Design Of CO_2 Removal System At Natural Gas Reserves

by

Norma Syahida binti Mazlan

Dissertation submitted in partial fulfillment of
the requirements for the
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Approved by,

____
(Dr .Murni Melati Ahmad)

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TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

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

NORMA SYAHIDA BINTI MAZLAN

ABSTRACT

Natural gas is one of the principle sources of energy for many of our day-to-day needs and activities. It burns to form carbon dioxide (CO_2) and water (H_2O) without or with minimal smoke subject to composition. The presence of carbon dioxide in natural gas prior to combustion would lower the heating value of the gas, increase the volume of gas that must be transported and increase the environmental impact. Most of the existing acid gas treatment systems in gas plants are limited in CO_2 removal capacity of 30 mol%. Hence this project aims to identify the feasible routes of the flowsheet for a CO_2 capture system at offshore gas platforms to reduce the CO_2 concentration in the raw natural gas from 20 – 90 mol% to 10 mol% before being sent to the acid gas treating plant in gas refineries using aminated resin. This feasibility of the CO_2 removal system is investigated using simulation based approach in PETRONAS iCON software. The simulation is used to investigate the effect of mass fraction of aminated resin, lean aminated resin temperature and lean aminated resin circulation rate within the range of 0.25-0.55, 37-45°C and 3000-8000 m^3/hr respectively on acid gas loading and percentage recovery of CO_2. Based on the simulation results, it is predicted that the aminated resin has the potential to reduce CO_2 from high CO_2 loaded natural gas to meet the objective which is less than 10 mol% CO_2 content. The best operating conditions are identified at mass fraction of 0.45, lean aminated resin temperature of $41°C$ and circulation rate of aminated resin of $7000m^3$/hr. A preliminary economic potential study shows that it is also economically viable.

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PROJECT BACKGROUND

1.1 Background of Study

1.1.1 Natural Gas

Natural gas is a gas consisting primarily of methane and varying amounts of ethane, propane, butane, and even higher molecular weight hydrocarbons, an amount of water vapor, small amounts of nonhydrocarbon gases such as hydrogen sulfide, carbon dioxide, and mercaptans such as methanethiol and ethanethiol, and even neutral gases such as nitrogen and helium.The gas composition depends on the geological area, as well as the underground deposit type, depth, and location (Avidan et al., 2001).

Natural gas is colorless, shapeless, and odorless in its pure form. It is also combustible, where it gives off energy when burned. However, it is clean burning and emits lower levels of potentially harmful byproducts into the air.

Due to the contaminants in natural gas such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other sulfur compounds such as mercaptans, it should be undergo gas processing to meet required specification for acceptance by a gas purchaser. As mentioned by Mallinson (2004), gas processing is the preparation of raw natural gas as it is produced from the reservoir for transportation to markets for utilization. Carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other sulfur compounds such as mercaptans are compounds that may require complete or partial removal. Natural gas from some wells contains significant amounts of hydrogen sulfide and carbon dioxide and is usually referred to as sour gas. Sour gas is undesirable because the sulfur compounds it contains can be extremely harmful, even lethal, to breathe, and the gas can be extremely corrosive (Kohl and Riesenfeld, 1985). The purpose of this removal is also to produce a sales gas stream that meets specifications. These specifications are mainly intended to meet pipeline requirements and the needs of industrial and domestic consumers.

1.1.2 History of Natural Gas

Natural gas is considered as nonrenewable fossil fuel. There are many different theories as to the origins of fossil fuels. The most widely accepted theory says that fossil fuels are formed from the remains of tiny sea animals and plants that died 200-400 million years ago. When these tiny sea animals and plants died, they sank to the bottom of the oceans where they were buried by layers of sand and silt. Over millions of years, these layers become thicker over the years. The enormous heat and pressure turned them into oil and gas. Based on the research, most scientists believe that the pressure, combined with the heat of the earth, changed this organic mixture into petroleum and natural gas.

1.1.3 Natural Gas Resources

Natural gas, as transported to domestic and industrial consumers, is much different from the natural gas that appears at the wellhead. According to Mokhatab, et al., natural gas used by consumers is composed almost entirely of methane (usually *>95%* by volume). However, natural gas found at the wellhead, although still composed primarily of methane (usually > *65%* by volume), is by no means as pure as required by sales specifications.

1.1.4 Market Survey for Natural Gas Demand

Findings from U.S. Energy Information Administration (2010) clearly indicates that total natural gas consumption worldwide increases 44 percent in the IEO2010 Reference Case, from 108 trillion cubic feet in 2007 to 156 trillion cubic feet in 2035 as in Figure 1.1. However, demand for natural gas slowed in 2008 as the global economic recession began to affect world energy markets, and in 2009 world consumption of natural gas contracted by an estimated 1.1 percent. As economies begin to recover, demand for natural gas rebound. In the Reference case, it can be estimated that the world natural gas demand would substantially increase for the coming few years as natural gas consumption expands by an average of 1.8 percent per year from 2007 to 2020. From

2020 to 2035, estimation shows the growth in consumption of natural gas slows to an average of 0.9 percent per year, as prices rise and increasingly expensive natural gas resources are brought to market. This shows that natural gas has the potential to become the future dominant fuel source since natural gas produces less carbon dioxide when it is burned than does either coal or petroleum, governments implementing national or regional policies to reduce greenhouse gas emissions may encourage its use to displace other fossil fuels.

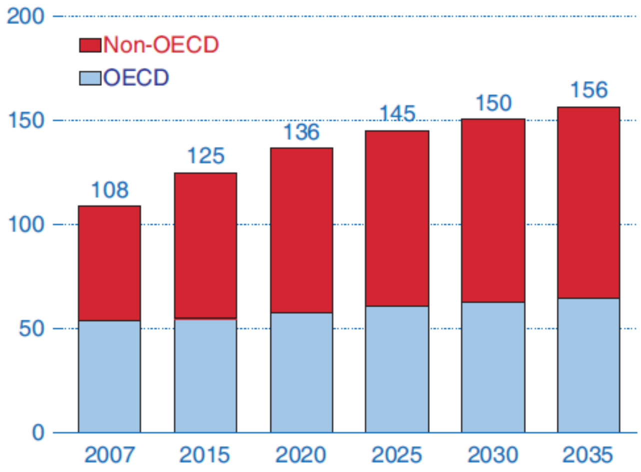


Figure 1.1 : World natural gas consumption 2007 -2035 (trillion cubic feet)

However, in addition to the routine production of low quality and sour natural gas reservoirs, in recent years reduced petroleum reserves have resulted in development of enhanced oil recovery techniques, such as CO_2 miscible flooding , which can result in production of gas streams having high acid gas content as high as 98% (Clifton et al., 1985). High CO_2 content in natural gas will result in low heating quality of the gas. It also release high amount of CO_2 which is one of the green house gases when it burned.

Thus, it is important to give attention towards the quality of natural gas in order to meet natural gas specification and reduce CO_2 gas emission. Hence, the project will consider producing a feasible flowsheet which would help the gas companies to meet their customers’ specifications in more environmentally friendly way.

1.1.5 Carbon Dioxide Content of Various Natural Gas Reserves in Malaysia

Abdul Rahim (2008) reported that, a total of 379 fields have been discovered in Malaysia as of January 2008 of which 163 are oil fields and 216 are gas fields. Table 1.1 below is the summary of high CO_2 content of natural gas reserves in Malaysia.

Table 1.1: Summary of High CO_2 Gas Fields in Malaysia (Nasir and Abd Rahman, 2006)

Peninsular Malaysia					
Holder	Field	Total EUR (TSCF)	EUR Net of CO_2 (TSCF)	CO_2 Content	CO_2 Volume (TSCF)
PETRONAS	Bujang	1.47	0.5	66%	0.97
PETRONAS	Sepat	1.2	0.48	60%	0.72
PETRONAS	Noring	0.58	0.23	60%	0.35
PETRONAS	Inas	1.04	0.42	60%	0.62
PETRONAS	Tangga Barat	0.33	0.22	32%	0.11
PCSB	Ular	0.14	0.07	50%	0.07
PCSB	Gajah	0.12	0.06	50%	0.06
PCSB	Bergading	1.36	0.82	40%	0.54
PCSB	Beranang	0.08	0.06	28%	0.02
EMEPMI	Palas NAG	0.38	0.2	46%	0.18
TOTAL		6.7	3.06		3.64
Sarawak					
Holder	Field	Total EUR (TSCF)	EUR Net of CO_2 (TSCF)	CO_2 Content	CO_2 Volume (TSCF)
PETRONAS	K5	25.65	7.7	70%	17.95
PETRONAS	J5	5.37	0.7	87%	4.67
PETRONAS	J1	1.43	0.59	59%	0.84
PETRONAS	T3	1.04	0.39	62%	0.65
PETRONAS	Tenggiri Mrn.	0.33	0.18	47%	0.15
TOTAL		33.82	9.56		24.26

Based on the table above, it shows that majority of natural gas field in Malaysia contain high CO_2 content of about 28 – 87% which proves the significance of the project.

1.2 Acid Gas Removal Process

Natural gas usually contains some impurities such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), water vapor and heavy hydrocarbons such as mercaptans. These compounds are known as "acid gases". 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 (Dow Chemical, 1998). The removal of acid gas (CO_2, H_2S and other sulfur components) from natural gas is often referred to as gas sweetening process. According to Abiodon (2005), acid gases present in the natural gas need to be removed in order to; increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and meet natural gas specification.

In this project, the main concern is to reduce the amount of CO_2 concentration in the natural gas before being distributed to other plant. There are a numbers of ways to remove carbon dioxide in natural gas. According to Ebenezer (2005), varieties of processes and improvements have been developed over the years to treat certain types of gas with the aim of optimizing capital and operating cost, meet gas specifications and for environment purpose. There are numbers of CO_2 removal processes available currently. Among those are;

1.2.1 Absorption Processes (Chemical and Physical absorption)

In an absorption process, one or more components in a gas phase transfer to a liquid phase. Removal of CO_2 by physical absorption process is based on the solubility of CO_2 within the solvents while chemical absorption process is based on exothermic reaction of the solvent with the gas stream to remove CO_2 present. The absorbed components can be regenerated by changing the equilibrium temperature or pressure, or by other chemical means. However, there are some limitations with the process such as formation of heat stable salt, foaming, corrosion problem, loss of solvent and high energy requirement (Ebenezer, 2005 and Andrew).

1.2.2 Adsorption Process (Solid Surface)

Adsorption process is the selective mass transfer of one or more solutes from a fluid phase (gas / liquid) to a batch of solid particles. In the process, a chemical reaction or ionic bonding between the solute and adsorbent surface will normally take place in a fixed bed reactor. But, there is possibility in adsorbent poisoning and hydrocarbon loss. Besides, temperature swing adsorption is expensive for bulk CO_2 removal. It is also suitable for small scales of operation only. However, this process is able to handle wide variation in flow and H_2S levels. It also produces high product gas purity (Ebenezer, 2005).

1.2.3 Physical Separation (Membrane, Cryogenic Separation)

In a membrane separation, the gas molecules permeate through a thin film from the high-pressure side to a lower pressure side by absorption and diffusion process. Gas separation therefore works on the principle that some gases are more soluble in, and pass more readily through polymeric membrane than other gases.

Cryogenic separation utilises the thermodynamic properties of the gases to remove a specific component at low temperature, produced through compression followed by cooling, refrigeration and Joule Thompson expansion. It is suitable for recovering CO_2 to high purity. However, with cryogenic process, it is difficult to sustain low energy requirement while avoiding CO_2 freezing (Ebenezer, 2005).

1.2.4 Hybrid Solution (Mixed Physical and Chemical Solvent)

Ebenezer (2005) states that the hybrid separation processes combines the properties of physical and chemical solvent for effective and selective removal of acid gas from natural gas. A hybrid system of membrane with absorption is desirable if the product is to contain less than 8mol% of CO_2.

The selection of the solvent for gas sweetening depends on process objectives and characteristics of the solvents, such as selectivity of CO_2, H_2S and etc, ease of handling water content in feed gas, ease of controlling water content of circulation solvent, concurrent hydrocarbon loss or removal with acid gas removal, solvent cost, solvent supply, chemical inertness, thermal stability and proven plant performance for various processing techniques (Ebenezer, 2005).

1.3 CO_2 Adsorption Mechanism

The aminated resin proposed to be utilized in the CO_2 removal system at the gas reserves is a solid material where adsorption process is expected to occur. Adsorption is basically the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid.

In this case, the aminated resin is the adsorbent which it adsorb the carbon dioxide (adsorbate). More often, for the adsorbents being used for CO_2 removal the adsorption process is considered to be gas-solid interaction. Coulson et al (1991) identifies the adsorption process occurs in three stages as it is described in Figure 1.2. Firstly, a single layer of molecules builds up over the surface of the solid. Then this monolayer may be chemisorbed and will be associated with a change in free energy which is characteristic of the forces which holds it. As the fluid concentration is further increased, second and third layer form a physical adsorption; the number of layers which can form may be limited by the size of the pores. Finally for the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate (Coulson et al., 1991).

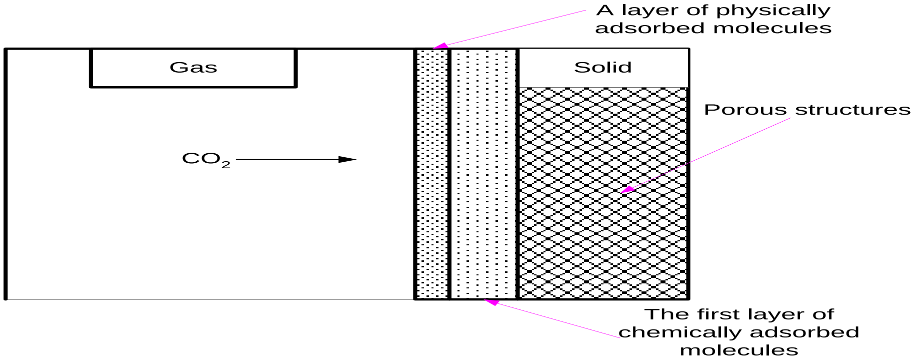


Figure 1.2: A Gas-Solid Carbon Dioxide Adsorption Mechanism

1.4 Problem Statement

Acid gas removal unit plays an important role in removing CO_2 and H_2S to achieve the gas specification requirement. In most plants that use the natural gas as their feed, the gas must pass through acid gas removal unit in order to remove acid gases before being processed in other systems. However, the existing proven and economically viable technologies being used for CO_2 removal from natural gas, such as absorption on liquid amines, adsorption on solid materials and membranes have a maximum of 30 mol% CO_2 removal efficiency (Brian and Swallow, 1984).

New sources of natural gas have been recently explored where new wells are drilled and it is discovered that this natural gas is having a carbon dioxide content of 20-90 mol% and flowing at high pressure. Therefore, the existing acid gas treating plant may not be able to remove high concentration of carbon dioxide content in the raw natural gas to a desired specification due to limitation of acid gas removal capability to remove high CO_2 concentration.

Thus, in order to minimize the CO_2 concentration in the raw natural gas and at the same time complement the existing CO_2 treatment unit in refineries, it is proposed to install a system of acid gas removal at the offshore that uses a newly and specially designed aminated resin. The system would be expected to reduce the concentration of carbon dioxide before the gas being directed to amine treating plants at the gas refineries.

1.5 Objectives

1. To identify the feasible routes of the flowsheet for a CO_2 removal system containing aminated resin at offshore gas platforms to reduce the CO_2 concentration in the raw natural gas from 20 – 90 mol% to 10 mol% before being sent to the acid gas treating plant in gas refineries.
2. To develop the feasible flowsheet for the CO_2 removal system and simulate the flowsheet in iCON to identify the best operating parameters for the system.
3. To perform a preliminary economic potential evaluation for the system.

1.6 Scope of Work

The overall scope of this study is to investigate the feasibility routes of CO_2 removal system at natural gas reserves that will provide cost effective, reliable and environmentally friendly. Conceptual studies, evaluation of processing options, economic evaluation and determination of optimal operating parameters are possible activities to be undertaken during the project.

Figure 1.3 illustrates the overall natural gas processing facilities including the proposed acid gas removal system of this project. It would consist of gas-oil separator, condensate separator, gas sweetening unit and plant operation.

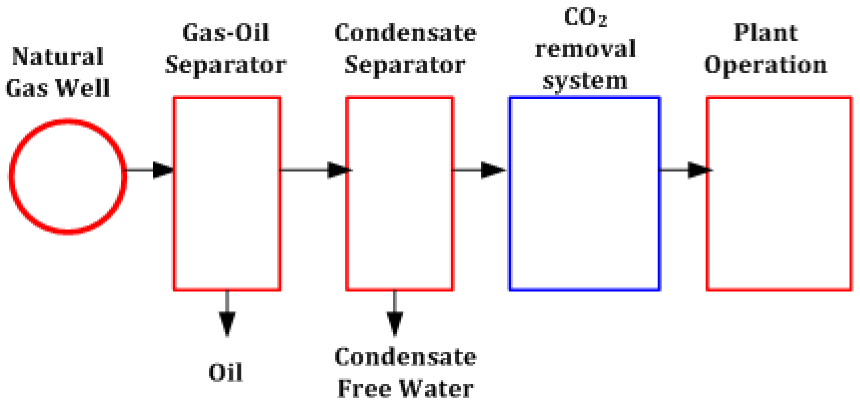


Figure 1.3: The proposed CO_2 removal system at offshore gas plant

Natural gas processing begins at the wellhead. Oil and natural gas are often found together in the same reservoir. Most natural gas production contains, to varying degrees, small (two to eight carbons) hydrocarbon molecules in addition to methane. Although they exist in a gaseous state at underground pressures, these molecules will become liquid (condense) at normal atmospheric pressure. Collectively, they are called condensates or natural gas liquids. The processing of wellhead natural gas into pipeline-quality dry natural gas can be quite complex and usually involves several processes to remove: oil, water; elements such as sulfur, helium, and carbon dioxide and natural gas liquids. Thus, it is usually passed through field separators at the reserves to remove those components. In addition to those four processes, it is often necessary to install scrubbers and heaters at or near the wellhead. The scrubbers serve primarily to remove sand and other large-particle impurities (Energy Information Administration, Natural Gas Annual, 2004).

The main focus of this project is more on developing a practical flowsheet of the acid gas removal and disposal system. Up on treatment in the proposed acid gas removal system with the target to achieve product specification of < 10mol% of CO_2, the gas will be sent to existing acid gas treatment plants for further purification to meet customer’s specifications.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas Sweetening

Natural gas usually contains some impurities such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), water vapor (H_2O), and heavy hydrocarbons such as mercaptans. These compounds are known as “acid gases”. Natural gas has a wide range of acid gas concentrations, depending on the nature of the rock formation from which it comes. The removal of acid gas (CO_2, H_2S and other sulfur components) from natural gas is often referred to as gas sweetening. According to Ebenezer (2005), acid gases present in the natural gas need to be removed in order to; increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and meet natural gas specification.

In this project, the main concern is to reduce the amount of CO_2 concentration in the natural gas before being distributed to other plant. Ebenezer (2005) have identified six potential carbon dioxide removal processes which are physical absorption process such as selexol process, fluor process and rectisol process, chemical absorption process, membrane process, adsorption process, cryogenic process and hybrid separation process.

Currently for industrial applications amine treating plants are used to remove CO_2 from natural gas streams. Amine has a natural affinity for CO_2 allowing it to be efficient and effective removal process.

2.2 Amine Process

Arnold and Maurice (1999) state that amine can be categorized into three groups which are primary, secondary and tertiary amine. Primary amine is stronger than secondary amines, which is stronger than tertiary amine. The stronger base the amine is, more reaction towards CO_2 and H_2S gases occurred and it will form stronger bond (Mallinson, 2004).

Jenkins and Haws (2001) points out that primary amine react directly with hydrogen sulphide (H_2S), carbon dioxide (CO_2) and carbonyl sulphide (COS). Examples of primary amines used in refineries include monoethanolamine (MEA) and the proprietary Diglycolamine agent (DGA). Secondary amines react directly with H_2S and CO_2, and react directly with some COS. The most common secondary amine used is diethanolamine (DEA) and diisopropanolamine (DIPA). Tertiary amines react directly with H2S, react indirectly with CO_2, and react indirectly with little COS. The most common example of tertiary amine used in refineries is methyldiethanolamine (MDEA) (Jenkins and Haws ,2001).

According to Polasek and Bullin (1994), there are a few important criteria to be considered in the selections of an amine for gas sweetening. The primary concern is that the sweetened gas should meet the required purification with respect to H_2S and CO_2. Then the selection of amine should optimize equipment size and minimizes plant operating costs. Other considerations in the selection of amines for design or existing plant evaluation include amine circulation rate, reboiler/ condenser size and duty, H_2S and CO_2 absorption from the sour gas and the corrosion problem.

Andrew clearly indicates that the following reactions may be used to represent the chemistry of acid gas absorption using aqueous amine solutions.

$CO_2 + H_2O + R_iNH_{3-i} \Leftrightarrow R_iNH_{4-i}^{+} + HCO_3^{-}$ ……………………………….. (2.1)

$H_2O + R_iNH_{2-i}COO \Leftrightarrow R_iNH_{3-i} + HCO_3^{-}$ …………………………………..(2.2)

$H_2S + R_iNH_{3-i} \Leftrightarrow R_iNH_{4-i}^{+} + HS^{-}$ …………………………………………..(2.3)

In the reaction above, R represents an organic attachment.The index *i* in Reactions 2.1 and 2.3 can vary between 1 and 3, representing primary, secondary and tertiary amines. The index *i* in Reaction 2.2 can vary between 1 and 2, representing primary and secondary amines. Only primary and secondary amines form carbamate so Reaction 2.2 applies to these amines.

Amine-based, wet scrubbing systems have been proposed as capture techniques for CO_2 removal from flue gas streams, but are energy intensive due to the large amount of water needed in these systems. Excessive water is required because of the mechanism, corrosiveness and air flow problems created by the use of monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) in these aqueous-based, CO_2-capture systems (Gray et al.,2005).

Gray et al. (2005) had proposed the reaction sequences in aqueous system using primary and secondary alkanolamines reacting with dissolved CO_2 as in Figure 2.1. According to Fig. 2.1, the majority of the CO_2 captured will result in the formation of bicarbonate in these liquid amine capture systems. In aqueous media, there is a requirement of 2 mol of amine/mol of CO_2 for the formation of stable bicarbonate compounds resulting in the capture of CO_2.

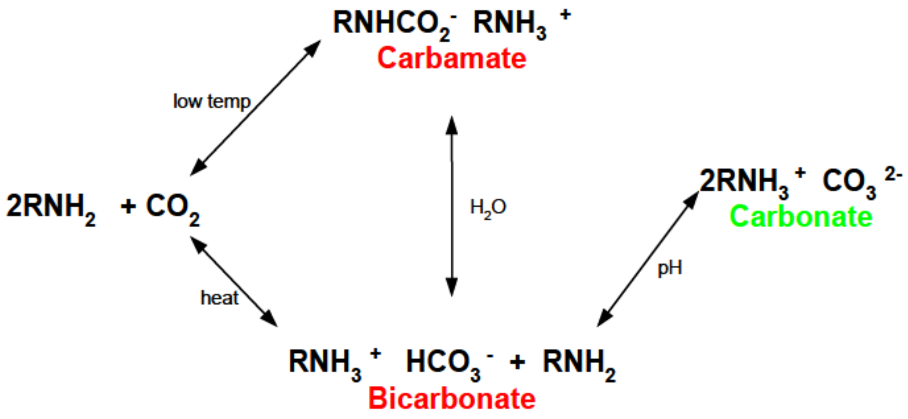


Figure 2.1 : Reaction Sequence using Liquid Solvents (Champagne et al.,2005)

2.3 Amine Contaminants

According to Haws (2001), amine contaminants can be grouped into five distinct categories:

(1) heat stable salts
(2)degradation,
(3) injection chemicals
(4) hydrocarbons
(5) particulates.

All of these contaminant categories can typically be present in any given amine system at the same time, although the amount of each one can vary from insignificant to several per cent.

2.3.1 Removal of Contaminants

Filtration is the preferred method if suspended solids are the only contaminant and charcoal filtration can be used to control hydrocarbon and injection chemicals. Heat stable salt can be neutralized, usually with sodium hydroxide, which will free up the amine bound to HSS anion. However, neutralization only changes the HSS from an amine HSS to a sodium HSS, but does not remove any contaminants from the system. Degradation product can be removed using reclaimer.

2.4 Methyldiethanolamine

The aminated resin used in this project is a resin that has been functionalized with methyldiethanol amine (MDEA) which is a type of tertiary amine. Bullin et al. (1990) states that MDEA is used in purifying the gases particularly natural gas for the bulk removable of CO_2 and also used as a scrubbing and extracting agent in gas treatment. MDEA is well known for its relatively slow reaction rate for CO_2. However it can be used in natural gas plant for removal bulk CO_2. Bulk carbon dioxide removal can be realized with methyldiethanolamine when the CO_2:H2S ratio ranges from 100 to 1,000 (Huntsman).

There are some characteristics of MDEA which make it attractive for CO_2 removal such as high solution concentration up to 50 – 55wt%, high acid gas loading with low corrosion problem, slow degradation rates, lower heats of reaction(600 BTU/lb CO_2 and 522 BTU/lb H_2S) and low vapor pressure and solution losses. But, there are also disadvantages associated with this MDEA which are slow reaction rate with CO_2, tendency to foam at high concentration and higher cost. These disadvantages with this MDEA is usually can be overcome to an acceptable level such as to increase reaction rates towards CO_2, small concentration amount of reactive primary or secondary amine can be added to form a mixtures of amines in water. Foaming problem can also be prevented by using silicon based and a few other types of antifoam agents. (Bullin et al.,1990).

According to Polasek and Bullin (1994), lower percentage of weight of MDEA are typically used in very low pressure. MDEA cannot be expose to oxygen otherwise it will form corrosive acid, where if not removed in the system, can result in the buildup of iron sulfide in the system. Polasek and Bullin (1994) also state that due to lower heat of reaction, MDEA can be employed in pressure swing plants for bulk CO_2 removal. In pressure swing plant, the rich amine is merely flashed at or near atmospheric pressure with little or no heat is added for stripping. Reaction of MDEA with CO_2:

$$CO_2 + R_1R_2R_3N + H_2O \leftarrow\rightarrow R_1R_2R_3NH^+ + HCO_3^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.4)$$

Since MDEA is a tertiary type of amine, it does not have a hydrogen atom attached to it. Therefore it cannot react directly with CO_2 to form carbamate. The CO_2 reaction can only occur after the CO_2 dissolves in water to form a bicarbonate ion.

2.5 Solid Sorbent

Recently, several solid sorbets have been utilized to remove CO_2 from gas streams. Champagne et al. (2005) state that the use of solid sorbents can reduce the energy intensity of current capture processes. Besides it can improve the capture capacity of sorbents compared to the solvent. The use of solid sorbent also can eliminate the corrosion problems associated with liquid amine system. This solid can increase the available contact surface as well, thus increasing the CO_2 removal from natural gas.

Gray et al. (2005) demonstrated the invention of producing low cost CO_2 capture sorbent. The sorbent are produced via simple reaction whereby the amine is modified to increase secondary amine functionalities, and the resulting amine is then incorporated into the pore volume of a solid substrate. Typically, the incorporation process is conducted in organic solvent media. The feature of this sorbent is that it is capable to adsorb CO_2 from 25 ^oC to 65 ^oC via a combination of both physical and chemical adsorption process. An advantage of this invention is that these sorbent can adsorb at temperature above normal ambient temperature and well above 30 ^oC. Regeneration of the sorbent can be accomplished by heating to around 90 ^oC and inexpensive.

Moreover, Hunter et al. (1986) elaborated the adsorption of CO_2 on polystyrene amine. The polystyrene resin has been functionalized with amine groups to chemically treat the surface of carbon-based material to improve its adsorptive capabilities. The resin of this invention is formed from chloromethylated polystyrene and tertiary amine with the chemical structure as in figure 2.2.

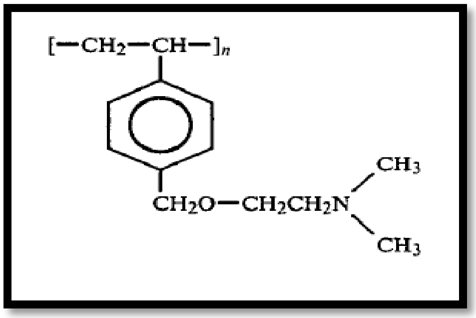


Figure 2.2 : Chemical Structure of tertiary polystyrene amine , Hunter et al. (1986)

Bjørnar et al. (2008) carried out experiment on three different porous metal organic framework (MOF) materials with and without uncoordinated amine functionalities inside the pores in order to prove the best adsorption capacity of amine functionalized adsorbents. The materials have been characterized and tested as adsorbents for carbon dioxide. At 298 K the materials adsorb significant amount of carbon dioxide, the amine functionalized adsorbents having the highest CO_2 adsorption capacities.

Zhang et al. (2004) reported the kinetics measurements for the adsorption of dissolved CO_2 on the immobilized amines (primary or secondary amines) and for desorption of CO_2-loaded immobilized amines (IA) with MDEA with the liquid medium fixed-bed column. The experimental work showed the adsorption rate of dissolved CO_2 with IA ($k_{liquid–solid} = 1.54\times10^{-7}$ m/s, 298 K) and the desorption rate of CO_2-loaded IA ($k_{solid–liquid} = 5.64\times10^{-8}$ m/s, 298 K) are the same order of magnitude and both constitute rate-limiting processes.

2.6 Flowsheet Designs for CO_2 removal system

Arnold and Steward (1999) state that in typical amine process, there are two main columns which are absorber and stripper. Before the sour gas enters the bottom of the absorber, it should passing through the inlet separator first to remove any entrained water or hydrocarbon liquids. In the absorber, the gas flows counter-currently with amine to remove acid gases. Then, the amine solution containing CO_2 and H_2S leaves the bottom of the absorber and flows through flash tank to remove almost all the dissolved hydrocarbon gases and entrained hydrocarbon condensates and small percentage of acid gas. After that, the gas passing through the Rich/Lean exchanger where it recovers some of the sensible heat from lean amine stream to decrease the heat duty on the amine reboiler. The heated rich amine then enters the amine stripper where the heat from reboiler breaks the bonds between acid gases and amines. The acid gases are removed overhead while lean amine is removed from the bottom of the stripper. Then the hot lean amine flows through rich/lean exchanger and through the cooler to reduce the temperature to no less than 10°F above the inlet gas temperature. The cooled lean amine solution is then pumped up to the absorber pressure and enters the top of the absorber (Mallinson, 2004).

In designing a gas sweetening plant, there are very basic gas treating fundamentals that need to be considered. Jenkins and Haws have identified the main fundamentals are the capacity which referring to the molarity basis, the relative bases strength and the maximum loading. A higher base strength indicates a higher affinity for the acid gas to be removed (Jenkins and Haws , 2001).

Posey et al., (1996) have presented a simple model to calculate acid gas vapor-liquid equilibrium (VLE) in alkanoamines so that the operating characteristics and behavior of absorption/ stripping system can be predicted. The model parameters were obtained from regression of experimental VLE data. This model is valid for total gas loading ranges from 0.003 to 0.8 and over wide ranges of temperatures and amine concentrations. The data based on model prediction of VLE, CO_2 partial pressure and heat of absorption agree with those of much more complicated models such as Ho and Equren model, Jou et al, and etc.

Since the solvent used for the removal of CO_2 in natural gas is aminated resin, the regeneration for this resin is different with existing regenerating system using amine solvent. The aminated resin can be regenerated using different methods based on its conditions. Lackner et al., (2010) had proposed a few steps in regenerating the resin. Firstly, the separation of CO_2 from the resin typically proceeds by washing the loaded resin with water, separating the resin from the wash water and heating the mixture of resin and entrained water to a temperature of about 40 to 95 °C. Then the carbon dioxide begins to be released by the resin and emitted therefrom.

Quinn (1998) stated that the tertiary amine containing resin can be partially regenerated by heating to 90 °C under vacuum. The resin containing tertiary amino group as a CO_2 absorbent can also be regenerated by purging with CO_2 free gas at 20 °C ot 50 °C.

2.7 Operating Paramaters Consideration

Addington and Ness have discussed on the general “rules of thumbs” in amine sweetening unit design. These rules are basically a guideline in designing the main operating parameters for the main equipments in the acid gas removal plant. The rules evaluated included the 5°C temperature approach in the absorber, the 0.12 kg/L specification for the reboiler steam, the 99°C lean/rich exchanger outlet temperature, and the pressure where the reboiler temperature is high but should not exceed 127°C For the regenerator, Bullin et al., (1990) have highlighted the consideration of operating parameters that should be carefully examined. For the case of bulk CO_2 removal using MDEA, the most sensitive parameters include liquid residence time on tray, lean amine temperature, circulation rate and steam stripping rate. Bullin et al., (1990) have suggested that the lean amine temperature should not reach 57-60 °C. Otherwise it will reduce the net CO_2 pickup. In general, CO_2 pickup can be achieve by longer liquid residence times on the trays, higher amine circulation rates and higher lean amine temperature that should not exceed 60°C.

According to Lunsford and Bullin (1996), increase the concentration of amine is advantageous but it should be less than corrosion limit. They also suggested that the lean amine temperature can be varied to get better performance of absorption but it should not exceed 60°C.

To get better performance of removing CO_2 in the absorber using MDEA, Miller and Roesler (2001) have propose to reduce the circulation rate, therefore the contact time between the feed gas and the amine will increase. Thus, it will increase the removal of CO_2.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

3.1.1 Process Information

By identifying background and problem statement of the project, conduct a research of the technical and pattern literature for the information on the project such as characteristic of the aminated resin, existing gas sweetening plant, new technology invention, process consideration and criteria. The information obtained from the literature is gathered, analyze and applied for new conceptual design.

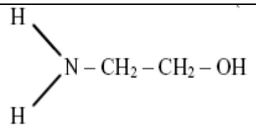
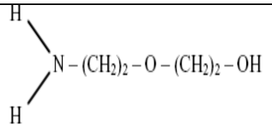
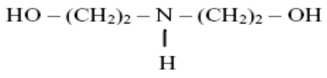
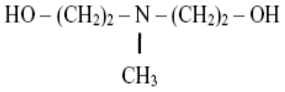
3.1.2 Critical Analysis

Based on the information obtained from the literature, critical analysis have to be done to analyze the information and relate to this project.

3.1.2.1 Aminated Resin

Aminated resin is basically a resin that has been functionalized with amine. Therefore, the characteristic of this resin is assumed to be similar with the type of amine attached to it. From the literature, it states that there are three main groups of amines that can be used in gas sweetening plant such as primary amine contains of MEA and DGA, secondary amine contains of DEA and tertiary amine contains of MDEA. All of these groups have different characteristic towards the selectivity of CO_2 and H_2S. Primary amine is stronger bases than secondary amines, which are stronger than tertiary amine. Amines with stronger bases properties will be more reactive towards CO_2 and H_2S gases and will form stronger bonds.

Table below is the comparison for each type of amine consists of MEA, DGA, DEA and MDEA (Bullin et al.,1994, Arnold et al.,1999, Polasek et al., 1990).

Solvent	Monoethanolamine (MEA)	Diglycolamine (DGA)	Diethanolamine (DEA)	Methyldiethanolamine (MDEA)
Type of Amine	Primary Amine	Primary Amine	Secondary Amine	Tertiary Amine
Molecular Structure			 $HO-(CH_2)_2-N(H)-(CH_2)_2-OH$	 $HO-(CH_2)_2-N(CH_3)-(CH_2)_2-OH$
Concentration	10 – 20 wt% If > 20 wt% MEA, corrosion inhibitors should be used	40-70 wt%	25 – 35 wt%	20- 50 wt%
Acid Gas Loading (for carbon steel equipment)	0.3 – 0.35 mole acid gas/mol of amine	Up to 0.35 mole/mole	0.3 – 0.35 mole/mole	0.7 – 0.8 mole/mole
Degradation rate	No degradation up to its normal boiling point	High degradation rates	N.A	Slow degradation rates
Degradation product	Extremely corrosive	N.A	Much less corrosive than those MEA	N.A
Selectivity towards CO_2 and H_2S	Meet pipeline specification for removing both CO_2 and H_2S	Tendency to preferentially react with CO_2 over H_2S	Reduce affinity for H_2S and CO_2 and may not be able to produce pipeline specifications gas	Selective absorption of H_2S Ability to slip CO_2 Slow reaction with CO_2
Reclaimer Required	Yes	Yes	No	N.A
Heat of	CO_2 – 825 Btu/lb	CO_2- 850 Btu/lb	CO_2- 653 Btu/lb	CO_2- 600 Btu/lb

reaction	H_2S – 550 Btu/lb	H_2S- 674 Btu/lb	H_2S- 511 Btu/lb	H_2S- 522 Btu/lb
Advantages	Easy to regenerate	- Higher DGA concentrations in the solution result in lower circulation rates and also in lower freezing points - Low vapor pressure (Pvap) - Work well at high T ambient if system operated at moderate pressure -	- Low vapor pressure - Fewer corrosion problem	- Lower vapor pressure and solution losses - Lower heat of reaction - Fewer corrosion problem - High acid gas loading - Higher resistance to degradation - Very low corrosion risk at high solution loadings
Disadvantages	High heat of reaction Irreversible reaction with CO_2 and H_2S can cause solution losses and degradation products Degradation or deactivation of MEA lowers the effective amine concentration but a reclaimer can recover most of the deactivated amine	- High heat of reaction	- Require higher operating pressure than MEA - Vacuum stripping may be required to fully regenerate	- Slow reaction rate with CO_2 - Tendency to foam at high concentration - Higher cost

Table 3.1: Table of comparison for each type of amine consists of MEA, DGA, DEA and MDE

3.1.3 Conceptual Process Design

Making use of existing design model, do the screening to examine all potential reaction paths. Then, evaluate and do comparison of the existing plant for the basic and fundamental knowledge. Based on that, design the process route for gas sweetening plant by considering the all the criteria obtained from the literature.

3.1.3.1 Process Screening

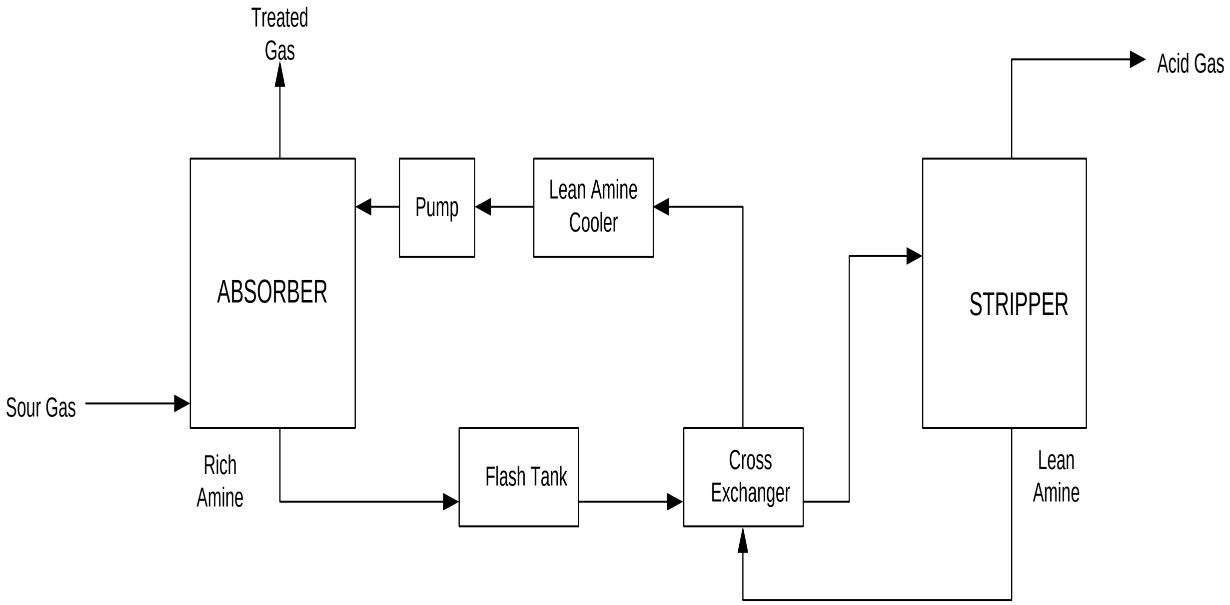


Figure 3.1: Acid Gas Removal Plant

Based on the literature review on the typical amine system, this is one of the process alternatives in the flowsheeting of acid gas removal plant as in Figure 3.1. Below are the process descriptions of the plant:

No table of contents entries found.

1

- The feed gas enters the bottom of Acid Gas Absorber
- Lean aminated resin enter the top of the Absorber and flow counter-currently to the feed gas.

2

- The treated gas leaves the top of the Absorber and is routed via pre-cooler to the water wash trays.

3

- The rich aminated (rich in acid gases) leaves the bottom of the Absorber and is routed to Flash Tank to flash off the hydrocarbons which are entrained and dissolved in the solution.

4

- The rich aminated is then heated in the Lean/Rich Exchanger and enters the Stripper in the top below wash trays in the stripping section, where it is being regenerated via heating (steam stripping)

5

- In stripper, stripping steam is generated in Reboiler to strip the acid gas from the solution.

6

- The lean aminated resin from the bottom of the Regenerator is routed to the Lean/Rich Exchanger, Lean Amine Cooler and Lean Amine Circulation Pump back to the Absorber.

7

- The gases leave the top of the Regenerator column and flow via the overhead Condenser to condensed and cooled.
- The condensed water is separated in the reflux drum and return to the Stripper top liquid distributor while the acid gases are vented to the acid flare.

In designing a plant, the basic gas treating fundamentals is important. According to Lenkins and Haws, the first fundamental is the capacity. Capacity is the circulating solution which is one of the most basic and critical principles in a treating plant. Capacity of the circulation solution is depending on the molarity of the aminated resin itself which mean that the capacity for each group is different with each others. The second fundamental is the relative base strength. A higher base strength indicates a higher affinity for the acid to be removed. The third fundamental is maximum loading. Rich loading on a mole-to-mole basis need to account for the relative base strength of the gas treating solution.

Based on the literature, Bullin et al., (1990) have identified important operating parameters that should be considered when using MDEA as the solvent. The first parameter is liquid residence time which has been suggested about 2-5 sec. The other parameter is the lean aminated resin temperature. Bullin et al., (1990) state that the lean amine temperature should not reaches about 57 – 60°C otherwise it will reduce the CO_2 pickup. Circulation rate is also one of the important parameters that should be considered. The circulation rate is related with liquid residence time. For tertiary amine, when circulation rate is increase, liquid residence time is decreasing, thus lower the CO_2 removal. The last parameter to be considered is the stripping rate. When the steam striping rate is increased, a leaner amine will be produced which will resulted in higher CO_2 pickup.

Since the solvent used in this project is aminated resin which is quite different with existing gas sweetening plant that mostly used amine solvent to absorb CO_2, the regeneration system is also different. Lackner et al., (2010) had proposed a regeneration system of resin by supplying heat to the resin-water mixture to release to CO_2 attach to it. Quinn (1998) stated that the resin containing tertiary amino group as a CO_2 absorbent can also be regenerated by purging with CO_2 free gas at 20 °C to 50 °C.

3.1.3.2 Develop Block Diagram and Subprocess

Referring on the literature, block diagram for gas sweetening system at gas offshore platform can be developed after identifying the possible route based on condition where high pressure, high concentration of CO_2 in natural gas, and the use of aminated resin. Below is the proposed block diagram for the acid gas removal system.

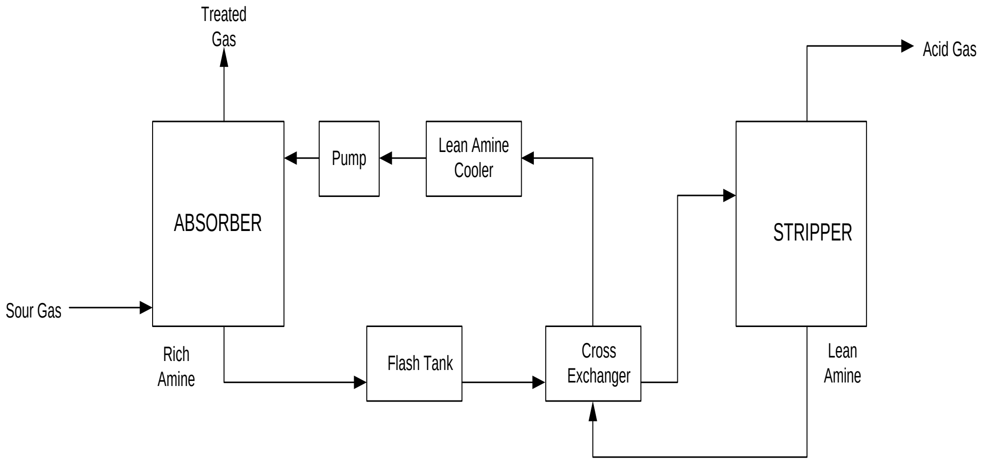


Figure 3.2: The Proposed Process Block Diagram for the Acid Gas Removal System

3.1.3.3 Develop Process Flowsheet

Based on the block diagram, a flowsheet of the process for gas sweetening unit can be developed in iCON. The most important things before simulate the process is to choose the appropriate property package. It is proposed to use Peng-Robinson property package instead of Amine property package since the process involving hypothetical component. Aminated resin is a new solvent which functionalized the polystyrene resin with tertiary amine, MDEA. Therefore, the substance is not in the components list. Thus, it is necessary to create hypothetical component for this aminated resin.

There are some assumptions used in this project which are:

- The system is operated under steady state conditions
- The reaction mechanism between aminated resin and carbon dioxide is as follow
  $CO_2 + H_2O + MDEA \Leftrightarrow MDEAH^+ + HCO_3^-$ ……………………………….(3.1)

- Regeneration process is expected to occur in the stripper where the aminated resin has been regenerated to remove the CO_2 content in the solvent and recycled back to the absorber. Regeneration has been achieved by introduce the heat inside the stripper and breaking the bond between acid gases and amines

3.1.3.4 Identify Operating Parameters

Below are the natural gas operating parameters that have been specified in this project.

i. Natural Gas Stream

Considering the case where CO_2 content in natural gas is in the range of 20-90mol% and flowing at high pressure, the study is conducted using the actual natural gas composition at Resak Platform, PETRONAS where the CO_2 content is about 22mol%.

Components	Composition (mol fraction)
C1	65.9058
C2	6.3686
C3	3.0650
iC4	0.6211
nC4	0.6936
iC5	0.2377
nC5	0.1973
C6+	0.2510
N2	0.1184
CO_2	22.5342
Total Flow (kg/day)	4,078,000
Temperature (°C)	36
Pressure (kPa)	8379
Volume (m^3/day)	3,849,000

Table 3.2: Natural Gas Feed Condition, Resak Platform,PETRONAS (27th March 2010)

ii. Lean Amine Stream

Temperature (°C)	41
Pressure (barg)	82
Flowrate (GPM)	39,445.72

Table 3.3 : Lean Amine Stream Properties

iii. Absorber Column

Stages	12
Pressure (barg) Top Bottom	 47 48

Table 3.4 : Absorber Column Properties

iv. Aminated Resin Properties

Molecular Weight (g/mol)	1106.65
Boiling Point (°C)	247
Liquid Density(kg/m^3)	10289
Critical Volume	0.8

Table 3.5: Aminated Resin Properties

CO_2 adsorption capability in aminated resin can be determined by the following main variables (Baying et al. 2009)

1. Lean aminated resin circulation rate
2. Lean aminated resin temperature
3. Mass Fraction of aminated resin

3.1.3.5 Evaluate System Performance

The system performance can be evaluated based on acid gas loading. Acid gas loading is basically the number of moles of acid gas in rich aminated resin stream divided by the number of moles of total amine in solution (Nathan & Ralph). High acid gas loading indicates that more CO_2 being adsorbed by the aminated resin. The other evaluation of the system performance is percentage recovery of CO_2 which indicates how much CO_2 being removed from the system.

3.1.3.6 Preliminary Economic Evaluation

Based on the design flowsheet, do the economic evaluation for the whole system to determine the feasibility of the project. This would give the insights on economic significance of the project. If the value calculated is positive, it means that the project is feasible, otherwise if it is negative, other methods of producing the desired product must be considered as the latter would not give a convincing return. According to Douglas (1988), the economic potential at level 1 can be calculated using the equation below;

Economic Potential 1= Product cost – Reactant cost

3.2 Tools/equipment required:

The Process simulation software called iCON will be used for this project. It is based on a thermodynamic and physical property calculation mechanism used to predict process behavior for upstream and downstream oil and gas applications.

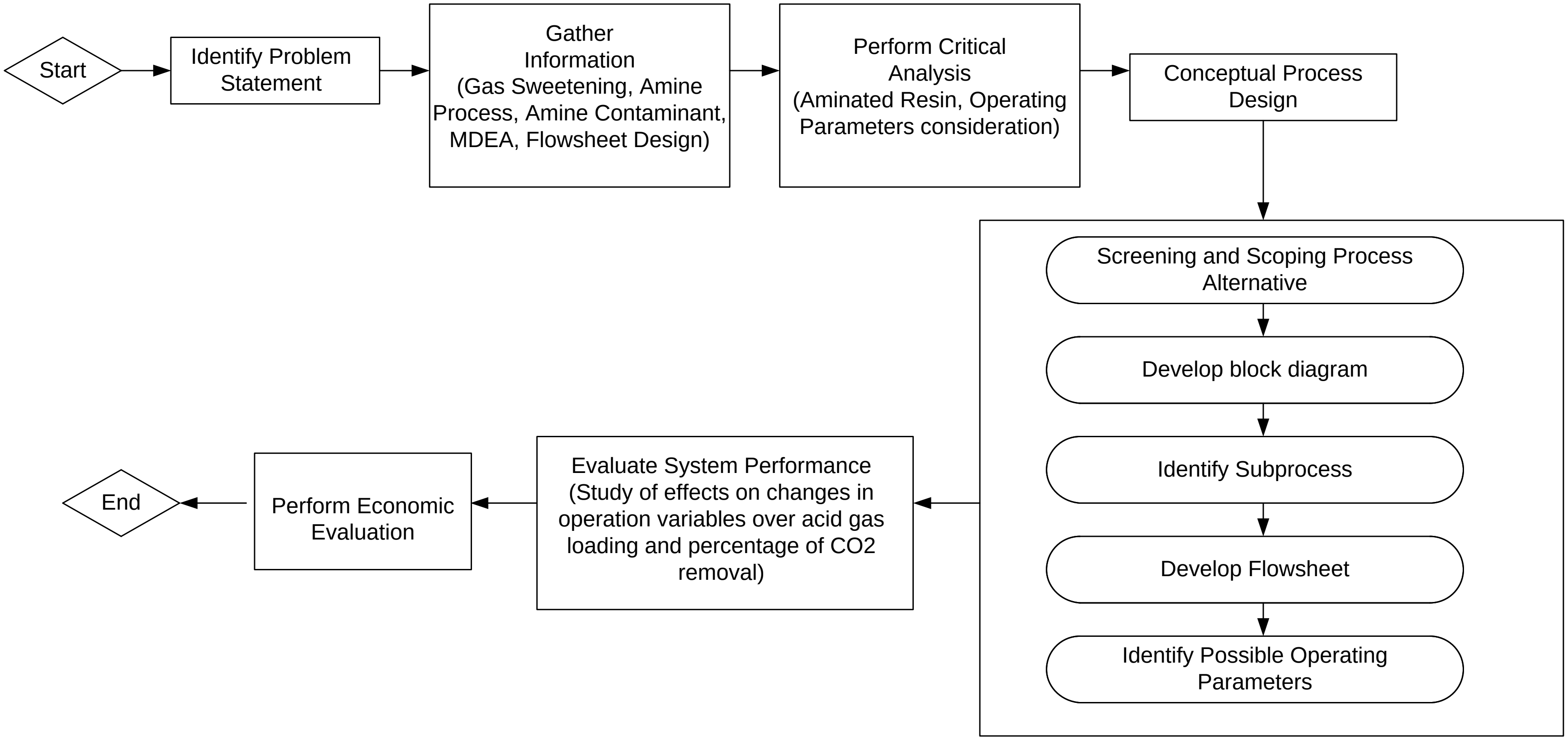


Figure 3.3: Process Flow of Methodology

3.3. Gannt Chart

.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Identify Problem Statement	🟪														
2	Gather Information	🟪														
3	Perform Critical Analysis	🟪														
4	Conceptual Process Design	🟪														
5	Screening and Scoping Process Alternative	🟪														
6	Develop Block Diagram		🟪													
7	Identify Subprocess			🟪												
8	Develop Flowsheet			🟪	🟪	🟪	🟪	🟪		🟪	🟪					
9	Identify Possible Operating Parameters			🟪	🟪	🟪	🟪	🟪		🟪	🟪					
10	Evaluate System Performance										🟪	🟪	🟪			
11	Perform Economic Evaluation												🟪	🟪	🟪	

Suggested milestone

🟪 Process

CHAPTER 4
RESULT AND DISCUSSION

4.1 Tertiary Aminated Resin

MDEA is frequently used for the removal of CO_2 from natural gas. It has a number of properties which make it attractive for CO_2 removal such as high solution concentration, high acid gas loading, high capacity to absorb CO_2, low corrosion problem even at high acid gas loading, lower heat of reactions and so on. However, MDEA is well known for its relatively slow reaction rate for CO_2. As a result, MDEA is not usually associated with situations where the removal of large amounts of CO_2 is desired. There are some modifications made to improve the removal of CO_2 using MDEA by combining high absorptive capacity of tertiary amines with high absorption rates of primary and secondary amines. However, the acceleration of CO_2 absorption via rapid formation of carbamates occurred in the column. In other parts of the absorption process homogeneous activating additives can give rise to undesirable side-effects, such as increased corrosion or higher energy demands for regeneration. Thus it would seem to be preferable to functionalize the resin with amine in which the porous support provides the amine with structural integrity and a surface for liquid/solid contact. In this way, the resin would also increase surface contact between MDEA and the natural gas, thus adsorbing more CO_2. It also helps the amine to withstand high pressure of natural gas (Zhang et al.,2005).

4.2 Adsorption Mechanism of CO_2 Removal with Tertiary Aminated Resin

Since the aminated resin is a new solvent, thus its exact kinetics model for reactive adsorption of CO_2 is yet to be developed. Therefore, a possible mechanism of adsorption of CO_2 is proposed. Figure 4.1 is a schematic reaction mechanism of adsorption of CO_2 into a resin.

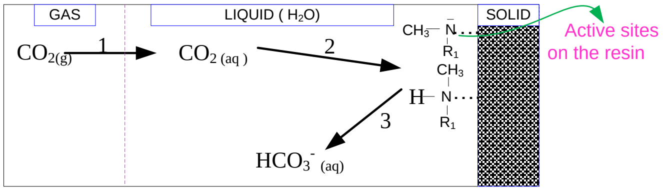


Figure 4.1: Mechanism of adsorption of CO_2 by aminated resin

The CO_2 firstly dissolves in the liquid phase (gas-liquid mass transfer). Then adsorption process takes place through the reaction of dissolves CO_2 with the aminated resin (liquid-solid adsorption) (Zhang et al.). The reaction release bicarbonate in the solution. According to Keith (2001), compound containing the ion HCO_3^- gives off carbon dioxide when heated or treated with dilute acids. In this project, it is proposed to use reboiler in the stripper column and generate stripping steam to release the carbon dioxide from aminated resin.

4.3 Flowsheet Design

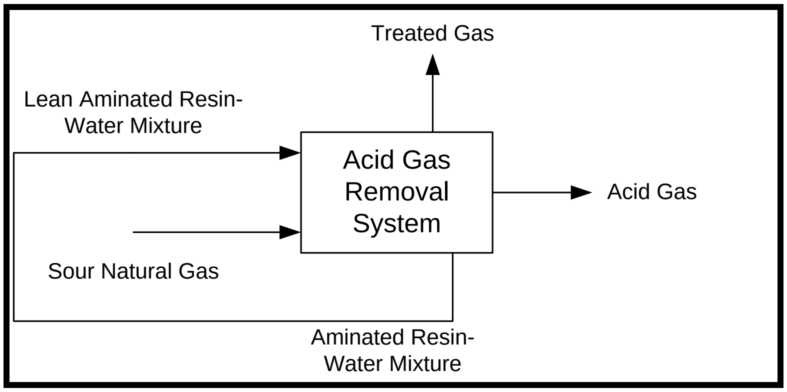


Figure 4.2: Simplified Block Diagram for Acid Gas Removal System

Figure 4.2 is the simplified block diagram for acid gas removal system. In this system, it uses aminated resin as the adsorbent to remove the CO_2 content in natural gas. The lean aminated resin-water mixture will come in contact with the sour gas to adsorb the CO_2 content in it. Then, the aminated resin mixture leaves the bottom of the absorber carrying with it the acid gases. This resin containing the CO_2 is referred to as the rich aminated resin. Then, the rich aminated resin is regenerated in the stripper to remove the CO_2 from the resin before recycle back to the absorber to be reused. This resin is called lean aminated resin.

In gas sweetening unit, there will be two main columns which are absorber and stripper column. The natural gas enters at the bottom of the absorber and flow upward, countercurrent- contact with aminated resin that flow downward to adsorb the CO_2 content in the natural gas. The rich aminated resin will flow into the flash tank to remove all the dissolved hydrocarbon gases and entrained hydrocarbon condensates. A small percentage of acid gas will also flash to the vapor phase in this vessel. The rich aminated resin is then heated in the Lean/Rich Exchanger and enters the stripper. The function of the stripper column is to regenerate the aminated resin to remove CO_2 attach to it before recycle back to the absorber. Aminated resin is regenerated by stripping stream generated in reboiler to strip acid gas from aminated resin. The lean aminated resin from the bottom of the regenerator is routed to Lean/Rich Exchanger, Lean Amine Cooler and Lean Amine Circulation Pump back to the absorber. There will be make-up water for lean aminated resin stream before entering the absorber as there would be loss of water from the process due to high temperature used in the regeneration step.

4.4 Process Simulation

4.4.1. Initial Amine Circulation Rate

In designing a CO_2 removal system, an estimation of initial amine circulation rate is important to ensure that effective adsorption occurred. The circulation rates for amine systems can be determine from the acid gas flow rates by selecting a solution concentration and an acid gas loading (Douglas et al., 2006).

$$Circulation\,rate(GPM) = 0.206 \times MM \times (H_2S + CO_2) \times (MWT) \Big/ ML \times WT$$

Where,

MM= gas flow MMSCFD,
H_2S = mol % of H_2S to be removed,
CO_2 = mol% of CO_2 to be removed,
MWT = mole wt of aminated resin =119.1,
ML = acid gas loading (moles acid gas/mole) recommended for aminated resin is 1,
WT= weight % of aminated resin.

Assuming that 100% of CO_2 concentration need to be removed. In this case, H2S concentration is neglected since its composition in the natural gas is too small. The aminated resin weight by percent is taken to be 50%.

$$Circulation\ rate(GPM) = 0.206 \times 192 \times (22.53 + 0) \times 2213.3 \Big/ 1 \times 50 = 39{,}445.72\ GPM$$

Thus, the initial estimate of lean aminated resin circulation rate is taken to be 39,445.72 *GPM*

4.4.2. Simulation Result

Figure 4.3 below shows the design of the proposed CO_2 removal system at natural gas reserves. Since this study focuses on absorber performance using aminated resin, thus the simulation for absorber column has been established using iCON as given in Figure 4.4.

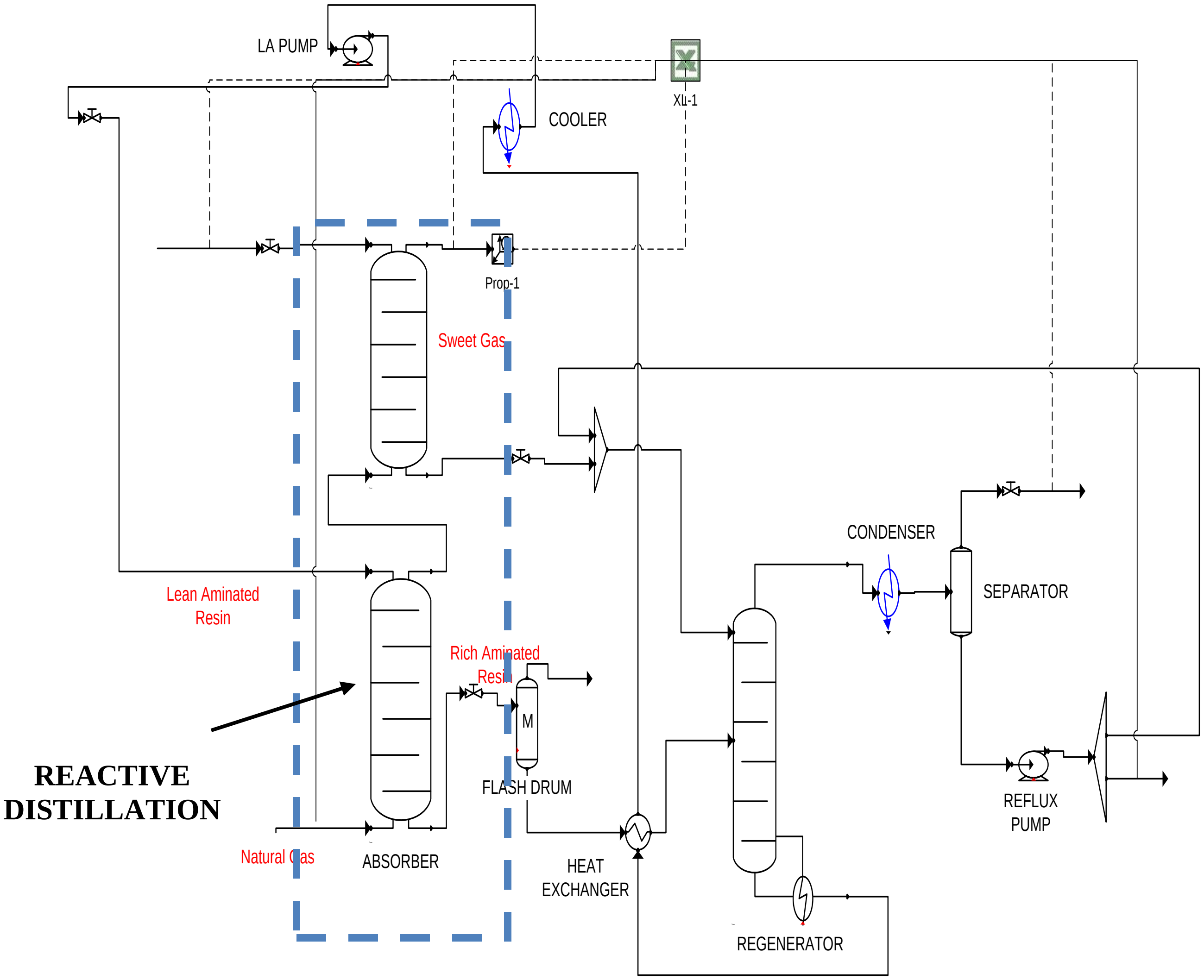


Figure 4.3: Proposed CO_2 Removal System

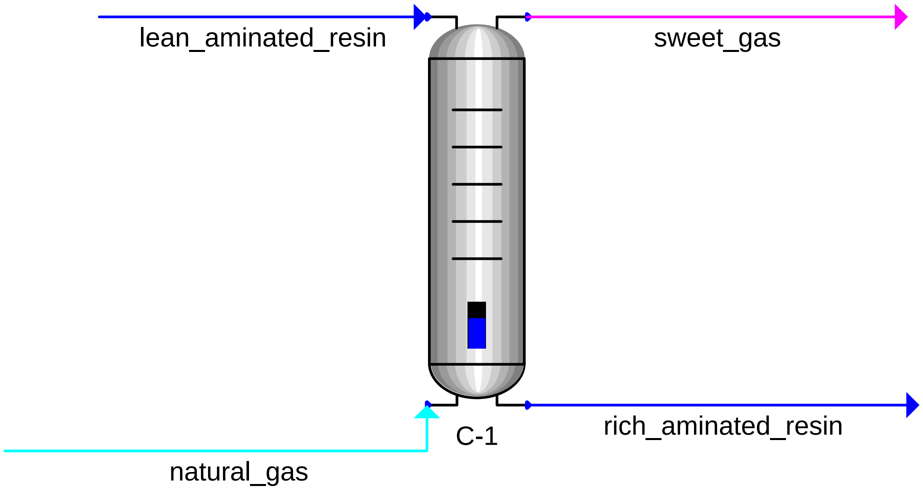
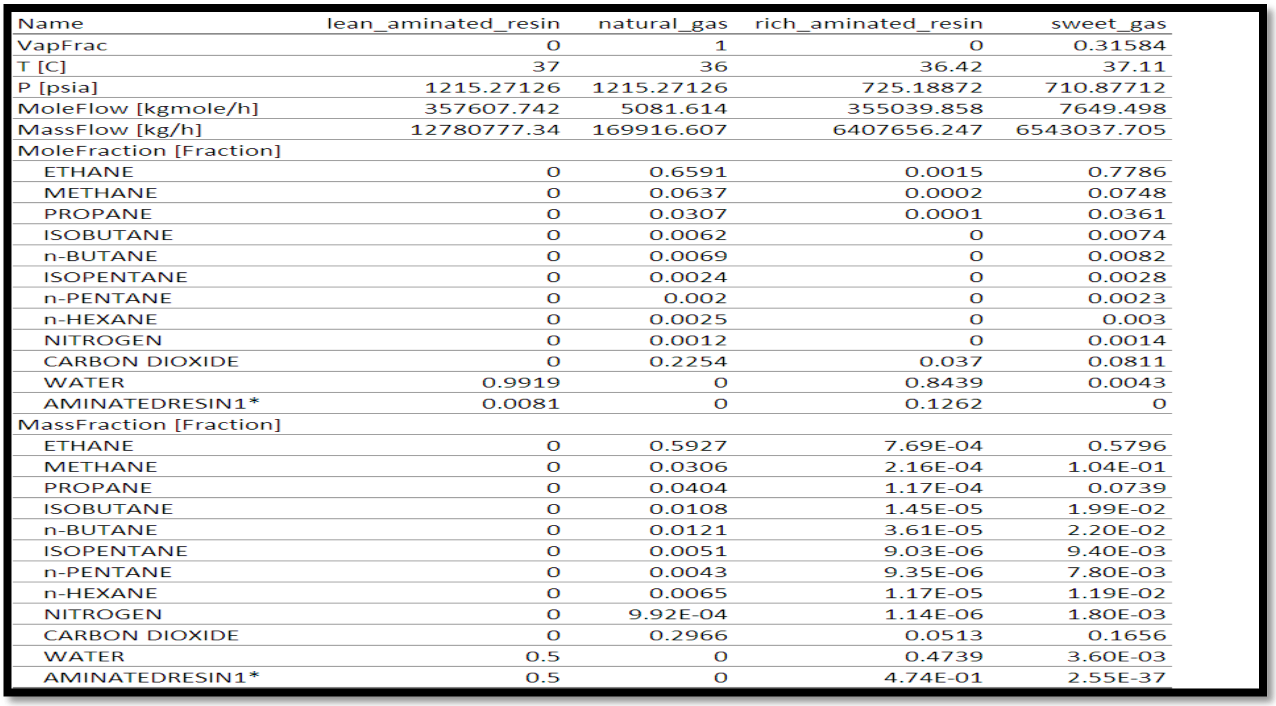


Figure 4.4: Reactive Distillation Column using iCON simulation software



Name	lean_aminated_resin	natural_gas	rich_aminated_resin	sweet_gas
VapFrac	0	1	0	0.31584
T [C]	37	36	36.42	37.11
P [psia]	1215.27126	1215.27126	725.18872	710.87712
MoleFlow [kgmole/h]	357607.742	5081.614	355039.858	7649.498
MassFlow [kg/h]	12780777.34	169916.607	6407656.247	6543037.705
MoleFraction [Fraction]				
ETHANE	0	0.6591	0.0015	0.7786
METHANE	0	0.0637	0.0002	0.0748
PROPANE	0	0.0307	0.0001	0.0361
ISOBUTANE	0	0.0062	0	0.0074
n-BUTANE	0	0.0069	0	0.0082
ISOPENTANE	0	0.0024	0	0.0028
n-PENTANE	0	0.002	0	0.0023
n-HEXANE	0	0.0025	0	0.003
NITROGEN	0	0.0012	0	0.0014
CARBON DIOXIDE	0	0.2254	0.037	0.0811
WATER	0.9919	0	0.8439	0.0043
AMINATEDRESIN1*	0.0081	0	0.1262	0
MassFraction [Fraction]				
ETHANE	0	0.5927	7.69E-04	0.5796
METHANE	0	0.0306	2.16E-04	1.04E-01
PROPANE	0	0.0404	1.17E-04	0.0739
ISOBUTANE	0	0.0108	1.45E-05	1.99E-02
n-BUTANE	0	0.0121	3.61E-05	2.20E-02
ISOPENTANE	0	0.0051	9.03E-06	9.40E-03
n-PENTANE	0	0.0043	9.35E-06	7.80E-03
n-HEXANE	0	0.0065	1.17E-05	1.19E-02
NITROGEN	0	9.92E-04	1.14E-06	1.80E-03
CARBON DIOXIDE	0	0.2966	0.0513	0.1656
WATER	0.5	0	0.4739	3.60E-03
AMINATEDRESIN1*	0.5	0	4.74E-01	2.55E-37

Table 4.1 : Mass balance and operating conditions of the Reactive Distillation Column

4.4.2.1 Effect of CO_2 Concentration

a) Effect of CO_2 concentration in natural gas on CO_2 loading using aminated resin

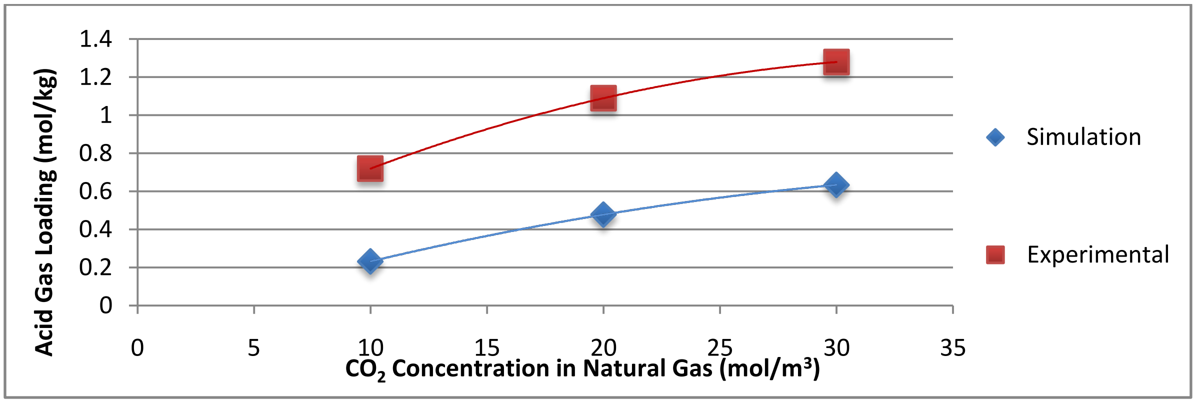


Figure 4.5: Acid Gas Loading vs CO_2 concentration in Natural Gas

The effect of CO_2 concentration in natural gas on acid gas loading is investigated for three different concentrations using simulation and experimental data and the results are presented in figure 4.5. The experimental data is based on the literature of Zhang et al. (2005). Its acid gas loading is determined based on single-site Langmuir model (Zhang et al.,2005).

$$q_{eq} = q_{\max} \frac{k_L c_L}{1 + k_L C_L}$$

where

q_{eq} = equilibrium solid phase concentration (mol/kg)

$q_{\max}$ = Langmuir model constant (mol/kg)

k_L = Langmuir model constant (mol/kg)

C_L = liquid phase concentration of CO_2 (mol/m^3)

Model parameter $q_{\max}$ and k_L are evaluated from the adsorption data derived from experiments.

Acid gas loading is basically the number of moles of acid gas in solution divided by the number of moles of total amine in solution (Nathan and Ralph). This is numerically equivalent to molar concentration of CO_2 in rich aminated resin divided by the molar concentration of aminated resin. All operating parameters are held constant in all runs except for CO_2 concentration in natural gas. The simulation data is taken based on the result using iCON software while the experimental data is taken from the literature. Figure 4.5 clearly shows that acid gas loading increase with increasing CO_2 concentration in natural gas for both trends. But, the values of acid gas loading for both trends are different since the operating parameters for both simulation and experimental are not exactly the same. However these trends result in more CO_2 being adsorb by the aminated resin.

The result can be explained further as when CO_2 concentration in solution is high while CO_2 concentration in the aminated resin is low, there will be molecular movement from high concentration to low concentration called diffusion. Thus, increasing the number of CO_2 in natural gas will increase the molecular movement to the resin, resulting in high acid gas loading. However, there is a limitation for the resin adsorption in terms of its loading. The resin is capable to adsorb CO_2 until it is fully loaded. Schubert et al. (2001) has reported that the use of aminated amine can improved solvent loading by virtue of the superior reactive mass transfer characteristics in identical equipment under otherwise similar conditions (e.g. residence time).

b) Effect of CO_2 concentration in Natural Gas on Percentage Recovery of CO_2

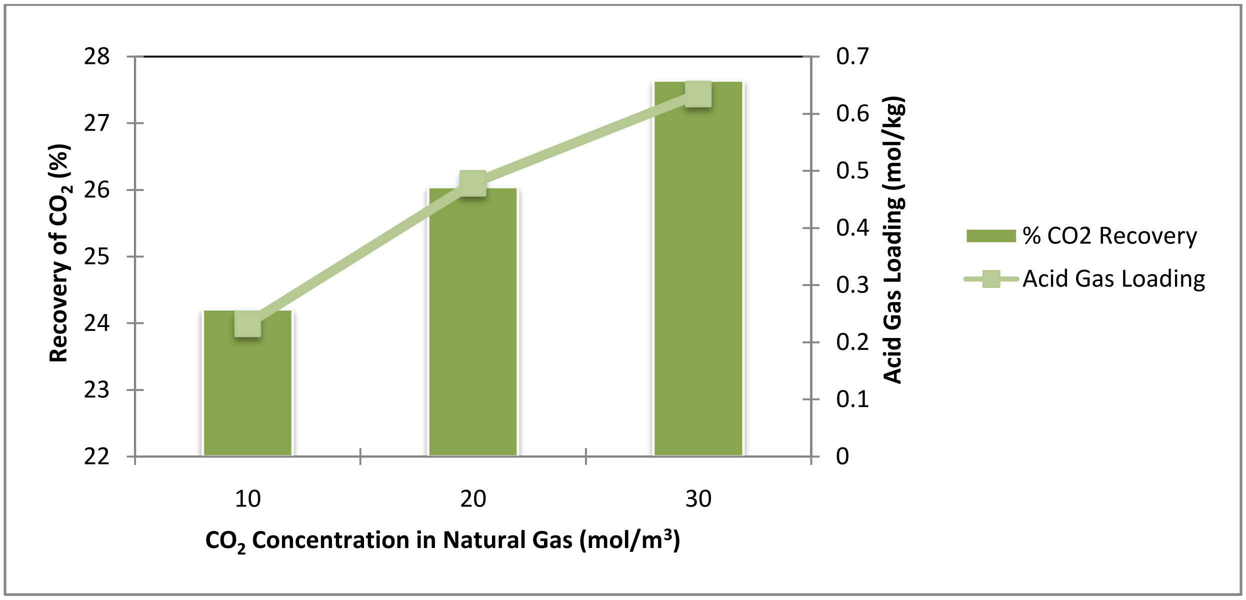


Figure 4.6 : Percentage Recovery of CO_2, Acid Gas Loading vs CO_2 concentration in Natural Gas

Figure 4.6 illustrates the percentage of CO_2 recovery in the system as a function of increasing CO_2-concentration in natural gas. Percentage recovery of CO_2 in this term can be defined as how much CO_2 is being removed from the system. Based on the graph, percentage recovery of CO_2 is directly proportional to Acid Gas Loading. As CO_2 concentration in natural gas increases, acid gas loading will increase as well resulting in high percentage recovery of CO_2.

4.4.2.2 Effect of Operating Parameters

a) Effect of mass fraction of Aminated Resin on CO_2 concentration in sweet gas

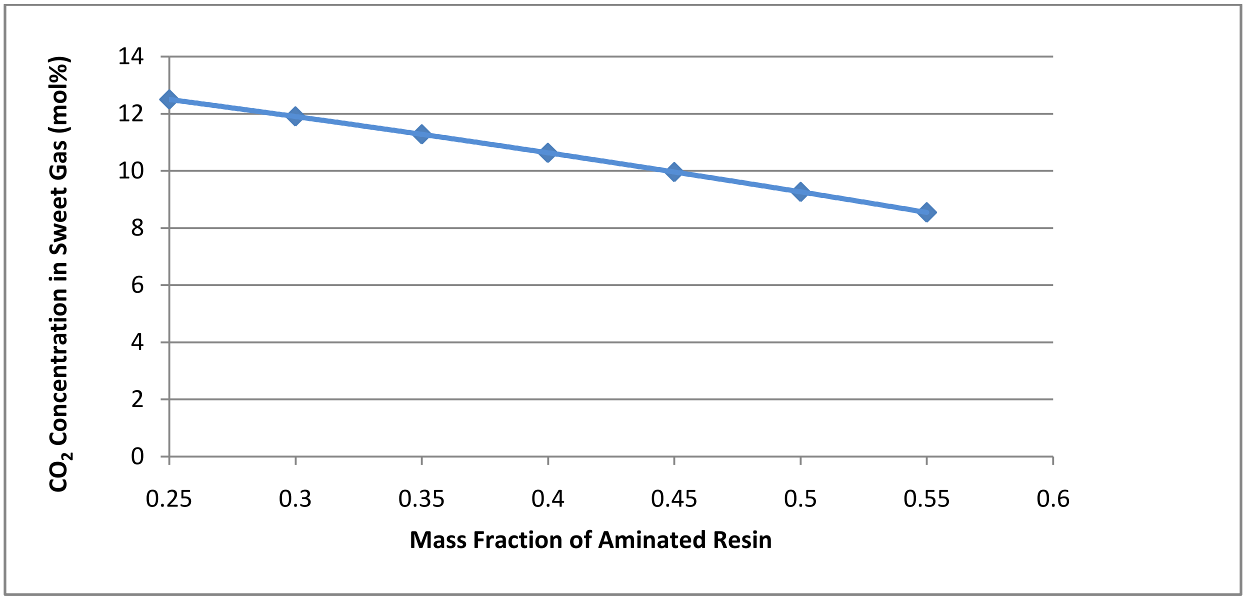


Figure 4.7: CO_2 concentration in Sweet Gas vs Mass Fraction of Aminated Resin

Figure 4.7 shows the effect of increasing mass fraction of Aminated Resin on molar percentage of CO_2 concentration in sweet gas. This system is simulated at 10 mol/m3 of CO_2 in natural gas and holding other process variables constant except the mass fraction of aminated resin. Figure 4.7 clearly shows that molar percentage of CO_2 in sweet gas is decreasing as mass fraction of aminated resin increase. This is due to the fact that high solvent concentration results in rich acid gas loading and tends to pick up a large amount of acid gas. However, rich acid gas loading may cause severe corrosion problem in the lean/rich exchanger and reboiler. Therefore, the use of aminated resin concentration must be within its range. The allowable use of mass fraction of aminated resin must be between 0.3 – 0.5. If the use is below the range, aminated resin will not be able to capture CO_2. However, if it is above the range, number of CO_2 being removed is high but will cause severe corrosion problem. According to Salako (2005), increasing the amine concentration attribute to increasing amine capacity. Thus, it will remove more CO_2 from natural gas.

b) Effect of Lean Aminated Resin Temperature

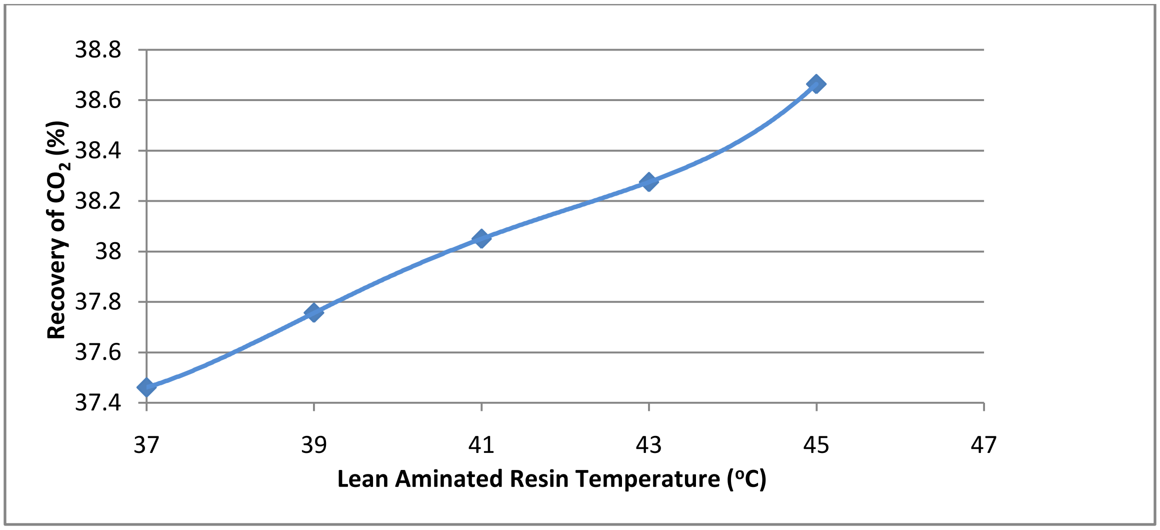


Figure 4.8: Percentage Recovery of CO2 vs Lean Amine Temperature

Similarly the simulation model was used to study how lean aminated resin temperature affects the percentage recovery of CO_2 while holding all other process variables constant. For this particular design, the mass fraction of aminated resin is 0.5. For the temperature between 37 to 45 ^oC, the trend clearly shows that increasing the lean aminated resin temperature will increase the percentage recovery of CO_2. Since the reaction with tertiary amine is kinetically controlled, the hotter the column the faster the reaction rate. Lunsforn and Bulllin (1996) stated that the higher temperature increases the kinetic effect to a greater extent relative to the decrease in solubility. However, this can be true up to certain temperature. When the temperature of lean aminated resin is too high, the solubility of CO_2 will decrease resulting in decreasing of CO_2 pickup. Addington and Ness suggested to maintain a minimum temperature approach of 5^oC. The temperature approach is defined as the temperature differential between the incoming acid gas and the lean amine feed. The reason for this guideline is to prevent the condensation of hydrocarbons in the contactor and avoid the subsequent problems that a second liquid phase causes an amine plant (Addington and Ness). Besides, high lean amine temperature also increases water and amine losses (Lunsford and Bullin, 1996). Since the natural gas feed temperature is 36 ^oC, it is suggested that the best temperature for lean aminated resin is 41 ^oC.

c) Effect of Lean Aminated Resin circulation rate

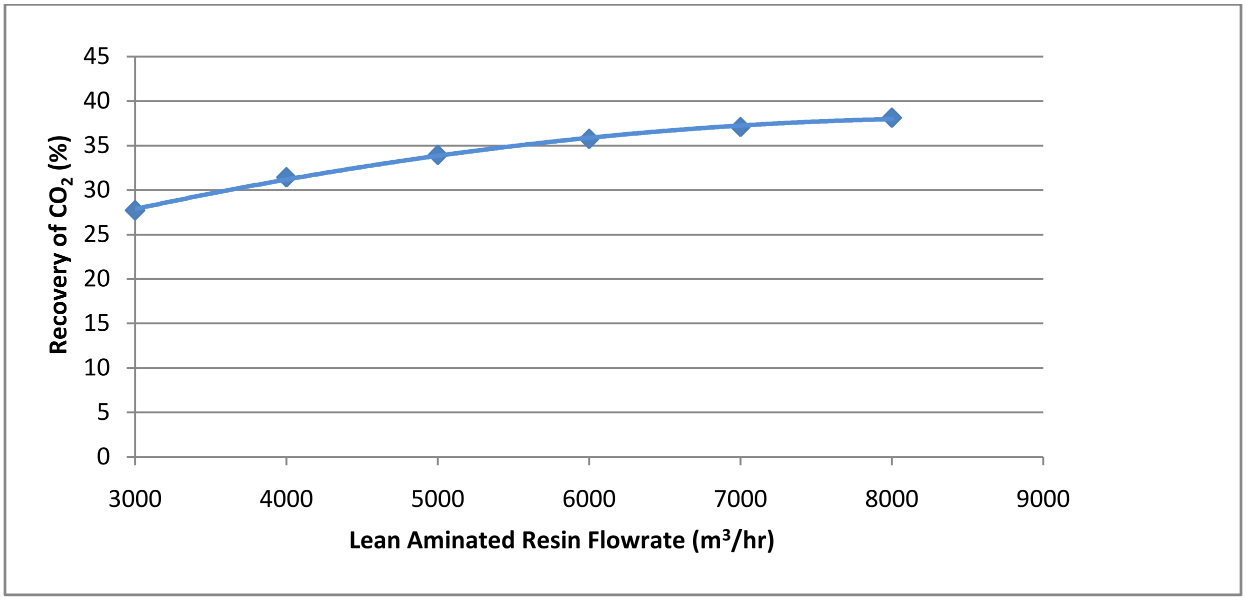


Figure 4.9: Percentage Recovery of CO_2 vs Lean Amine Circulation Rate

The effect of lean amine circulation rate is investigated to study the percentage recovery of CO_2. This design is simulated using the lean amine concentration in the range of 3000 to 8000 m3/hr while holding other parameters constant. Figure 4.9 clearly shows that increasing lean aminated resin circulation rate increase the percentage recovery of CO_2. This usually holds true for the amine in a column of fixed diameter eventhough the liquid residence time on a tray will decreased with increased circulation (Aliabadi et al.,2009).

4.5 Preliminary Economic Evaluation

The following preliminary economic evaluation is done to evaluate the potential of the plant with respect to the raw materials and product cost. Since the aminated resin is a polystyrene resin that has been functionalized with tertiary amine, the price of aminated resin is expected to be higher than the price of solvent MDEA and polystyrene resin Table 4.2 below is the summary of the price of raw materials and the product.

Table 4.2: Price of Raw Materials and Products

Material	Price (RM per m^3)	Amount being consumed or produced and produced in simulation model (m^3/hr)	Total price (RM per year)
Aminated resin (estimated)	326 (ICIS 2009)	7,000	1.8 x 10^{10}
Water	0.337 ((Industrial Water Tariff for Terengganu)		
Natural gas (processed)	458 (ICIS 2009)	160,375	5.82 x 10^{11}
▪ **Note**: The price for the aminated resin is considered to be a bit higher than the price of the reactants (solvent MDEA and Polystyrene) for making this product (aminated resin).			

The corresponding amount of fresh aminated resin required on hourly basis is 7000 m^3/hr. A total of 320 operational days in a year have been considered for obtaining the estimate for economic potential level 1 (EP1).

Economic Potential 1= Product cost – Reactant cost

$$= (\text{RM}5.82 \text{ x } 10^{11} - \text{RM}1.8 \text{ x } 10^{10}) = \text{RM}5.64 \text{ x } 10^{11}$$

The calculated positive value of EP1 indicates the proposed CO_2 removal system is economically viable.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A CO_2 removal system has been designed for an application at natural gas reserves. Via simulation approach, this system is predicted to be capable of reducing the CO_2 concentration in the raw natural gas from 20 – 90 mol% to less than 10 mol% before being sent to the acid gas treating plant in gas refineries using aminated resin. Based on the simulation result, it shows that the aminated resin has the potential to reduce CO_2 from high CO_2 loaded natural gas to less than 10 mol% CO_2 content using the best operating conditions have been identified.

The important operating parameters that were identified are mass fraction of aminated resin, lean amine temperature and flowrate of lean amine. According to the results, the mass fraction of 0.45 is capable to remove 10 mol/m^3 of CO_2 (22 mol%) to less than 10 mol%. In addition, it is suggested to maintain a minimum temperature approach of 5^{o}C for lean amine temperature. This is due to the fact that when the temperature of lean aminated resin is too high, the solubility of CO_2 will decrease resulting in decreasing of CO_2 pickup. Therefore, the best temperature for lean amine is 41^{o}C. The effect of lean amine circulation rate is also investigated to study the percentage recovery of CO_2. This design is simulated using the lean amine concentration in the range of 3000 to 8000 m^3/hr while holding other parameters constant. Based on the result, the best flowrate of lean aminated resin is 7000 m3/hr as it can reduce the CO_2 content to less than 10mol%.

Based on a preliminary economic evaluation, it is shown that the proposed CO2 removal system displayed a positive value of EP1, indicating that it is economically viable.

5.2 Recommendations

In order to get more accurate result on the performance of CO_2 removal system using specially designed aminated resin, it is recommended to setup experimental system for CO_2 removal using aminated resin to verify the kinetics data of this resin. By having this information, the aminated resin can be simulated using a series of reactors and separator (reactive adsorption) in place of the absorber to investigate the performance of aminated resin accurately. In our suggested design, the reactors are expected to capture newly added contribution of the resin to the CO_2 adsorption process when compared to adsorption by aminated resin created in the hypothetical component

Then, simulate the whole CO_2 removal system at natural gas reserve to see its performance in terms of energy consumption as well. Besides, it is suggested to study the economic potential by performing the comparison between aminated resin and amine liquid to see which one is more economical.

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APPENDICES

SAMPLE CALCULATION

a) Effect of CO_2 concentration in natural gas on CO_2 loading using aminated resin

CO_2 conc in NG	CO_2 (rich aminated resin)	lean aminated resin	Acid Gas Loading	Acid Gas Loading
mol/m^3	kgmole/hr	kgmole/hr	kgmole/kgmole	mol/kg
10	355.17	690.68	0.51	0.23
20	730.89	690.68	1.05	0.47
30	969.64	690.68	1.40	0.63

$$\text{Acid Gas Loading} = \; = \frac{Lean\ \ Aminated\ \ \mathrm{Resin}}{CO_2\ \ (rich\ \ aminated\ \ resin)}$$

$$= \frac{690.68}{355.17} = 0.5142 kgmole / kgmole$$

$$= \frac{0.5142 \times 1000}{2213.3} = 0.232337 mol / kg$$

b) Effect of CO_2 concentration in Natural Gas on Percentage Recovery of CO_2

	Natural Gas		Sweet gas		% CO_2 recovery
CO_2 conc in NG	mol fraction CO_2	molar flow	mol frac CO_2	molar flow	
mol/m3		kgmole/hr		kgmole/hr	
10	0.30	5008.07	0.21	5361.16	24.20
20	0.65	4350.49	0.48	4356.92	26.04
30	0.90	3987.21	0.66	3934.12	27.64

Percentage of CO_2 Recovery $= \frac{CO_2 \text{ molar flow in NG} - CO_2 \text{ molar flow in sweet gas}}{CO_2 \text{ molar flow in NG}}$

$$= \frac{0.3(5008.7) - 0.2124(5361.16)}{0.3(5008.07)} \times 100 = 24.2083$$

c) Effect of mass fraction of Aminated Resin on CO_2 concentration in sweet gas

Mass Fraction	CO_2 in Sweet Gas (mol%)
0.25	12.49
0.30	11.89
0.35	11.27
0.40	10.62
0.45	9.95
0.50	9.25
0.55	8.53

d) Effect of Lean Aminated Resin Temperature

Temp	Natural gas		Sweet Gas		% recovery
	mol frac CO$_2$	total flow	mol frac CO$_2$	total flow	
		kgmole/hr		kgmole/hr	
37	0.22	5081.61	0.0933	7675.40	37.46
39	0.22	5081.61	0.0929	7668.68	37.75
41	0.22	5081.61	0.0925	7662.14	38.05
43	0.22	5081.61	0.0922	7665.76	38.27
45	0.22	5081.61	0.0918	7649.8	38.66

e) Effect of Lean Aminated Resin circulation rate

	Natural Gas		Sweet Gas		% recovery
Lean Amine Flowrate	mol frac CO$_2$	total flow	mol frac CO$_2$	total flow	
m^3/hr		kgmole/hr		kgmole/hr	
3000	0.22	5081.61	0.1408	5879.38	27.68
4000	0.22	5081.61	0.1264	6214.37	31.40
5000	0.22	5081.61	0.1152	6566.71	33.91
6000	0.22	5081.61	0.1062	6930.66	35.72
7000	0.22	5081.61	0.0987	7302.89	37.05
8000	0.22	5081.61	0.0922	7681.36	38.09