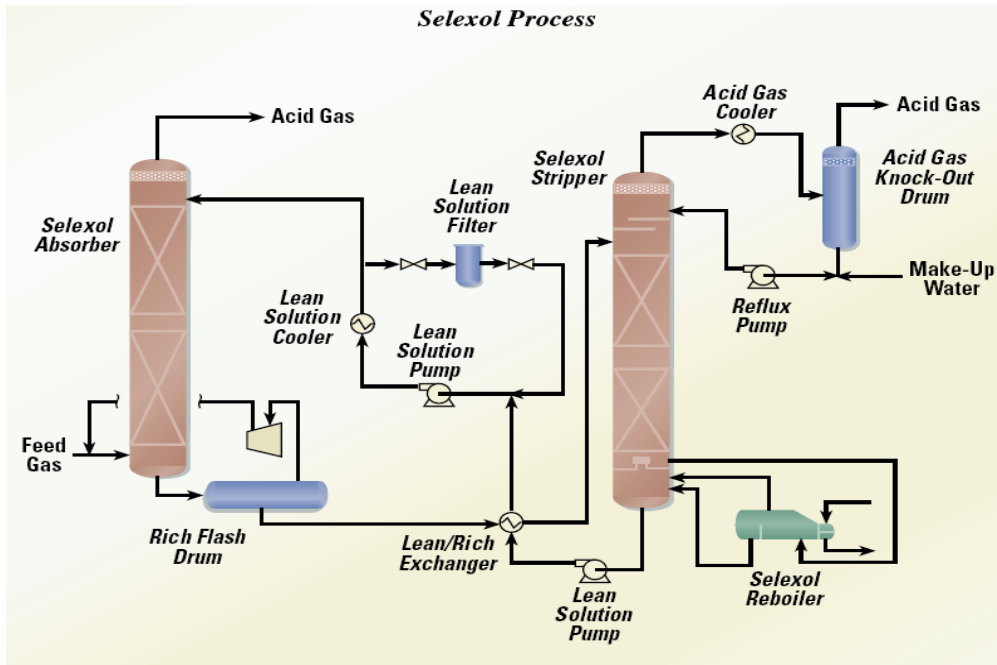
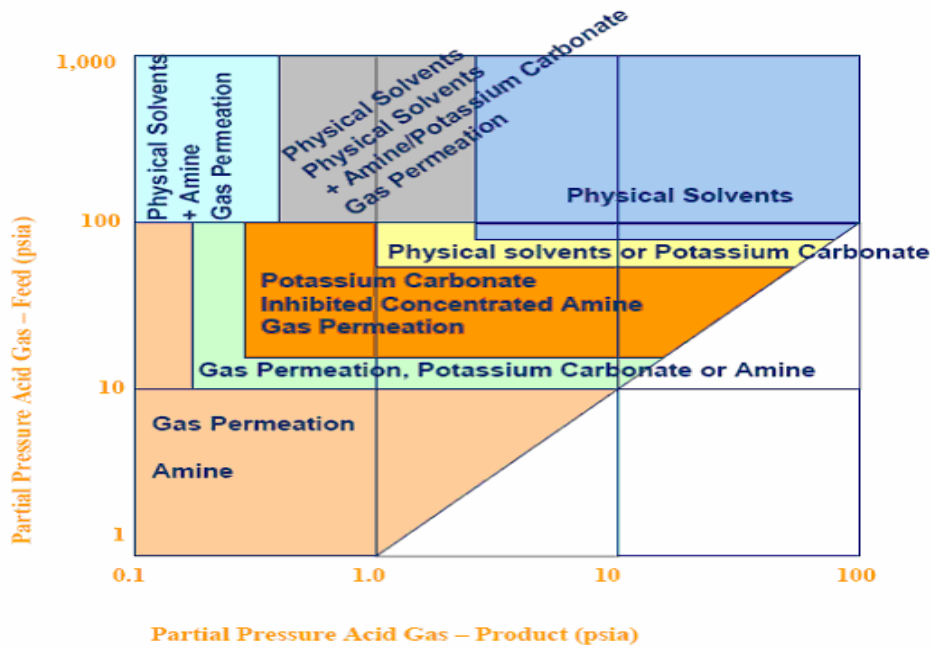


Figure 19 Process Capabilities for gas treating process



Source TEP 30 “ Gas Processing Course Material, 2005

Figure 20 Cooling Curve of Natural Gas and Evaporating temperature in Cascade Process

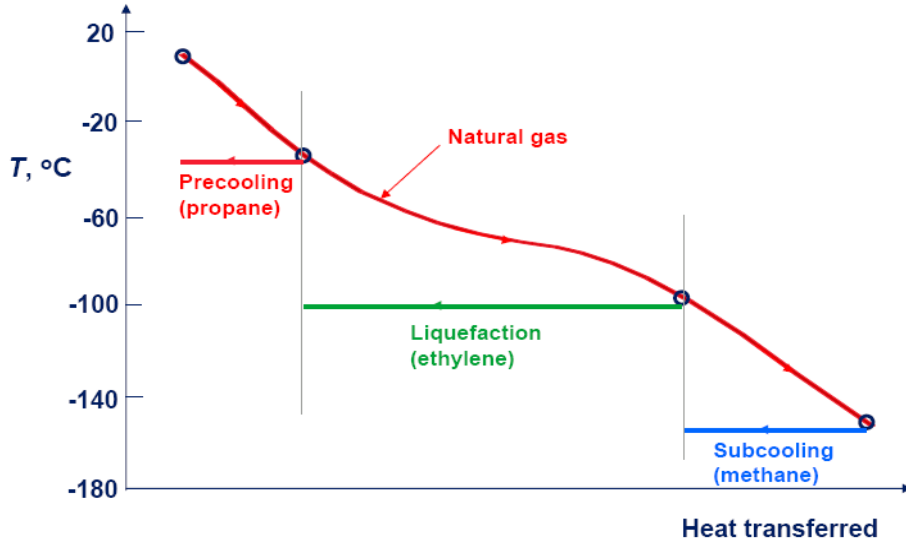


Figure 21 Typical LNG liquefaction Cascade arrangements

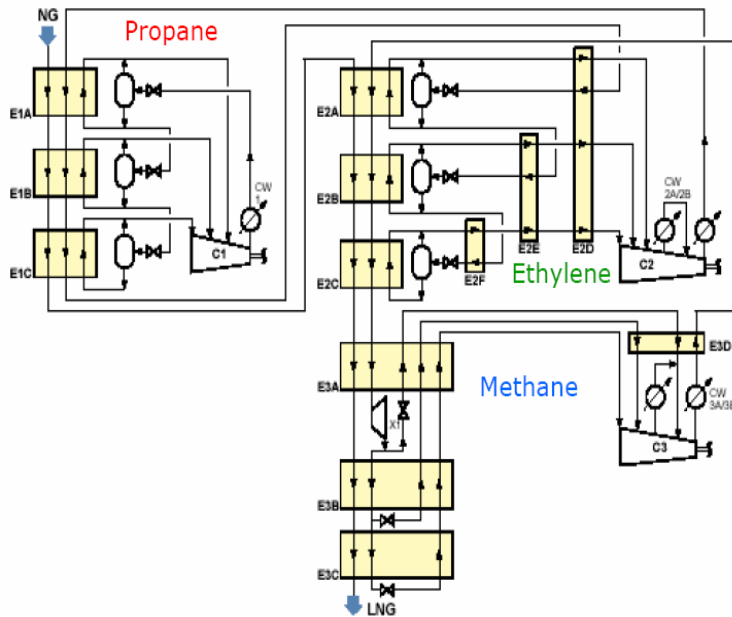


Figure 22 Typical LNG Liquefaction Mixed refrigerant arrangements (Statoil/Linde)

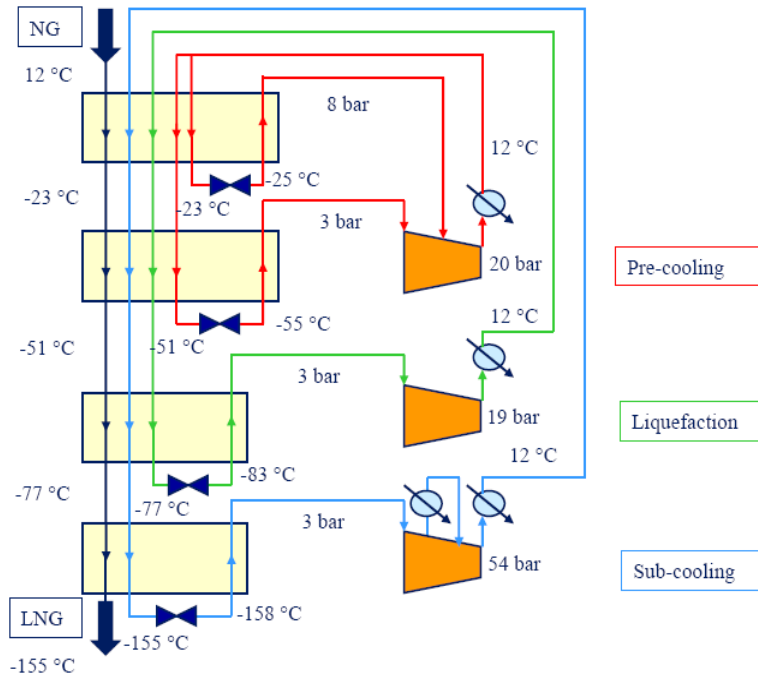


Table 8 Water Content from HYSYS Simulator in [mg/Sm<sup>3</sup>]

Pressure [kpa]	Temperature , °C						
	-40	-20	0	20	40	60	80
100	135,881	916,528	4531,066	17542,497	55863,199	151869,421	362793,548
500	28,2398954	189,218225	930,501231	3587,49789	11386,30367	30872,41487	73591,29911
1000	15,05	98,56	481,08	1754,93	5830,10	15753,94	37450,76762
1500	10,36948747	68,4429878	331,788826	1265,10053	3980,607815	10718,96278	25411,00264

Table 9 Water Content from GPSA Chart in [mg/Sm<sup>3</sup>]

Pressure [kpa]	Temperature , °C						
	-40	-20	0	20	40	60	80
100	170	998	4500	17500	55000	149000	350000
500	38	220	880	3500	11000	30000	75000
1000	21	110	500	1750	5500	14900	36000
1500	15	80	350	1200	3700	10000	25000

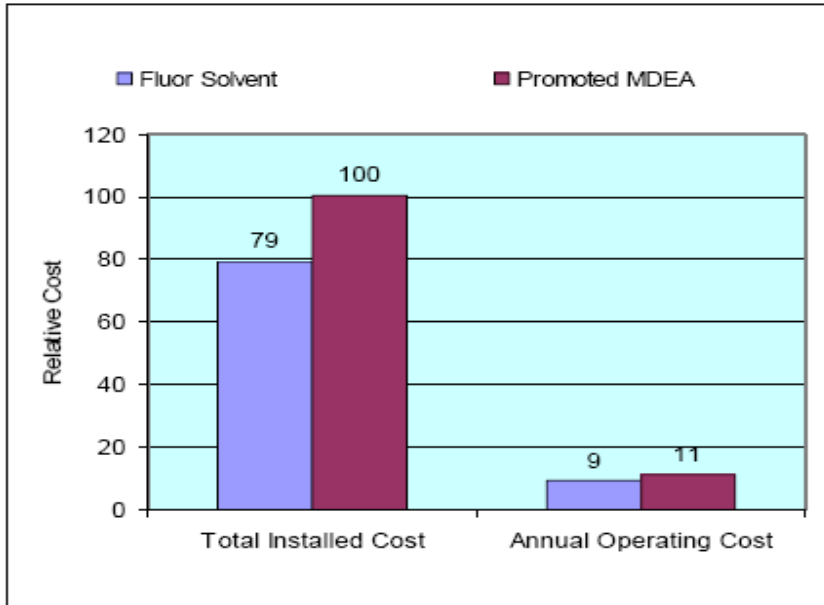
**Table 10** Water Content Comparison in [mg/Sm<sup>3</sup>] for 100 and 500 kpa

	Pressure =100 kpa			Pressure = 500 kpa		
Temperature °C	H2O content from HYSYS	H2O Content from GPSA	% Difference	H2O content from HYSYS	H2O Content from GPSA	% Difference
-40	135.81	170	0.2	28.24	38	0.25
-20	916.528	998	0.08	189.22	220	0.14
0	4,531.066	4,500	0.0069	930.50	880	0.057
20	17,542.49	17,500	0.0024	3,587.50	3,500	0.025
40	55,863.199	55,000	0.016	11,386.30	11,000	0.035
60	151,869.421	149,000	0.019	30,872.41	30,000	0.029
80	362,793.548	350,000	0.036	73,591.30	75,000	0.018

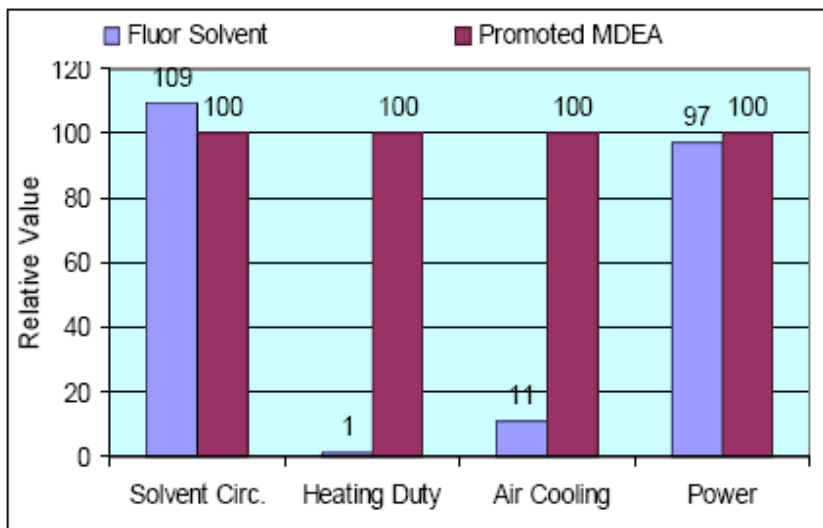
**Table 11** Water Content Comparison in [mg/Sm<sup>3</sup>] for 1000 and 1500 kpa

	Pressure =1000 kpa			Pressure = 1500 kpa		
Temperature °C	H2O content from HYSYS	H2O Content from GPSA	% Difference	H2O content from HYSYS	H2O Content from GPSA	% Difference
-40	15.05	21	0.28	10.37	15	0.31
-20	98.56	110	0.10	68.44	80	0.14
0	481.08	500	0.038	331,79	350	0.052
20	1,754.93	1,750	0.003	1,265.10	1,200	0.054
40	5,830.10	5,500	0.06	3,980.61	3,700	0.076
60	15,753.94	14,900	0.057	10,718.96	10,000	0.072
80	37,450.77	36,000	0.04	25,411.00	25,000	0.016

**Figure 23** Comparison of Fluor solvent and Promoted MDEA process relative cost



**Figure 24** Comparison of Fluor Solvent and Promoted MDEA process Parameters.



**Table 12** Approximate Guideline for amine Processes (Kensell, 1979)

	<b>MEA</b>	<b>DEA</b>	<b>DGA</b>	<b>MDEA</b>
Acid gas pickup, mol/mol amine, Normal Range	0.33 – 0.4	0.35 – 0.65	0.25– 0.3	0.2 – 0.55
Solution Concentration, wt%, Normal Range	15 - 25	25 - 35	50 - 70	40 - 50
Approximate Reboiler heat Duty kJ/L	280 - 335	245 - 280	300 – 360	220 - 335
Reboiler Temperature, Normal Operation in °C	107 – 127	110 - 121	121 - 127	110 - 127
Approximate Heat of Reaction, kJ/kg CO <sub>2</sub>	1445 - 1630	1350 - 1515	2000	1325 - 1390

**Table 13** Physical Properties of Amines (Source from GPSA)

	<b>MEA</b>	<b>DEA</b>	<b>TEA</b>	<b>MDEA</b>	<b>DIPA</b>	<b>DGA</b>
Overall Chemical formula	C <sub>2</sub> H <sub>7</sub> NO	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>15</sub> NO <sub>3</sub>	C <sub>5</sub> H <sub>13</sub> NO <sub>2</sub>	C <sub>6</sub> H <sub>15</sub> NO <sub>2</sub>	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>
Molecular weight (kg/kmol)	61.08	105.14	149.19	119.17	133.19	105.14
Boiling Point at 101325 pa , °C	170.6	269.2	360	247.4	248.9	221.3
Specific Gravity (20°C/20°C)	1.0179	1.0919 (30°C/20°C)	1.1258	1.0418	0.9890 (45°C/20°C)	1.0572
Absolute Viscosity at 20°C (pa.s)	0.0241	0.380 (30°C)	0.1030	0.1010	0.198 (45°C)	0.0400 (15.6°C)
Melting point, °C	10.5	28.0	22.4	-23.0	42.0	-12.5
Specific Heat at 15.6 (J/kg.K)	2546 (20°C)	2512	2931	2238	2889 (30°C)	2391
Flash Point °C	93.3	137.8	185.0	129.4	123.9	126.7

**Figure 25** Flow Process for Determination of Water Content

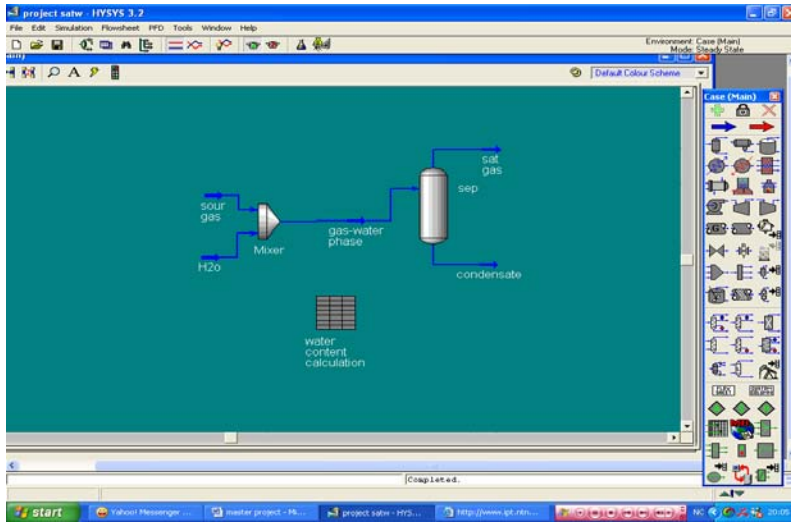
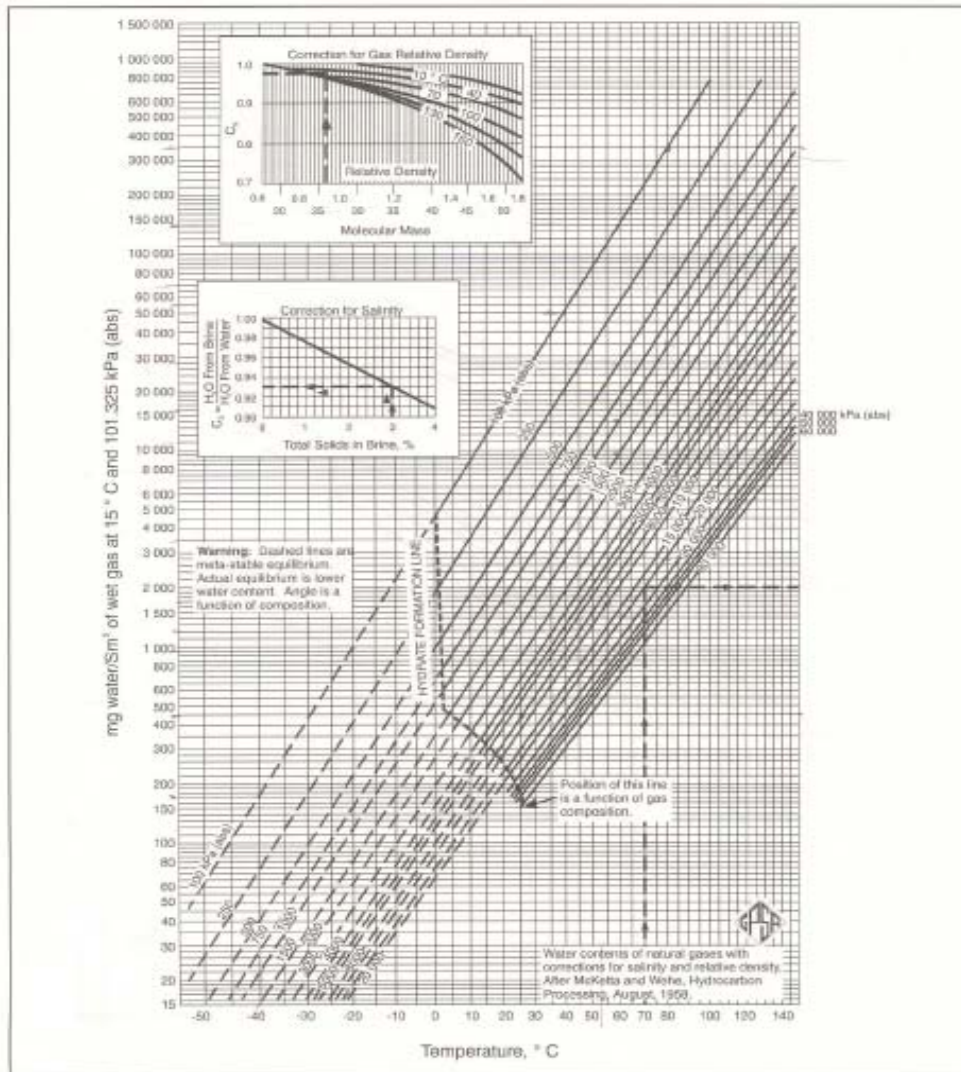


Figure 26 Water Content of Hydrocarbon Gas from GPSA



## APPENDIX A: Basic Raw Data and Base Case Simulation Data

Table 14 Sour Gas Feed Composition Parameters

Temperature	30 °C
Pressure	6900 kpa ( 69 bara)
Molar Flow rate	1250 kgmol/h
Components	Mole Fraction
Nitrogen	0.001372
Hydrogen sulfide	0.000
Carbon dioxide	0.0568
Methane	0.8991
Ethane	0.0257
Propane	0.0061
n-Butane	0.001902
n-Pentane	0.00078
Water	0.000

Table 15 Amine Lean-Rich Heat Exchanger

L/R HX	
Tube Outlet Temperature	95 °C
Tube Side Pressure Drop	70 kpa
Shell Side Pressure Drop	70 kpa

Table 16 Lean Amine to the Contactor

Temperature	35 °C
Pressure	6865 kpa
Std Ideal Volume Flow	43 m <sup>3</sup> /h
Comp Mass Fraction (H <sub>2</sub> O)	0.7181
Comp Mass Fraction (DEAmine)	0.2801

## APPENDICES B: Water Content Determination Procedures

### WICHERT AND AZIZ CORRELATION FOR PSEUDO CRITICAL PROPERTIES OF GAS WITH CO<sub>2</sub> AND H<sub>2</sub>S PRESENT

Critical Temperature of Hydrocarbon Content in the Gas

$$T_{pcHc} = \sum_{i=1}^N y_i T_{ciHC}$$

Critical Pressure of Hydrocarbon Content in the Gas

$$P_{pcHc} = \sum_{i=1}^N y_i P_{ciHC}$$

Critical Temperature Adjusted for Non Hydrocarbon present

$$T_{pc}^* = (1 - y_{N_2} - y_{CO_2} - y_{H_2S}) * T_{pcHc} + y_{N_2} T_{cN_2} + y_{CO_2} T_{cCO_2} + y_{H_2S} T_{cH_2S}$$

Critical Pressure Adjusted for Non Hydrocarbon present

$$P_{pc}^* = (1 - y_{N_2} - y_{CO_2} - y_{H_2S}) * P_{pcHc} + y_{N_2} P_{cN_2} + y_{CO_2} P_{cCO_2} + y_{H_2S} P_{cH_2S}$$

$$\epsilon = 120 \left[ (y_{CO_2} + y_{H_2S})^{0.9} - (y_{CO_2} + y_{H_2S})^{1.6} \right] + 15 (y_{H_2S}^{0.5} - y_{H_2S}^4)$$

$$T_{pc} = T_{pc}^* - \epsilon$$

$$P_{pc} = \frac{P_{pc}^* (T_{pc}^* - \epsilon)}{T_{pc}^* + y_{H_2S} (1 - y_{H_2S}) * \epsilon}$$

$$P_r = \frac{P}{P_c}$$

$$T_r = \frac{T}{T_c}$$

Compressibility factor using Hall and Yarborough correlation

$$Z = \frac{\alpha P_{pr}}{y}$$

$$\alpha = 0.06125t * \exp[-1.2(1-t)^2]$$

Where;

$$t = \frac{1}{T_{pr}}$$

y = the reduced density parameter (the product of a van der Waals covolume and density) is obtained by solving

$$f(y) = 0 = -ap_{pr} + \frac{y + y^2 + y^3 - y^4}{(1 - y)^3}$$

This equation is solved using Newton Raphson

iteration

Z = function (Tr, Pr)

DETERMINATION OF WATER CONTENT USING HYSYS SIMULATOR AND WICHERT AND AZIZ CORRELATION

EXAMPLE:

Determination of water content present in a given Feed Gas at T= -40°C and P = 100kpa

Data from HYSYS application

Molecular weight of water Mw = 18.02 kg/kmol

Molecular weight of gas with water Mg\_w = 16.46115 kg/kmol

Mole fraction of pure water Cw = 1.78\*10<sup>-4</sup>

Mass density of water- gas mixture ρg-w = 0.853289 kg/m<sup>3</sup>

Therefore the number of mole of water present is  $n_{g-w} = \frac{1 * 0.853289 kg}{16.46115 \frac{kg}{kmol}} = 0.05184 kmol$

From real gas equation PV = nZRT

And

Clapeyron equation  $\frac{P_{sc} V_{sc}}{T_{sc}} = \frac{PV}{T}$

Calculation of mole of gas is determined by combination of real gas and Clapeyron equation

This gives;

$$n_{sc} Z_{sc} R = n_{H_2O} ZR$$

n<sub>H<sub>2</sub>O</sub> = is the mole of water present at a given feed gas conditions.

$$n_{H_2O} = \frac{n_{sc} * Z_{sc}}{Z}$$

Where; Z<sub>sc</sub> = 1

Z – Factor = 0,995188 Compressibility factor of the feed gas at a given T, P obtained from Hall and Yarborough correlation.

$$m_{w,lm} = n_{g-w,im} * C_w * M_w$$

$$m_{w,lm} = 0.05184 * 1.78 * 10^{-4} * 18.0151 \left[ \frac{kg}{kmol} \right] = kg$$

$$m_{w,lm} = 1.6623 * 10^{-4} kg$$

Using clapeyron equation to convert 1 mole of gas to standard condition

$$V_{sc} = 1.22553 kg/Sm^3$$

See table A below.

Mass of water per 1 Sm<sup>3</sup>

$$M_{H_2O} = \frac{1.6623 * 10^{-4}}{1,2256} [kg / Sm^3]$$

$$M_{H_2O} = 1.35881 * 10^{-4} kg / Sm^3 * 10^6 = 135.881 [mg / Sm^3]$$

**Table 17** Water Content Evaluated

Name	Satgas	Satgas	Satgas	Satgas	Satgas	Satgas	Satgas
Temperature, oc	-40	-20	0	20	40	60	80
Pressure, kpa	100	100	100	100	100	100	100
Pr	0,022898782	0,022898782	0,02289878	0,02289878	0,02289878	0,022898782	0,022898782
Tr	1,199442763	1,302332985	1,40522321	1,50811343	1,61100365	1,713893873	1,816784095
Z <sub>fac</sub>	0,995266924	0,99631001	0,99709873	0,9977037	0,99817291	0,998540929	0,998832586
M <sub>H<sub>2</sub>O</sub> per 1m <sup>3</sup> of gas, kg	1,67E-04	1,03E-03	4,73E-03	1,71E-02	5,08E-02	1,30E-01	2,92E-01
V <sub>sc</sub>	1,225538674	1,127533843	1,04414941	0,97232293	0,90979556	0,854862612	0,80621356
W <sub>H<sub>2</sub>O_gas</sub> mg/Sm <sup>3</sup>	135,881	916,528	4531,066	17542,497	55863,199	151869,421	362793,548