

**PROCESS SIMULATION AND IMPROVEMENT OF INDUSTRIAL ACID
GAS REMOVAL UNIT (AGRU)**

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**PROCESS SIMULATION AND IMPROVEMENT OF INDUSTRIAL ACID
GAS REMOVAL UNIT (AGRU)**

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical & Natural Resources Engineering
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APRIL 2009

“I hereby declare that the work in this thesis entitled Process Simulation and Improvement of Industrial Acid Gas Removal Unit (AGRU) is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree”.

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To Whom It May Concern
My responsible dad alongside my lovely mom,
Brothers and Sisters.

To my supportive friends.
Friend in need is a friend indeed.
Friends forever.

To my beloved Fairuz.
Always give me support and motivation.
Thanks for having me.

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ABSTRACT

Acid gas removal process, which is also known as gas sweetening process, is a very important industrial operation that has been described in many works. The main processes installed are based on absorption, and the selection of the solvent is based on its capability to absorb or remove acid gases such as carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Realizing such acid gases can cause operational problems such as corrosion and equipment plugging, the solvent used for absorption can be classified into chemical and physical types. The widely used absorption processes to sweeten natural gas are using chemical solvent such as alkanolamines or simply called “amine”. In this context, monoethanolamine (MEA) and methyldiethanolamine (MDEA) are among the most common amine used in the aqueous solution to remove both CO_2 and H_2S gases from natural gas stream. In this research, existing process flow diagram of industrial Acid Gas Removal Unit (AGRU) has been modified in terms of solvent used for absorption process. The mixture of MEA and MDEA in aqueous amine solution replaces the existing solvent known as Benfield solution. Simulation using Aspen Hysys is then performed to compare both existing and modified absorption processes according to four parameters, which are absorption column removal efficiency, power consumption, heating duty and cooling duty. The simulation results shows amine solution offers attractive solvent option to be used in improving existing AGRU system. For the same absorption column removal efficiency, amine solution can save 11.2% annual power consumption, which is equivalent to RM 967270 per year. Even though there is no change for heating duty, the cooling duty requirement however can be reduced by 17%, which saves about RM 27324 per year for the amine solution. These savings can be further analyzed when considering and comparing other aspects of operational experiences such as foaming, solvent degradation and corrosion problems.

ABSTRAK

Proses penyingkiran gas asid yang turut dikenali sebagai proses pemanisan gas, adalah satu operasi penting industri. Proses-proses utama adalah berdasarkan keupayaan penyerapan, dan pemilihan pelarut adalah diasaskan keupayaannya bagi menyerap atau membuang gas asid seperti karbon dioksida (CO_2) dan hidrogen sulfida (H_2S). Menyedari gas asid boleh menyebabkan masalah operasi seperti kakisan dan penyumbatan alat, pelarut yang digunakan untuk penyerapan dapat diklasifikasikan kepada sifat-sifat kimia dan fizikal. Proses penyerapan digunakan secara meluas untuk memaniskan gas asli dengan menggunakan pelarut kimia seperti alkanolamines atau dipanggil hanya "amina". Dalam konteks ini, monoethanolamine (MEA) dan methyldiethanolamine (MDEA) adalah antara amina yang paling biasa digunakan dalam larutan bagi membuang kedua gas CO_2 dan H_2S dari saluran gas asli. Dalam penyelidikan ini, gambar rajah aliran proses perindustrian Acid Gas Removal Unit (AGRU) telah diubah suai berdasarkan pelarut yang digunakan untuk proses penyerapan. Campuran larutan MEA dan MDEA dalam larutan amina bagi menggantikan pelarut sedia ada yang dikenali sebagai larutan Benfield. Simulasi menggunakan Aspen Hysys dilaksanakan untuk membandingkan kedua-dua keadaan dan perubahan proses penyerapan berdasarkan empat parameter iaitu kecekapan penyingkiran turus penyerapan, penggunaan kuasa, proses pemanasan dan penyejukan. Keputusan simulasi menunjukkan larutan amina menjadi pilihan pelarut yang menarik diguna pakai dalam meningkatkan sistem AGRU sedia ada. Bagi turus penyerapan yang mempunyai kecekapan penyingkiran yang sama, penyelesaian amina boleh dijimatkan sebanyak 11.2% penggunaan kuasa tahunan bersamaan RM 967,270 setiap tahun. Walaupun tiada perubahan untuk proses pemanasan, proses pendinginan bagaimanapun boleh dikurangkan sebanyak 17% iaitu penjimatan sebanyak RM 27,324 setiap tahun untuk larutan amina. Penjimatan ini masih boleh dianalisis selanjutnya dengan menitik beratkan dan membandingkan aspek-aspek operasi seperti berbuih, degradasi pelarut dan masalah kakisan.

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LIST OF NOMENCLATURE

ppm	= Part per million, volume
°C	= Temperature in deg C
wt%	= percentage water content
kW	= Mechanical shaft work , kilowatt
m ³	= cubic meters, volume
LLP Steam	= Low Low Pressure Steam
MDEA	= Methyldiethanolamine
MEA	= Methylethanolamine
CO ₂	= Carbon Dioxide
H ₂ S	= Hydrogen Sulfide

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CHAPTER 1

INTRODUCTION

1.1 Natural Gas and Natural Gas Industry.

The natural gas industry began in early 1900s in the United State and is still evolving. This high quality fuel and chemicals feedstock plays an important role in the industrial world and is becoming an important export for other countries.

1.1.1 History of Natural Gas

The Chinese are reputed to have been the first to use natural gas commercially, some 2400 years ago. The gas was obtained from shallow wells, transported in bamboo pipes and used to produce salt from brine in gas-fired evaporators. Manufactured, or town gas (gas manufactured from coal) was used in both Britain and the United States in the late 17th and early 18th centuries for streetlights and house lighting. The next recorded commercial use of natural gas occurred in 1821. During following years, a number of small, local programs involved natural gas, but large-scale activity began in the early years of the 20th century. The major boom in gas usage occurred after World War II, when engineering advances allowed the construction of safe, reliable, long distance pipelines for gas transportation. At the end of 2004, the United State had more than 479,000 kilometers of gas pipelines, both interstate and intrastate. In 2004, the U.S was the world's second largest producer of natural gas 543 billion standard cubic meters (BSm³) and the leading world consumer 647 BSm³.

Although the primary use of natural gas is as fuel, it is also a source of hydrocarbons for petrochemicals feedstock and a major source of elemental sulfur, an important industrial chemical. Its popularity as an energy source is expected to grow substantially in the future because natural gas presents many environmental advantages over petroleum and coal.

1.1.2 Natural Gas Industry In Malaysia.

Natural gas is amongst one of the fastest growing component of the world primary energy consumption. Consumption of natural gas worldwide of 2660 Bm³ in 2005 is forecasted to increase by more than 90 per cent by year 2030. Globally, the industrial and electric power sectors are the largest consumers of natural gas. The total world gas reserves currently stand at 171136 Bm³ with Russia, holding 27 per cent having the largest reserves.

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

Malaysia is endowed with natural gas reserves that are three times larger than its oil reserves. With total proven natural gas reserves of 2400 Bm³, Malaysia is ranked the 13th largest in the world. Most of these gas reserves are located offshore Peninsular Malaysia, Sarawak and Sabah.

These natural gas resources are carefully harnessed to serve as the main source of fuel for Malaysia's industrialisation through the Industrial Master Plan, charting out the long-term energy utilisation strategy for Malaysia. This saw Malaysia ushering in the gas era in the 1980s with the introduction of natural gas as a source of fuel for power generation and industrial development as well as the

harnessing of the gas resources for foreign exchange earnings in the form of liquefied natural gas exports.

The natural gas resources in Malaysia are distributed almost equally between Peninsular Malaysia in the west and Sarawak and Sabah in the east. Due to the low population density in the states of Sarawak and Sabah on the island of Borneo, the natural gas resources found offshore Sarawak are harnessed to produce liquefied natural gas (LNG) for exports.

1.1.3 Sources of Natural Gas

Conventional natural gas generally occurs in deep reservoirs, associated either with crude oil also known as associated gas, which is found in association with crude oil either dissolved in the oil or as a cap of free gas above the oil or in reservoirs that contain little or no crude oil. Associated gas is produced with the oil and separated at the casing head or wellhead. Gas produced in this fashion is also referred to as casing head gas, oil well gas, or dissolved gas. Non-associated gas is sometimes referred to as gas-well gas or dry gas. However, this dry gas can still contain significant amounts of natural gas liquid (NGL) components. The differences of associated gas and non-associated gas in term of the compositions as shown in Table 1.1 below.

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

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

Hydrogen Sulphate	15.3	1.5
Carbon Dioxide	9.3	8.9

1.1.4 Compositions of Natural Gas

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

Table 1.2: Typical Composition of Natural Gas

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

1.2 Acid Gas in Natural Gas Flow

Acid gas removal or gas treating involves reduction of the acid gases such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S), along with other sulfur species, to sufficiently low levels. This removal process is required in order to meet contractual specifications or permit additional processing in the plant without corrosion and plugging problems.

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

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

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

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

1.3 Acid Gas Removal Processes.

Acid gas removal process as shown in Figure 1.1 is a very important industrial operation, which has been described in many works. The main processes used are based on absorption, and the selectivity of the solvent with respect to acid gasses is based on an affinity of the chemical or physical type. Adsorption is also used for intensive purification. Gas permeation has a substantial potential, but today, industrial applications are limited.

Many factors must be considered in selecting an acid gas removal process including, natural gas composition, acid gas content of the gas to be processed, final specifications, gas throughput to be processed, inlet pressure and temperature conditions, H₂S removal conditions with or without sulfur recovery, acid gas disposal method and relative cost.

1.3.1 Process Based on Chemical Solvents

1.3.1.1 Using Amine Solution

From Figure 1.2, the sour gas feed enters the bottom of the contactor at pressure to 1000 psi and the temperature in the range of 32°C. The sour gas flows upward, countercurrent to the lean amine solution, which flows down from the top. The lean amine that returns to the contactor is maintained at the temperature above the vapor that exits the contactor to prevent any condensation of heavier liquid hydrocarbon. Intimate contact between the gas and the amine solution is achieved by use of either trays or packing in the contactor

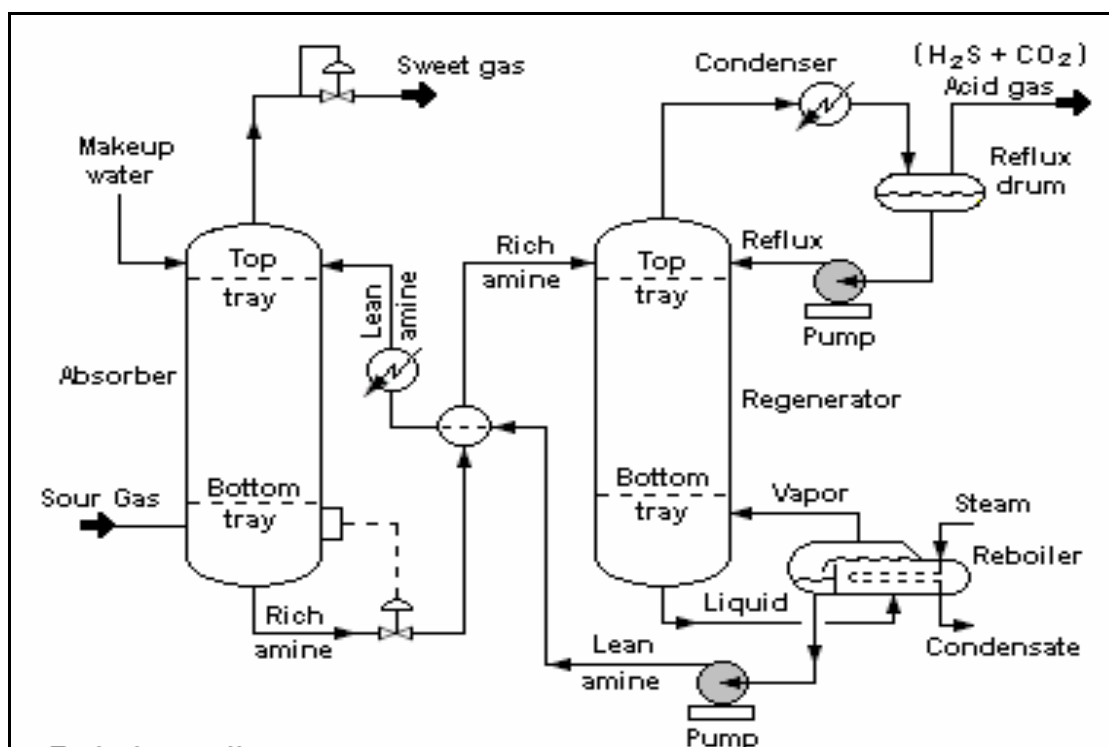


Figure 1.2: Process Flow Diagram for Amine Treating.

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

The treated gas leaves the top of the tower water saturated and at a temperature controlled by the temperature of the lean amine that enters, usually around 38°C.

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

The lean amine exits the bottom of the stripper at about 130°C and is pumped to the contactor pressure, exchanges heat with the rich amine stream, and is further cooled before it enters the top of the contactor.

1.3.1.2 Using Benfield Solution.

Benfield solution normally contain Potassium Carbonate (K₂CO₃), Diethanolamine (DEA), Vanadium (V₂O₅), Thiosulfate and Chloride. From Figure 1.3, in a typical application, the contactor will operate at approximately 300 psig, with the lean carbonate solution entering near 110°C and leaving at 115°C. The rich carbonate pressure is reducing approximately 5 psig as it enters the stripper. Approximately one-third to two third of the absorbed CO₂ is released by the pressure reduction, reducing the amount of steam required for stripping (Kohl and Nielsen, 1997).

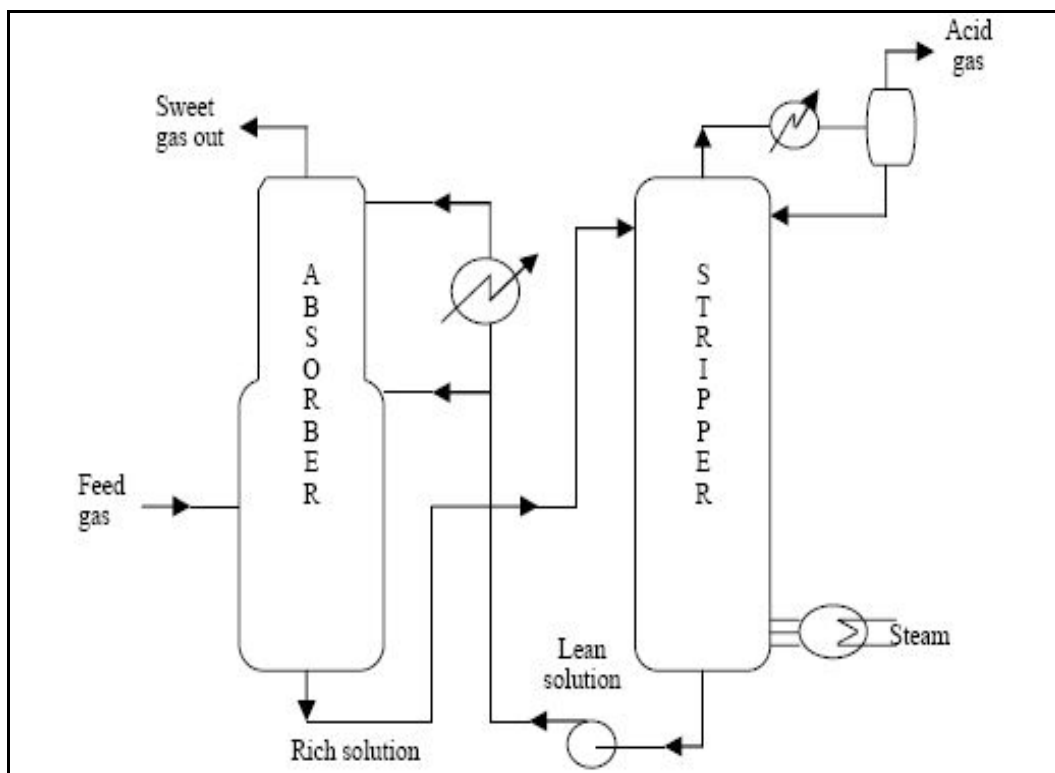


Figure 1.3.: Process Flow Diagram for Hot Potassium Carbonate Process.

The lean carbonate solution leaves the stripper at the same temperature as it enters the contactor, and eliminates the need for the heat exchange between the rich and the lean stream. The heat of solution for absorption of CO_2 in potassium carbonate is small, approximately 32 Btu/ft^3 of CO_2 (Bensen et al., 1954), and consequently the temperature rise in the contactor is small and less energy is required for regeneration.

1.3.2 Processes Based on Physical Solvents.

These processes offer the advantages of requiring little or no heat to desorb the acid gases. On the other hand, they are sensitive to the presence of the heavy hydrocarbon in the gas, which are absorbed by the solvent and then desorbed with the acid gases. The use of the process based on the physical solvent is favored by the following conditions, which are gas available at relatively high pressure, low concentration of heavy hydrocarbon in the feed, high acid gas content in the feed and desired $\text{H}_2\text{S}/\text{CO}_2$.

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

1.3.3 Acid Gas Removal Process by Adsorption.

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

1.3.4 Acid Gas Removal by Gas Permeation

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

1.4 Using Amine as a Solvent for Chemical Absorption

Amines are compounds formed from ammonia (NH_3) by replacing one or more of the hydrogen atoms with another hydrocarbon group. Replacement of single hydrogen produces a primary amine, replacement of two hydrogen atoms produces a secondary amine, and replacement of all three of the hydrogen atoms produces a tertiary amine. Primary amines are the most reactive, followed by secondary and tertiary amines. Sterically hindered amines are compounds in which the reactive center (the nitrogen) is partially shielded by neighboring group so that larger molecules cannot easily approach and react with the nitrogen. The amines are used in water solutions in concentration ranging from approximately 10 to 65 wt% amines. Amines removed H_2S and CO_2 in two steps process, which are by dissolving the gas in the liquid (physical absorption) and the dissolved gas, which is weak acid, reacts with the weakly basic amines.

1.4.1 Primary Amines

Monoethanolamine (MEA) is the most basic of the amines used in acid treating and thus the most reactive for acid gas removal. It has the advantage of a high solution capacity at moderate concentrations, and it is generally use for gas streams with moderate levels of CO_2 and H_2S when complete removal of both impurities is required. MEA also a relatively high vapor pressure that is results in high vaporization losses, higher corrosion rates than most other amines if the MEA concentration exceeds 20% at high level of acid gas loading (Kohl and Nielsen, 1997) and inability to selectively remove H_2S in the presence of CO_2 .

1.4.2 Secondary Amines

Diethanolamine (DEA), a secondary amine, is less basic and reactive than MEA. Compared with MEA, it has a lower vapor pressure and thus, lower evaporation losses; it can operate at higher acid gas loadings, typically 0.35 to 0.8 mole acid gas/mole of amine versus 0.3 to 0.4 mole acid-gas /mole; and it has a lower energy requirement for reactivation. Concentration ranges for DEA are 30-50

wt% and are primarily limited by corrosion. DEA forms regenerate able compounds with COS and CS₂ and, thus, can be used for their partial removal without significant solution loss. DEA has disadvantage of undergoing irreversible side reactions with CO₂ and forming corrosive degradation products; thus, it may not be the best choice for high CO₂ gases.

1.4.3 Tertiary Amines

Methyldiethanolamine (MDEA), a tertiary amine, selectively removes H₂S to pipeline specifications while “slipping” some of the CO. As noted previously, the CO₂ slippage occurs because H₂S hydrolysis is much faster than for CO₂, and the carbonate formation reaction does not occur with a tertiary amine. Consequently, short contact times in the absorber are used to obtain the selectivity. MDEA has a low vapor pressure and thus, can be used at concentrations up to 60wt% without appreciable vaporization losses. Even with its relatively slow kinetics with CO₂, MDEA is used for bulk removal of CO₂ from high concentration gases because energy requirement for regeneration are lower than those for the other amines (Veroba and Stewart, 2003).

1.5 Problem Statement

Problem statement in this research refers to a problem occur that need to be solve. Problem statement will describe the cause and effect of the problem and help to choose the wise solution to overcome it.

The typical operating problem occurs in Acid Gas Removal Unit using Benfield solution are foaming, corrosion and solvent losses (Gary T. Rochelle, 2006). Foaming is the common problem happen in this process. Foaming of the liquid benfield solution because it results in poor vapor-liquid contact, poor distribution, and solution holdup with resulting carryover and off spec gas. Among the causes of foaming are suspended solids, liquid hydrocarbons, and surface-active

agents, such as those contained in inhibitors and compressor oils. One obvious cure is to remove the offending materials; the other is to add antifoaming agents.

Various plant inspections have indicated localized corrosion of absorber tower walls. Deep, smooth edged pits and some sharp-edged, partly undercut areas characterize the corrosion morphology. Some reports have also indicted outgrowths of corrosion products within some of the pits. The corrosion problem presents a significant safety issue since if not monitored; it may lead to loss of pressure containment. The corrosion may require vessel de-rating because of corrosion allowance consumption. Production may be reduced because of the time required to undertake repair work. The financial losses may be quite significant and encompasses direct financial losses such as those incurred because of loss of production due to absorber down time (usually 3 weeks) and cost of repair costs. In addition, there is the cost of managing corrosion, which is inhibitor usage, plant air supply and usage, corrosion monitoring equipment and procedures.

Solvent losses are one of the problems that occur in acid gas removal process. The major degradation products among these include formic acid, acetic acid, oxalic acid and glycolic acid. The oxygen stoichiometry necessary to produce these degradation products varies for each individual component; overall, it varies anywhere from 0.5 to 2.5 (Goff, 2004). Goff's work on Benfield degradation was limited to analyzing Benfield degradation rates via the evolution of NH_3 . The ammonia evolution rates were measured using a Fourier Transform Infrared (FT-IR) analyzer. The oxidative degradation of the Benfield may significantly affect the economics and environmental impact of these solvent systems. Oxidative degradation results in fragmentation of the Benfield solvent. The identity and quantity of degradation products is required to assess their impact on the environment and the process economics and to design for corrosion prevention and solvent reclaiming (Gary T. Rochelle, 2006).

1.6 Objectives

This research contains two main objectives. The first objective is to evaluate existing process flow diagram of industrial AGRU based on four parameters that include absorption column removal efficiency, power consumption, heating duty and cooling duty. The second objective is to replaced Benfield solution with Amine solution which process take place. Process improvement can be realized after making comparison for the four parameters highlighted above.

1.7 Scopes of the Research

This project will be focusing on simulation thru Aspen Hysys, which is will be done based on the industrial Acid Gas Removal process flow sheet that use Amine solution instead of Benfield solution. Comparisons between AGRU which used Benfield solution and AGRU that will be using Amine solution are being made in terms of absorption column removal efficiency power consumption, heating duty and cooling duty.

1.8 Rationale and Significance

In this research, the motivation to use Amine solution instead of Benfield solution for industrial AGRU system are based on overall process and economic performances. While typical AGRU has operational problems such as solvent losses and degradation, foaming and corrosion, the selection of solvent is therefore very important. Replacing Benfield solution with Amine solution is theoretically offers both process and economic advantages.

CHAPTER 2

LITERATURE REVIEW

Natural gas has a wide range of acid gas concentrations, from parts per million to 50 volume percent and higher, depending on the nature of the rock formation from which it comes. Because of the corrosiveness of H₂S and CO₂ in the presence of water and because of the toxicity of H₂S and the lack of heating value of CO₂, sales gas is required to be sweetened. The most widely used processes to sweeten natural gas are those, which are using the alkanolamines such as monoethanolamine (MEA) and mdiethanolamine (MDEA).

2.1 AGRU's Process Description

Figure 2.1 shows that the sour gas is introduced at the bottom of an absorber and flows up the tower countercurrent to an aqueous amine stream. Within the tower, the acid gases are absorbed by the amine.

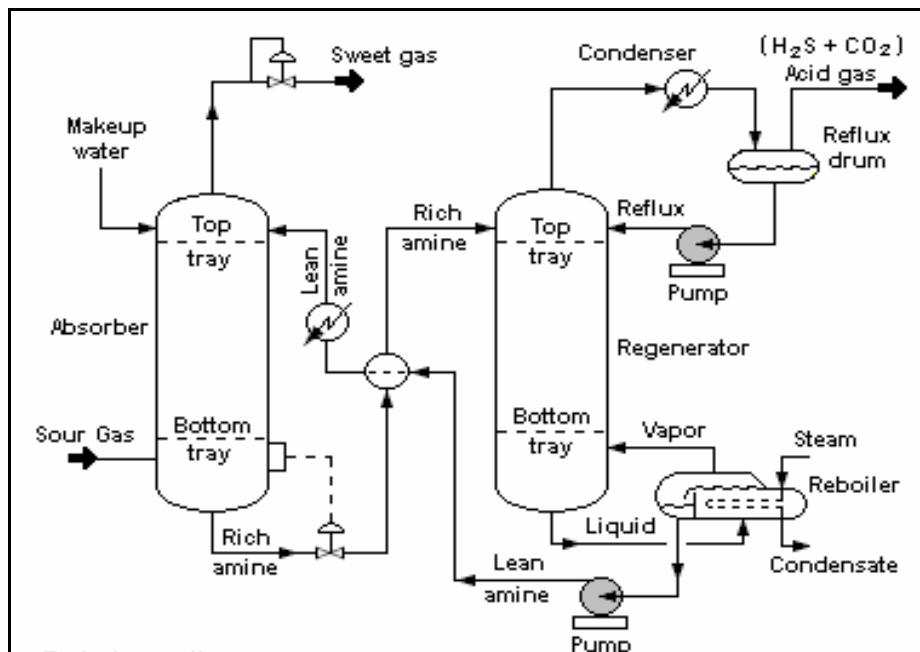


Figure 2.1: Acid Gas Removal Process Flow Diagram

The amine is described as being lean in acid gas as it enters the top of the absorber, and rich as it exits the bottom, loaded with acid gas. From the absorber the rich amine is directed to the top of a stripping tower where a drop in pressure and application of heat enables the solvent to be stripped of the acid gases. The amine, again lean, is circulated back to the absorber for sweetening.

2.1.1 Inlet Gas Knockout

Before entering the absorber, the gas is passed through an inlet separator where entrained droplets or slugs of liquid are removed from the gas stream by impaction devices. Baffles remove a portion of the liquids. Mist eliminator pads, located near the gas outlet of the tank, trap the rest. Typical contaminants in natural gas streams may be liquid hydrocarbons, salt water, sands, well treating compounds, pipeline treating chemicals, and compressor oils. It is important that these contaminants be removed before the gas reaches the absorber. Once in the sweetening system, these contaminants can cause a number of operational problems including foaming, equipment fouling, and high corrosion rates, usually resulting in solvent loss and difficulty in meeting sweet gas specifications.

2.1.2 Absorber

The sour gas, freed of entrained liquids by the inlet separator, enters the bottom of the absorber. Usually the absorber is a tray column although packed columns are also used. In either case, the objective is to provide intimate contact between the gas and the amine solvent so that the H₂S and CO₂ molecules can transfer from the gas phase to the solvent liquid phase. In tray columns, a liquid level is maintained on each tray by a weir usually 2 or 3 inches high. The gas passes up from underneath the trays through openings in the trays such as perforations, bubble caps, or valves, and disperses into bubbles through the liquid, forming froth.

The gas disengages from the froth, travels through a vapor space, providing time for entrained amine solution to fall back down to the liquid on the tray, and passes through the next tray above. Nearly all absorption of H₂S and CO₂ takes place on the trays, and not in the vapor space between the trays. In packed columns, the liquid solvent is dispersed in the gas stream, by forming a film over the packing, providing a large surface area for CO₂ and H₂S transfer from the gas to the liquid solvent. The degree of sweetening achieved is largely dependent on the number of trays or the height of packing available in the absorber. Twenty trays or the equivalent height in packing are common, and are often a standard design. A water wash consisting of 2 to 5 trays at the top of the absorber can be used to minimize vaporization losses of amine, and is often found in low-pressure monoethanolamine systems. In most cases, a mist eliminator pad is installed near the gas outlet of the absorber to trap entrained solvent, and an outlet knockout drum, similar to the inlet separator for the gas feed, is provided to collect solvent carryover.

2.1.3 Regenerator

Like the absorber, the stripper is either a tray or packed column with approximately 20 trays or the equivalent height in packing. To minimize amine vaporization loss, there may be a water wash section at the top of the column with an additional four to six trays. The preheated rich amine enters near the top of the column and flows down countercurrent to a gas stream of steam, H₂S, and CO₂. The

steam is generated in the re-boiler, lowering the partial pressure of H₂S and CO₂ in the gas stream, enhancing driving force of the acid gases from the amine solution. The overhead gas passed through a condenser to recover water and the small amount of amine that is vaporized in the regenerator.

The overhead condenser, the re-boiler tube bundle, and the upper third of the stripping column shell are all susceptible to high corrosion rates, and may need to be manufactured out of stainless steel. Thermal degradation, which can contribute to corrosion, can be minimized by designing the re-boiler to use a low temperature-heating medium such as low-pressure steam. The ratio moles of steam to moles of acid gas in the overhead gas upstream of the condenser, called the reflux ratio, commonly ranges from 1.5:1 to 4:1, depending upon the required degree of regeneration.

2.2 Amine Solvent Selection

2.2.1 Selective Absorption with MDEA

Vidaurri and Kahre, (1977); reported on a number of tests related to selective absorption. The authors conducted three series of experiments. The first series consisted of batch absorptions using four different amines. This data showed that all amines could be used selectively if conditions could be arranged properly. The next phase consisted of operating a small-scale pilot plant with various amines under a wide variety of conditions.

This phase showed that MDEA could give the best selectivity under typical operating conditions encountered in the industry. The last phase consisted of the conversion of an industrial sweetening unit from DEA to MDEA. The data showed that significant selectivity was obtained from the updated unit. The data from this unit are used for comparison in the present work. The inlet gas was at 78 psig and contained 8% H₂S and 1.5% CO₂. The absorber was 6 ft in diameter with 20 trays

and a pressure drop of 3.5 in. of water per tray. The scrubbing solution was 15 wt% MDEA. Average operating conditions and a residence time of 2.5 seconds per tray were used for the simulation.

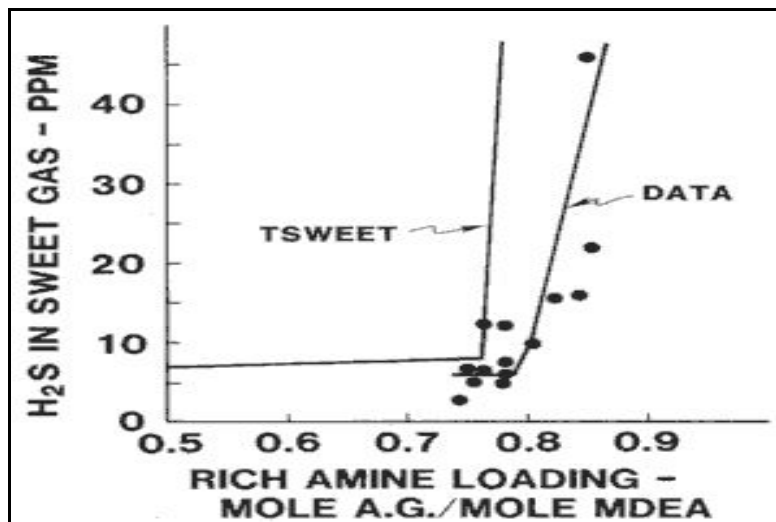


Figure 2.2: Comparison of TSWREET to data of Vidaurri and Kahre, (1977)
(John C Polasek, 2006)

The data for the H₂S in the sweet gas are shown in Figure.2.2.1 long with the program results. The values calculated by the program are well within the scatter of the data. The scatter is about +/-6 part per million (ppm) about the data curve. The total solution loading where H₂S breakthrough occurs can also be compared in Figure.2.2.1. The breakthrough value of 0.76 mole a.g./mole MDEA calculated by the program is about 6% lower than the value of about 0.81 mole a.g./mole MDEA from the data. CO₂ rejections of about 70% were reported for the absorber. The values calculated by the program were near 80% and were thus about 10% high. CO₂ rejections of about 70% were reported for the absorber. The values calculated by the program were near 80% and were thus about 10% high. (John Polasek, 2006)

2.3 General Trends for Selective Absorption with MDEA

Selective absorption is dependent on several process variables, some of which cannot be specified or controlled by the design engineer. The variables include absorber pressure, amine temperature, concentration of acid gases, residuals in lean amine, residence time and wt% of amine. Furthermore, each of these variables interacts to give a very complex system.

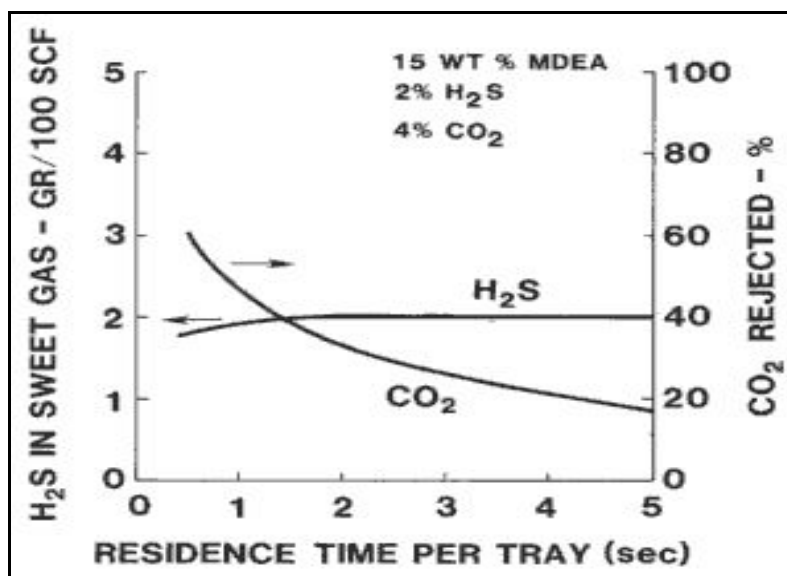


Figure 2.3 (a): Effect of Residence Time on CO₂ Rejection (John C Polasek, 2006)

The influence of residence time and acid gas loading were chosen for presentation in the current work. The effect of residence time on each tray for a typical example is shown in Fig. 2.3 (a). Obviously, the amine loading also varies as the CO₂ pickup increases. The H₂S concentration is nearly constant over the 1 to 5-second range for this case.

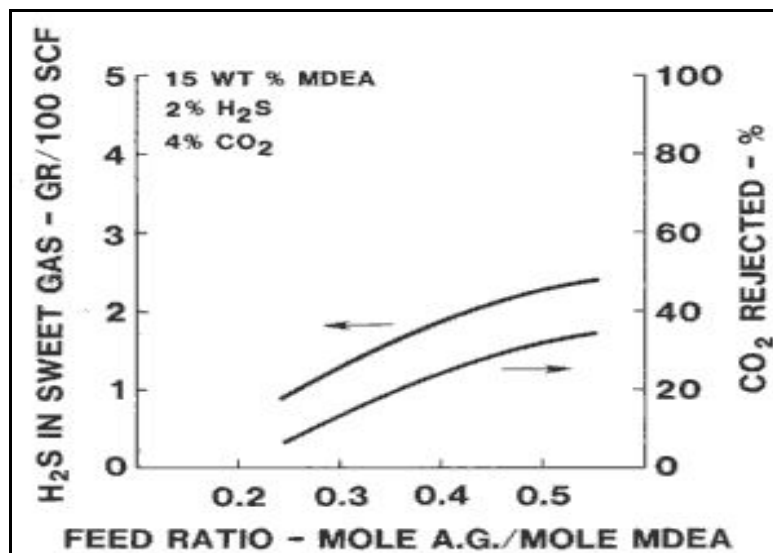


Figure 2.3 (b): Effect of Amine Loading on CO₂ Rejection. (John Polasek, 2006)

The effect of amine loading is shown in Figure. 2.3 (b). The CO₂ rejection increases sharply with loading. The H₂S in the sweet gas also increases with loading over this range.

2.4 Lower Gas Treating Cost

Methyldiethanolamine (MDEA) has become the amine molecule chosen to remove hydrogen sulfide, carbon dioxide and other contaminants from hydrocarbon streams (John Polasek, 2006). Amine formulations based on MDEA can significantly reduce the costs of acid gas treating. Under the right circumstances, MDEA based solutions can boost plant capacity, lower energy requirements or reduce the capital required. Most amine units can be readily converted to specialty amines. The benefits of conversion can produce paybacks in less than six months. It is therefore no surprise that hundreds of acid gas treatment plants have converted from generic to specialty amines.

The term 'gas treating' covers many applications, each with its own unique gas characteristics and with differing objectives for the treated gas streams. Specialized MDEA based products were developed to answer these needs. One key

difference among the various specialty amines is selectivity towards hydrogen sulfide, instead of removing both hydrogen sulfide and carbon dioxide, as generic amines such as MEA and DEA do, some products readily remove hydrogen sulfide to specifications, but allow controlled amounts of carbon dioxide to slip through. Alternatively, products that are designed for carbon dioxide removal are also available.

2.4.1 Higher Amine Concentrations

Specialty amines can be used in concentrations of up to 50%. More corrosive amines, such as MEA or DEA, are generally limited to a maximum of 15% and 30% respectively. With higher concentrations, the MDEA based amines make amines that are more active available for acid gas removal. Therefore, each gallon of solution has more gas treating capacity. As a result, the gas treating ability of each plant is significantly increased. This requires no plant expansion or expense in capital costs. Even for plants that do not require expansion, specialty amines may still be relevant. While maintaining current capacity, operating expenses can be cut significantly, by reducing energy consumption. Each gallon of solution has more gas treating capacity, therefore operators can reduce the circulation rate, and as a result, less power is needed to operate the pumps. Energy savings also occur in the re-boiler because less energy is required to break the bonds between the acid gas and the amine. This lower reaction heat requires less energy for regeneration. The selectivity of MDEA based products can lead to more energy savings. For example, allowing carbon dioxide to remain in the treated gas reduces the amount of acid gas in the amine that needs to be regenerated, thus reducing the amount of energy required.

2.5 Advantages of MDEA in Gas Treating

Historically, MDEA has been recognized primarily for its ability to selectively absorb H₂S from a gas while leaving large amounts of CO₂ in the gas. The selective absorption characteristics of MDEA have been widely reported in the literature.¹⁻⁹ MDEA's selective absorption ability is due to its relatively slow

reaction rate with CO₂. Until the last few years, MDEA has not been associated with cases where the removal of large amounts of CO₂ is desired.

As reported in the literature, MDEA has a number of properties, which make it desirable for broader application such as, high solution concentration (up 50 to 55 wt %), high acid gas loading, low corrosion even at high solution loadings, slow degradation rates, lower heats of reaction, low vapor pressure and solution losses, and MDEA also delivers energy savings from reduced reboiler duties (reflux ratio of 0.5 to 1.0) and lower overhead condenser duties. It has proved to be highly selective for absorption of H₂S when compared to CO₂ resulting in even lower circulation rates and higher quality acid gas for recycle to sulfur recovery unit. MDEA also as tertiary amine and therefore carbamate formation with CO₂ does not take place in MDEA based system. MEA and DEA form Carbamates with CO₂. Therefore, operation with MDEA is far more stable with no spurious shutdowns over longer periods.

Due to the above advantages, MDEA is the most desirable amine to use even in cases where large amounts of CO₂ must be removed.

2.6 Carbon Dioxide Removal by Amine Absorption using Aspen HYSYS

The actual method for CO₂ removal is by absorption in an amine-based solvent followed by de-sorption. The simplest and most used amine for CO₂ removal is monoethanol amine (MEA). This removal process has a high consumption of thermal energy, and one of the main aims of improvement is to minimize this energy consumption. Because testing at large scale is so expensive, it is natural to use process simulation to evaluate such processes. There are however few literature references on process simulation of CO₂ removal from exhaust gases at atmospheric pressure. AspenTech bought the program HYSYS from Hypro-Tech in 2002, and in 2006 the program name was changed to Aspen HYSYS. (Lars Erik Øi, 2007).

An important advantage with using a process simulation program for such calculations, is that the available models for thermodynamic properties can be used. Aspen Plus has an MEA property insert model (Aspen Plus, AspenTech, Cambridge Mass., 2006). Aspen HYSYS has an Amines Property Package (Aspen HYSYS 2004, AspenTech, and Calgary 2007). Within the Amines Property Package, one of the two models, Kent Eisenberg or Li-Mather, can be selected. Even though Aspen HYSYS is probably the most used process simulation program in the world, there has not been found any journal references on CO₂ removal from atmospheric exhaust gas using this program. There is however much literature on CO₂ removal from natural gas at high pressure. Other process simulation programs containing amine packages are ProVision and ProMax. (Lars Erik Øi, 2007).

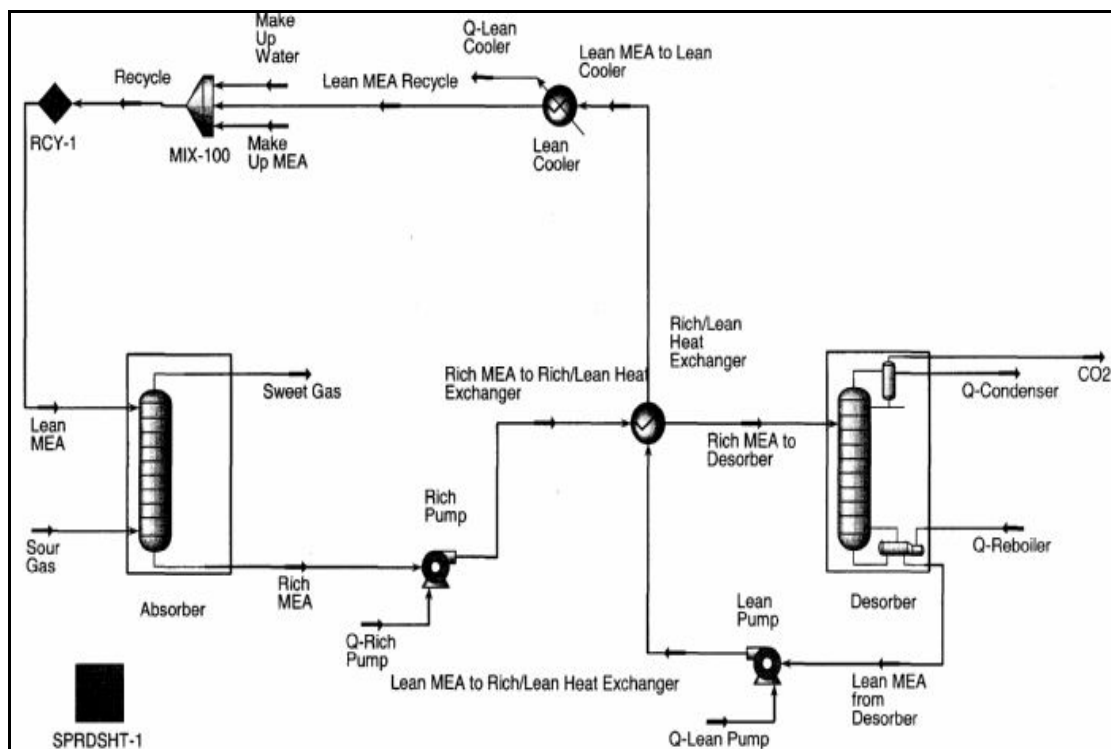
2.6.1 Simulation of CO₂ Removal Base case

An absorption and de-sorption process for CO₂ removal with an aqueous MEA solution has been simulated. The exhaust gas from the power plant model is used as the feed to this model. The absorption column is specified with 10 stages each with a Murphree efficiency of 0.25 (An estimated Height Equivalent to a Theoretical plate of 4 meter is about equivalent to 0.25 efficiency for each meter of packing.) Traditional concentrations, temperatures and pressures are used in the base case simulation. An Amines Property Package available in Aspen HYSYS describes the thermodynamics for this mixture. The Kent Eisenberg (Kent, R.L., Eisenberg, B., 1976) model is selected in the Amines Property Package. Specifications for the calculation are listed in Table 1.

Table 2.1: Specifications for Base Case CO₂ removal (Lars Erik Øi, 2007).

Specifications	Values
Inlet gas temperature	40 °C
Inlet gas pressure	1.1 bar (a)
Inlet gas flow	85000 kmole/hr
CO ₂ in inlet gas	3.73 mole %
Water in inlet gas	6.71 mole %
Lean amine temperature	40 °C
Lean amine pressure	1.1 bar (a)
Lean amine rate	120000 kmole/hr *
MEA content in lean amine	29 mass % *
CO ₂ in lean amine	5.5 mass % *
Number of stages in absorber	10
Murphree efficiency in absorber	0.25
Rich amine pump pressure	2 bar
Heated rich amine temperature	104.5 °C
Number of stages in stripper	6 (3+3)
Murphree efficiency in stripper	1.0
Reflux ratio in stripper	0.3
Reboiler temperature	120 °C
Lean amine pump pressure	2 bar
Minimum deltaT in heat exch	10 °C

* In first iteration

**Figure 2.4:** Aspen HYSYS model of CO₂ Removal

The Aspen HYSYS CO₂ removal model is presented in Figure 2.6.1. Different versions of this model have been developed in several student projects. Trine Amundsen (Amundsen, T, 2007) bases the version in figure 2.6.1 on a Master Project work. 85% CO₂ removal can be specified in the process. The Kent Eisenberg equilibrium model has been compared with the Li-Mather equilibrium model (Lee, I.J., Otto, F.D., Mather, A.E., 1975). The CO₂ removal calculated by Aspen HYSYS was reduced from 85 to 82%, and the heat consumption was reduced from 3.65 to 3.4 MJ/kg CO₂. (Lars Erik Øi, 2007).

2.7 Carbon Dioxide Removal Sensitivity Calculations

2.7.1 Variables Held Constant

The model has been used to evaluate the effects of changing the most important parameters. In most of the calculations, the CO₂ removal and the stripping heat consumption were calculated, while keeping all the other parameters in table 1 constant. From a calculation viewpoint, this is probably the simplest. Another possibility had been to keep the percentage CO₂ removal constant, and calculate the heat duty and the necessary column height. This would give the possibility to optimize the trade-off between operation cost (due to heat consumption) and capital cost (due to column height). In the cases where the default Inside-Out algorithm did not converge, the Modified Hysim Inside-Out algorithm with adaptive damping was tried to obtain convergence. (Lars Erik Øi, 2007).

2.7.2 Circulation Rate

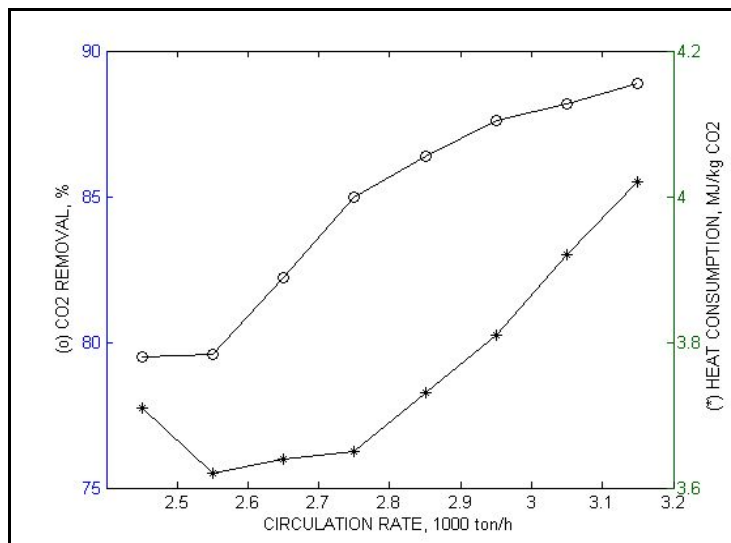


Figure 2.5: Circulation rate dependence (Lars Erik Øi, 2007)

The effect of increased circulation rate is that the removal grade increases. The results of the simulations are shown in Figure 2.7.2. A minimum calculated steam consumption is calculated to 3.62 MJ/kg CO₂ removed. (Lars Erik Øi, 2007).

2.7.3 Absorption Pressure

The absorption pressure is set to atmospheric pressure at the outlet and atmospheric pressure plus pressure drop at the inlet. The pressure inlet in the base case was 1.1 bars. In the case of a pressure drop of 0.5 bar, the percentage CO₂ removal increased to 87.1 % and the energy consumption was reduced to 3.59 MJ/kg CO₂ removed. (Lars Erik Øi, 2007).

2.7.4 Re-boiler Temperature

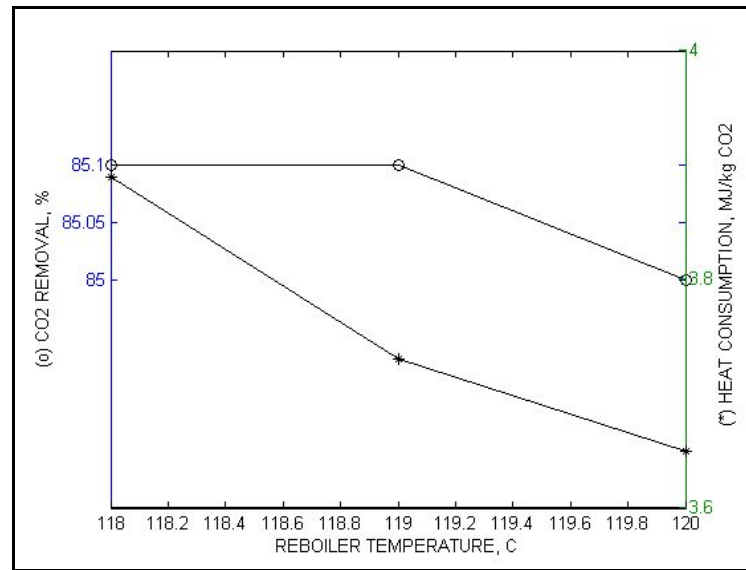


Figure 2.6: Re-boiler temperature dependence (Lars Erik Øi, 2007).

Increased re-boiler temperature gives purer amine solution and better CO₂ removal efficiency. However, amine degradation problems arise above 120°C. The temperature was varied between 118 and 121 °C. It was difficult to get converged solutions outside this range. At 121°C, an outside range warning was given. The results up to 120°C are shown in figure 2.7.4. (Lars Erik Øi, 2007).

2.7.5 Stripper Pressure

The stripper pressure was specified to 2 bar(abs) in the calculation. It was very difficult to get a converged solution at other pressures. A solution with a warning (outside range) was achieved with a pressure at 1.9 bar(abs). (Lars Erik Øi, 2007).

2.8.6 Minimization of heat consumption

There have been performed many Aspen HYSYS calculations at different conditions. One aim is to reduce the heat duty as much as possible. The lowest heat consumption calculated was 3.39 MW/kg CO₂ removed. The CO₂ removal efficiency

was then 93.8 %. This was obtained with gas temperature at 30°C, 16 absorption stages, stripper pressure 2.0 bars and re-boiler temperature at 200°C. At lower temperatures or more absorption stages, the calculation did not converge. (Lars Erik Øi, 2007).

CHAPTER 3

METHODOLOGY

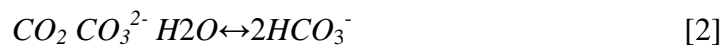
3.1 Flowsheet Analysis of the Industrial Acid Gas Removal Unit (AGRU)

Existing process flow diagram of Industrial AGRU is operated using Benfield process for removal of carbon dioxide (CO₂) and hydrogen sulfide (H₂S) from the feed gas to the plants. The removal of CO₂ from the feed gas is crucial in order to prevent dry ice formation in the downstream low temperature equipment which could lead to equipment plugging and production losses. It is also required to achieve ethane production specification.

The basic reaction for aqueous hot potassium carbonate solution and CO₂ is



Since the solution is strong electrolyte, it may be assumed that the metal is present only in the form of K⁺ ions, so reaction [1] may be more realistically represented in the ionic terms as:



The above reaction is evidently made up of a sequence of elementary steps. The carbonate ion first reacts with water to generate hydroxyl ions, which then react with CO₂ as follows :



Since reaction (3) is instantaneous reaction, reaction (4) is the rate-controlling step, so that rate equation for the reaction of carbon dioxide with un-promoted hot potassium carbonate leads to

$$r_{OH} = k_{OH}[OH][CO_2] - k_{-OH}[HCO_3^-] \quad [5]$$

where k_{OH} and k_{-OH} are forward and backward rate constants of reaction (4)

The unit is designed to remove CO₂ in the feed gas less than 0.2% from up to 8.0% CO₂ in the feed gas. The flowsheet of such acid gas removal process is shown in Figure 3.1.

The heated sour gas enters the bottom of the absorber tower at a temperature of around 90°C. In the absorber, the gas will flow countercurrent to the Benfield solution and removes the acid gases from the gas. At the top of the absorber, the sour gas will be washed to remove the entrained Benfield solution in tray section above a full drawn chimney tray at the top of absorber.

The water used for washing comes from condensate recovered from the CO₂ and pumped back to absorber through the acid knock out drum. The gas will then leave the AGRU. The Benfield solution in absorber, which is now rich with acid gases and impurities absorbed from the sour gas, leaves absorber to the hydraulic turbine and enter the top of regenerator. The pressure of the solution when leaving absorber is 601 kPa abs, but reduce to 557 kPa abs when entering top of the regenerator. The rich solution descends through the packed beds countercurrent to hot CO₂ and steam. The steam being produce by carbonate reboiler. The CO₂ was pulled from the lean solution in flash tank by motive steam. The CO₂ leaves regenerator contains water, hydrogen sulphide, mercaptans and small amount of the impurities. The water, which may contain some of Benfield chemicals will be condensed, knocked, and return to the solution in circulation in two stages. The water condensed will be knocked at acid gas knock out pot. The water recovered will used as wash water at the top of absorber.

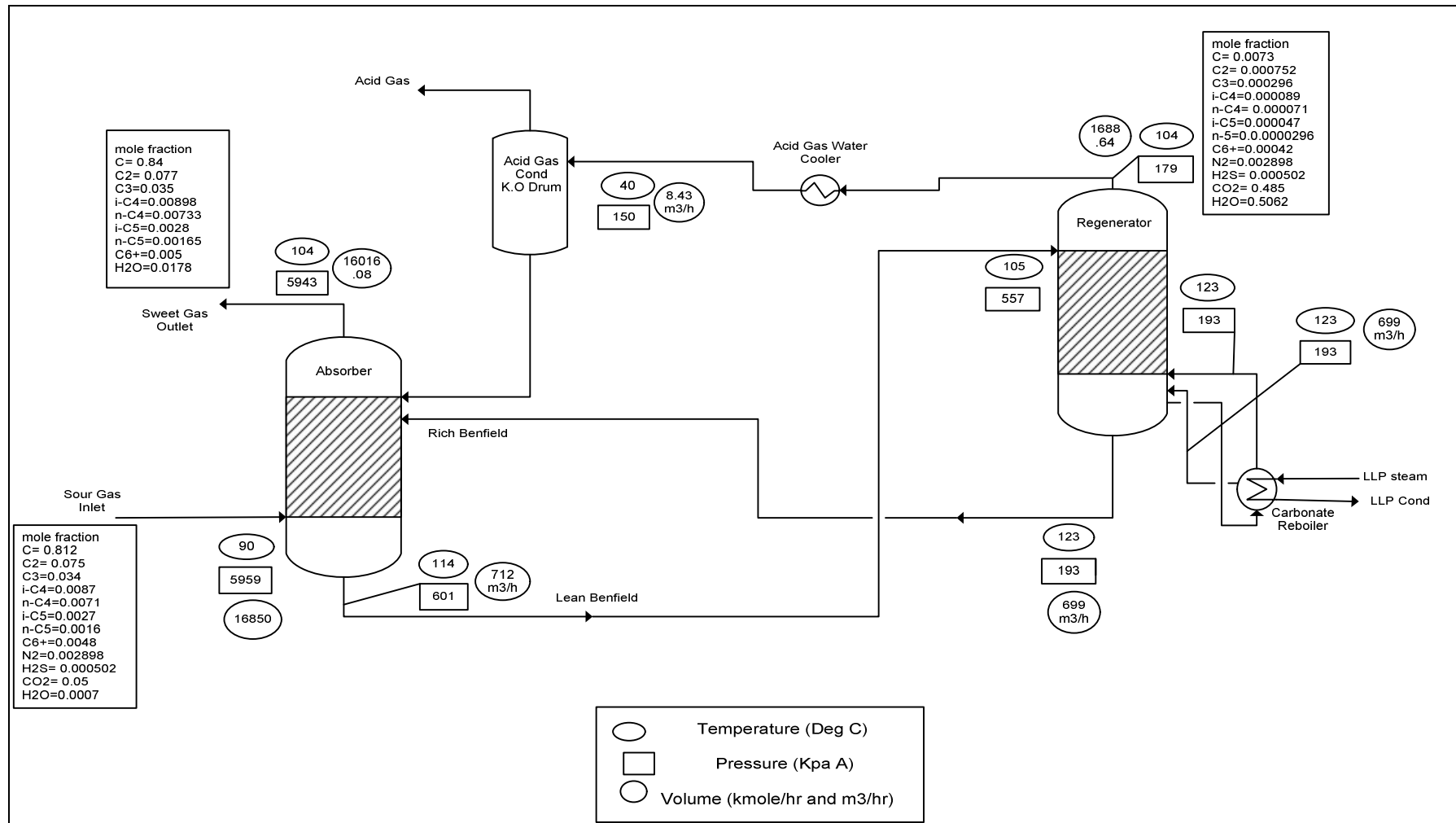


Figure 3.1: Flow sheet of Industrial Acid Gas Removal Unit (AGRU) using Benfield solution.

The regenerated solution will leave regenerator to lean solution flash tank for further removal CO₂. The hot CO₂ from lean solution flash tank will go to the booster pump and delivered to absorber. (Sanjay, 2003)

Table 3.1 : Benfield System Design Data (Sanjay, 2003)

Feed Gas Specification	<ul style="list-style-type: none"> • CO₂ – 8.0 mole % = 850.93 kmole/h • H₂S – 10 ppmV
Treated Gas Specification (AGRU outlet)	<ul style="list-style-type: none"> • CO₂ – 8.0 mole % = 850.93 kmole/h • H₂S – 10 ppmV

Table 3.1 above show that the design data for acid gas specification inlet and after treated. In real situation, the gas is not fully treated. The sour gas enter contain 850.93 kmole/h of CO₂ and sweet gas outlet contain 32.03 kmole/h CO₂. That means CO₂ are not fully removed from the gas. For H₂S, inlet 10ppmV, and in sweet gas still have 2.5ppmV H₂S.

3.2 Acid Gas Removal Unit Modification and Improvement using HYSYS Software

Aspen Hysys is the process-modeling tool for steady state simulation, design, performance monitoring, optimization and business planning for oil & gas production. With this software, rigorous steady state and dynamic models for plant design, performance monitoring, troubleshooting, operational improvement, and business planning and asset management can be performed. In HYSYS, many equations of state are applicable such as Peng-Robinson (PR), Lee-Kesler-Plocker (LKP), Soave-Redlich-Kwong (SRK) etc. The accuracy for each equation of states however is subjected to the thermodynamic behaviors of the system.

For this simulation, Peng-Robinson equation of state (PR EOS) is used because of the accuracy in calculating different unit operations like heat exchangers, pumps, distillation columns etc. The Peng-Robinson EOS has become the most popular equation of state for natural gas systems in the petroleum industry. The performance of the PR EOS and the SRK EOS, they are pretty close to a tie; they are “neck to neck,” except for a slightly better behavior by the PR EOS at the critical point. A slightly better performance around critical conditions makes the PR EOS somewhat better suited to gas/condensate systems. Earlier researchers prove this, which is, the Peng-Robinson equation, on the other hand, represents adsorption of a supercritical fluid such as ethane accurately on flat surfaces. It is capable of predicting the isotherm crossovers above the critical pressure found in experimental data. (Subramanian, R.; Pyada, H.; Lira, C. T, 1995). In porous materials, some success has been obtained, (Chen, J.; Tan, C.; Wong, D.; Lira, C. T.; Subramanian, R.; Orth, M, 1997) but the temperature dependence of adsorption is typically too weak. (Aaron D. Soule, 2000). Aspen HYSYS recommends Peng Robinson (Peng, D., Robinson, D.B., 1976).

Peng Robinson is regarded to be suitable to handle systems containing hydrocarbons, water, air and combustion gases, the typical components in a natural gas based power plant. Traditional equation of state models is not regarded to be suitable for non-ideal liquid systems. An amine solution is an electrolytic system and comprises chemical reactions. This is not expected to be well described with traditional equations of state. In this research, the researcher found that the calculated heat consumption of 3.65 MJ/kg CO₂ is regarded as realistic. This is slightly lower than normally found in literature, eg. Desideri^[8] which has a list of references with values mostly above 4.0 MJ/kg CO₂. If water wash is included in the highest value, this can explain the difference. The lowest calculated value of 3.39 MJ/kg CO₂ is regarded as an optimistic value. It might be regarded as a potential value for improvements. The optimum cost for heat consumption will probably be a trade-off between investment and operational cost (Lars Erik Øi, 2007). The CO₂ removal model developed in Aspen HYSYS is useful for evaluating the effects of changing amine circulation rate, absorption column height, absorption temperature and re-

boiler temperature. The reduced total efficiency in a gas-based power plant can be calculated. (Lars Erik Øi, 2007).

Modifications and improvement in term of column performance, energy consumption and pump duty schemes design are applied to the base case of acid gas removal process flow sheet. The main objective of such modifications and improvement is intently to reduce the current energy consumption, which is usually used in re-boiler to generate steam. In this work, the energy consumption reduction, column performance and pump duty schemes are being applied using the HYSYS software. Then, the obtained energy consumption reduction, column performance, pump duty value of each option is compared to the current energy consumption, column performance and pump duty requirement at which the percentages saving can be calculated.

Furthermore, in order to ensure that the designs of this scheme are performed successfully, the different solution will be use from the current solution used. Amine solution will replaced benfield solution to see the improvement in energy consumption, column performance and pump duty and will be comparing with the current process that is used benfield solvent as a solution. Finally, the result will be compare to the current or existing data to prove that by using amine the objectives of this project are achieve successfully. Below is the flowchart of the project from the beginning until the end of this project.

3.3 Summary of Methodology

In summary, methodology for evaluate existing process flow diagram of industrial AGRU based on four parameters that include absorption column removal efficiency, power consumption, heating duty and cooling duty is depleted in Figure 3.2

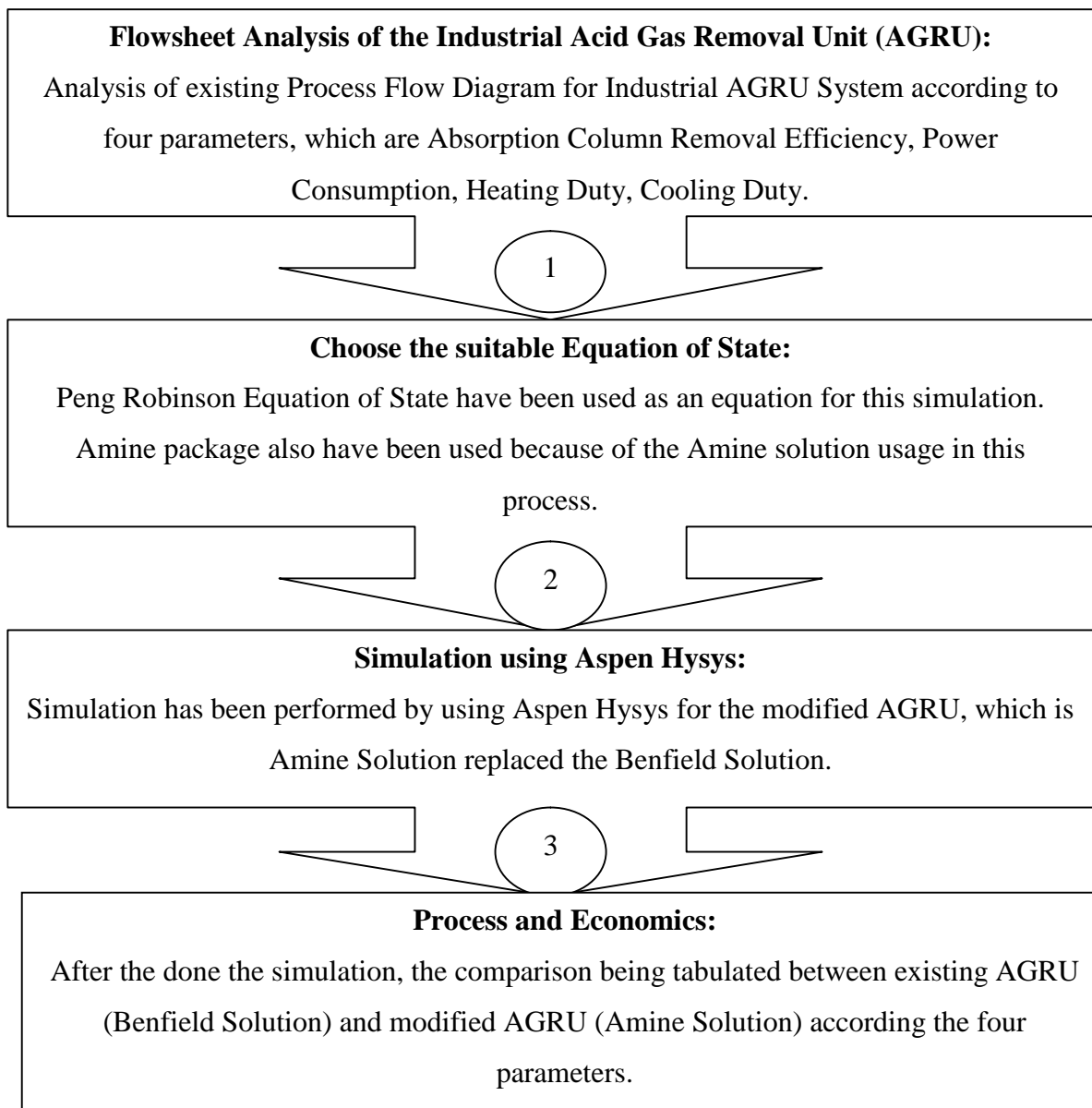


Figure 3.2: The Work Flowchart for evaluate existing process flow diagram of industrial AGRU

CHAPTER 4

RESULTS AND DISCUSSION

For this research, the main objective is to evaluate existing process flow diagram of industrial AGRU based on four parameters that include absorption column removal efficiency, power consumption, heating duty and cooling duty. The second objective is to replaced Benfield solution with Amine solution which process take place. Process improvement can be realized after making comparison for the four parameters highlighted above. Qualitative research is to gain an understanding of underlying reasons and motivations and to provide insights into the setting of a problem, generating ideas or hypothesis for later quantitative research. Meanwhile this research will also uncover prevalent trends in thought and opinion. Exploratory or investigative findings are not conclusive and cannot be used to generalize about the population of interest but able to develop an initial understanding and sound base for further decision making.

4.1 AGRU Modeling and Simulation

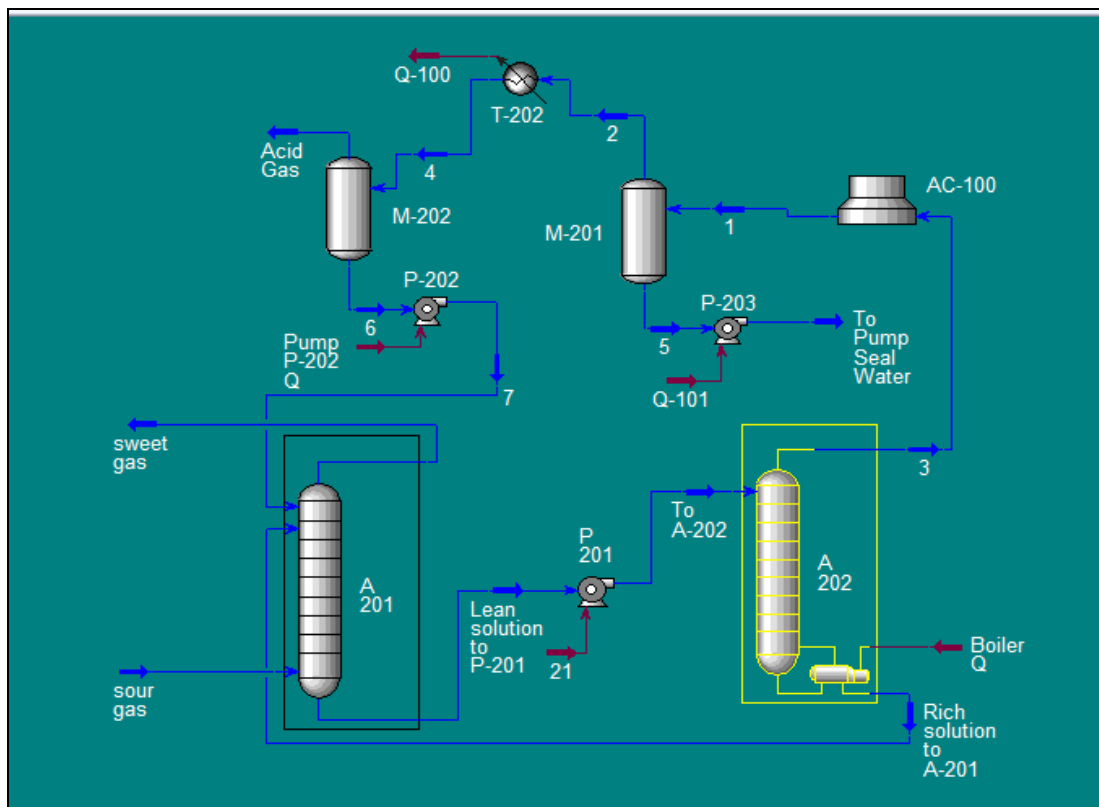


Figure 4.1: Aspen HYSYS model of CO₂ removal (Amine Solution)

The Aspen Hysys for CO₂ removal model is presented in Figure 4.1. Earlier simulation has been performed the same process data of existing AGRU using Benfield solution but with different equation of state. In AGRU using Amine solution, the Amine package has been used for fluid package and also Peng Robinson equation of state. Because of the difference in using equation of state, stripper column was over specified and no process equipments were converged. The other ways to make this process converge, some process data have been modified at P203, P202, T202, AC100 and stripping reboiler. As the result, the process equipment has been converged successfully.

4.2 Comparison between existing AGRU and modified AGRU

Comparison between manual calculation from data taken from existing process flow diagram of Industrial AGRU with Aspen Hysys results are shown in Table 4.1 below. The detailed are shown in APPENDIX A and B .

Table 4.1: Comparison between manual calculation and simulation results

Parameters	Existing AGRU that use Benfield Solution (manual calculation)	Modified AGRU that use Amine Solution (simulation result)	Saving (%)
Column Efficiency (%)	96	96	-
Power Consumption (kW)	2367.74	2102.24	11.21
Cost Power Consumption (RM/ year)	RM 8626150.40	RM 7658880.77	11.21
Heating Duty (Stripping reboiler using LLP steam kW)	5180	5180	-
Cost Heating Duty (RM/year)	RM 172656	RM 172656	-
Cooling Duty (gas water cooler ,kW)	2.6	2.3	11.54
Cost Cooling Duty (RM/year)	RM 32788.80	RM 27324	17
Total cost saving (%)			28.12

The comparison between existing conditions data calculation and simulation calculation is shown in Table 5 above in term of column efficiency, cooling duty, heating duty and power consumption. As we can see from the table, the values of cooling duty using Amine Solution (HYSYS) are decrease from 2.6 kW using

Benfield solution to 2.3 kW. The decreasing of cooling duty also effect the operating cost for cooling system, which is from RM 32788.80/year using Benfield solution decrease to RM 27324/year using Amine solution. It is about 17% of cost saving for cooling system per year.

It goes with power consumption for electricity usage. Total power consumption using Amine solution is about 2094.5 kW per month is lower than total power consumption using Benfield solution, which is 2360 kW per month. The electricity cost is decreasing perpendicular with decreasing of power consumption using Amine solution. It is 11.25 % cost saving in comparison to electricity cost using Benfield solution, which is RM 8597952 per year to RM 7630682.40 per year using Amine solution The same heat consumption calculated was 5180 kW per month CO₂ removed. The CO₂ removal efficiency was then 96 %. This was obtained with gas temperature at 30°C, 10 absorption stages, and stripper pressure 2.0 bars and re-boiler temperature at 123°C. At lower temperatures or more absorption stages, the calculation did not converge.

By using Amine solution, this unit can save about 29% of operating cost, which is about RM 972734.40 per year. This is because MDEA is tertiary amine and therefore carbamate formation with CO₂ does not take place in MDEA based system. MEA and DEA form Carbamates with CO₂. Therefore, operation with MDEA is far more stable with no spurious shutdowns over longer periods. MDEA also delivers energy savings from reduced reboiler duties (reflux ratio of 0.5 to 1.0) and lower overhead condenser duties. It has proved to be highly selective for absorption of H₂S when compared to CO₂ resulting in even lower circulation rates.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project has achieved their objectives, which are to evaluate existing process flow diagram of industrial AGRU based on four parameters that include absorption column removal efficiency, power consumption, heating duty and cooling duty. and to replace Benfield solution with Amine solution (MDEA). The CO₂ removal model developed in Aspen HYSYS is useful for evaluating the effects of changing amine reboiler temperature, heat and cooling consumption minimization, and column efficiency. The developed models can be developed further to improve amine absorption processes for CO₂ removal.

5.2 Recommendations

As the end of the study, there are some recommendations that should be made for next phase of this research. The calculated CO₂ removal process is a simplified process. Heat losses and some pressure losses are neglected. A real process contains more equipment, pipes and valves, and all this equipment has heat losses and pressure losses.

For the first step to improve the quality of the result is by using mixture of three type of amine solution although it has already used mixture of methyldiethanolamine (MDEA), and monoethanolamine (MEA), the addition of

secondary amine, diethanolamine (DEA) will make the solution more reactive and CO₂ reaction rate with the primary (MEA) and secondary (DEA) amines is much faster than with MDEA. Hence, by using mixture of primary, secondary and tertiary amine usually improve the plant performance

Amine gas sweetening plants can experience operating difficulties including foaming, failure to meet sweet gas specification, high solvent losses, corrosion, fouling of equipment, and contamination of the amine solution. To prevent this problems occur, for example foaming. An immediate method to control a foaming problem is the addition of antifoam at a location just upstream of the foam. Effective foam inhibitors for amine sweetening systems are silicone antifoams and polyalkylene glycols and use concentrated aqueous amine solutions. This is because concentrated amine solvent do not foam. By maintaining the temperature in Absorption column also can prevent problem occur.

As to improve the process Amine, absorbers should be change with structured packing to meet the H₂S requirement to meet pipeline specification. Amine Absorber structured packing can successfully meet a pipeline H₂S removal specification while slipping CO₂, and provide a cost savings due to decreased solvent consumption.

REFERENCES

Aspen Plus, AspenTech, Cambridge Mass., 2006.

Aspen HYSYS 2004.2, AspenTech, Calgary 2007.

Amundsen, T. (2007). CO₂-renewable Aspen HYSYS, Master Project, Telemark University College.

Ballard, D, "Cut Energy Costs for Amine Units" Proceedings of 59th GPA convention.

Bullin, J.A., John Polasek, and Joe Holmes. "Optimization of New and Existing Amine Sweetening Plants by Computer Simulation," Proceedings of the GPA meeting, San Antonio, Texas, March, 1981.

Bullin, J.A., John Polasek, and Joe Holmes. "Alternative Flow Schemes to Reduce Capital and Operating Costs of Amine Sweetening Units" Bryan Research & Engineering, Inc., Bryan, Texas, 2006.

Butwell, K. F., D. J. Kubek and P. W. Sigmund, "Alkanolamine Treating", Hydrocarbon Processing, March (1982).

Campbell, J. M., Gas Conditioning and Processing, Vol. 2, Campbell Petroleum Series, -Forman, Oklahoma 19/9).

Calgon Corporation, "Purification of Amines with Granular Activated Carbon", Brochure.

Chen, J.; Tan, C.; Wong, D.; Lira, C. T.; Subramanian, R.; Orth, M. *Ind. Eng. Chem. Res.* 1997, 36, 2808.

Gas Conditioning Fact Book, Dow Chemical Co, Midland, Michigan, (19-6 Scheirman, W. L, "Filter DEA Treating Solution" Hydrocarbon Processing August 1973).

Kidnay, A.J. and Parrish, William (2006). *Fundamentals of Natural Gas Processing*, CRC Press, Taylor & Francis Group.

Kohl, A. L. and F. C. Riesenfeld, Gas Purification, 3rd Ed., Gulf Publishing Co., Houston, 1979)

Lars Erik Øi. "Aspen HYSYS Simulation of CO₂ Removal by Amine Absorption from a Gas Based Power Plant". *Telemark University College, Norway*, October 2007.

Lee, I.J., Otto, F.D., Mather, A.E. (1975). Solubility of Mixtures of Carbon Dioxide and Hydrogen Sulfide in 5.0 N Monoethanolamine Solution, J. Chem. Eng. Data, 20, 161-163.

Peng, D., Robinson, D.B. (1976). A New Two-Constant Equation of State, Ind. Eng. Chem. Fundamental., 15 No.1, 59-64.

Perry Engineering Corporation, "Activated-Carbon Filter", Brochure.

Subramanan, R.; Pyada, H.; Lira, C. T. *Ind. Eng. Chem. Res.* 1995, 34, 3830

Vidaurri, F. C., and L. C. Kahre. "Recover H₂S Selectively from Sour Gas streams. *Hydrocarbon Processing*" pp. 333-337, Nov. 1977.

APPENDIX A

A.1 Power Consumption Calculation for Benfield Solution

I) Electricity cost for pump (AGRU PFD)

Operation time = 24 hrs = 330 days (35 days shutdown for maintenance)

Industry usage, electricity tariff = RM0.46/ kWh

i P-203 (A, B)

Duty = 7kW

$$\text{Duty per year basis} = 7kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{55440kWh}{year}$$

$$\text{Electricity cost} = \frac{RM0.46}{kWh} \times \frac{55440kWh}{year} = RM\ 25502.40 / year$$

ii P-202 (A, B, C)

Duty = 1565 kW

$$\text{Duty per year basis} = 1565kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{12394800kWh}{year}$$

$$\text{Electricity cost} = \frac{RM0.46}{kWh} \times \frac{12394800kWh}{year} = RM\ 5701608 / year$$

iii P-201 (Lean Solution Pump)

Duty = 788 kW

$$\text{Duty per year basis} = 788kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{6240960kWh}{year}$$

Electricity cost =

$$\frac{RM0.46}{kWh} \times \frac{6240960kWh}{year} = RM2870841.60/year$$

A.2 Heating Duty Calculation

I) Steam cost calculation for Stripping reboiler.

Use LLP Steam

LLP Steam price = RM2/ton

Duty = 5180 kW

Flow = 10.9 ton/ hr = 10.9 m³/ hr

$$\text{Steam cost} = \frac{10.9ton}{hr} \times \frac{RM2.00}{ton} \times \frac{24hr}{1day} \times \frac{330days}{1year} = RM172656/year$$

A.3 Cooling Duty Calculation

I) cooling water cost calculation for Gas Water Cooler

Duty = 2.6 kW

Flow = 3.6 m³/hr

Operation time = 24 hr = 330 days

Water Tariff = RM1.15/ m³

$$\text{Cooling water cost} = \frac{3.6m^3}{hr} \times \frac{24hr}{1day} \times \frac{330day}{1year} \times \frac{RM1.15}{m^3} = RM32788.80/year$$

A.4 Column Efficiency

I) Column efficiency based on CO₂ removal

$$\text{Column efficiency} = \left(\frac{850.93 \frac{kmole}{hr} - 32.03 \frac{kmole}{hr}}{850.93 \frac{kmole}{hr}} \right) \times 100\% = 96.23\%$$

APPENDIX B

B.1 Power Consumption Calculation for Amine Solution (HYSIS)

I) Electricity cost for pump

Operation time = 24 hrs = 330 days (35 days shutdown for maintenance)

Industry usage, electricity tariff = RM0.46/ kWh

i P-203 (A, B)

Duty = 6.5kW

$$\text{Duty per year basis} = 6.5kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{51480kWh}{year}$$

$$\text{Electricity cost} = \frac{RM0.46}{kWh} \times \frac{51480kWh}{year} = RM 23680.80 / year$$

ii P-202 (A, B, C)

Duty = 1300 kW

$$\text{Duty per year basis} = 1300kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{10296000kWh}{year}$$

$$\text{Electricity cost} = \frac{RM0.46}{kWh} \times \frac{10296000kWh}{year} = RM 4736160 / year$$

iii P-201 (Lean Solution Pump)

Duty = 788 kW

$$\text{Duty per year basis} = 788kW \times \frac{24hr}{1day} \times \frac{330days}{1year} = \frac{6240960kWh}{year}$$

$$\text{Electricity cost} = \frac{RM 0.46}{kWh} \times \frac{6240960 kWh}{year} = RM 2870841.60 / year$$

B.2 Heating Duty Calculation

I) Steam cost calculation for Stripping reboiler.

Use LLP Steam

LLP Steam price = RM2/ton

Duty = 5180 kW

Flow = 10.9 ton/ hr = 10.9 m³/ hr

$$\text{Steam cost} = \frac{10.9 \text{ ton}}{\text{hr}} \times \frac{RM 2.00}{\text{ton}} \times \frac{24 \text{ hr}}{1 \text{ day}} \times \frac{330 \text{ days}}{1 \text{ year}} = RM 172656 / year$$

B.3 Cooling Duty Calculation

I) cooling water cost calculation for Gas Water Cooler

Duty = 2.3 kW

Flow = 3000 kg/ hr = 3 m³/ hr

Operation time = 24 hr = 330 days

Water Tariff = RM1.15/ m³

$$\text{Cooling water cost} = \frac{3 \text{ m}^3}{\text{hr}} \times \frac{24 \text{ hr}}{1 \text{ day}} \times \frac{330 \text{ day}}{1 \text{ year}} \times \frac{RM 1.15}{\text{m}^3} = RM 27324 / year$$

B.4 Column Efficiency

I) Column efficiency based on CO₂ removal

$$\text{Column efficiency} = \left(\frac{850.93 \frac{\text{kmole}}{\text{hr}} - 32.03 \frac{\text{kmole}}{\text{hr}}}{850.93 \frac{\text{kmole}}{\text{hr}}} \right) \times 100\% = 96.23\%$$