Flowsheet Design Of CO_2 Adsorption System With Aminated Resin At Natural Gas Reserves

by

Tigabwa Yosef Ahmed

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

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Approved by,

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TRONOH, PERAK

June 11, 2010

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.

TIGABWA YOSEF AHMED

ABSTRACT

Natural gas is efficient, convenient and relatively clean energy source and its global use is growing rapidly. 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% to 40 mol%. Hence, this project aims to investigate the potential of an onsite application of adsorption column with aminated resin to capture CO_2 at the natural gas reserves using flowsheet simulation based approach. The simulation of this CO_2 removal plant that reduces the CO_2 content down to 30 mol%, i.e. the gas processing plant's limitation, is done. The effects of temperature, pressure, adsorbent concentration and its flow rate on performance of CO_2 removal are investigated using the model.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

1.1.1 Natural Gas

Natural gas has been preferred as energy source over some existing energy sources such as coal and petroleum .This is because natural gas is found to be relatively environment-friendly and high effective source of energy. Natural gas is used as fuel in such sectors as transportation, industrial, agricultural, and a raw material for petrochemical industry. Furthermore, natural gas can be used in a cooling system. However, to bring natural gas to this desirable composition the natural gas mixture derived from reserves needs to go through separation processes for the removal of some contaminating gases such as CO_2 for optimal results.

Natural gas is a mixture of various hydrocarbon gases known in scientific names i.e. methane, ethane, propane, and butane. Commonly, methane constitutes around 70% of the gas. In addition to hydrocarbon, other components, such as carbon dioxide, hydrogen sulfide, nitrogen and water can also be found.

Natural gas can also be used to produce various products through gas separation process. As natural gas is made up from many beneficial compositions, at gas separation plants, those compositions can be extracted for a number of products (Steve, 1997) such as methane, ethane, propane and butane, heavier hydrocarbons and Natural Gasoline (NGL) in which each of them has a wide variety of uses.

Natural gas is fossil fuel formed from plant and animal remains millions of years ago. And it has the following physical properties (Steve, 1997)

- It is hydrocarbon component with methane as a major component.
- It is colorless and odorless.
- It is lighter than air with a specific gravity of about 0.6-0.8.

- It is inflamed during a range of 5-15% by volume of gas in air. The self-ignition temperature of natural gas is 537-540 ^{0}C.
- As it is a clean fuel with cleaner burning nature, natural gas has lower environmental impact when compared with other types of fuel.

1.1.2 Market Survey for Natural Gas Demand

Public domain information (Mark, 2009) shows that (Figure 1.1) world natural gas consumption grew by 2.5% in year 2008. As natural gas consumption is determined by both supply and demand , based on upward trend of the graph it can be estimated that the world natural gas demand would substantially increase for the coming few years. This shows that natural gas has the potential to become the future dominant fuel source.

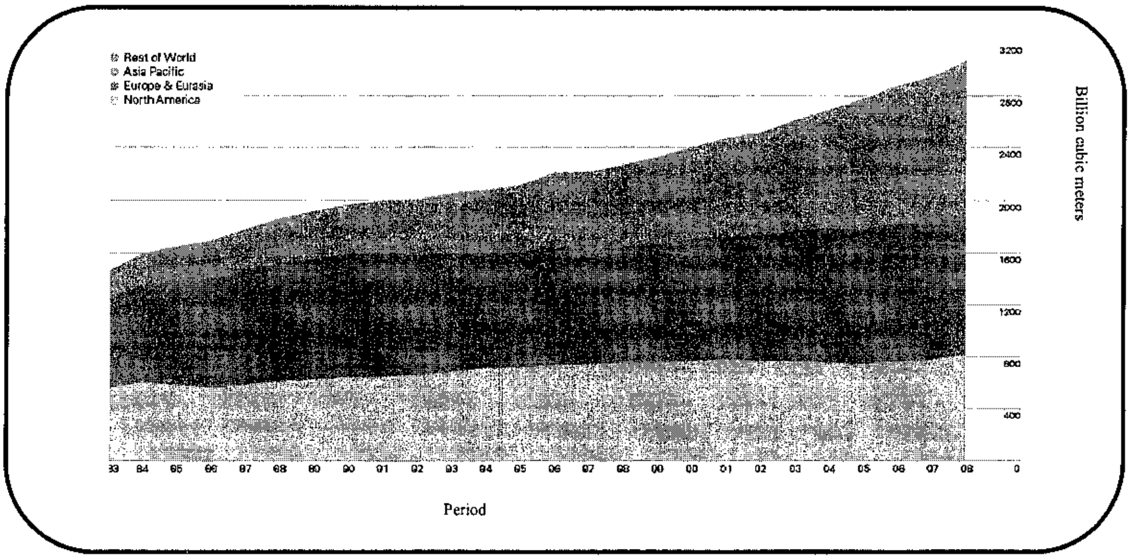


Figure 1.1: Statistical Review of World Natural Gas Consumption (Mark, 2009)

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). This CO_2 content can potentially reduce heating quality of the gas and when burned it results in emission of high amount of CO_2 which is one of the green house gases. Consequently, giving much more attention towards the quality of natural gas in order to meet the customers' specifications would be the major task to gas companies. Hence, the project considers producing a feasible flowsheet which would help the gas companies to meet their customers' specifications in more environmentally friendly way.

1.1.3 Carbon Dioxide Content of Various Natural Gas Reserves in Malaysia

In Malaysia as of January 2008, a total of 379 fields have been discovered, of which 163 are oil fields and 216 are gas fields (Abdul Rahim, 2008). Later for the validation of this project we might need to undergo industrial case studies. Thus, knowing the carbon dioxide content for the reserves in Malaysia is more justifiable than otherwise. Table 1.1 shows the summary of high CO_2 gas fields 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

Table 1.1 illustrates that the majority of natural gas fields in Malaysia have carbon dioxide content of 50 to 74%, which proves the significance of the project.

1.1.4 Technology Options for CO_2 Capture

There are many possible processes for CO_2 removal in which the variations are best suited to a certain operating conditions. In selection of appropriate separation techniques for CO_2 removal from natural gas, the conditions at which the feed gas is available for processing, final product specification, capital and operating costs are the key factors which should be taken into consideration. The major separation techniques (Salako, 2005) which have been implemented for CO_2 removal in natural gas can be grouped as follows:

a. Absorption Process
    - Physical absorption
    - Chemical absorption

b. Adsorption Process
    - Physical adsorption
    - Chemical adsorption

c. Physical Separation (Membrane, Cryogenic Separation)

a. Absorption: refers to processes in which a substance penetrates (diffuses) into the actual interior of crystals, of blocks of amorphous solids, or of liquids. Physical absorption involves the removal of CO_2 using organic solvents (Salako, 2005). Here, the acid gas components get absorbed physically by the absorbent. Selexol process, rectisol process and fluor processes are some of the common physical absorption processes used for CO_2 removal. The selexol process uses a mixture of polypropyleneglycoldimethyl ethers as a solvent whereas rectisol and fluor process use methanol and propylene carbonate respectively (Salako, 2005).

On the other hand, chemical absorption is based on exothermic reaction of the solvent with gas stream to remove the CO_2 present. Chemical absorption processes are particularly applicable where acid gas (CO_2) partial pressure are low and for low level of acid gas requirement in the residue gas (Salako, 2005). An example of chemical absorption is the uses of potassium carbonate (K_2CO_3) to remove CO_2.

Amine-based, solvent-capture systems have been extensively used for the removal of CO_2 from gas streams in many industries. This process based on the principles of chemical absorption of CO_2 via alkanolamines is considered to be a potential technique for capturing CO_2 from natural gas. Aqueous alkanolamines such as monoethanolamine (MEA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), diglycolamine (DGA), triethanolamine (TEA) and 2-amino-2-methyl-1-propanol (AMP) have been widely used chemical absorbents for removal of acid gases (CO_2, H_2S) (Song et al., 2006). The particular choice of alkanolamine is primarily dictated by the requirements of a specific application. However, at high CO_2 levels due to the high energy requirement for regenerating the absorbents other processes become rather desirable (Clifton et al., 1985).

b. Adsorption: refers to the collecting of molecules by the external surface or internal surface (walls of capillaries or crevices) of solids or by the surface of liquids. The removal processes is either by chemical reaction (Chemical adsorption) or by ionic bonding of solid particles with the acid gas.

Due to the limited lifetime, susceptibility to degradation through oxidation and corrosion problems observed in aqueous amine processes (Philip et al., 1999) recently there is a need to utilize solid sorbents for CO_2 removal. Activated carbon (George and Coraopolis, 1970), phenolic resin-based carbon spheres (Przepiórski et al., 2002), molecular sieve (Zeolite) (Wei et al., 2009) and silica gel (Leal et al., 2000) process are some of the common adsorption processes for CO_2 removal from natural gas. Leal et al. (2000) demonstrated the reversible adsorption of CO_2 on amine surface-bonded silica gel in which the porous support provides the amine with structural integrity and a surface for gas/solid contact. Hence, a development of synthetic and higher capacity, more selective adsorbent would greatly improve the overall performance of the adsorption separation process.

c. Membrane Separation: Carbon dioxide membranes operate on the principle of selective permeation. Polymer membrane systems are commercially proven technology for natural gas treatment applications (Salako, 2005). However, there would be high amount of hydrocarbons loss due to some tendency of diffusion through the membrane.

Accordingly, it can be stated that the process selection for CO_2 removal depends on the raw gas conditions and treated gas specifications. As preliminary laboratory-scale research indicated the specially designed aminated resin of this project has been proved to be a good solid adsorbent to remove CO_2 from high CO_2 loaded natural gas stream. Hence, in this project flowsheet of the acid gas plant is developed and simulated to prove the industrial scale performance of this particular adsorbent.

1.1.5 CO_2 Adsorption Mechanisms

The aminated resin of this project is a solid material where adsorption of carbon dioxide is expected to take place. Thus, knowing adsorption mechanisms of the carbon dioxide onto solid adsorbents would help to understand the system better. More often, for the adsorbents being used for CO_2 removal the adsorption process is considered to be gas-solid interaction. Adsorption occurs in three stages (Coulson et al., 1991) as it is described in Figure 1.2.

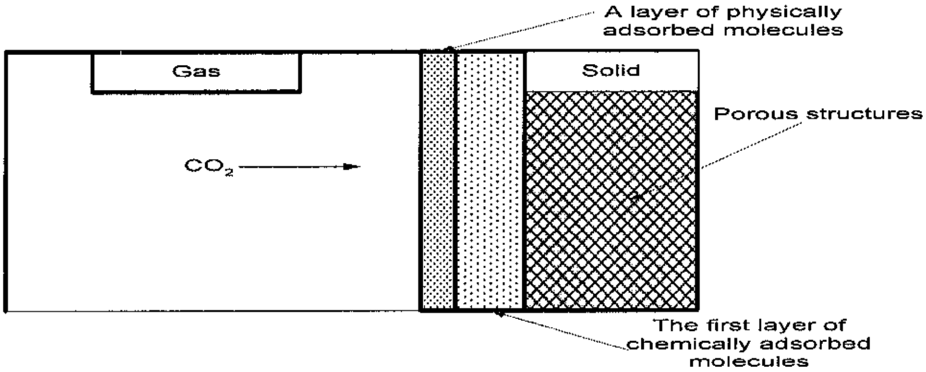


Figure 1.2: A Gas-Solid Carbon Dioxide Adsorption Mechanism

Figure 1.2 shows that at first a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and will be associated with a change in free energy which is characteristic of the forces which holds it. And the fluid concentration is further increased, second and third etc., 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).

However, an adsorption mechanism might differ from one system to another depending on nature of interaction in a system. For instance, there might be a three phase interaction (gas-liquid-solid) in a system as it has been discussed by Zhang et al.(2004). In such systems, the adsorption mechanism would vary accordingly.

Zhang et al. (2004) reported a possible mechanism for a novel three-phase (gas-solid-liquid) CO_2 absorption system with primary or secondary immobilized amine and methyldiethanolamine (MDEA). In the mechanism (Figure 1.3) CO_2 from the gas phase dissolves in the liquid phase (gas–liquid mass transfer). The formation of carbamate then takes place as a kind of chemical adsorption process through the reaction of dissolved CO_2 with the immobilized amine (liquid–solid 'adsorption'), which would be continuously regenerated by hydrolysis reaction between the aqueous MDEA solution in the liquid phase flowing over the immobilized amine and the carbamate releasing bicarbonate into the solution (solid–liquid 'desorption').

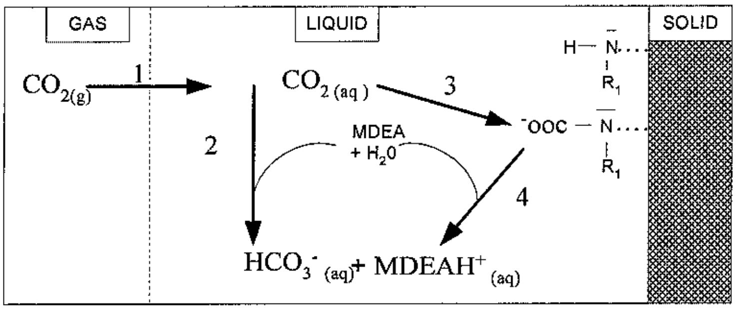


Figure 1.3: A Gas-Liquid-Solid-Liquid Mechanism (Zhang et al., 2004)

1.2 PROBLEM STATEMENT

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% to 40 mol% CO_2 removal efficiency (Brian and Swallow, 1984). However, having natural gas mixture straight from reserves containing about 10 to 70 mol% methane and carbon dioxide content of 30 to 90 mol% (Brian and Swallow, 1984), the existing natural gas treating plants will be ineffective for this high carbon dioxide loaded stream due to their limited absorption capacity i.e. as high as 30 mol% to 40 mol%. As it is also shown in Table 1.1 the majority of natural gas fields in Malaysia have carbon dioxide content of 50 to 74 mol%, which proves the significance of the project.

Thus, in order to minimize CO_2 amounts in natural gas mixture and at the same time complement the existing CO_2 treatment unit in refineries, it is proposed to install an adsorption based separation system that uses a newly and specially designed aminated resin. The system would be expected to reduce the concentration of carbon dioxide up to 30% or less before the gas being directed to amine treating plants at the gas refineries.

1.3 OBJECTIVES

The main objective of this project is investigate the potential of an onsite application of adsorption column with a newly designed aminated resin to capture CO_2 at natural gas reserves using flowsheet simulation based approach. Below are the specific objectives of the study:

1. To synthesize feasible routes for CO_2 adsorption system that uses a specially designed aminated resin which can be applied to a high CO_2 content and high pressure natural gas stream at natural gas reserves.
2. To develop feasible flowsheet and simulate it in ICON and HYSYS to identify best operating parameters for the system.
3. To perform preliminary economic evaluation for the system.

1.4 SCOPE OF WORK

The overall scope of work for this study is to provide cost effective and environmentally friendly CO_2 capture plant design from natural gas from reserves. Conceptual studies, evaluation of processing options and determination of optimal operating parameters are possible activities to be undertaken during the project.

Figure 1.4 demonstrates the overall natural gas processing facilities including the proposed acid gas removal system of this project. It would consist of gas reception facilities, acid gas removal system, existing gas sweetening plants and gas processing plant.

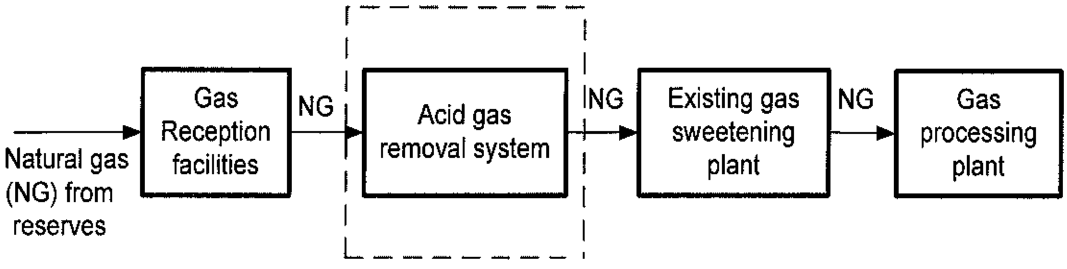


Figure 1.4: The Overall Process for Natural Gas Processing System

Natural gas delivered from reserves contains hydrocarbon condensate and water. Thus, it is usually passed through field separators at the reserves to remove those components. Slug catcher and stabilizer are used mainly for that separation (Al-Sobhi, et al., 2009). Such activities are conducted in the gas reception facilities shown in Figure 1.4. However, 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, the gas will be sent to existing acid gas treatment plants for further purification to meet customer's specifications.

A sour natural gas is a natural gas which contains, in addition to hydrocarbon components, one or more acid gas components such as CO_2 and H_2S. Figure 1.5 illustrates that the natural gas delivered from offshore reserves would go through the proposed acid gas removal system at the reserves. Once the target product specification is achieved (< 30 mol% of CO_2), the gas will be sent to existing refineries for further processing. The desired natural gas product specification will be used for simulation to study process alternatives, process design to optimize flowsheet, assess feasibility and preliminary economics, and plant operation to reduce energy use, increase yield and improve pollution control.

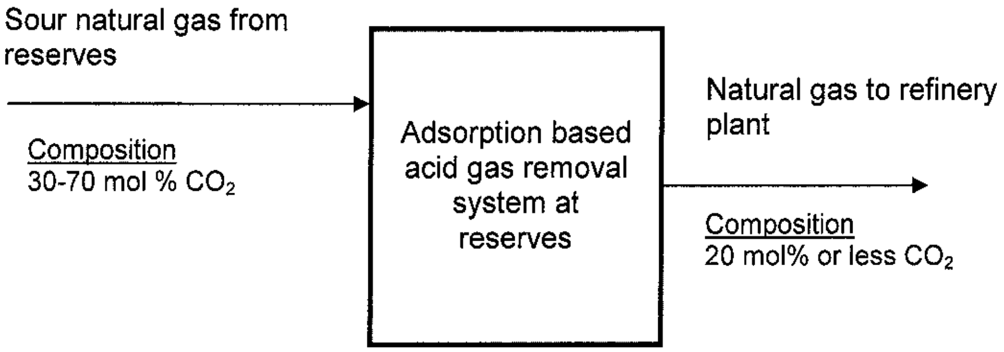


Figure 1.5: Block Diagram Representation of the General Streams Conditions of a Near-Shore Onsite Acid Gas Removal System

CHAPTER 2

LITERATURE REVIEW

2.1 CARBON DIOXIDE REMOVAL TECHNIQUES

Understanding the behavior of the CO_2 removal system would help to design a reasonable flowsheet. It has been highlighted in Chapter 1 that generally three different approaches have been used for CO_2 removal from gas streams. Those are absorption on liquid amines, adsorption on solid materials and membrane technology (Leal et al., 2000).

Recently, several solid sorbets have been utilized to remove CO_2 from gas streams. Leal et al. demonstrated the reversible adsorption of CO_2 on amine surface-bonded silica gel. Moreover, Hermann et al. (1989) elaborated the adsorption of CO_2 on aminated carbon molecular sieves. In this process the gas to be treated is contacted with the material at room temperature and atmospheric pressure. The carbon molecular sieve-based material has been functionalized with amine groups to chemically treat the surface of carbon-based material to improve its adsorptive capabilities. Regeneration was done by heating to moderate temperature. However, George and Coraopolis (1970) reported another way of reactivation of monoethanolamine impregnated activated carbon by passing monoethanolamine vapors through the exhaust carbon to sweep out the CO_2, carbon disulphide (CS_2) and H_2S.

In the same area of study, in order to prove the best adsorption capacity of amine functionalized adsorbents, 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. 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, the best adsorbing around 14 wt% CO_2 at 1.0atm CO_2 pressure. At 25atm CO_2 pressure, up to 60 wt% CO_2 can be adsorbed.

The use of membranes top remove carbon dioxide and other acid gases were assessed by Bhide and Stern (1993). Besides, Anjan and Pradip (2006) reported on optimization of membrane unit for removing carbon dioxide from natural gas. Aromatic polyimide separation membranes are particularly useful for CO_2 enrichment, because they are able to achieve high flow rates with good selectivity and relatively low temperature (Orland et al., 2000). These procedures proved effective to remove carbon dioxide in concentration ranging between 5 and 40% (Orland et al., 2000). However, membrane saturation might produce gas losses.

2.2 REACTION MECHANISMS OF CO_2 REMOVAL BY ALKANOLAMINES

For many years among other alkanolamines, methanolamine (MEA) was exclusively used for removal of CO_2 and H_2S. This amine increases the CO_2 pickup but has higher heat of absorption than methyldiethanolamine (MDEA) and tends to be more corrosive (John et al., 1990). Thus, to reduce operating costs (lowest regeneration heat) and corrosion rates, the use of MDEA (tertiary amine) solvents became more common as an alternative to the primary and secondary amines in bulk CO_2 removal (Wang et al., 2004). In addition, MDEA offers various important features, such as high-acid gas loading, slow degradation, lower heats of reaction, low vapor pressure and solution losses (John et al., 1990).

The slower rate of reaction of CO_2 with MDEA could be compensated through the addition of small amounts of rate-promoting agents such as diethanolamine (DEA), which is a secondary amine, and piperazine (Fürhacker et al., 2003). Here is where researchers found out the idea of using blends of primary or secondary amine with tertiary amines (e.g. MDEA) for CO_2 removal. Primary amines MEA and diglycolamine (DGA) offer no selectivity in normal operating units, absorbing CO_2 as completely as H_2O. However, secondary and tertiary amines DEA, diisopropanolamine (DIPA) and MDEA are selective amines and more effective for high pressure application (>300 psi, 20 kPa) (Kevin and Jerry, 2006). Hence, the blend of primary or secondary with tertiary amine is advantageous since it combine the high absorption capacity of the tertiary amines with the high absorption rates achievable with primary or secondary amine (Zhang et al., 2004).

Considering such importance of blend of primary or secondary amines with tertiary amines, 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.

The most significant observation from a plant design perspective is relatively simple (Douglas et al., 2006). All of amines, as well as the tertiary amines, react with H_2S instantaneously since it is a proton donor acid.

$$H_2S + R_1R_2NCH_3 \Leftrightarrow R_1R_2NHCH_4^+ + HS^- \text{..........} \quad (2.1)$$

,where R corresponds to alkyl or alkanol groups.

Only the primary and secondary amines can form carbamate by reacting with CO_2, which is an electron acceptor lewis acid (Olgac and Erdo, 1999). Here, CO_2 replaces a proton from the amino site as follows

$$2R_1R_2NH + CO_2 \Leftrightarrow R_1R_2NH_2{}^+ + R_1R_2NCOO^- \text{.....} \quad (2.2)$$

However, MDEA do not react with CO_2 directly (Zhang et al., 2004). Since MDEA is a tertiary amine and doesn't have hydrogen atom attached to the nitrogen, the CO_2 reaction can only occur after the CO_2 dissolves in the water to form a bicarbonate ion (Douglas et al., 2006).

$$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+ \ldots\ldots\ldots\ldots\ldots \tag{2.3}$$

The bicarbonate formation is slow and only occurs in the liquid phase (Douglas et al., 2006). The bicarbonate then undertakes an acid-base reaction with the amine to yield an overall CO_2 reaction.

$$CO_2 + H_2O + R_1R_2NCH_3 \Leftrightarrow R_1R_2NCH_4^+ + HCO_3^- \ldots\ldots\ldots \tag{2.4}$$

The tertiary amine MDEA has two ethanol groups attached to the nitrogen atom along with a methyl group (Wang et al., 2004).

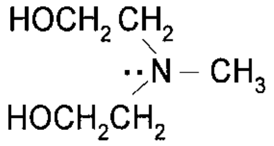


Figure 2.1: Chemical Structure of MDEA (Huttenhuis et al., 2006)

Thus, the reaction of CO_2 with MDEA can be rewritten as follow (Bolhàr-Nordenkampf et al., 2004).

$$CO_2 + H_2O + MDEA \Leftrightarrow MDEAH^+ + HCO_3^- \ldots\ldots\ldots\ldots \tag{2.5}$$

Hydrogencarbonate (HCO_3^-) is an acid salt of carbonic acid (solution of carbon dioxide in water). It gives off carbon dioxide when heated or treated with dilute acids (Keith, 2001).

2.3 METHYLDIETHANOLAMINE (MDEA)

2.3.1 Physical Properties of MDEA

MDEA is a clear, water-white, hygroscopic liquid with an ammoniacal odor (Huntsman, 2000). It absorbs carbon dioxide and hydrogen sulfide at lower temperatures and releases the acid gases at higher temperatures. MDEA is used in natural gas plants for bulk removal of carbon dioxide while producing a gas stream containing 0.25 grains hydrogen sulfide/100scf (Huntsman, 2000). Bulk carbon dioxide removal can be realized with MDEA when the CO_2 H_2S ratio ranges from 100 to 1,000 (Huntsman, 2000). Table 2.1 contains a list of some physical properties of MDEA.

Table 2.1: Physical Properties of Methyldiethanolamine (Stephen, 2007) and (Fine Chem Trading, 2000)

Physical properties of Methyldiethanolamine	
Chemical formula	$C_5H_{13}NO_2$
Boiling point (°C)	247.3
Flash point (PMCC, °F)	240
Freezing point (°C)	-21
Specific gravity (20/20 °C)	1.0431
Vapor pressure (20 °C, mm Hg)	< 0.01
Viscosity (100 °F, cst)	36.8
Water solubility (in water)	Complete
Weight (20 °C, lb/gal)	8.69
Molecular Weight	119.1
pKa	8.52

2.3.2 Storage and Handling

The solvent and alkaline properties of MDEA should be considered when using handling and storage facilities (Fine Chem Trading, 2000). MDEA will react with copper to form complex salts, so the use of copper and alloys containing copper should be avoided. Carbon steel storage tanks are considered satisfactory. Centrifugal pumps are preferred with methyldiethanolamine, although carbon steel rotary pumps can be used (Fine Chem Trading, 2000).

2.3.3 Safety Measures

MDEA is considered slightly toxic by single oral dose and practically nontoxic in single dermal application. MDEA is moderately irritating to the eyes, but only slightly irritating to the skin (Fine Chem Trading, 2000). Because of the low vapor pressure of methyldiethanolamine, exposure to vapors is not expected to present a significant hazard under normal workplace conditions (Fine Chem Trading, 2000). However, care must be taken in handling the compound for extra safety measure.

2.4 CONTAMINANTS IN AMINE GAS TREATING

The knowledge of contaminants that are normally found in amine system would help not to ignore their significant impact on the overall process performance. Performance limiting contaminants can build up in amine solutions over an extended period of operation. Amine contaminants can be grouped into five categories (Randy, 2001); heat stable salts, degradation, injection chemicals, hydrocarbons and particulates. Randy (2001) has explained in detail about each of them.

Such contaminant found in amine systems come from three sources which are makeup water or feed gas and derived contaminants formed by reactions of amine with contaminants from makeup water (Randy, 2001). And the best approach to avoid contaminate, such as heat stable amine salt, problem is to address the conditions that led to the problem.

2.5 FLOWSHEET DESIGN AND STEADY STATE SIMULATION FOR CO_2 REMOVAL SYSTEM

Flowsheet design is the overall development of a process flowsheet by combining individual steps (equipment and operating conditions) into an optimal arrangement. The simulation would provide a set of experimental data on feasibility of separation.

2.5.1 Flowsheet Design for CO_2 Removal System

The primary selection of a particular process for carbon dioxide removal from natural gas may be based on feed parameters such as composition, pressure, temperature, and the nature of the impurities, as well as product specifications. The second selection of a particular process may be based on acid/sour gas percent in the feed, whether all CO_2, all H_2S, or mixed. The third selection could be based on content of heavy hydrocarbon, such as C3+, in the feed gas and the size of the unit. Final selection is ultimately based on process economics, reliability, and environmental constraints.

Commonly the absorption of acid gases (H_2S, SO_2, and CO_2) in amine solution is conducted with a two column operation. The first column is used to absorb the acid gas into the absorbent amine while the second column is used to regenerate the amine. Kevin and Jerry (2006) disclosed a process configuration for CO_2 removal plant (Figure 2.2) using MDEA. The process is based on counter current flow to achieve optimum mixing. A lean solution (low acid gas) enters the top of the absorber and flows to the bottom; acid gas enters the bottom of the absorber tower and bubbles to the top. The rich amine (high acid gas) enters the stripper were the acid gases are released and the clean amine is returned to the absorber. The acid gases exit from the top of the stripper.

The MDEA is regenerated in the stripper column. In the regeneration process the amine can degrade or be depleted. Filtration of reaction and corrosion by-products is done with a slipstream so the total amine concentration is not depleted on each pass and the make-up is based on the amount of filtration (Kevin and Jerry, 2006).

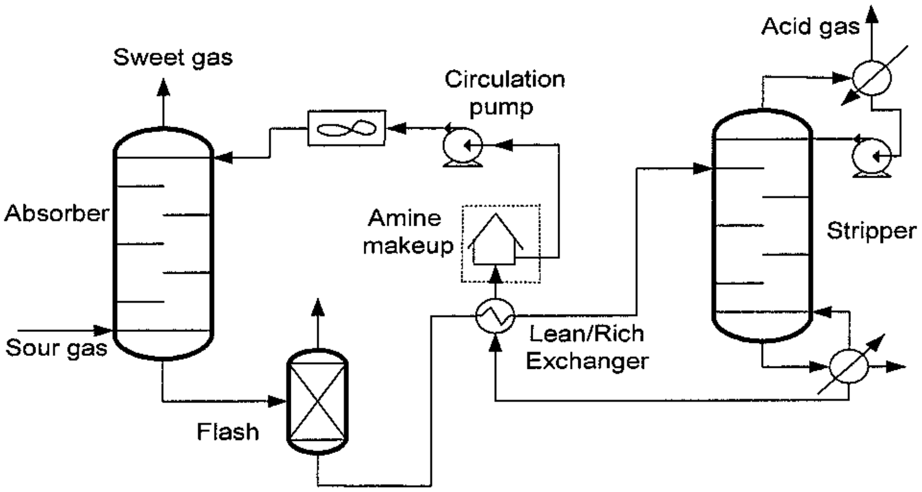


Figure 2.2: Schematic of Amine Sweetening Plant (Kevin and Jerry, 2006)

Douglas et al. (2006) reported the design and operation of a selective sweetening plant using MDEA for Signalta Forestburg plant. Figure 2.3 shows the process flow diagram for the plant. A sour natural gas will come in contact with 50% MDEA amine solution in the contactor. Once treated the sweet gas will leave the column at the top while the bottom product will be lean amine solution. The solution will be sent to the regeneration column where the regeneration is being achieved by the increase in the column temperature.

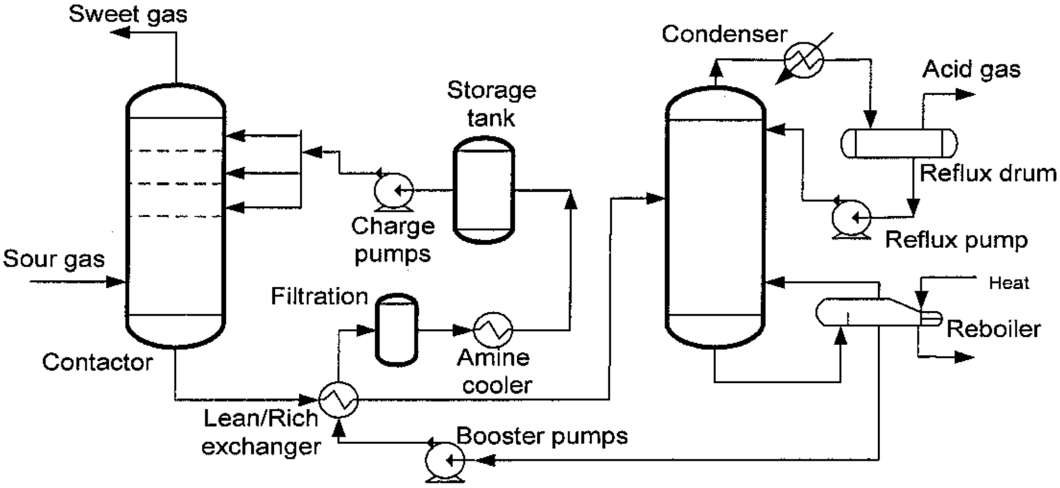


Figure 2.3: Process Flow Diagram for the Forestburg Sweetening Plant (Douglas et al., 2006)

A full flow amine filter was incorporated into the foresburg amine plant. Directly ahead of the amine contactor in the gas stream a large filter separator removes any particulate or liquids mists that might be present after inlet separation. A plate/plate heat exchanger was used as the lean/rich amine exchanger. This type of heat exchanger offers large surface areas and high transfer rates in small volumes. The overhead condenser and the lean amine cooler were mounted in a common unit. Air recirculation and two speed fan motors were also used to prevent freezing problems at low ambient conditions.

Clifton et al. (1985) disclosed another method for removing carbon dioxide from high carbon dioxide content hydrocarbon containing gaseous streams. The process is for CO_2 removal from gaseous stream by CO_2 solution absorption in two or more stages with hydrocarbon control before one or more of the stages to prevent operating problem due to hydrocarbon condensation as CO_2 is removed. According to the invention, the gaseous stream can contain from about 20 mol% CO_2 to about 99 mol% CO_2, since above about 20 mol% CO_2 this particular CO_2 solution absorption process become increasingly significant and economic.

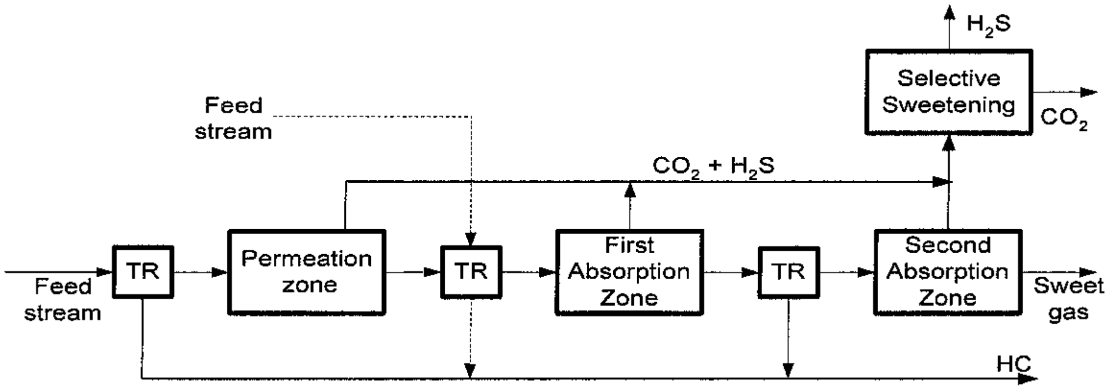


Figure 2.4: Block Diagram of Sour Gas Processing Plant (Clifton et al., 1985)

The process (Figure 2.4) is treating the gaseous stream comprising separating at least the first portion of hydrocarbons from the gaseous stream to produce the first stream having a reduced hydrocarbon content to prevent the presence of heavy (C3 and higher) hydrocarbon from causing operating inefficiencies by hydrocarbon condensation in the absorber during CO_2 removal.

2.5.2 Flowsheet Simulation of CO_2 Removal System

Once the process flowsheet is developed, the process is simulated to investigate the necessity of recycles, product quality and to refine the operating conditions in order to optimize the process yield, utilities, and cost.

HYSYS process simulator has been used (Salako, 2005) to predict the CO_2 removal process operating conditions range at which hydrocarbon and chemical loss (amine solvent) can be minimized. For the amine process simulation, amine fluid package and Kent-Eisenberg thermodynamics and non-ideal vapor phase model was found to be accurate and applicable (Salako, 2005) . In his work the behavior of different process variables for reference state condition and the influence of changes in operating conditions for an industrial packed column for reactive absorption column have been recorded.

Gøteborg (2007) reported Aspen HYSYS simulation of a monoethanolamine based CO_2 removal by amine absorption from a gas based power plant. The thermodynamic properties were calculated with the Peng Robinson and Amines Property Package models which are available in Aspen HYSYS.

Seok and Hyung-Taek (2004) elaborated Aspen Plus simulation of CO_2 absorption system with various amine solutions. The study focused on minimizing the amount of energy required in the regeneration process through the simulation of various process concepts of solvent absorption and to suggest the optimum operation conditions to the actual experimental setup. Bench-scale, continuous CO_2 absorption reactor (capacity = 5 Nm^3/hr) located in the Korea institute of energy research was modeled and simulated with Aspen Plus. Kevin and Jerry (2006) used TSWEET® process simulator to analyze an amine sweetening unit with regard to amine concentration, use of amine mixture and lean amine temperature. The authors reported that the use of mixture of amines appeared to be the best alternative for increasing CO_2 pickup for DEA and MDEA based solution.

CHAPTER 3

METHODOLOGY

3.1 CONCEPTUAL PROCESS DESIGN

This project has got two major phases: phase one, designing a flowsheet of the proposed plant and phase two, simulating the flowsheet in order to access the feasibility and operating condition of the plant.

Conceptual design generates potentially profitable alternatives based on characteristics of a system. In order to design flowsheet of the CO_2 removal plant, the well-known heuristic-based method proposed by Douglas (1988) will be implemented for the purpose of hierarchical decision making. Heuristics-based methods are often used during industrial process synthesis. The hierarchical procedure for conceptual design (Douglas, 1988) decomposes the design into a series of sub-problems. Figure 3.2 shows the hierarchical procedures for conceptual design to be applied for this project.

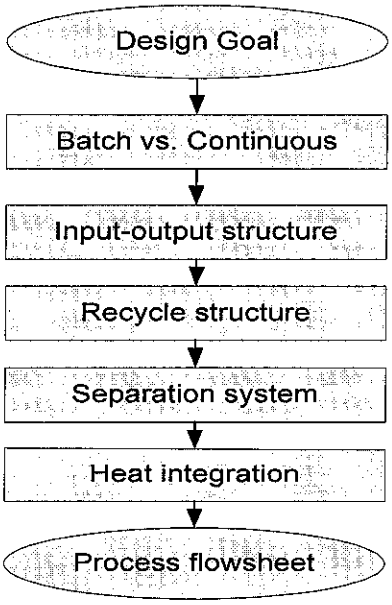


Figure 3.1: Conventional Design Procedures (Douglas, 1988)

3.2 FLOW CHART FOR PROJECT METHODOLOGY

Considering the role of the hierarchical design procedure (Figure 3.2), Figure 3.1 shows the detailed flowchart for the project methodology. Given a product that is to be manufactured, which in this case is sweet natural gas, conducting a search of technical and patent literatures for information about reaction kinetics , flowsheet design and flowsheet simulation of the proposed CO_2 removal system is the first crucial step in doing the project. Then by the use of existing process design models such as onion model, the flowsheet design of the aminated resin based CO_2 removal plant would be done step by step.

Furthermore, constructing input-output structure of the CO_2 removal process would simplify and make the whole picture of the process clearer. At this stage it would be necessary to identify and examine all the necessary steps to be accomplished in the separation of CO_2 from natural gas. Once the base flowsheet is obtained, a study on the effect of change of parameters on the process would be conducted. Finally, in order to access the practicality of the flowsheet a preliminary economics analysis of the flowsheet will be done.

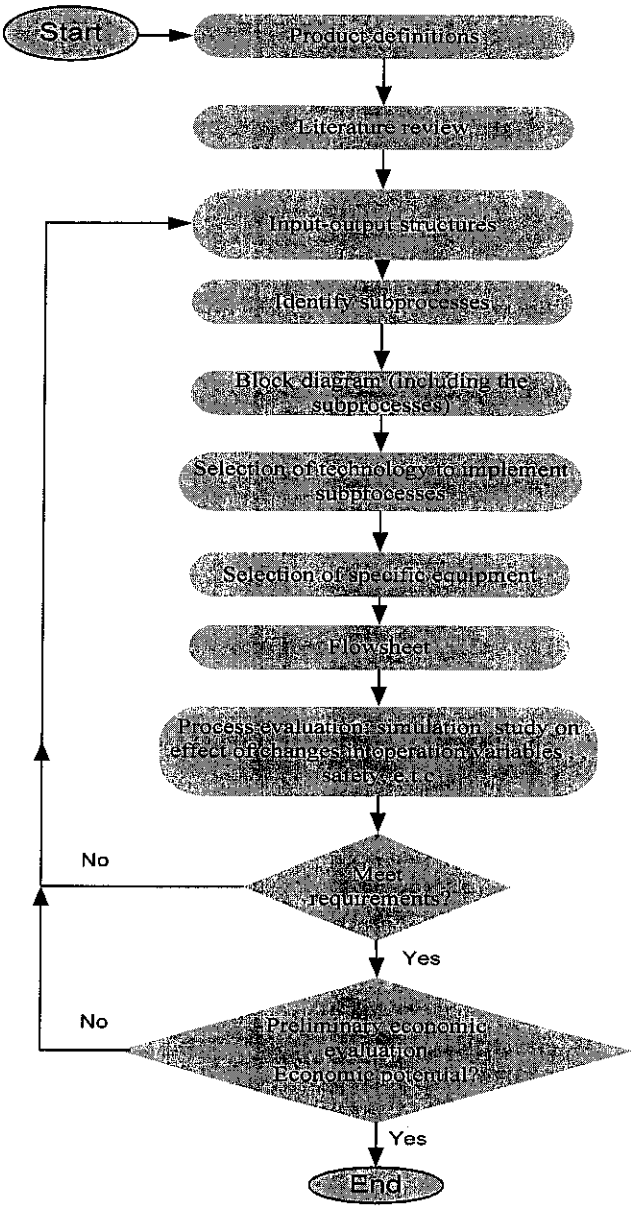


Figure 3.2: Flow Chart for Project Methodology

3.2 TOOLS REQUIRED FOR THE PROJECT

Since testing at a large scale is so expensive, it is natural to use process simulation to evaluate such process. The rigorous unit operations models and fast simulation algorithms contained in process simulators enable to generate accurate data about a process plant. Besides, a computerized approach to the process design calculations is necessary to optimize the design in any reasonable time frame.

For the process simulation, ICON and HYSYS are the simulators used for this project. Since the aminated resin is a new adsorbent these two process simulators are used to validate the simulation data found from one of the simulators using the data found from the other.

The ICON process simulator is a process modeling tool for conceptual design and optimization which is developed by PETRONAS, the Malaysia's national oil corporation in collaboration with Virtual Materials Group (VMG) Inc. It is based on a thermodynamic and physical property calculation mechanism used to predict process behavior for upstream and downstream oil and gas applications.

The HYSYS process simulator is also powerful software for simulation of chemical plants and oil refineries. It includes tools for estimation of physical properties and liquid-vapor phase equilibria, heat and material balances, and simulation of many types of chemical engineering equipment. Moreover, Microsoft Excel will also be used to do analysis on data obtained from the simulators mentioned above.

CHAPTER 4
RESULT AND DISCUSSION

4.1 ADSORPTION MECHANISM OF CO_2 REMOVAL WITH AMINATED RESIN

Since the exact kinetics model for this particular reactive adsorption process on aminated resin is yet to be developed, a possible mechanism of CO_2 adsorption onto the aminated resin is proposed. Figure 4.1 demonstrated the reversible adsorption of CO_2 on amine surface-bonded resin in which the porous support provides the amine with structural integrity and a surface for liquid/solid contact. Hence, the resin would help the amine to with stand high pressure contributing to its durability.

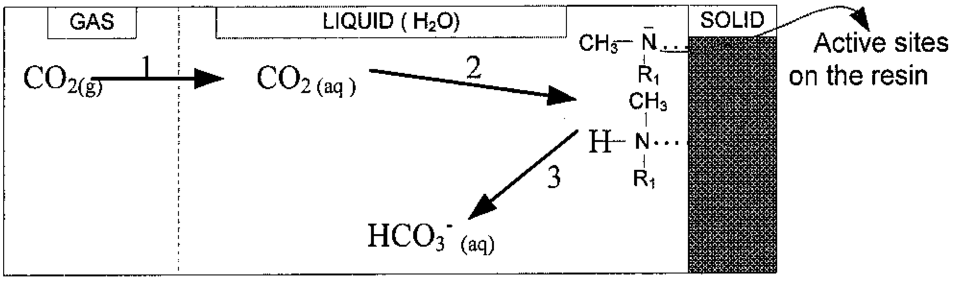


Figure 4.1: A Gas-Liquid-Solid Mechanism for CO_2 Removal with Aminated Resin

Figure 4.1 illustrates that the CO_2 from the gas phase dissolves in the liquid phase (gas–liquid mass transfer). The chemical adsorption process happens through the reaction of dissolved CO_2 with the aminated resin (liquid–solid 'adsorption'). Then the reaction will result in releasing bicarbonate (hydrogencarbonate) into the solution. As hydrogencarbonate gives off carbon dioxide when heated or treated with dilute acids (Keith, 2001), for this project it is proposed to use heat to release the carbon dioxide.

4.2 KEY DESIGN ASSUMPTIONS

The basic assumptions made for this project are summarized below:

1. Carbon dioxide in natural gas is adsorbed by an aminated resin, an amine functionalized adsorbent i.e. methyldiethanolamine (MDEA) is the amine group in the resin.

2. The reaction mechanism for the carbon dioxide removal by the aminated resin is considered to be similar to that of the kinetics of carbon dioxide absorption with solvent MDEA. Thus, the basic reactions that govern MDEA selectivity are as follows as it has been discussed in detail in literature review section too.

$$H_2S + MDEA \Leftrightarrow MDEAH^+ + HS^- \ldots\ldots\ldots\ldots\ldots\ (4.1)$$

$$CO_2 + H_2O + MDEA \Leftrightarrow MDEAH^+ + HCO_3^- \ldots\ldots\ldots\ldots\ (4.2)$$

3. The resin is considered as inert solid in the separation process apart from its contribution to enhancement of carbon dioxide adsorption in MDEA by allowing the amine to withstand high pressure.
4. Regeneration is expected to happen in a distillation column where the regeneration is being achieved by the increase in the column temperature.
5. Heat stable salts and other process solid contaminants (Randy, 2001) which might be accumulated over some run times shall be removed from the cycle by an appropriate filtration process.

4.3 FLOWSHEET DESIGN

The selection criteria for gas processing is highly related to the selection of gas treating configurations to complete the gas processing in order to meet product specification and to satisfy environmental regulatory requirements. Although there are many different types of amines and different configurations for amine sweetening facilities (section 2.5.1), the fundamental process is the same in nearly all cases.

4.4 PROCESS FLOW DESCRIPTION

Figure 4.2 presents a simplified input–output structure of the acid gas removal process. As the aminated resin–water mixture is the media being used for CO_2 adsorption; it will come in contact with the sour natural gas for effective removal of the acid gas (CO_2 and H_2S).

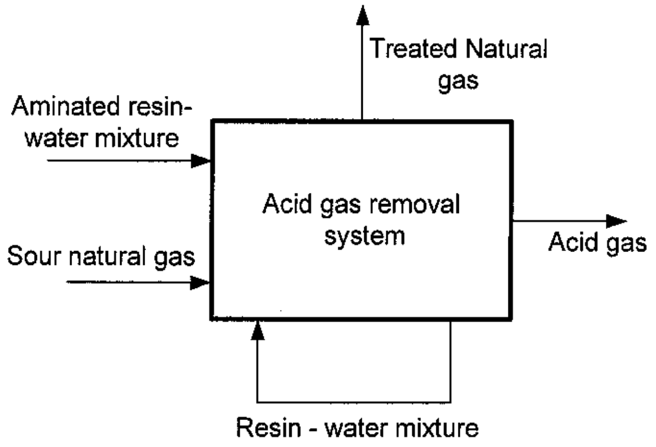


Figure 4.2: The Input-Output Structure for the Acid Gas Removal System

Based on input-output structure in Figure 4.2 the block diagram for the system is illustrated in Figure 4.3. In Figure 4.3, the sour natural gas would go through the CO_2 removal section. Upon sweetening using the aminated resin the natural gas will be sent to existing acid gas removal plants (e.g. amine treating plant in refineries) for further processing as desired. On the other hand, the exhausted resin-water mixture from the carbon dioxide removal section would go through another separation process which will be used to recover some of the hydrocarbons components carried over. The exhausted aminated resin-water mixture (i.e. saturated) then passes through a separation process to separate adsorbed carbon dioxide from the resin. Once regenerated, the aminated resin is recycled to the carbon dioxide removal section for carbon dioxide adsorption.

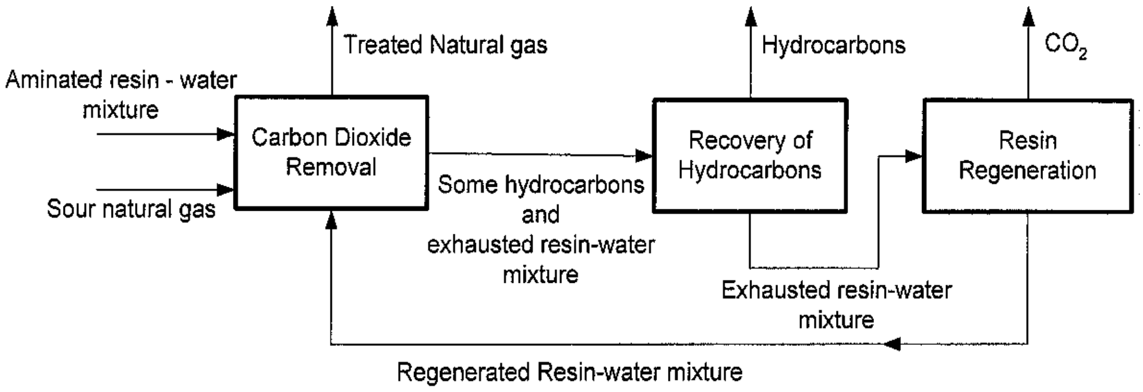


Figure 4.3: The Block Diagram for the Acid Gas Removal System

It is a common knowledge that recycling of materials can reduce cost and has environmental benefit too. In addition, makeup water is necessary as there would be loss of water from the process due to high temperature used in the regeneration step.

At the start of this project, there was a need to consider a simple vessel allowing a contact between the sour gas and the specially designed adsorbent to benefit from the design simplicity and economic aspect of the separation process. However, due to the characteristics of the amine (MDEA), slow reaction rate with CO_2, for this project it was necessary to use tray column to give more time for the reaction to happen getting better gas-liquid-solid contacting efficiency. In addition, since the solid resin is present in the towers are also preferred because it permits easier cleaning too.

Once the CO_2 is adsorbed on to the resin, the treated natural gas leaves from the top of the column while the exhausted aminated resin-water mixture leaves the column from the bottom. The exhausted resin–water mixture will be flowed to a flash tank to remove the hydrocarbon components carried over with it. The flashed overhead product containing the hydrocarbons can be used as a fuel. To make the resin ready for reuse a regeneration section using a distillation column (CO_2 stripping column) to remove the adsorbed carbon dioxide from the resin is proposed. During the regeneration, carbon dioxide and some water evolve from the mixture and water can be separated by condensing the mixture.

Some of the aminated resin might degrade along the regeneration process and there might also be some other contaminants such as heat stable salts (Randy, 2001). Since the deposition of such contaminants occurs in a long run, early consideration of there existence is beneficial than otherwise. Filtration of those contaminants can be done either by introducing a continuous filtration process right ahead of the regeneration process or it can also be done manually depending on its suitability.

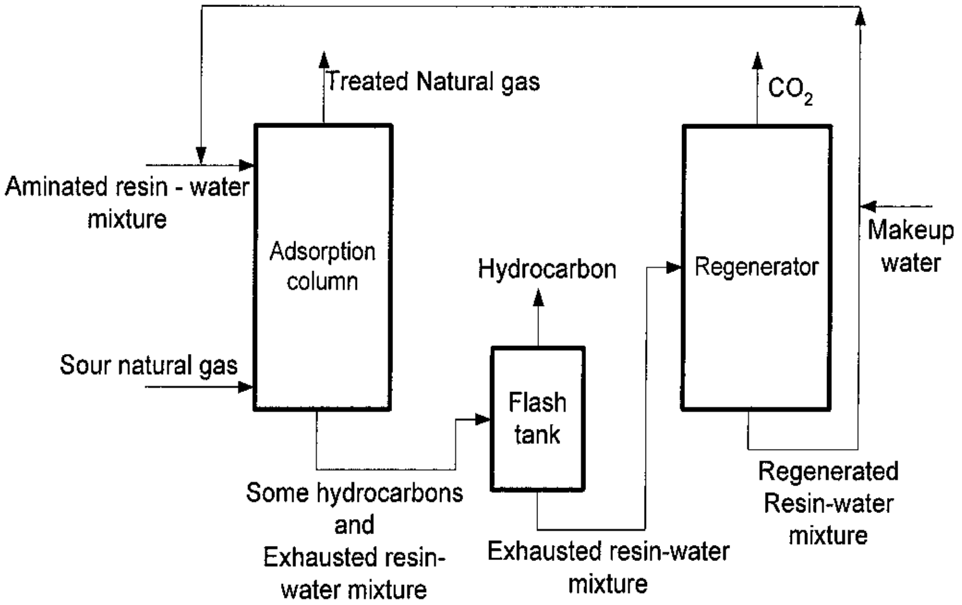


Figure 4.4: The Proposed Process Block Diagram for the Acid Gas Removal System

Based on the block diagram in Figure 4.4, the process flow diagram for the system is illustrated in Figure 4.5. The process flow diagram makes the process representation clearer and ready to be entered to simulation environment for simulation.

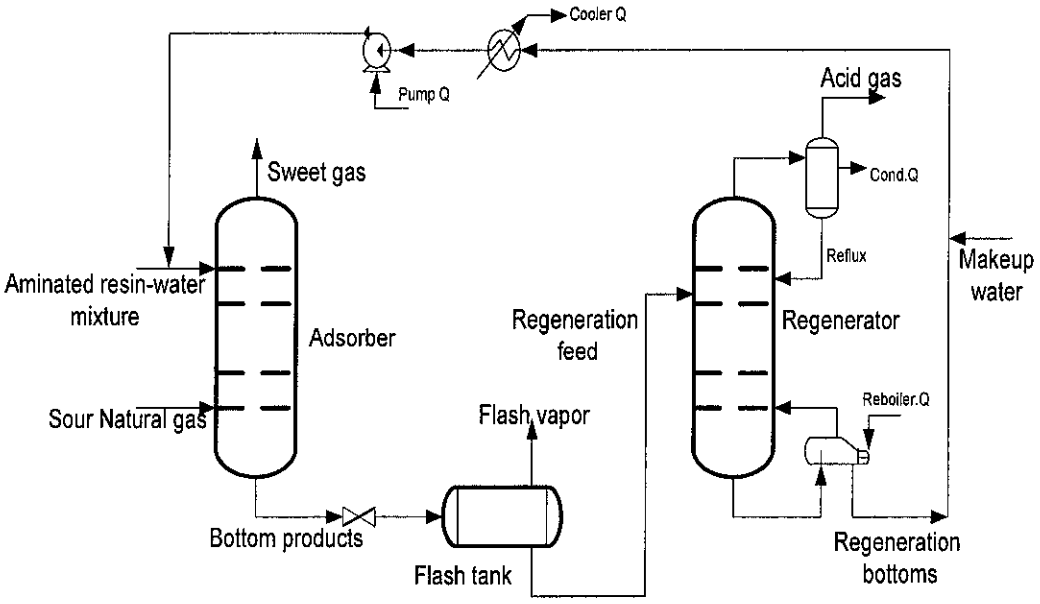


Figure 4.5: The Proposed Process Flow Diagram for the Acid Gas Removal System

4.5 PROCESS SIMULATION

Considering the presence of other trace amount elements in case of the real natural gas feed condition, the composition of the sour gas is considered to be as shown in the Table 4.1. The amount of carbon dioxide is taken to be 70 mol% of the natural gas in line with the project objective.

4.5.1 Natural Gas Feed Condition

If simulation result for the particular natural gas stream condition (Table 4.1) is evaluated and found to have certain pattern of performance, then for a case where there are no other trace elements in the natural gas stream other than carbon dioxide and methane, the designed plant performance would obviously be better as there wouldn't be any other compound such as that of H_2S competing with carbon dioxide for adsorption onto the aminated resin.

Table 4.1: Natural Gas Feed Conditions (Douglas et al., 2006)

Components	Composition (mol fraction)	Composition (mass fraction)
N_2	0.0016	0.001
CO_2	0.70	0.813
H_2S	0.0172	0.015
C1	0.2105	0.089
C2	0.0393	0.031
C3	0.0093	0.011
iC4	0.0026	0.004
nC4	0.0029	0.004
iC5	0.0014	0.003
nC5	0.0012	0.002
nC6	0.0018	0.004
nC7	0.0072	0.019
H_2O	0.005	0.002
Temperature (°F)	86	
Pressure (psia)	1000.0	

4.5.2 Initial Amine Circulation Rate

When initially designing an MDEA facility, a first estimate of the amine circulation rate is required. That is because, the amine circulation rate is important to ensure effective treatment of the sour gas. It is also important because it is a major contribution to the operating cost. Douglas et al. (2006) reported the following formula (4.3) to be used to estimate preliminary amine circulation rate.

$$Circulation\,rate(GPM) = {0.206 \times MM \times (H_2S + CO_2)} / {ML \times WT} \cdots\cdots\cdots\cdots (4.3)$$

, 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 MDEA =119.1,
ML = acid gas loading (moles acid gas/mole) recommended for MDEA 0.4 to 0.6,
WT= weight % of solvent amine MDEA.

Taking the composition of natural gas in Table 4.2, the initial estimate for amine circulation rate can be calculated as follows assuming 50% of the CO_2 and 100% of the H_2S to be removed. Moreover, the amine solution weight by percent is taken to be 50%.

$$Circulation\ rate\,(GPM) = {0.206 \times 25 \times (35 + 1.72) \times 119.1} / {0.6 \times 50} = 750.55$$

Thus, the initial estimate for the amine circulation rate is taken to be 750.55 USGPM, equivalent to 170.47 m^3/hr.

Mafarahi et al. (2008) reported some of the different operating conditions that are tested and proven with a particular amine and become accepted on industry-wide basis. Table 4.2 shows the operating conditions for common amines used for CO_2 removal.

Table 4.2: Typical Operating Conditions and Data for Amines (Mafarahi et al., 2008)

Amine	**MEA**	**DEA**	**DGA**	**MDEA**
Solution concentration (wt %)	15–30	25–35	50–70	20–50
Maximum concentration (wt %)	30	50	70	50
Temperature (°F)	77–260	77–260	77–260	77–260
Acid gas loading (mol/mol)	0.3–0.35	0.3–0.35	0.3–0.35	Unlimited

4.5.3 Theoretical Number of Trays

There are several accepted methods to calculate theoretical trays in amine contactors. Among these are the McCabe Thiele- Graphical Method and the calculation method (Jones and Peter, 2006). This calculation method is considered by many to be the sounder and more accurate of the methods available. The formula (4.4) is known being used for design of absorption column for H_2S removal from natural gas. For this project, the same formula is adapted for calculation for carbon dioxide removal. In this project, the number of trays used is 20.

$$N = \frac{Log(1/q(A-1))}{(Log\,A)} - 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.4)$$

Where N= number of theoretical trays

q = mole of CO_2 in the lean gas/mole CO_2 in feed gas

A= the absorption factor L/V .K

For the regeneration purpose the reboiler duty is chosen based on the guidelines provided below, which should provide an acceptable H_2S and CO_2 loading in the lean amine (Jones and Peter, 2006).

Table 4.3: Recommended Steam Rates Per Lean Amine for Different Type of Amines

Recommended Steam Rates lb Steam / USGAL lean amine (based on 1000 BUT /lb steam)	
Primary Amine (e.g., MEA)	0.80
Secondary Amine (e.g., DEA)	1
Tertiary Amine (e.g., MDEA)	1.20
DGA	1.30

4.6 SIMULATION RESULTS

Using ICON process simulator, with the convergence of the absorber and the regenerator units a complete amine simulation was established as shown in Figure 4.6. One basic assumption made for simulation is that the tray efficiency of the absorption column is taken to 15% for CO_2 and 80% for that of H_2S. This is because H_2S can instantly react with MDEA unlike CO_2.

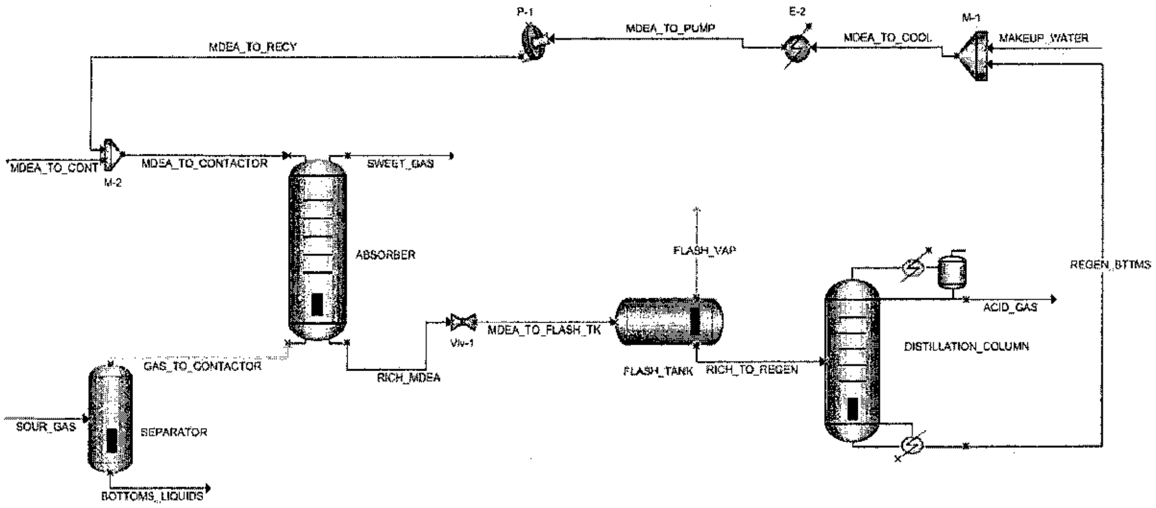


Figure 4.6: Complete Simulations Unit using ICON Process Simulator

The material balance table for the simulation done using ICON process simulator is presented in Table 4.4.

Table 4.4: Material Balance for the Acid gas Removal system using ICON

Name	ACID_GAS	BOTTOMS_LIQUIDS	FLASH_VAP	GAS_TO_CONTACTOR	MAKEUP_WATER	MDEA_TO_CONTACTOR	MDEA_TO_COOL	MDEA_TO_FLASH_TK	MDEA_TO_PUMP	REGEN_BTTMS	RICH_MDEA	RICH_TO_REGEN	S1	SOUR_GAS	SWEET_GAS
VapFrac	0	0	1	1	0	0	0.1668	0.007	0.1672	0	0	0	0.134	0.997	0.9377
T [C]	-77.2727	30	62.4766	30	21.1111	35	-13.5303	62.4766	-13.5303	52.9742	65.4148	62.4766	35	30	35.2999
P [kPa]	189.606	8106	620.528	8106	148.237	6860.283	148.237	620.528	113.763	217.185	8106	620.528	113	8106	6860.283
MoleFlow [kgmole/h]	123.01	3.71	122.33	1241.39	-11812.84	16582.89	5374.24	17432.42	5374.24	17187.08	17432.42	17310.09	5374.24	1245.1	391.87
MassFlow [kg/h]	5412.42	68.75	5264.01	47096.1	-212811.63	456556.19	270165.64	493653.69	270165.64	482977.27	493653.69	488389.68	270165.64	47164.85	9998.6
VolumeFlow [m3/hr]	4.322	0.071	536.411	205.755	-213.25	419.866	13055.675	959.506	17053.939	421.198	423.178	423.094	16357.845	205.826	110.94
Energy [W]	-2465829.027	-34455.0718	350207.6717	1897576.397	114164423.2	-183963339.8	-72079622.87	-183046166	-72030875.65	-186244046.1	-183046166	-183396383.5	-65435143.55	1863121.325	884573.168
MoleFraction.NITROGEN [Fraction]	1.98E-05	1.96E-06	6.94E-04	0.0016	0	0	8.97E-34	5.01E-06	8.97E-34	2.80E-34	5.01E-06	1.40E-07	8.97E-34	0.0016	0.0049
MoleFraction.WATER [Fraction]	3.55E-11	0.9795	0.0318	0.0021	1	0.8854	0.5337	0.8424	0.5337	0.8542	0.8424	0.8481	0.5337	0.005	8.22E-04
MoleFraction.HYDROGEN SULFIDE [Fraction]	8.94E-04	0.0014	2.92E-04	0.0172	0	8.01E-04	0.0064	0.002	0.0064	0.002	0.002	0.002	0.0064	0.0172	9.85E-07
MoleFraction.CARBON DIOXIDE [Fraction]	0.9991	0.0191	0.9622	0.702	0	0.0267	0.1911	0.0727	0.1911	0.0598	0.0727	0.0664	0.1911	0.7	0.1183
MoleFraction.METHANE [Fraction]	7.61E-06	9.67E-08	0.0048	0.2111	0	0	7.99E-57	3.37E-05	7.99E-57	2.50E-57	3.37E-05	5.41E-08	7.99E-57	0.2105	0.6673
MoleFraction.ETHANE [Fraction]	7.24E-08	1.89E-10	1.73E-04	0.0394	0	0	4.31E-69	1.21E-06	4.31E-69	1.35E-69	1.21E-06	5.14E-10	4.31E-69	0.0393	0.1248
MoleFraction.PROPANE [Fraction]	1.52E-10	1.38E-13	3.41E-06	0.0093	0	0	5.18E-89	2.39E-08	5.18E-89	1.62E-89	2.39E-08	1.08E-12	5.18E-89	0.0093	0.0295
MoleFraction.ISOBUTANE [Fraction]	3.73E-13	1.93E-16	8.16E-08	0.0026	0	0	3.20E-100	5.73E-10	3.20E-100	1.00E-100	5.73E-10	2.65E-15	3.20E-100	0.0026	0.0083
MoleFraction.n-BUTANE [Fraction]	1.41E-12	4.99E-16	1.62E-07	0.0029	0	0	3.20E-100	1.14E-09	3.20E-100	1.00E-100	1.14E-09	1.01E-14	3.20E-100	0.0029	0.0092
MoleFraction.ISOPENTANE [Fraction]	6.86E-09	1.22E-18	4.87E-11	0.0014	0	0	3.20E-100	4.87E-11	3.20E-100	1.00E-100	4.87E-11	4.87E-11	3.20E-100	0.0014	0.0044
MoleFraction.n-PENTANE [Fraction]	5.01E-09	6.09E-19	3.56E-11	0.0012	0	0	3.20E-100	3.56E-11	3.20E-100	1.00E-100	3.56E-11	3.56E-11	3.20E-100	0.0012	0.0038
MoleFraction.n-HEXANE [Fraction]	3.43E-10	1.02E-21	2.44E-12	0.0018	0	0	3.20E-100	2.44E-12	3.20E-100	1.00E-100	2.44E-12	2.44E-12	3.20E-100	0.0018	0.0057
MoleFraction.n-HEPTANE [Fraction]	6.45E-11	5.13E-24	4.58E-13	0.0072	0	0	3.20E-100	4.58E-13	3.20E-100	1.00E-100	4.58E-13	4.58E-13	3.20E-100	0.0072	0.0229
MoleFraction.METHYL DIETHANOLAMINE [Fraction]	5.53E-38	0	2.87E-08	0	0	0.0871	0.2688	0.0829	0.2688	0.084	0.0829	0.0834	0.2688	0	4.94E-09
MassFraction.NITROGEN	1.26E-05	2.96E-06	4.52E-04	0.0012	0	0	5.00E-34	4.96E-06	5.00E-34	2.80E-34	4.96E-06	1.39E-07	5.00E-34	0.0012	0.0053
MassFraction.WATER	1.45E-11	0.9521	0.0133	9.92E-04	1	0.5794	0.1913	0.5359	0.1913	0.5476	0.5359	0.5415	0.1913	0.0024	5.81E-04
MassFraction.HYDROGEN SULFIDE	6.93E-04	0.0026	2.31E-04	0.0155	0	9.92E-04	0.0044	0.0024	0.0044	0.0024	0.0024	0.0024	0.0044	0.0155	1.32E-06
MassFraction.CARBON DIOXIDE	0.9993	0.0453	0.9841	0.8144	0	0.0427	0.1673	0.113	0.1673	0.0936	0.113	0.1036	0.1673	0.8133	0.204
MassFraction.METHANE	2.77E-06	8.37E-08	0.0018	0.0893	0	0	2.55E-57	1.91E-05	2.55E-57	1.43E-57	1.91E-05	3.07E-08	2.55E-57	0.0891	0.4196
MassFraction.ETHANE	4.95E-08	3.06E-10	1.21E-04	0.0312	0	0	2.58E-69	1.29E-06	2.58E-69	1.44E-69	1.29E-06	5.48E-10	2.58E-69	0.0312	0.1471
MassFraction.PROPANE	1.52E-10	3.29E-13	3.50E-06	0.0108	0	0	4.54E-89	3.73E-08	4.54E-89	2.54E-89	3.73E-08	1.69E-12	4.54E-89	0.0108	0.0511
MassFraction.ISOBUTANE	4.92E-13	6.05E-16	1.10E-07	0.004	0	0	3.70E-100	1.18E-09	3.70E-100	2.07E-100	1.18E-09	5.46E-15	3.70E-100	0.004	0.0188
MassFraction.n-BUTANE	1.87E-12	1.56E-15	2.19E-07	0.0045	0	0	3.70E-100	2.34E-09	3.70E-100	2.07E-100	2.34E-09	2.07E-14	3.70E-100	0.0044	0.021
MassFraction.ISOPENTANE	1.12E-08	4.75E-18	8.17E-11	0.0027	0	0	4.59E-100	1.24E-10	4.59E-100	2.57E-100	1.24E-10	1.25E-10	4.59E-100	0.0027	0.0126
MassFraction.n-PENTANE	8.22E-09	2.37E-18	5.97E-11	0.0023	0	0	4.59E-100	9.08E-11	4.59E-100	2.57E-100	9.08E-11	9.11E-11	4.59E-100	0.0023	0.0108
MassFraction.n-HEXANE	6.71E-10	4.74E-21	4.88E-12	0.0041	0	0	5.48E-100	7.41E-12	5.48E-100	3.07E-100	7.41E-12	7.44E-12	5.48E-100	0.0041	0.0193
MassFraction.n-HEPTANE	1.47E-10	2.77E-23	1.07E-12	0.0191	0	0	6.37E-100	1.62E-12	6.37E-100	3.57E-100	1.62E-12	1.63E-12	6.37E-100	0.019	0.0898
MassFraction.METHYL DIETHANOLAMINE	1.50E-37	0	7.94E-08	0	0	0.377	0.6371	0.3487	0.6371	0.3564	0.3487	0.3524	0.6371	0	2.31E-08

Having the project objective of producing a treated natural gas containing less than 30% of carbon dioxide, the natural gas from the proposed simulated natural gas plant meets the requirement as shown in Table 4.4 i.e. 11.8 mol% which is around 20 wt% of the sweet gas stream.

Using HYSYS process simulator with the convergence of the absorber and the regenerator units a complete amine simulation was established as shown in Figure 4.7. The amount CO_2 in the treated natural gas stream is found to be 14 mol% consistent with the project objective of producing less than 30 mol% CO_2 in the product stream.

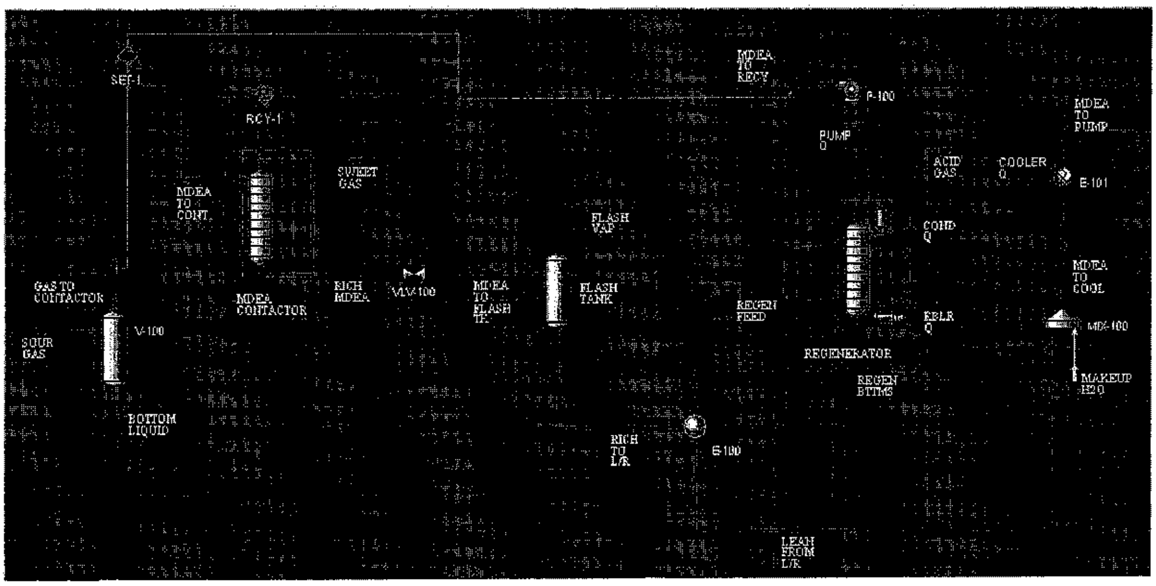
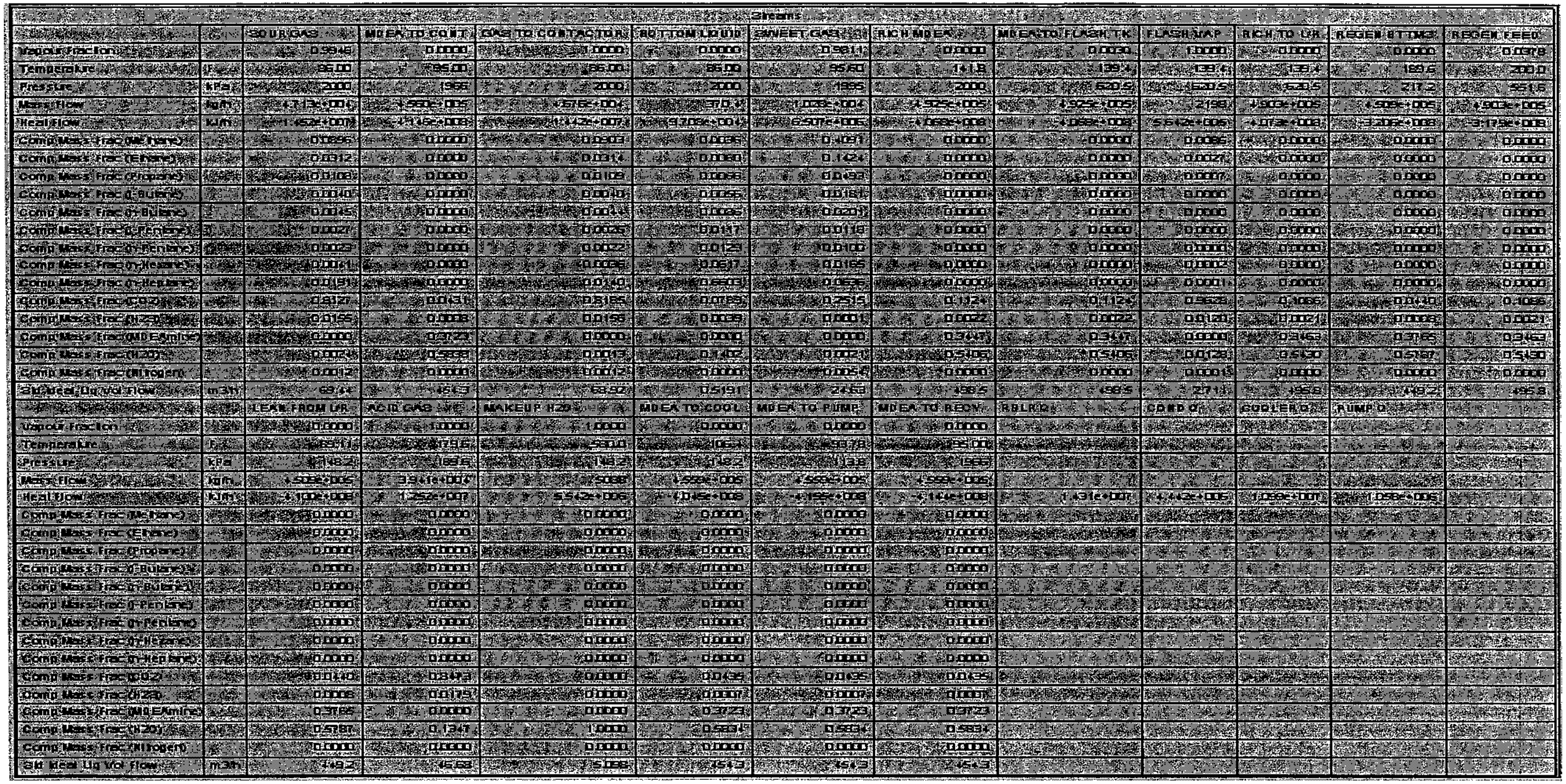


Figure 4.7: Complete Simulations Unit Using HYSYS Process Simulator

The material balance table for the simulation done using HYSYS process simulator is presented in Table 4.5.

Table 4.5: Material Balance for the Acid gas Removal system using HYSYS



Streams												
		SOUR GAS	MDEA TO CONT	GAS TO CONTACTOR	BOTTOM LIQUID	SWEET GAS	RICH MDEA	MDEA TO FLASH TK	FLASH VAP	RICH TO L/R	REGEN BTTMS	REGEN FEED
Vapour Fraction		0.9946	0.0000	1.0000	0.0000	0.9811	0.0000	0.0030	1.0000	0.0000	0.0000	0.0378
Temperature	F	86.00	95.00	86.00	86.00	95.60	141.8	139.4	139.4	139.4	189.6	200.0
Pressure	kPa	2000	1966	2000	2000	1995	2000	620.5	620.5	620.5	217.2	551.6
Mass Flow	kg/h	4.713e+004	4.550e+005	4.676e+004	370.4	1.028e+004	4.925e+005	4.925e+005	2198	4.903e+005	4.509e+005	4.903e+005
Heat Flow	kJ/h	-1.452e+007	-7.116e+008	-1.142e+007	-9.709e+004	-6.507e+006	-7.068e+008	-7.068e+008	-5.642e+006	-7.073e+008	-3.206e+008	-3.175e+008
Comp Mass Frac (Methane)		0.0896	0.0000	0.0903	0.0036	0.4091	0.0000	0.0000	0.0086	0.0000	0.0000	0.0000
Comp Mass Frac (Ethane)		0.0312	0.0000	0.0314	0.0060	0.1424	0.0000	0.0000	0.0027	0.0000	0.0000	0.0000
Comp Mass Frac (Propane)		0.0108	0.0000	0.0109	0.0098	0.0493	0.0000	0.0000	0.0007	0.0000	0.0000	0.0000
Comp Mass Frac (i-Butane)		0.0040	0.0000	0.0040	0.0056	0.0181	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mass Frac (n-Butane)		0.0045	0.0000	0.0044	0.0026	0.0201	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mass Frac (i-Pentane)		0.0027	0.0000	0.0026	0.0117	0.0118	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mass Frac (n-Pentane)		0.0023	0.0000	0.0022	0.0129	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Comp Mass Frac (n-Hexane)		0.0041	0.0000	0.0036	0.0617	0.0165	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000
Comp Mass Frac (n-Heptane)		0.0191	0.0000	0.0140	0.6603	0.0636	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Comp Mass Frac (CO2)		0.8127	0.0431	0.8185	0.0785	0.2515	0.1124	0.1124	0.9628	0.1066	0.0040	0.1066
Comp Mass Frac (H2S)		0.0156	0.0008	0.0158	0.0039	0.0001	0.0022	0.0022	0.0120	0.0021	0.0008	0.0021
Comp Mass Frac (MDEAmine)		0.0000	0.3723	0.0000	0.0000	0.0000	0.3447	0.3447	0.0000	0.3463	0.3765	0.3463
Comp Mass Frac (H2O)		0.0024	0.5838	0.0013	0.1402	0.0021	0.5406	0.5406	0.0128	0.5430	0.5787	0.5450
Comp Mass Frac (Nitrogen)		0.0012	0.0000	0.0012	0.0000	0.0054	0.0000	0.0000	0.0013	0.0000	0.0000	0.0000
Std Ideal Liq Vol Flow	m3/h	69.44	451.3	68.92	0.5191	24.53	498.5	498.5	2.711	495.8	449.2	495.8
		LEAN FROM L/R	ACID GAS	MAKEUP H2O	MDEA TO COOL	MDEA TO PUMP	MDEA TO RECY	RBLR Q	COND Q	COOLER Q	PUMP Q	
Vapour Fraction		0.0000	1.0000	1.0000	0.0000	0.0000	0.0000					
Temperature	F	189.1	179.5	530.0	106.4	99.78	95.00					
Pressure	kPa	148.2	189.6	148.2	148.2	133.8	1966					
Mass Flow	kg/h	4.509e+005	3.941e+004	5088	4.559e+005	4.559e+005	4.559e+005					
Heat Flow	kJ/h	-7.100e+008	-1.252e+007	5.542e+006	-7.045e+008	-7.195e+008	-7.144e+008	1.431e+007	4.442e+006	1.089e+007	1.058e+006	
Comp Mass Frac (Methane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (Ethane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (Propane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (i-Butane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (n-Butane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (i-Pentane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (n-Pentane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (n-Hexane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (n-Heptane)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Comp Mass Frac (CO2)		0.0140	0.8473	0.0000	0.0435	0.0435	0.0435					
Comp Mass Frac (H2S)		0.0008	0.0179	0.0000	0.0007	0.0007	0.0007					
Comp Mass Frac (MDEAmine)		0.3765	0.0000	0.0000	0.3723	0.3723	0.3723					
Comp Mass Frac (H2O)		0.5787	0.1347	1.0000	0.5834	0.5834	0.5834					
Comp Mass Frac (Nitrogen)		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000					
Std Ideal Liq Vol Flow	m3/h	449.2	45.68	5.098	451.3	451.3	451.3					

4.7 EFFECT OF OPERATING PARAMETERS

CO_2 absorption capability in solvent can be determined by the following main variables (Baying et al. 2009)

1. Solvent circulation rate
2. Solvent feed temperature to the absorber
3. Absorber operating pressure
4. Absorber column height

In this work, the effects of the first three parameters listed are investigated except the column height. The simulated models are used to study how operating parameters affect the CO_2 composition of the sweet gas while holding all other process variables constant when studying the effect of one parameter.

Table 4.6: An Overview on Results With Respect to Each Simulator

Parameters	Observation on effects of the changes in the parameters with respect to each simulators	
	HYSYS	ICON
Fluid package	• Amine fluid package	• MDEA fluid package
Pressure	• Simulator converged for each ΔP attempted and shown consistent trend • However, the simulator couldn't converge for $P >$ 2000 kPa	• Simulator converged for each ΔP attempted and shown consistent trend
Temperature	• Simulator converged for each ΔT attempted and shown consistent tread	• Simulator didn't converge for various ΔT attempted. Therefore, couldn't observe the profile
Amine circulation rate	• Simulator converged and shown consistent trend	• Simulation didn't converge for various attempted changes in amine rate. Therefore , couldn't observe the profile

In addition, the identification of best operating parameters were done in a two dimensional search i.e. not identifying the best performance with respect to all parameters simultaneously.

4.7.1 Effect of MDEA Concentration and Its Flow rate on CO_2 Removal

Figure 4.7 compares the CO_2 removal performance of 38 wt% MDEA with 48 wt% MDEA when increasing the MDEA flow rate. As the concentration of MDEA increases, the absorber performance would increase i.e. resulting in low amount of CO_2 in the treated natural gas stream (sweet gas). The result can be explained further as, when highest quantity of reactive (amine) is present, a major quantity of CO_2 absorbed in the liquid phase reacts with amine i.e. the higher the amine flow rate the better the performance would be. Moreover, Douglas et al. (2006) reported that for MDEA when the circulation rate is increased for any given column, the CO_2 pickup increases in a column of fixed diameter even though the liquid residence time on a tray decreases with increased circulation.

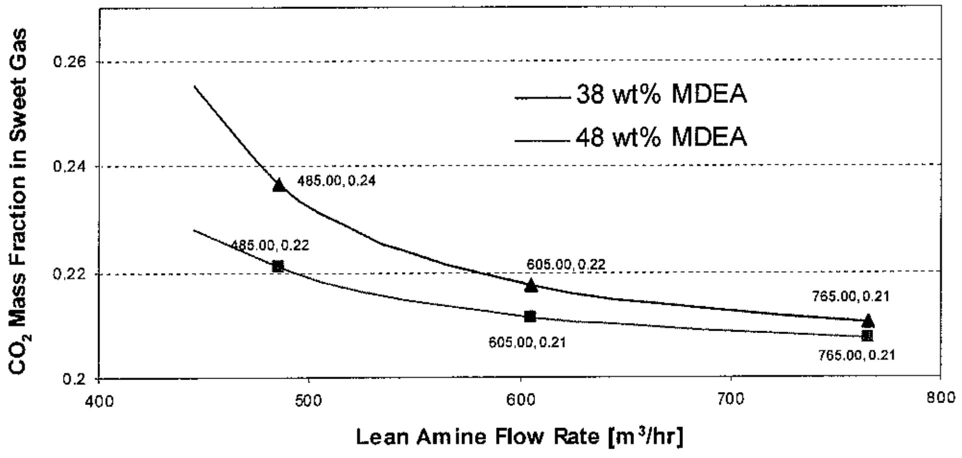


Figure 4.7: Effect of MDEA Flow Rate on Amount of CO_2 in Sweet Gas for 38 Wt% and 48 wt% MDEA Using HYSYS (T=35 °c and P= 6860.28 kPa)

4.7.2 Curve Fitting

A Polynomial regression method can be applied to produce a mathematical model which shows the relation between the amine circulation rate and the amount of CO_2 in the sweet gas shown in Figure 4.7. The equation can be used to make quick estimate for the amount of CO_2 for any given amount of amine flow rate. Microsoft Excel is the software used while doing this task.

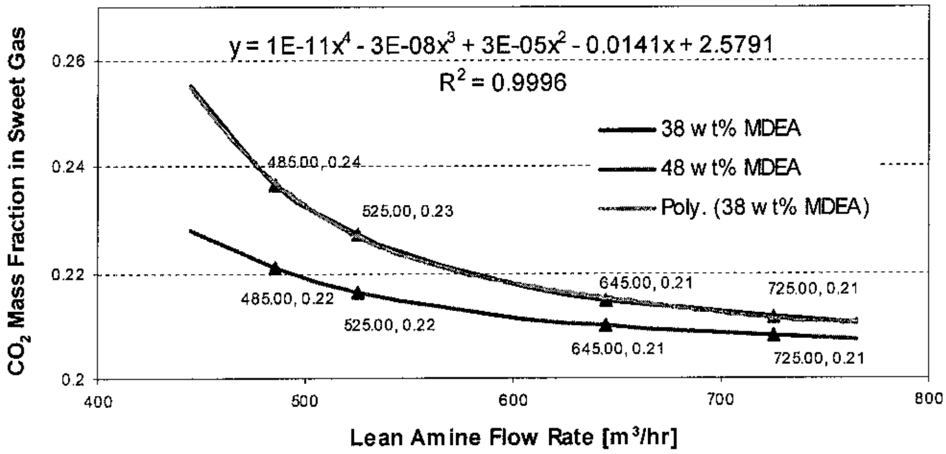


Figure 4.8: Curve Fitting for Effects of MDEA Concentration and Its Flow Rate on CO_2 Removal

Table 4.7 shows the polynomial equations for concentrations of 38 wt% MDEA and 48 wt% MDEA.

Table 4.7: The Polynomial Equation Models for Relation between Amine Flow Rate and Amount of CO_2 in Sweet Gas

Amine concentration	Polynomial equation	Value of R^2
38 %	$y = 1E\text{-}11x^4 - 3E\text{-}08x^3 + 3E\text{-}05x^2 - 0.0141x + 2.5791$	0.9996
48 %	$y = 3E\text{-}12x^4 - 9E\text{-}09x^3 + 9E\text{-}06x^2 - 0.0041x + 0.9343$	0.9999

- **Note**: "y" in the equations, represents the mass fraction of CO_2 in the treated natural gas (sweet gas) while "x" represents the amine flow rate.
- The R-square value is an indicator of how well the model fits the data (e.g. an R-square close to 1.0 indicates that the model accounted for almost all of the variability)

4.7.3 Effect of Lean Amine Temperature on CO_2 Removal

Figure 4.8 illustrates the acid gas concentration in the sweet gas as a function lean amine temperature for 38 wt% concentration of MDEA. For this particular designed plant the only parameter available for control of the column temperature is the lean amine temperature. Since the reaction with MDEA is kinetically controlled, the hotter the column the faster the reaction rate. From figure 4.8, for temperature region up to around 130 °F increase in temperature increases CO_2 removal capacity of the system. This is because the higher temperature increases the kinetic effect to a greater extent relative to the decrease in CO_2 solubility. However, after a certain temperature (i.e. about 130 °F), the decrease in solubility of the CO_2 in the amine solution becomes the overriding factor and the net CO_2 pickup begins to decrease. A similar trend was reported by Jerry and John (2006). In the absence of other chemicals the amine does not suffer degradation or decomposition at temperature up to its normal boiling point (247.3 °C) (Jones and Peter, 2006). Hence, from the graph at temperature of around 130 °F the plant operates very well.

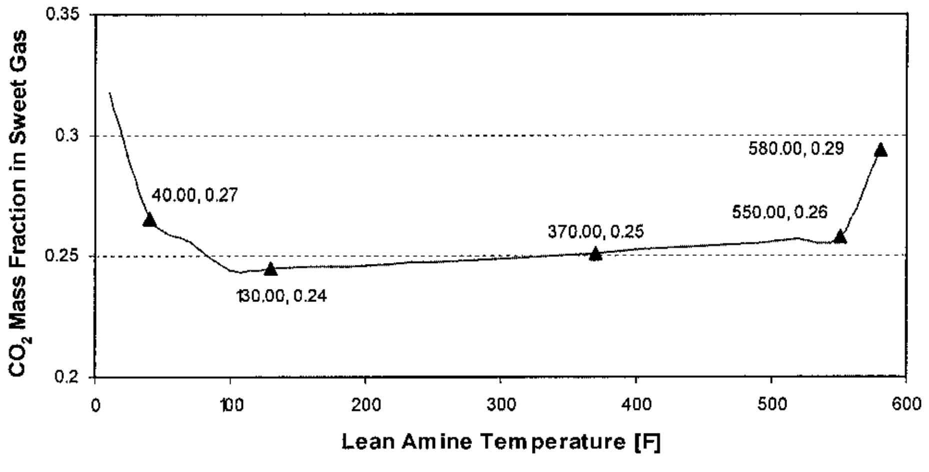


Figure 4.8: Effect of the Lean MDEA Temperature on amount of CO_2 in the Sweet Gas for 38 wt% MDEA using HYSYS (P= 6860.283 kPa)

4.7.4 Effect of Sour Gas Pressure on CO_2 Removal

Using both process simulators (HYSYS and ICON), the impact of the sour gas pressure on the CO_2 adsorption system has been recorded. As the sour natural gas comes from different reserves, pressure of the sour gas might vary from time to time. Thus, knowing the impact of the increase in pressure on the system would help to give attention on pressure of the sour natural gas stream and to take corrective measures as necessary.

Figure 4.9 illustrates that both of the models generated using HYSYS and ICON show a similar trend. Up to the pressure of around 1500 kPa, the increase in pressure did not have the significant change on CO_2 absorption capacity of the amine. This shows as the CO_2 reaction is driven by kinetics, it is less affected by lowered pressure. However, sudden slight increase in pressure caused the decrease in the efficiency of carbon dioxide adsorption.

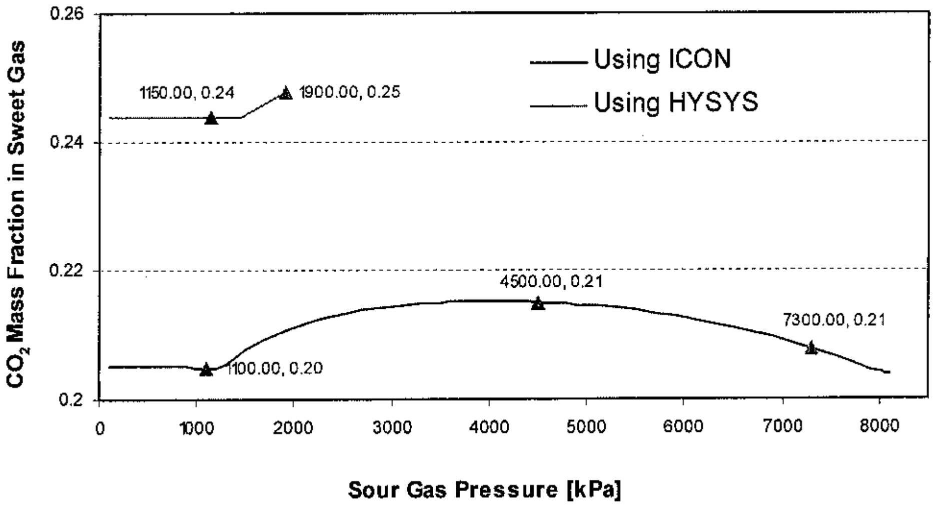


Figure 4.9: Effect of the Sour Natural Gas Pressure on amount of CO_2 in the Sweet Gas for 38 wt% MDEA using HYSYS and ICON (T=30 °C)

However, Figure 4.9 also illustrates that high pressure enhances CO_2 removal. As it happens in pressure swing adsorption the higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. Hence, in this work as we need to enhance the CO_2 removal capacity of the resin, the increase in pressure leads to better CO_2 removal. Hence, operating at higher pressure more that 4500 kPa will bring high CO_2 removal efficiency to the plant i.e. the higher the pressure the better the performance would be.

Deviation for results from the simulated models using HYSYS and ICON can be calculated as follows:

$$Deviation = \frac{x_{co_2}\, from\, HYSYS - x_{co_2}\, from\, ICON}{x_{co_2}\, from\, ICON} \times 100\%$$

Table 4.8: Data Points chosen for Calculating Deviation for Results

No.	Data Points			
	HYSYS		ICON	
	Pressure (kPa)	Mass fraction of CO_2 in sweet gas	Pressure (kPa)	Mass fraction of CO_2 in sweet gas
1	700	0.24402632	700	0.205027
2	1900	0.24762771	1900	0.21061736

For point 1 the deviation is calculated as 19% while for point 2 is 17%. These results can be interpreted as, the results found from ICON model deviates 19% and 17 % from results found form HYSYS model for two random points selected from the graph (Figure 4.9)

4.8 PRELIMINARY ECONOMIC EVALUATION

The following preliminary calculation is done to evaluate economic potential of the plant with respect to the raw material and product cost. The aminated resin of this project is expected to have a higher price than price of solvent MDEA and normal resin since it is the combination of the two. The price of the aminated resin is estimated considering the price of the two materials as listed in the Table 4.8. Based on the project objective of reducing CO_2 content down to 30 mol%, the corresponding amount of fresh

MDEA required on hourly bases is 175 m^3/hr. A total of 330 operational days in a year have been considered for obtaining the estimate for economic potential one.

Table 4.9: Price of Raw Materials and Products

Material	Price	Amount being consumed or produced in simulation model	Total price ($ per year)
Aminated resin (estimated)	$0.70 per lb	273 m^3/hr	26,872,673
Water	$0.337 per m^3		
Natural gas (processed)	$154.47 per m^3	206 m^3/hr	252,020,894

- **Note**: The price for the aminated resin is considered to be a bit higher than the price of the reactants (solvent MDEA and Polyethylene) for making this product (aminated resin).
- Industrial water tariff for Terengganu as of 2008 is taken for the calculation
- The calculation is done for 30 mol% of CO_2 in the sweet gas

Based on the calculation in Table 4.9, the price of the raw material seems to be higher that the product price based on hourly operation. However, it should be noted that the aminated resin is being recycled so depending the life time of the resin the plant would obviously be profitable. The concept applied here is provided in the formula below

Economic Potential 1= Product cost – Reactant cost

= ($252,020,894- $27,235,673)

= $225,148,221 per year

The calculated positive value of EP1 indicates building the CO_2 removal plant is economically viable.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The ultimate goal of this project was to design amine sweetening plant which is capable of producing specification quality product as economically as possible. The project is done based on the basic engineering assumption that; the methyldiethanolamine functionalized resin of this project behaves almost the same way as the solvent methyldiethanolamine. The same assumption makes the resin to be considered as inert solid in the separation process apart from its contribution to enhancement of carbon dioxide absorption in MDEA by allowing the amine to withstand high pressure. It has been discussed in the earlier parts of this report that solid adsorbents (section 1.1.4) have a good feature in which the porous support provides the amine with structural integrity and a surface for gas/solid contact (Leal et al. 2000).

Based on the simulation performed, the specially designed aminated resin has the expected potential to capture carbon dioxide from high CO_2 loaded natural gas steam, provided the amine circulation rate and column size are large enough. The carbon dioxide content in the treated gas stream from the designed plant is found to meet the project objective of having less than 30 mol% carbon dioxide content, i.e. 11.8 mol% from the ICON process simulator and 14 mol % from HYSYS. In addition, the best operating parameters have been identified for best performance of the resin. The higher the amine flow rate and concentration, the better the performance. At temperature of around 130 °F the plant operates very well. Operating the plant at higher pressure greater than 4500 kPa brings high CO_2 removal efficiency to the plant i.e. the higher the pressure the better the performance would be.

5.2 RECOMMENDATION

Knowing more about the specially designed aminated resin of this project such as its reaction kinetics and other relevant physical properties of the reactions products (e.g. the physical properties of products resulted from the reaction between CO_2 and the aminated resin) would help to design the plant more efficiently. For future work it is suggested to study the kinetic characteristics of the reaction by actual experiment and incorporate the result into the proposed design. Such results would allow to implement reactive adsorption with use of series of reactors and separators in place of the absorber (Figure 4.5 & 4.6) for simulation. 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 solvent MDEA.

A single heat exchanger the details of which has been discussed in literature review part of this report (Chapter 2) is used in acid gas treatment plants as it has been simulated in HYSYS. The heat exchanger allows heat transfer between the lean and rich amine. For this particular design project, an attempt in terms specifying the pressure drop among the parts of a shell and tube type of heat exchanger has been made to include the effect of the heat integration in ICON simulator. However, the ICON was unable to simulate it. Thus, further work it is recommended to do the detail heat integration analysis for the system to come up with detail design specification to provide the simulators with.

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APPENDIX 1

Table A.1 Project Schedule

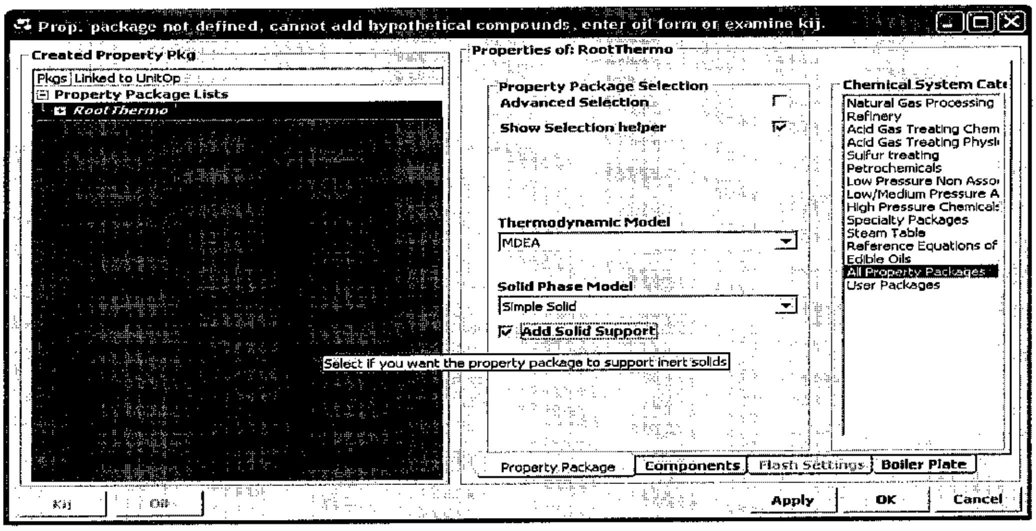
Gantt Chart			Week Number													
	No.	Task Detail	1	2	3	4	5	6	7		8	9	10	12	13	14
Semester 1	1	Selection of project topic	▨							Semester break						
	2	Preliminary research work		▨	▨	▨										
	3	Submission of preliminary report					●									
	4	Seminar 1						●								
	5	Project work (Letrature review)[1]					▨	▨	▨							
	6	Submission of progress report									●					
	7	Seminar 2											●			
	8	Project work continues (input-output structure)[2]									▨	▨	▨	▨		
	9	Submission of interim report draft													●	
	10	Oral presentaion														●
Semester 2	1	Identifying subprocesses/ Construct a block diagram[3]	▨	▨												
	2	Selection of specific equipment[4]			▨	▨										
	3	Developing Flowsheet[5]					▨	▨								
	4	Simulation/ Process evaluation[6]							▨		▨	▨				
	5	Preliminary economics evaluation[7]											▨	▨		
	6	Submission of interim report													●	
	7	Final oral presentation														●

	No	The project objective
▨	a	To synthesize the feasible routes for CO_2 adsorption systemthat uses a specially designed solvent at the natural gas reserves which can remove CO_2 at high pressure and high CO_2 content (**1,2,3 and 4**)
	b	To develop the feasible flowsheet and simulate it in ICON and identify the best operating parameters for the system (**5 and 6**)
	c	To perform preliminary economic evaluation for the system (**7**)

APPENDIX 2

ICON Simulation Procedures

The simulation of the plant (Figure 4.4) was carried was using the following steps. The first step is to select the appropriate fluid package; here MDEA fluid package which can be found in ICON process simulator is selected. Considering the presence of the resin in the process, solid support model was also selected which can also be found in ICON process simulator (Figure A.1).



Prop. package not defined, cannot add hypothetical compounds, enter oil form or examine kij.

Properties of: RootThermo

Property Package Selection

Advanced Selection ☐

Show Selection helper ☑

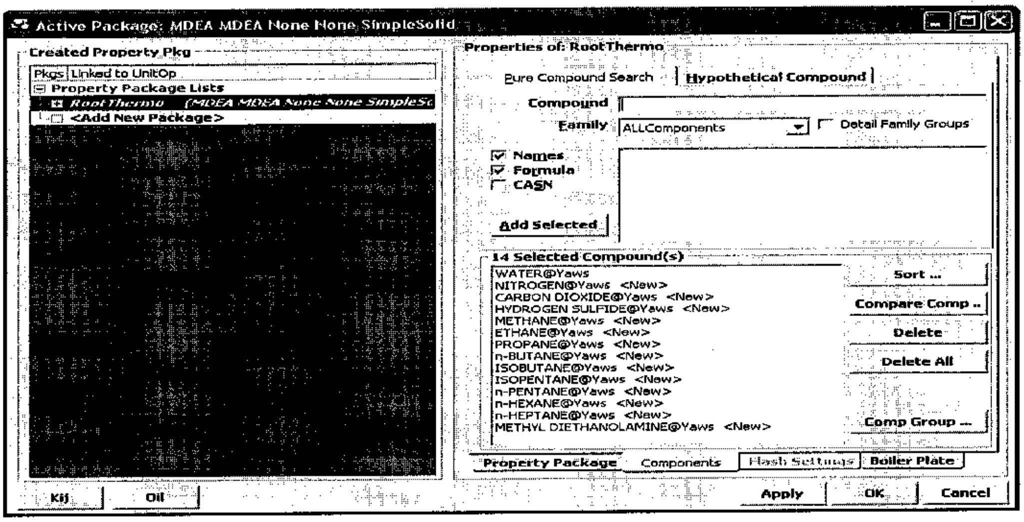
Thermodynamic Model: MDEA

Solid Phase Model: Simple Solid

☑ Add Solid Support

Select if you want the property package to support inert solids

Figure A.1 Fluid Package Basis (MDEA fluid Package)



Active Package: MDEA MDEA None None SimpleSolid

Properties of: RootThermo

RootThermo (MDEA MDEA None None SimpleSo

Family: ALLComponents

☐ Detail Family Groups

☑ Names

☑ Formula

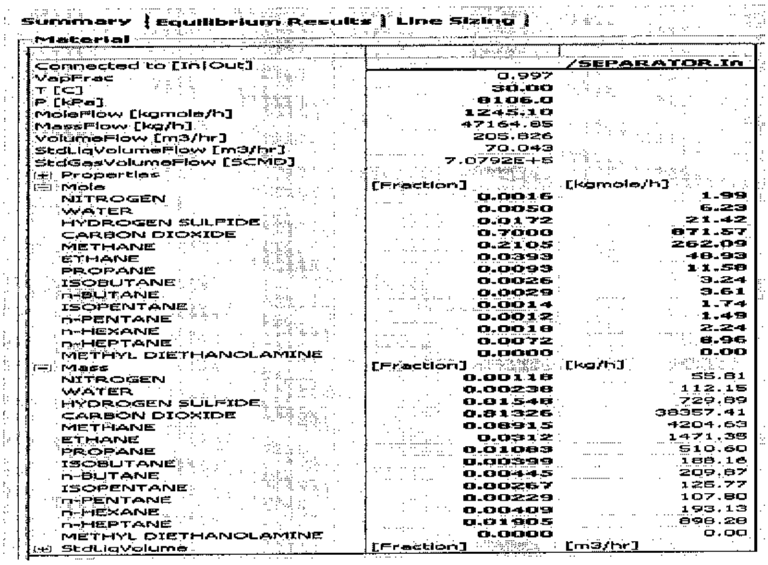
☐ CASN

14 Selected Compound(s)

WATER@Yaws
NITROGEN@Yaws <New>
CARBON DIOXIDE@Yaws <New>
HYDROGEN SULFIDE@Yaws <New>
METHANE@Yaws <New>
ETHANE@Yaws <New>
PROPANE@Yaws <New>
n-BUTANE@Yaws <New>
ISOBUTANE@Yaws <New>
ISOPENTANE@Yaws <New>
n-PENTANE@Yaws <New>
n-HEXANE@Yaws <New>
n-HEPTANE@Yaws <New>
METHYL DIETHANOLAMINE@Yaws <New>

Figure A.2 Dialog Window for Components Selection

Once the components of the fluid are selected, one can enter the simulation environment. The simulation environment is where process flow diagram is built. The simulation of the process begins with the simulation of the feed sour gas stream by specifying the gas temperature, pressure and flow rate and ICON calculates the remaining parameters as shown in Figure 4.7. As shown in Figure A.3, the percent composition of CO_2 of the feed gas is taken to be 70% which is above the maximum of 40 % capacity of existing acid gas plants.

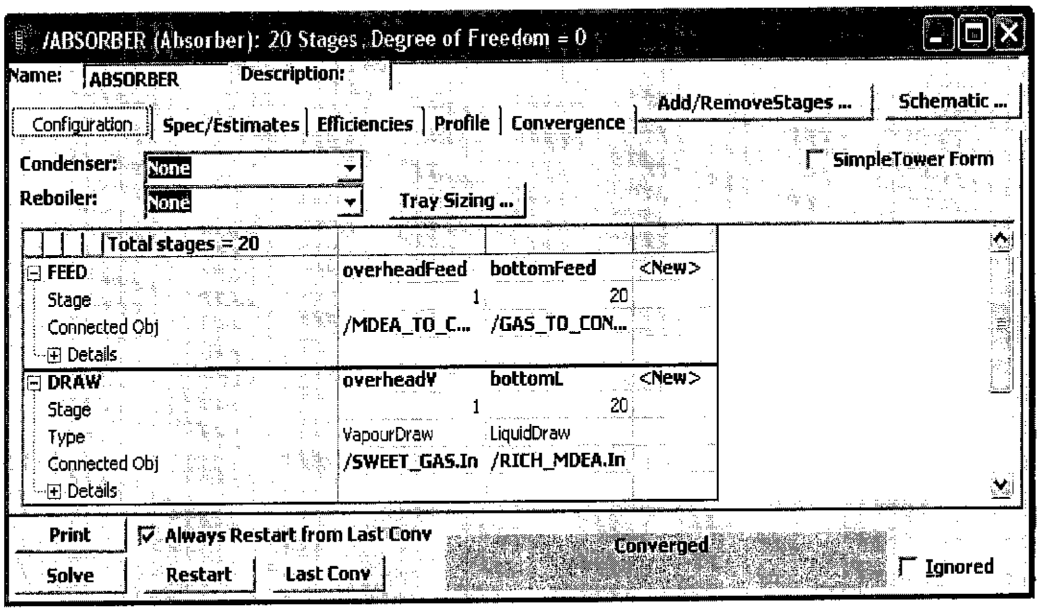


Connected to [In|Out]		/SEPARATOR.In
VapFrac	0.997	
T [C]	30.00	
P [kPa]	8106.0	
MoleFlow [kgmole/h]	1245.10	
MassFlow [kg/h]	47164.85	
VolumeFlow [m3/hr]	205.826	
StdLiqVolumeFlow [m3/hr]	70.043	
StdGasVolumeFlow [SCMD]	7.0792E+5	
[+] Properties		
[−] Mole	[Fraction]	[kgmole/h]
NITROGEN	0.0016	1.99
WATER	0.0050	6.23
HYDROGEN SULFIDE	0.0172	21.42
CARBON DIOXIDE	0.7000	871.57
METHANE	0.2105	262.09
ETHANE	0.0393	48.93
PROPANE	0.0093	11.58
ISOBUTANE	0.0026	3.24
n-BUTANE	0.0029	3.61
ISOPENTANE	0.0014	1.74
n-PENTANE	0.0012	1.49
n-HEXANE	0.0018	2.24
n-HEPTANE	0.0072	8.96
METHYL DIETHANOLAMINE	0.0000	0.00
[−] Mass	[Fraction]	[kg/h]
NITROGEN	0.00118	55.81
WATER	0.00238	112.15
HYDROGEN SULFIDE	0.01548	729.89
CARBON DIOXIDE	0.81326	38357.41
METHANE	0.08915	4204.63
ETHANE	0.0312	1471.35
PROPANE	0.01083	510.60
ISOBUTANE	0.00399	188.16
n-BUTANE	0.00445	209.87
ISOPENTANE	0.00267	125.77
n-PENTANE	0.00229	107.80
n-HEXANE	0.00409	193.13
n-HEPTANE	0.01905	898.28
METHYL DIETHANOLAMINE	0.0000	0.00
[+] StdLiqVolume	[Fraction]	[m3/hr]

Figure A.3 Sour Gas Specification Window

Usually the feed gas stream (the sour gas) would contain trace amount of water vapor. Hence, separating the water vapor from the gas stream would be important to avoid operation problems due to condensation in the adsorption column. For this specific purpose a separator is being utilized.

Other streams specifications made are, MDEA to contactor temperature, pressure and flow rate, make up water temperature and MDEA to recycle temperature. With these specifications made, ICON make use of its flexibility of calculating forward and backward to completely simulate the process. One of the rigorous tasks is the convergence of the absorber and the regenerator. To converge the absorber (Figure A.4), its top and bottom temperature and pressure were specified. Unlike HYSYS process simulator ICON does not provide users with calculated component efficiencies (H_2S and CO_2) in the absorber. Hence, the alternative way considered was to simulate the same plant (Figure 4.4) and get the estimated component efficiencies for the base simulation in ICON.



/ABSORBER (Absorber): 20 Stages, Degree of Freedom = 0

Name: ABSORBER
Description:

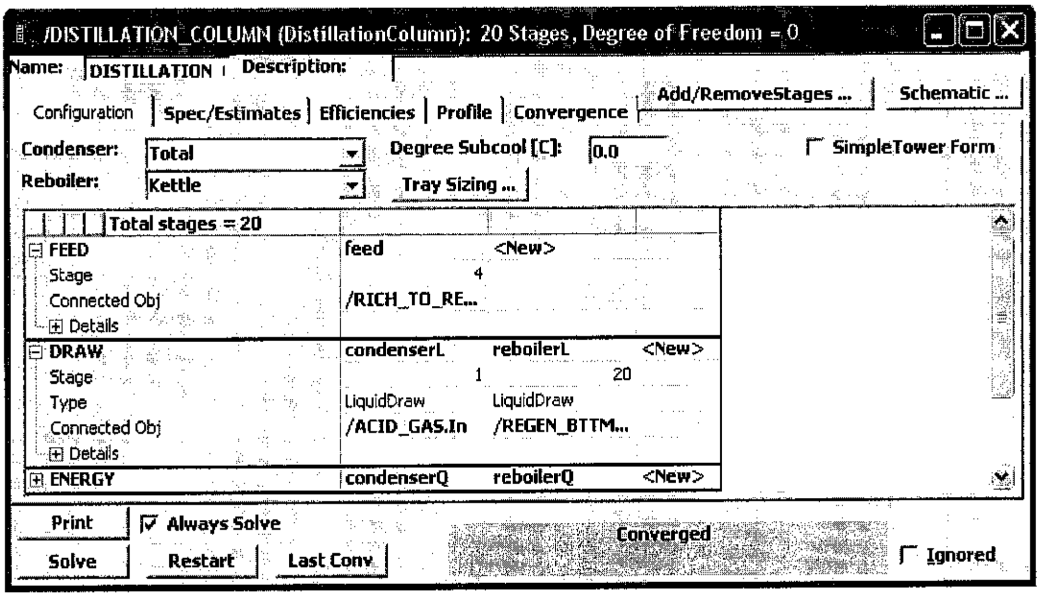
Condenser: None
Reboiler: None
☐ SimpleTower Form

Total stages = 20			
FEED	overheadFeed	bottomFeed	<New>
Stage	1	20	
Connected Obj	/MDEA_TO_C...	/GAS_TO_CON...	
Details			
DRAW	overheadV	bottomL	<New>
Stage	1	20	
Type	VapourDraw	LiquidDraw	
Connected Obj	/SWEET_GAS.In	/RICH_MDEA.In	
Details			

☑ Always Restart from Last Conv
☐ Ignored

Figure A.4 Converged Window of the Absorber

The bottom product of the absorber need to go through a flash tank (separator) to remove the hydrocarbons components carried along with the rich amine. The regenerator (distillation column) is converged by specifying the condenser and re-boiler pressure, the reflux ratio (full reflux) and components efficiencies (H_2S and CO_2) the column is then run (Figure A.5).



Name: DISTILLATION Description:

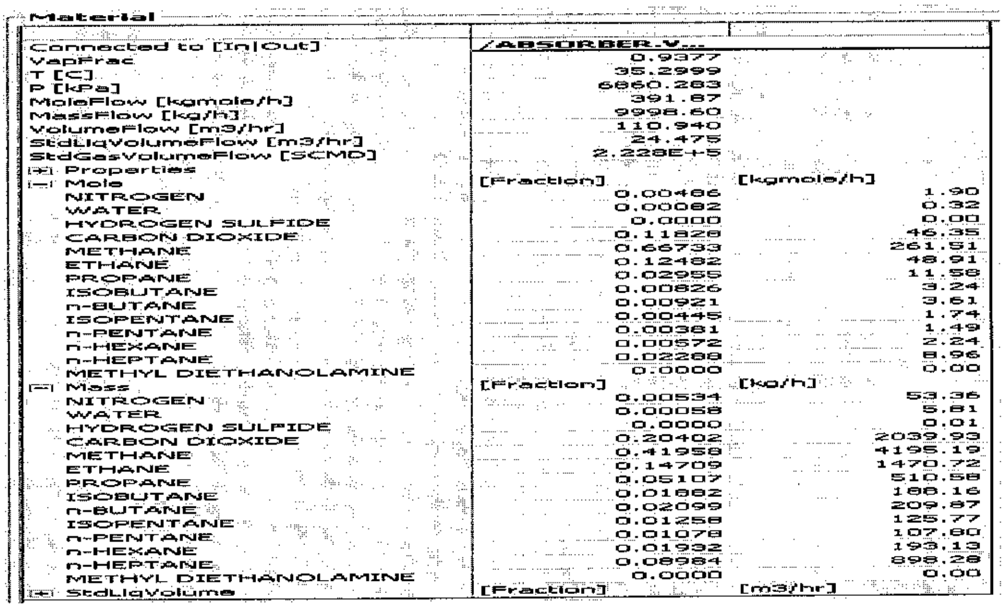
Condenser: Total Degree Subcool [C]: 0.0 ☐ SimpleTower Form

Reboiler: Kettle

Total stages = 20			
FEED	feed	<New>	
Stage	4		
Connected Obj	/RICH_TO_RE...		
Details			
DRAW	condenserL	reboilerL	<New>
Stage	1	20	
Type	LiquidDraw	LiquidDraw	
Connected Obj	/ACID_GAS.In	/REGEN_BTTM...	
Details			
ENERGY	condenserQ	reboilerQ	<New>

☑ Always Solve ☐ Ignored

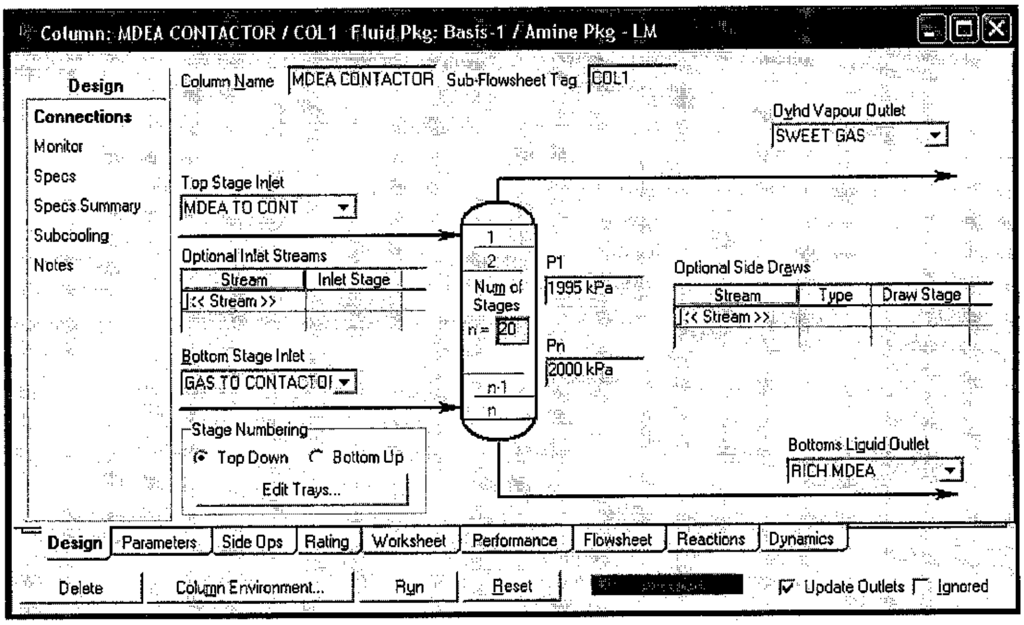
Figure A.5 Converged Windows for Regenerator Unit



Connected to [In|Out]	/ABSORBER.V...	
VapFrac	0.9377	
T [C]	35.2999	
P [kPa]	6860.283	
MoleFlow [kgmole/h]	391.87	
MassFlow [kg/h]	9998.60	
VolumeFlow [m3/hr]	110.940	
StdLiqVolumeFlow [m3/hr]	24.475	
StdGasVolumeFlow [SCMD]	2.228E+5	
Properties		
Mole	[Fraction]	[kgmole/h]
NITROGEN	0.00486	1.90
WATER	0.00082	0.32
HYDROGEN SULFIDE	0.0000	0.00
CARBON DIOXIDE	0.11828	46.35
METHANE	0.66733	261.51
ETHANE	0.12482	48.91
PROPANE	0.02955	11.58
ISOBUTANE	0.00826	3.24
n-BUTANE	0.00921	3.61
ISOPENTANE	0.00445	1.74
n-PENTANE	0.00381	1.49
n-HEXANE	0.00572	2.24
n-HEPTANE	0.02288	8.96
METHYL DIETHANOLAMINE	0.0000	0.00
Mass	[Fraction]	[kg/h]
NITROGEN	0.00534	53.36
WATER	0.00058	5.81
HYDROGEN SULFIDE	0.0000	0.01
CARBON DIOXIDE	0.20402	2039.93
METHANE	0.41958	4195.19
ETHANE	0.14709	1470.72
PROPANE	0.05107	510.58
ISOBUTANE	0.01882	188.16
n-BUTANE	0.02099	209.87
ISOPENTANE	0.01258	125.77
n-PENTANE	0.01078	107.80
n-HEXANE	0.01932	193.13
n-HEPTANE	0.08984	898.28
METHYL DIETHANOLAMINE	0.0000	0.00
StdLiqVolume	[Fraction]	[m3/hr]

Figure A.6 Sweet Gas Stream Conditions using ICON Process Simulation

Figure A.7 and A.8 shows the converged absorber and regenerator units using HYSYS process simulator.


Column: MDEA CONTACTOR / COL1 Fluid Pkg: Basis-1 / Amine Pkg - LM

Column Name: MDEA CONTACTOR

Sub-Flowsheet Tag: COL1

Top Stage Inlet: MDEA TO CONT

Bottom Stage Inlet: GAS TO CONTACTOI

Ovhd Vapour Outlet: SWEET GAS

Bottoms Liquid Outlet: RICH MDEA

P1: 1995 kPa

Pn: 2000 kPa

Num of Stages n = 20

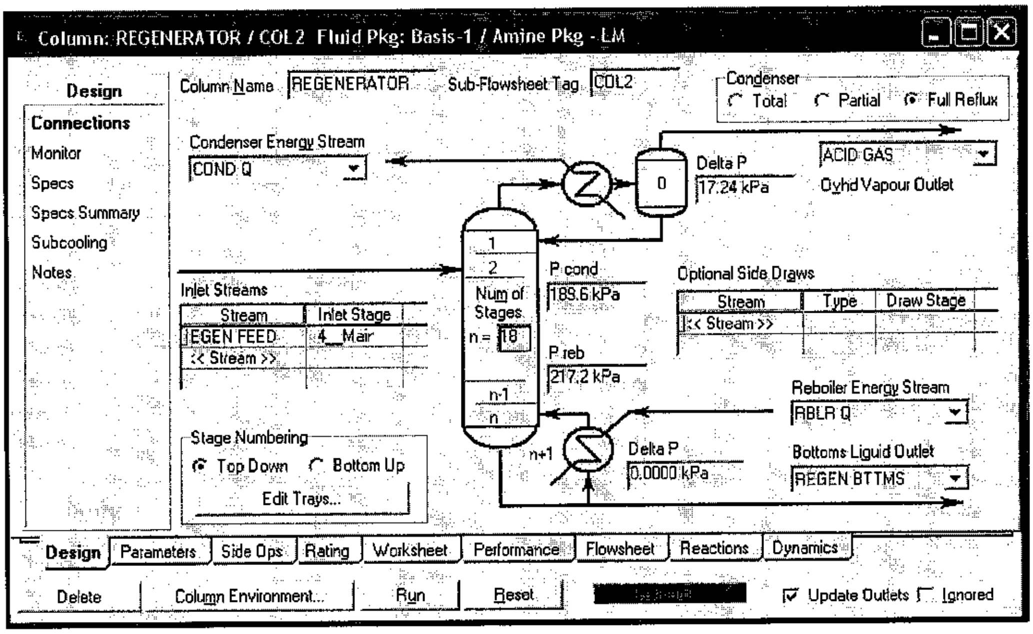
Stage Numbering: ● Top Down ○ Bottom Up

Stream	Inlet Stage
<< Stream >>	

Stream	Type	Draw Stage
<< Stream >>		

☑ Update Outlets ☐ Ignored

Figure A.7 Converged Windows for Absorber


Column: REGENERATOR / COL2 Fluid Pkg: Basis-1 / Amine Pkg - LM

Column Name: REGENERATOR

Sub-Flowsheet Tag: COL2

Condenser: ○ Total ○ Partial ● Full Reflux

Condenser Energy Stream: COND Q

Ovhd Vapour Outlet: ACID GAS

Delta P: 17.24 kPa

P cond: 189.6 kPa

P reb: 217.2 kPa

Num of Stages n = 18

Reboiler Energy Stream: RBLR Q

Delta P: 0.0000 kPa

Bottoms Liquid Outlet: REGEN BTTMS

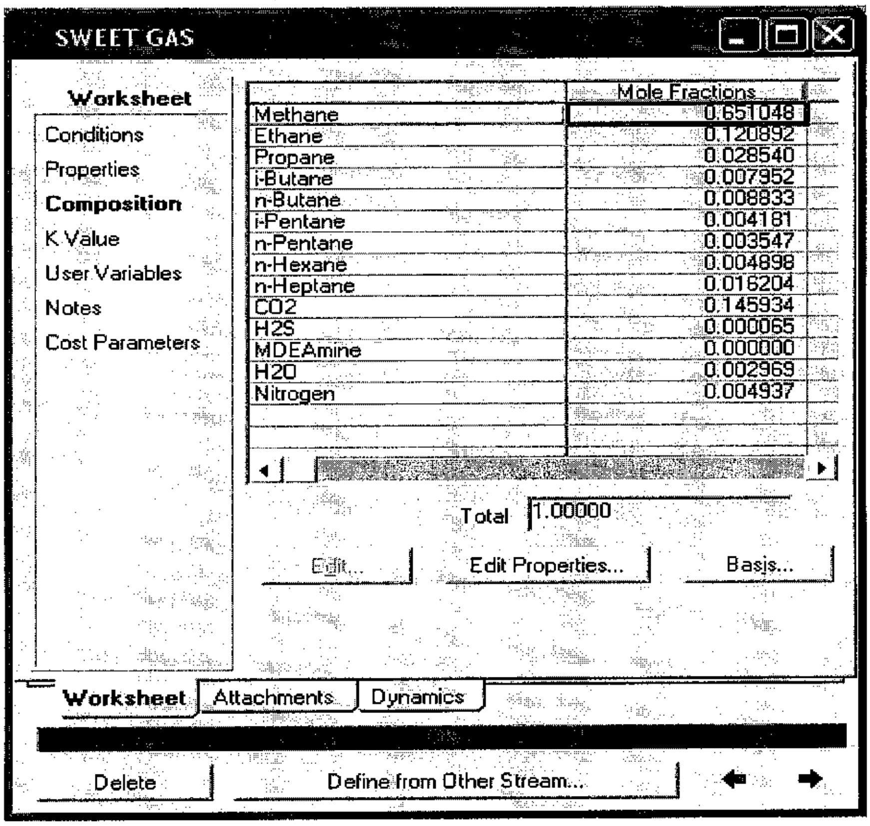
Stage Numbering: ● Top Down ○ Bottom Up

Stream	Inlet Stage
EGEN FEED	4__Mair
<< Stream >>	

Stream	Type	Draw Stage
<< Stream >>		

☑ Update Outlets ☐ Ignored

Figure A.8 Converged Windows for Regenerator



	Mole Fractions
Methane	0.651048
Ethane	0.120892
Propane	0.028540
i-Butane	0.007952
n-Butane	0.008833
i-Pentane	0.004181
n-Pentane	0.003547
n-Hexane	0.004898
n-Heptane	0.016204
CO2	0.145934
H2S	0.000065
MDEAmine	0.000000
H2O	0.002969
Nitrogen	0.004937

Total 1.00000

Figure A.9 Sweet Gas Stream Conditions using HYSYS Process Simulation