Energy Conservation Study in MDEA-Based CO₂ Removal System

by

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

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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BACHELOR OF ENGINEERING (Hons)
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Approved by,

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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.

NURUL SHAKIRA BINTI HAMID

ABSTRACT

Carbon dioxide (CO₂) removal section in Ammonia Plant is highly energy intensive. Many developments have been made to make it more energy efficient and environmentally friendly. Absorption of carbon dioxide in an amine based solution followed by desorption is one of the best available processes to meet the specific plant conditions of high carbon dioxide purity, minimum hydrogen loss, less corrosion, low energy requirement and low capital investment. A simplified carbon dioxide removal system using methydiethanolamine (MDEA) solution have been simulated with the Aspen HYSYS process simulation tool. Analysis on the operating parameters such as the absorption temperature and pressure, and also the concentration of MDEA in lean amine solution have been performed to observe the effect of operating parameters changes on the absorption rate of carbon dioxide, reboiler duty and CO₂ ventilation rate. The comparative study on the structural changes of the absorption system also is being done to observe the energy performance of the system which apparently can reduce the capital investment if optimization of the energy requirement can be accomplished. Based on the base case simulation, 8278.8 kg/hr of CO₂ has successfully being removed from the system with energy requirement of 10.7 MW. Increasing the temperature and pressure of the lean amine stream has decreased the CO₂ absorption rate, CO₂ removal rate and reboiler duty. In contrast, raising the concentration of MDEA in the lean amine solution has caused the declining of CO₂ absorption rate, CO₂ removal rate and energy requirement of the reboiler. Subsequently, new configurations of the CO2 removal system including usage of hydraulic turbine do not contribute in reducing energy requirement of the system. Hence, the energy cost could not be reduced much.

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ABBREVIATIONS AND NOMENCLATURES

CO₂ - carbon dioxide

MDEA - methyldiethanolamine

ppm - part per million

PP - polypropylene

MEA - monoethanolamine

DEA - diethanolamine

kW - kilowatt

PEP - Phulpur Expansion Project

AEP - Aonla Expansion Project

PZ - piperazine

IGCC - Integrated Gasification Combined Cycle

TEA - triethanolamine

H₂ - hydrogen

N₂ - nitrogen

CO - carbon monoxide

CH₄ - methane

H₂O - water

MW - megawatt

CHAPTER 1: INTRODUCTION

1.1 Background of Study

1.1.1 CO₂ Removal Process

Carbon dioxide (CO₂) emission has become the center of attention of the world today.

The environmental effects of carbon dioxide are of significant interest. CO2 is a

greenhouse gas which plays a major role in global warming and anthropogenic climate

change. CO2 is mainly produced as an unrecovered side product of four technologies

which are combustion of fossil fuels, production of hydrogen by steam reforming,

ammonia synthesis and fermentation.

Ammonia is one of the most highly-produced inorganic chemicals because it has many

applications in the industry. The typical modern ammonia-producing plant uses natural

gas as the main feedstock which then being converted into synthesis gas via steam

methane reforming process. The synthesis gas generally consists of hydrogen, nitrogen,

methane, carbon monoxide and also carbon dioxide. CO2 is an undesirable constituent in

the synthesis gas because it poisons the ammonia synthesis catalysts in the reactor.

According to Kunjunny et al. (2007); carbon dioxide content in the synthesis gas must

be reduced to 5 to 10 part per million (ppm) by volume.

There are several of technologies used to remove CO₂ from the synthesis gas. Wang et

al. (2011) have reviewed that post-combustion of CO₂ can be captured with chemical

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solvent absorption method while Xu et al. (2005) have developed a novel nanoporous CO₂ "molecular basket" adsorbent to separate CO₂ from the flue gas of a natural gas fired boiler. Besides, Kumar et al. (2011) have used approach in biological fixation for CO₂ sequestration by developing suitable photo bioreactors by using cyanobacteria and green algae. On the other hand, polypropylene (PP) hollow fiber membrane contactors are used by Yan et al. (2007) to remove the CO₂ from the flue gas.

Among the broad variety of techniques for CO₂ separation, absorption is the best process to separate CO₂ from the synthesis gas. Absorption, in chemistry is a physical or chemical phenomenon or a process in which atoms, molecules, or ions enter some bulk phase. This is a different process from adsorption, since molecules undergoing absorption are taken up by the volume, not by the surface (as in the case for adsorption). Based on the process used, the gas absorption can be classified as physical or chemical absorption.

Wang et al. (2011) state that physical absorption of CO₂ into a solvent based on Henry's law. The process generally uses an organic solvent which absorbs carbon dioxide as a function of partial pressure. The advantages of this process are high carbon dioxide loadings, low circulation rates and less utility costs. The most common used physical absorption process is Selexol process where solvent used is a homologue of diethyl ether of polyethylene-glycols.

Chemical absorption involves the reaction of CO₂ with a chemical solvent to form a weakly bonded intermediate compound which may be regenerated with the application of heat producing the original solvent and a CO₂ stream (IPCC, 2005). The selectivity of this form of separation is relatively high. In addition, a relatively pure CO₂ stream could be produced. These factors make chemical absorption well suited for CO₂ capture for industrial flue gases. The chemical absorption process can be classified in three main

categories; the hot potassium carbonate process, the alkanoamines process and other chemical absorption process (Kunjunny et al., 2007). Commercially available hot potassium carbonate processes are Benfield process, Glycine Vetrocoke process and Cataract process. In alkanoamines process, most used solutions are monoethanolamine (MEA), diethanolamine (DEA) etc. Present day, the most preferred solution in alkanoamines process is activated methyldiethanolamine (MDEA).

Activated MDEA process for carbon dioxide removal is a physical/chemical absorption process (Kunjunny et al., 2007). It behaves as a physical absorption process at higher partial pressure of carbon dioxide and as a chemical absorption process at low carbon dioxide partial pressure. The bulk solution can be regenerated by simple flashing, leading to very low energy consumption.

1.1.2 Hydraulic Turbine

The hydraulic turbine has a long period of development, its oldest and simplest form being the waterwheel, first used in ancient Greece and subsequently adopted throughout medieval Europe for the grinding of grain, etc (S.L. Dizon and C. A. Hall, 2010). The first commercially successful hydraulic turbine (circa 1830) is developed by a French engineer, Benoit Fourneyron. Later, Fourneyron built turbines for industrial purposes that achieved a speed of 2300 rev/min, developing about 50 kilowatt (kW) at efficiency of over 80%.

Hydraulic turbine transfers the energy from a flowing fluid to a rotating shaft (Naveenagrawal, 2009). The turbine itself means a thing which rotates or spins. Hydraulic turbine has a row of blades fitted to the rotating shaft or rotating plate. When passing the turbine, the flowing fluid mostly water will strikes the blades and makes the

shaft to rotate. The velocity and pressure of the liquid reduce as the fluid flows through the hydraulic turbine. These result in the development of torque and rotation of turbine shaft.

There are different forms of hydraulic turbines used in the industry, depending on the operational requirements. Each type of hydraulic turbine has their specific use which can provide the optimum output. Hydraulic turbines can be classified into two categories which are based on flow path and pressure change. Based on the flow path of the liquid, hydraulic turbine can be categorized into three types (Naveenagrawal, 2009);

i. Axial flow hydraulic turbines (Prasad V., 2012)

The turbine has the flow path of the liquid mainly parallel to the axis of rotation. Kaplan Turbines has liquid flow mainly in axial direction.

ii. Radial flow hydraulic turbines

The turbine has the liquid flowing mainly in a plane perpendicular to the axis of the rotation.

iii. Mixed flow hydraulic turbine

Francis Turbine is an example of mixed flow type, where the water enters the turbine in radial direction and exits in axial direction.

Based on the pressure change, hydraulic turbines can be classified into two types (Naveenagrawal, 2009);

i. Impulse turbine

The pressure of liquid does not change while flowing through the rotor of the machine. The pressure change only occurs in the nozzle of the machine. Example of the impulse turbine is Pelton Wheel.

ii. Reaction turbine

The pressure of liquid change while flowing through the rotor of the machine. The change in fluid velocity and reduction in its pressure causes a reaction on the turbine blades. Examples of the reaction turbine are Francis and Kaplan Turbines.

1.2 Problem Statement

Carbon dioxide removal is a significant step in ammonia production as removing the gas can reduce the effect of ammonia synthesis catalyst damage. The most actual method for the removal is by absorption in an amine based solvent followed by desorption. Figure 1 below shows the basic flow diagram of the removal process:

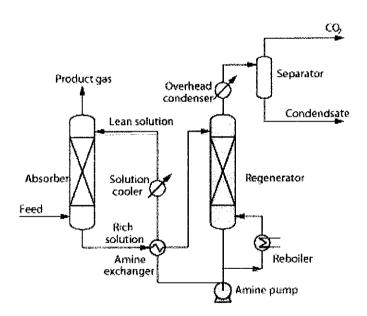


Figure 1: Principle for CO₂ removal process based on absorption in amine solution

The simplest and most used amine for carbon dioxide removal nowadays is MDEA. The effectiveness of the MDEA solution to absorb all the CO₂ in the natural gas is considered as the best among the other solvents. However, this removal process has a high consumption of thermal energy especially at the stripper section, where the reboiler duty is extremely large. More than 90% of the energy requirement of the system is contributed by the reboiler duty. Therefore, study on the configuration of the system has to be done to reduce the energy requirement and at the same time large amount of CO₂ is being removed.

1.3 Objective

This project aims to develop a new configuration of \overline{CO}_2 removal system with lower energy requirement and higher CO_2 removal rate which subsequently reduces the energy cost. Hence, base case problem has been chosen where all the data and information for the removal system are taken from the existing ammonia plant. Thus, the objectives of this project are:

- i. To simulate chosen CO₂ removal system case using Aspen HYSYS
- ii. To perform analysis on the CO₂ absorption rate, CO₂ removal rate and reboiler duty when changing the operating parameters; pressure, temperature and concentration
- iii. To study different configuration of the removal system on the energy requirement and amount of CO₂ which is removed from the synthesis gas

1.4 Scope of Study

The main focus of this study is to conduct the simulation of CO₂ removal system using Aspen HYSYS under different operating conditions such as pressure and temperature of lean amine stream and also the concentration of MDEA in the amine solution. Then, a few changes on the system configuration are being done to compare the energy requirement and energy performance including amount of CO₂ which is being removed from the feed gas.

CHAPTER 2: LITERATURE REVIEW

According to Chaudhary et al. (2011), the selection and design of carbon dioxide removal system was the most difficult engineering job of the Phulpur Expansion Project (PEP), an ammonia plant in India. PEP is a repeat of Aonla Expansion Project (AEP). The new ammonia plant was consuming higher energy per ton of ammonia as compared to the design value and the carbon dioxide removal system was identified as one of the higher energy consuming areas. This situation generally happens in all plants that run the carbon dioxide removal system including gas based power plant and natural gas processing plant. Many studies have been done to observe the performance of the carbon dioxide removal system.

Lars (2007) says that the most actual method for carbon dioxide removal is by absorption in an amine based solvent followed by desorption. According to Dubois (2011), two major criteria must be considered to choose the adequate amine solution; the absorption performance (generally higher with primary and secondary amines) and the energy requirement for the solvent regeneration (lower with tertiary and sterically hindered amines). The different types of amines can also be mixed in order to combine the specific advantages of each type of amines and obtain the highest absorption rate.

According to Yang et al. (2010), CO₂ capture on monoethanolamine (MEA) is one of the most mature chemical absorption methods of post-combustion technologies. Mangalapally et al. (2012) have done a pilot plant study of four new solvents for post

combustion carbon dioxide capture by reactive absorption. The results are being compared to MEA. While Jerry et al. (1990) has explored the use of MDEA and mixtures of amines for bulk CO₂ removal. It has been proved that MDEA can be used quite advantageously for bulk CO₂ removal and the performance is often very sensitive to the operating parameters such as lean amine temperature.

The simplest and most used amine for the removal these days is MDEA (Lars, 2007). The advantages of using MDEA are:

- High solution concentration (up to 50 to 55 wt %)
- High acid gas loading
- Low corrosion even at high solution loadings
- Slow degradation rates
- Lower heats of reaction
- Low vapor pressure and solution losses.

In alkanoamine technology, usage of activated amine solutions which consist of a conventional amine doped with small amounts of an accelerator or activator has been developed (Ali et al., 2004). Activator is used to enhance the overall CO₂ absorption rate. Piperazine (PZ) is one activator that has been the focus of many researchers. The piperazine has been mixed with MDEA and MEA (Ali et al, 2004; Dugas et al., 2009) to observe the effect of PZ on the absorption and desorption rate of CO₂. Besides, aqueous ammonia also has been used as the solvent to absorb CO₂ (Puxty et al., 2010; Zeng et al., 2012).

Carbon dioxide removal by absorption using MDEA solution is highly energy intensive. Studies have been done to perform some analysis on the system to improve the performance and reduce the energy consumption. Based on Lars (2007), because testing at large scale is so expensive, it is natural to use process simulation to evaluate such processes. Before this, Aspen Plus is one of the process simulation tool used in the industry but in 2002, AspenTech company bought the program HYSYS from HyproTech and changed the program name Aspen HYSYS in 2006. An important advantage of using a process simulation program for such analysis is that the available models for thermodynamic properties that can be used. Aspen HYSYS has an Amine Property Package. Within the package, one of the two models, Kent Eisenberg or Li-Mather can be selected.

Based on simulation of carbon dioxide removal with an aqueous MEA solution done by Lars (2007), Sohbi (2007) and Desideri (1999), changing some of the important parameters can give effect to the process. Table 1 below shows the parameters that can be changed to evaluate the performance of the process and the energy consumption.

Table 1: Important parameters for CO₂ removal system (Lars, 2007)

No.	Parameter	Remark
1	Variables held constant	- Percentage CO ₂ removal
2	Circulation rate	 The effect of increased circulation rate is that the removal grade increases. The steam consumption also increases.
3	Number of absorption stages	 Removal grade increases and heat requirement decreases with increased number of stages.
4	Absorption temperature	 An increase in gas and liquid inlet temperature leads to reduced absorption at equilibrium.
5	Absorption pressure	 In case of pressure drop, the percentage of CO₂ removal increases and the energy consumption reduces.
6	Reboiler temperature	 Increased reboiler temperature gives purer amine solution and better CO₂ removal efficiency. But amine degradation problems arise above 120°C.
7	Stripper pressure	- The stripper pressure was specified at to 2 bars as it was difficult to get a converged solution at other pressures.

Based on gas-liquid absorption study done by Padurean (2012) for Integrated Gasification Combined Cycle (IGCC) power plant, packing and absorber/desorber height give effect to the reboiler duty in case of acid gas removal using Selexol® as solvent. The following figure is the result of the study from Aspen Plus simulation:

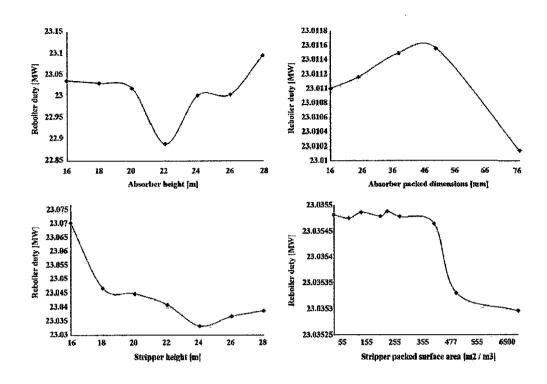


Figure 2: Packing and absorber/desorber effect on the reboiler duty

However, stripping section still requires a lot of energy to make sure the regeneration of MDEA solution happens effectively. Roland E. M. et al (1984) stated that amine solution that is regenerated by flashing results in large energy savings compared to stripping. This is proved by the first triethanolamine (TEA) wash plant operation commenced in Ludwigshafen, West Germany in 1966. The following figure shows the BASF TEA wash process flow diagram:

BASF TEA WASH PROCESS

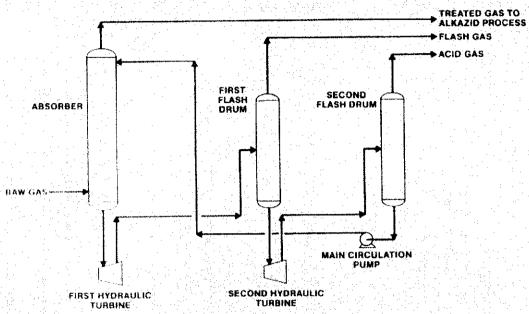


Figure 3: BASF TEA wash process flow diagram

The plant removed CO₂ from a raw synthesis gas at a pressure of about 70 bars. With the high pressure system, rich solution coming out from the bottom of the absorber is being fed to a hydraulic turbine where the pressure of the solution is reduced. Fluid energy is thus converted to mechanical energy which supplements the power required for the main circulation pump. The rich amine solution is then flashed into the first flash drum where the CO₂ and other minor constituents are expelled from the solution. The semi-rich solution is then fed to the second hydraulic turbine for further pressure reduction and energy recovery. Then, the solution is fed into second flash drum where most of the remaining CO₂ is expelled from the solution. The semi-lean solution is recycled back to the absorber, thus completing the circulation loop.

CHAPTER 3: METHODOLOGY

3.1 Aspen HYSYS Process Simulation Tool

The simulation study for the carbon dioxide removal system using MDEA has been

done via Aspen HYSYS process simulation tool. Aspen HYSYS is a market-leading

process modeling tool for conceptual design, optimization, business planning, asset

management and performance monitoring for oil and gas production, gas processing,

petroleum refining and air separation industries. Aspen HYSYS is a core element of

Aspen Tech's aspen ONE® Engineering applications. Some features of the Aspen

HYSYS are easy to use, easy to train, and best in class physical properties method and

data. It also has comprehensive library of unit operation models and introduce the novel

approach of steady state and dynamic simulations in the same platform.

3.2 Aspen HYSYS Input Data

All the data and information used for the system are taken from the existing ammonia

plant. The following table shows the information used for the system:

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Table 2: Operating parameters for CO₂ removal process

Operating parameter	Value
Feed gas inlet temperature (°C)	45
Feed gas inlet pressure (kg/cm ² g)	20.4
Feed gas molar flow rate (Nm ³ /h)	142 459
Lean amine inlet temperature (°C)	60
Lean amine inlet pressure (kg/cm ² g)	20.4
Lean amine mass flow rate (kg/hr)	236 001
Concentration of MDEA (wt %)	40
Composition of feed gas (mol %)	
Hydrogen (H ₂)	67.91
Nitrogen (N ₂)	0.14
Carbon monoxide (CO)	22.93
Carbon dioxide (CO ₂)	4.13
Methane (CH ₄)	4.43
Water (H ₂ O)	0.46

3.3 Description of Process Equipment

For the CO₂ removal units the following is a brief description of the major equipment necessary for successful of amine unit.

The absorber allows counter-current flow of lean amine from the top and sour gas (feed gas) from the bottom. The rich amine is flowing to the bottom while the sweet gas (treated gas) is collected at the top for further reaction to produce ammonia. The rich/lean amine exchanger is a heat conservation device where hot lean solvent preheats

cooler rich amine solution. The rich amine flows into stripping unit to separate CO₂ from the amine solution. Separated CO₂ is collected at the top of the column while lean amine solvent from the reboiler is further cool through a cooler before entering the absorber again. The centrifugal pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber.

3.4 Aspen HYSYS Simulation Procedure

The first step in doing HYSYS simulation is to select the appropriate fluid package. In this work, Amine Fluid Package with Kent-Eisenberg thermodynamic model is selected. The component selection window is opened by selecting view in the component-list as in the following figure:

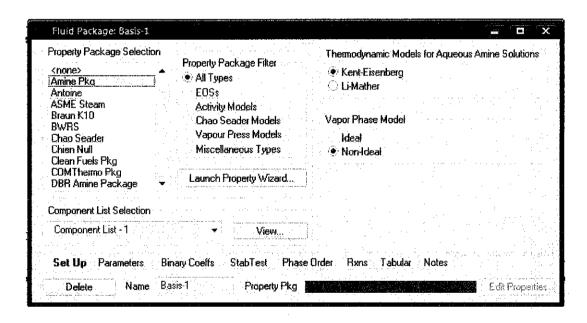


Figure 4: Fluid package basis (Amine Fluid Package)

Figure 5 shows dialog window is used for components selection:

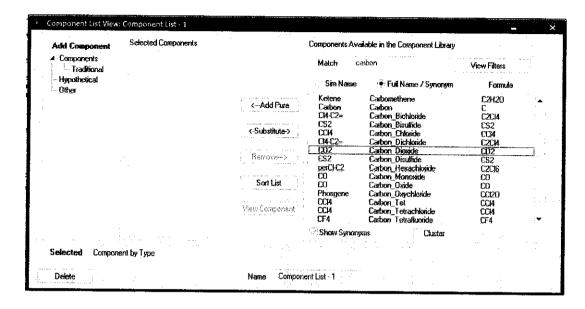


Figure 5: Component selection window

After selecting the component of the fluid, the simulation environment can enter where the process flow diagram is built. Stream specifications are made for lean amine and feed gas inlet temperature, pressure and flow rate. The compositions of the inlet streams are also specified. Other streams specifications made are tube and shell pressure drop for the heat exchanger, stages of the absorber and desorber, outlet temperature of CO₂ vent streams, outlet pressure of pump and outlet temperature of the cooler.

One of the rigorous tasks is the convergence of the absorber and desorber, to converge the absorber top and bottom temperature and pressure was specified and run, as in Figure 6. The desorber is converged by specifying the condenser temperature, distillate rate and reflux rate, the column is then run, as in Figure 7.

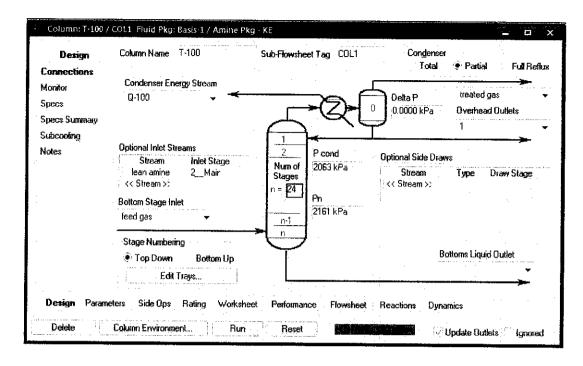


Figure 6: Converged window of the absorber column

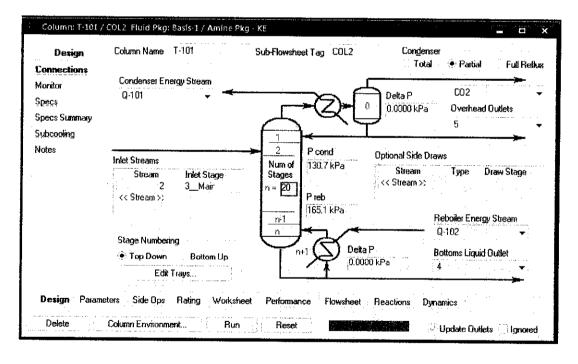


Figure 7: Converged window for desorber unit

With the convergence of the absorber and desorber units, a complete amine simulation for the base case is established. Then, a few changes have been done to the arrangement of the system. Hydraulic turbine has been used to convert the energy from the high pressure rich amine solution into electrical power. However, there is no turbine in the simulation tool, Aspen HYSYS. Hence, expander has been used to replace the hydraulic turbine usage. Different in pressure has to be set to get a converge expander but there will be error stating that there is liquid in the stream as expander is used for gas stream. Then, separation of CO₂ from the solution is done using flash drum or separator.

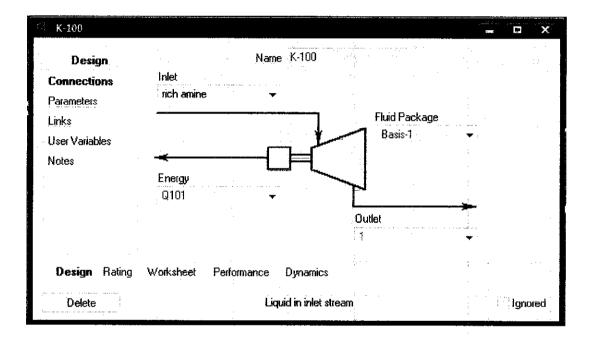


Figure 8: Expander (hydraulic turbine)

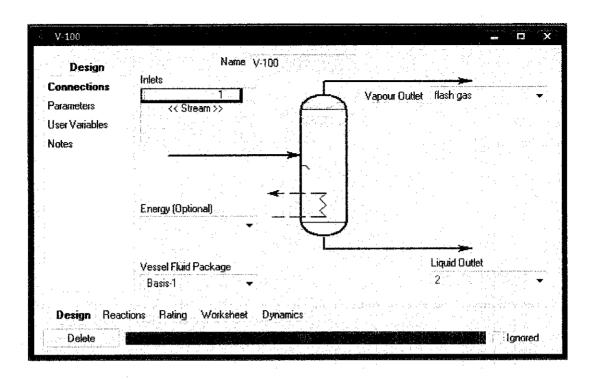


Figure 9: Separator (flash tank)

3.5 Procedure to change the operating parameters of absorber

Analysis need to be performed to observe the effect of changing the operating parameters on the CO₂ absorption rate, CO₂ removal rate and reboiler duty. The operating parameters that have been changed are pressure of the lean amine stream, temperature of lean amine stream and concentration of MDEA in the lean amine solution.

The CO₂ absorption rate is defined as shown in the following equation:

Absorption rate (%) = $\underline{\text{CO}_2 \text{ content in the rich amine stream (kg/hr)}}$ X 100% $\underline{\text{CO}_2 \text{ mass flow in the inlet stream (kg/hr)}}$ CO₂ mass flow in the inlet stream (kg/hr)

= CO₂ mass flow in the feed gas stream + CO₂ mass flow in the lean amine stream

Besides that, the CO₂ removal rate also is calculated by using the following equation:

 CO_2 removal rate (%) = $\underline{CO_2}$ content in the $\underline{CO_2}$ vent stream (kg/hr) \underline{X} 100% $\underline{CO_2}$ mass flow in the feed gas stream (kg/hr)

3.5.1 Procedure to change the pressure of the lean amine stream

Following is the procedure to change the pressure of the lean amine stream based on the base case simulation:

- i. Others parameters are remained constant.
- ii. Pressure of the lean amine stream is changed gradually from 10 kg/cm²g to 90 kg/cm²g.
- iii. The outlet pressure of the centrifugal pump is adjusted according to the pressure of the lean amine stream.
- iv. The changes in CO₂ mass flow in the rich amine stream, lean amine stream and CO₂ vent stream are recorded to observe the effects of changes on the CO₂ absorption and removal rate.
- v. The changes in the reboiler duty also are recorded.

3.5.2 Procedure to change the temperature of the lean amine stream

Following is the procedure to change the temperature of the lean amine stream based on the base case simulation:

- i. Others parameters are remained constant.
- ii. Temperature of the lean amine stream is changed gradually from 45 °C to 90 °C.
- iii. Temperature used must be in between 25 °C to 125 °C (Amine Package Range).
- iv. The outlet temperature of the cooler is adjusted according to the temperature of the lean amine stream.
- v. The outlet temperature of the cooler must be lower than the inlet temperature.
- vi. The changes in CO₂ mass flow in the rich amine stream, lean amine stream and CO₂ vent stream are recorded to observe the effects of the changes on the CO₂ absorption and removal rate.
- vii. The changes in the reboiler duty also are recorded.

3.5.3 Procedure to change the concentration of MDEA in the lean amine solution

Following is the procedure to change the concentration of MDEA in the lean amine solution based on the base case simulation:

- i. Others parameters are remained constant.
- ii. Concentration of MDEA in the lean amine solution is changed gradually from 10 wt% to 45 wt%.
- iii. Concentration used must be in between 0 wt% to 50 wt% (Amine Package Range).
- iv. The changes in CO_2 mass flow in the rich amine stream, lean amine stream and CO_2 vent stream are recorded to observe the effects of the changes on the CO_2 absorption and removal rate.
- v. The changes in the reboiler duty also are recorded.

3.6 Procedure to change the configuration of the removal system

Different configurations of the CO_2 removal system need to be performed to observe the changes of the configuration on the energy requirement of the system and amount of CO_2 that is being removed from the feed gas. Following is the procedure to change the configuration of the system based on the base case simulation:

3.6.1 Procedure to install hydraulic turbine in the system

Hydraulic turbine is used to decrease the pressure of the rich amine stream and at the same time generate power from the flowing fluid. Following is the procedure to apply the hydraulic turbine in the system:

- i. Others equipments are remained except the rich/amine heat exchanger (as there will be no convergence of the system if the heat exchanger is used).
- ii. The expander model is used to represent hydraulic turbine (unavailability of hydraulic turbine model in the software) to decrease the pressure of the rich amine stream.
- iii. The lowest pressure that can be dropped off is 101.3 kPa so that the solution did not enter the stripping unit at vacuum pressure.
- iv. Multiple expanders are used also to observe the effect of different pressure drop to the power generation of the turbine.

3.6.2 Procedure to install valve in the system

Valve is used to decrease the pressure of the rich amine stream but it cannot generate power from the flowing fluid. Following is the procedure to use the valve in the system:

i. Others equipments are remained except the rich/amine heat exchanger (as there will be no convergence of the system if the heat exchanger is used).

- ii. The valve is instead of hydraulic turbine to decrease the pressure of the rich amine stream.
- iii. The lowest pressure that can be dropped off is 101.3 kPa so that the solution did not enter the stripping unit at vacuum pressure.
- iv. Multiple valves are used also to observe the effect of different pressure drop to the separation of CO₂ from the rich amine solution.

3.6.3 Procedure to apply separator/flash tank in the system

Flash tank is used to separate the gas and liquid phase in the rich amine solution after going out from expander. Following is the procedure to apply the separator in the system:

- i. The separator is placed after the expander of valve.
- ii. The outlet stream of the separator is attached to the desorber for further separation of CO₂ from the amine solution.

3.6.4 Procedure to install heater in the system

Heater is used to increase the temperature of the rich amine stream after going out from the expander or valve. Following is the procedure to use the heater in the system:

- i. Others equipments are remained except the rich/amine heat exchanger (as there will be no convergence of the system if the heat exchanger is used).
- ii. The heater is used after expander or valve to increase the temperature of the rich amine stream.
- iii. The temperature must be lower than 100°C so that the water in the solution did not vaporize as steam or gas as the boiling point of water is 100 °C.
- iv. Multiple heaters are used also to observe the effect of temperature difference to the separation of CO₂ from the rich amine solution.

3.6.5 Procedure to install make up water stream in the system

Make up water stream is used to increase the flow rate of water in the lean amine stream so that the concentration of water is 60 wt%. Following is the procedure to install the makeup water stream in the system:

- i. The makeup water stream is installed before the absorber as the recycle lean amine solution will mix with the makeup water.
- ii. The flow rate of makeup water must fulfill the concentration of water in the lean amine solution.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Base case simulation

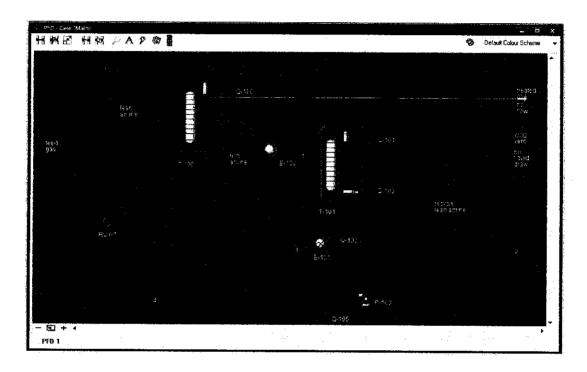


Figure 10: Complete simulation unit

Figure 10 clearly shows the simulation of the base case as per data from existing ammonia plant. To simulate the base case problem, the property package, Amine Package has been chosen. It is preferred as the process uses MDEA as the solvent to separate the carbon dioxide (CO₂) from the feed gas. According to the base case simulation, there are about 11, 552 kg/hr of CO₂ in the feed gas that has to be removed through the absorption process. Via the absorption system that uses absorber and

desorber as the main equipments, 8278.8 kg/hr of CO₂ has successfully being removed from the feed gas. However, the desorber that functions to separate the CO₂ from the rich amine solution requires about 10, 700 kW (10.7 MW) of energy to operate the boiler. It is a large value and has to be reduced to minimize the operating cost and save the energy. In order to do that, operating parameters have been changed to examine the effect of the adjustment to the reboiler duty and at the same time the CO₂ absorption and removal rate. Besides, modifications on the current carbon dioxide removal system also have been done to observe any changes of the type of equipment used and equipment arrangement to the amount of CO₂ removed and the energy requirement for the reboiler.

4.2 Effect of changing operating parameters to the absorption rate and the reboiler duty

One of the aim of the study is to investigate the effect of changing the operating parameters on the CO₂ removal system using the process simulation program HYSYS. Operating parameters that have been tested are the pressure and temperature of the lean amine stream as it is the stream that can be manipulated to get desired amount of CO₂ that can be removed. Concentration of the MDEA in the solution also has been changed to study the effect of different solvent concentration on the absorption rate of the CO₂.

4.2.1 Pressure of lean amine stream

The simulation result, Figure 11 shows the effect of changing the pressure of the lean amine stream on the absorption rate at different lean amine temperature while other parameters are remained constant. The CO_2 absorption rate decreases when increasing the pressure of lean amine stream. The trend is same for all temperatures. The highest absorption rate, 76.40% is achieved at 50° C and 10° kg/cm²g.

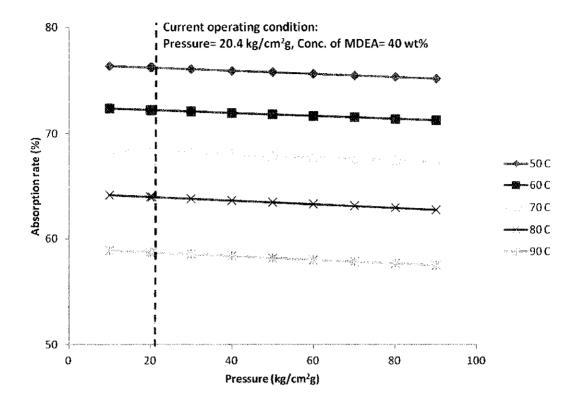


Figure 11: The effect of different lean amine pressure upon the CO2 absorption rate at different temperature

In Figure 12, increasing lean amine pressure has lead to the decreasing in reboiler duty which is good for the system but at the same time decreases the CO₂ ventilation rate which is not preferrable. The highest CO₂ ventilation rate is 71.78% with 10.70 MW energy requirement.

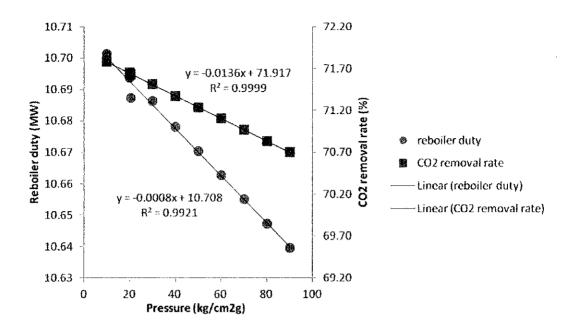


Figure 12: The effect of different lean amine pressure upon the reboiler duty and CO₂ ventilation rate

Figure 13 shows the correlation between the reboiler duty and CO₂ removal rate at different pressure of lean amine stream. It can be concluded that CO₂ ventilation rate is increasing linearly with increament of reboiler duty. There is a point wich disturbing the relationship and it can be considered as error from the process simulation.

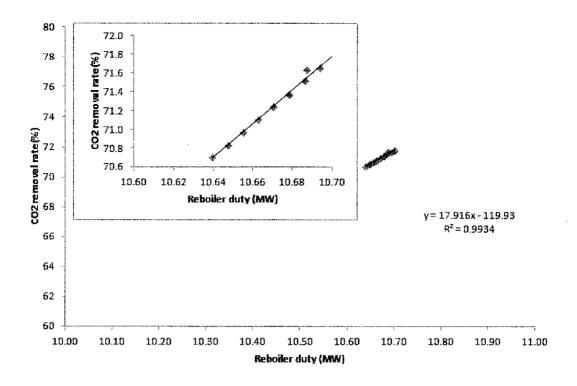


Figure 13: Correlation between reboiler duty and CO₂ removal rate at different pressure of lean amine stream

4.2.2 Temperature of lean amine stream

Figure 14 shows the effect of different lean amine temperature upon the absorption rate of CO₂ at different lean amine pressure. Limitation of the cooler usage (before lean amine solution fed up into absorber from desorber) has restricted the study of the temperature effect as the lean amine temperature only can be changed in range of 45°C - 90°C only. From the figure, it can be concluded that increasing temperature will decrease the absorption rate of CO₂.

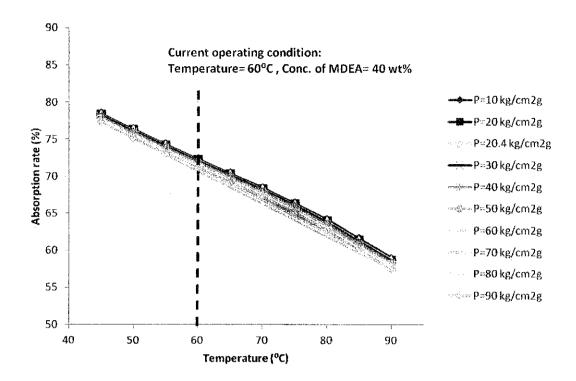


Figure 14: The effect of different lean amine temperature upon the absorption rate at different pressure

In Figure 15, it can be seen that increasing lean amine temperature led to decreasing reboiler duty and also CO_2 ventilation rate. Reboiler duty is at lowest value (10.09 MW) when the temperature is at 90° C.

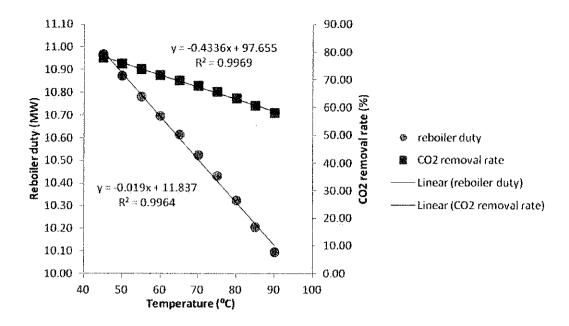


Figure 15: The effect of different lean amine temperature upon reboiler duty and CO₂ ventilation rate

4.2.3 Concentration of MDEA (wt %)

Figure 16 shows the effect of different concentration of MDEA (wt %) in the lean amine solution upon the absorption rate at current operating pressure (20.4 kg/cm²g). The absorption rate increases when the concentration of MDEA increases. However, there is limitation on concentration of MDEA used as using Amine Fluid Package; the system can only be converged if the range of the MDEA's concentration is in between 10-50 wt%. The figure also shows that the highest absorption rate which is 75.83% can be obtained when using 45 wt% of MDEA in the solution.

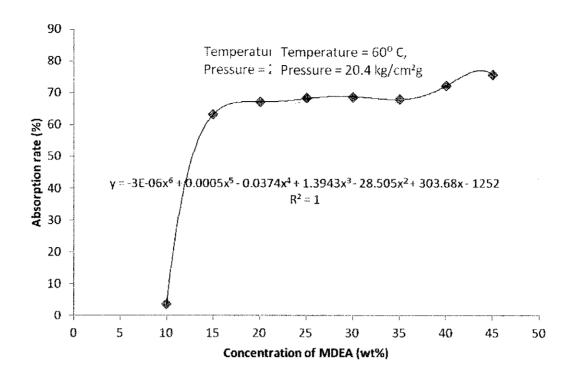


Figure 16: The effect of different concentration of amine solution upon the absorption rate at different pressure

Figure 17 shows the effect of different concentration of MDEA in amine solution upon reboiler duty and CO₂ ventilation rate. Increasing the concentration of MDEA has increased the reboiler duty and CO₂ ventilation rate. For current operation (40 wt% MDEA), the system is already vented huge amount of CO₂ but also consume large amount of energy for the reboiler operation at the desorber unit.

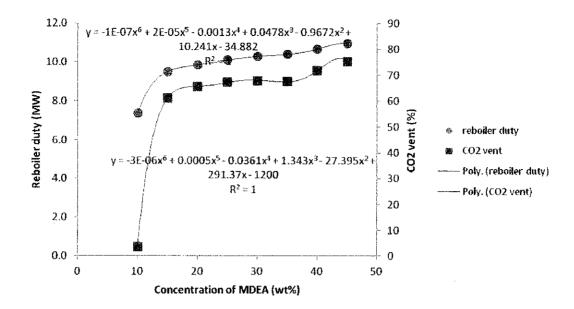


Figure 17: The effect of different concentration of amine solution upon reboiler duty and CO₂ ventilation rate

4.3 Comparative study

Comparative study has been done to observe the effect of different arrangement of the CO₂ separation system to the energy performance and amount of CO₂ being removed from the system. All changes are compared to base case simulation.

4.3.1 Usage of Two Hydraulic Turbine and Flash Tanks

According to BASF TEA wash process flow diagram (Roland E. M. et al., 1984), hydraulic turbines were used in the system. Hydraulic turbine can transfer the energy from a flowing fluid to a rotating shaft and producing the electrical power. For this problem, the rich amine solution that is going out from the absorber has potential to generate energy as the absorber column is operated at high pressure. Therefore,

hydraulic turbine is used to generate energy from the solution as shown in the following figure:

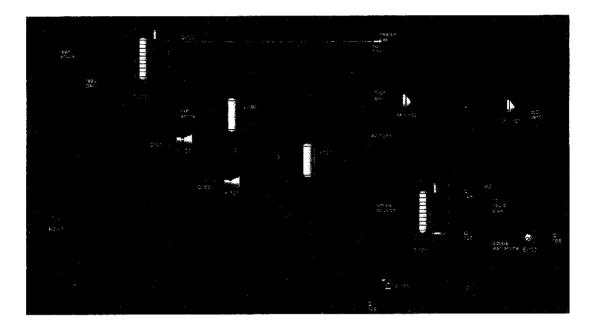


Figure 18: Usage of Hydraulic Turbine and flash tanks

Based on the simulation, power generated from the turbine is extremely small as shown in Table 3. The highest total power generated from the hydraulic turbines is 47.189 kW which is only 0.5% from the energy requirement of the reboiler in the base case. This means that the usage of the hydraulic turbine is not effective in the problem.

Table 3: Power generated from the hydraulic turbine

	1 st Hydrauli	c Turbine	2 nd Hydrau	ulic Turbine	
Trial	Pressure drop (kPa)	Power generated (kW)	Pressure drop (kPa)	Power generated (kW)	Total power generated (kW)
4	250	2.329	1809.7	44.86	47.189
1	500	4.772	1559.7	38.94	43.712
5	750	7.353	1309.7	33.64	40.993
2	1000	10.15	1059.7	28.14	38.29
6	1250	13.24	809.7	21.85	35.09
3	1500	16.92	559.7	15.81	32.73
7	1750	21.87	309.7	10.46	32.33
8	2000	34.53	59.7	12.36	46.89

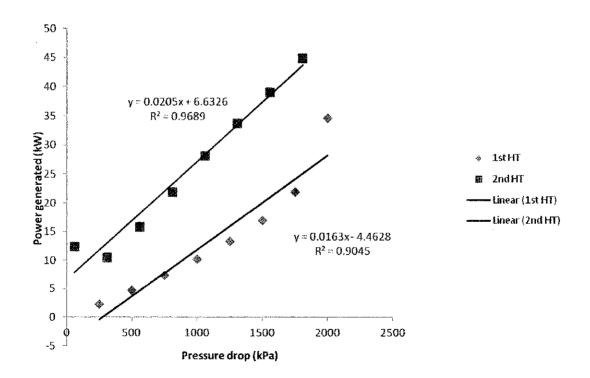


Figure 19: Power generated by the hydraulic turbine at different pressure drop

The possible cause of the small amount of power generated from the turbine is because the limitation of the software Aspen HYSYS. There is no specific equipment of hydraulic turbine in the software. Hence, instead of turbine, expander is used to represent the turbine. However, expander or commonly known as gas turbine is used for gas flow; rich amine solution is liquid solution, therefore the model that specifically designed for gas purpose is not applicable for liquid problem. The enthalpy calculated by the model is different from the actual enthalpy. Besides, energy produced basically depends on pressure, temperature, volume and the compressibility of the fluid. Supposedly for large pressure difference, the temperature difference also should be large. Nevertheless, in the case, the difference of the temperature is tremendously small. Thus, the power generated is small.

4.3.2 Usage of Multiple Hydraulic Turbines and Flash Tanks

Instead of using two hydraulic turbines, other configurations using different number of hydraulic turbines also are simulated to observe the power generated by the turbines as shown in the following figures:

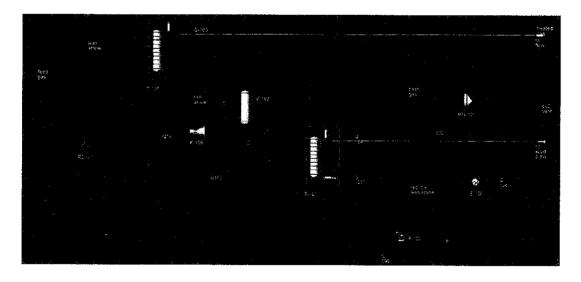


Figure 20: Usage of 1 hydraulic turbine and 1 flash tank

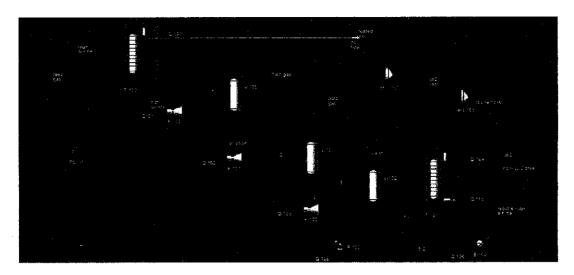


Figure 21: Usage of 3 hydraulic turbines and 3 flash tanks

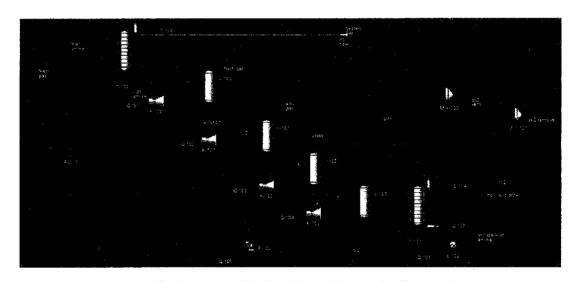


Figure 22: Usage of 4 hydraulic turbines and 4 flash tanks

According to the Table 4, it is clearly shown that the highest power generated is when using 1 hydraulic turbine. With 51.96 kW of power generated, total CO2 that is successfully being separated is about 109.7615 kg/hr. However, compared to base case simulation the amount of power generated is extremely small and cannot accommodate the energy requirement by the reboiler.

Table 4: Power generated from the multiple hydraulic turbines and flash tanks

Number of flash drum/ hydraulic turbine	Power generated by hydraulic turbine	total power generated (hydraulic turbine)	P _{in} (kPa)	P _{out} (kPa)	ΔP (kPa)	CO2 separated (kg/hr)	total CO ₂ separated (kg/hr)
1	51.96	51.96	2160.72	101.3	2059.42	109.7615	109.7615
ä	10.49	38.73	2160.72	1131	1029.72	1.9791	59.9145
2	28.24	30./3	1131.00	101.3	1029.70	57.9354	59.9145
	6.681		2160.72	1474	686.72	1.0013	
3	7.668	33.309	1474.00	787	687.00	1.9415	42.3089
	18.96		787.00	101.3	685.70	39.3661	
	4.918		2160.72	1646	514.72	0.6697	
4	5.382	30.708	1646.00	1131	515.00	0.9884	22 4205
4	6.058	30.700	1131.00	616	515.00	1.9050	33.4305
	14.35		616.00	101.3	514.70	29.8674	

4.3.3 Usage of flash tanks and valves

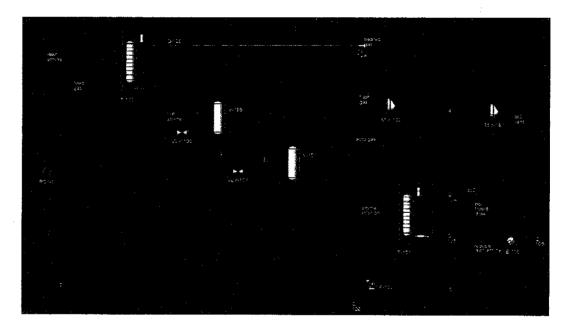


Figure 23: Usage of valves and flash tanks

Instead of using hydraulic turbine, valve is used to reduce the pressure of the rich amine solution. However, there is no power generated if using the valve. A valve is a device that regulates, directs or controls the flow of fluid by opening, closing or partially obstructing various passageways manually or automatically. Only 100.94 kg/hr of CO₂ is being separated during flashing the solution. This is extremely small if compared to the total CO₂ that has to be removed. The reason of the small amount of the CO₂ separated is possibly because of no temperature difference in the rich amine solution stream. Separation needs changes in temperature and pressure to make sure the separation process takes place effectively. In addition, using the arrangement as shown in Figure 15, the reboiler duty of the desorber increases to 20, 490 kW which is unacceptable as it increases the energy requirement of the system. Therefore, this arrangement is not applicable for the problem.

4.3.4 Usage of flash tanks, heaters and valves



Figure 24: Usage of valves, heaters and flash tanks

Upgrading the simulation in Figure 23, heaters have been added before the separator to increase the temperature of the stream. Adding the heaters increase the amount of CO₂ that is being separated during flashing process which is 6, 483.655 kg/hr. The reboiler duty also decreases from 10, 700 kW to 9, 839 kW. However, extra energy (18, 500 kW) is required when using the heater because the heater is operated with the aid of hot utility such as steam. Therefore, this configuration is not preferable.

4.3.5 Usage of hydraulic turbine and make up water stream

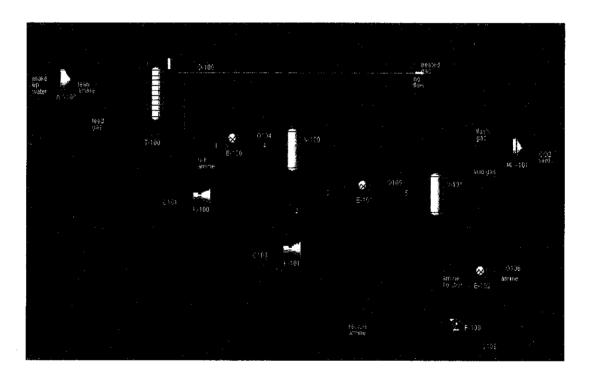


Figure 25: Usage of hydraulic turbine and make up water stream

Figure 25 shows different configuration where there is no desorber used in the system. The new configuration uses 2 hydraulic turbines, 2 heaters and 2 flash tanks to separate the CO₂ from the rich amine stream. After going through second flash tank, the amount of water decreases as it goes out with the CO₂ in the gas stream. Therefore, make up

water stream is added to top up the amount of water so that the concentration of water in the lean amine solution is 60 wt%. According to the configuration, there is about 7,078.8 kg/hr of CO₂ being removed from the system and 623.11 kW of power generated by the hydraulic turbines. However, the energy requirement has increased to 27, 327 kW which is larger from the base case simulation. Consequently, this configuration is not preferable as it cannot achieve the objective of the study.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the study that had been done, Aspen HYSYS process simulation tool has successfully simulated the chosen base case simulation. The analysis on CO₂ absorption rate, CO₂ removal rate and reboiler duty when changing the operating parameters of the system also have been carried out. It can be concluded that when increasing the pressure of the lean amine stream, the CO₂ absorption rate and CO₂ removal rate decrease. The reboiler duty also decreases when the pressure increases. Similar with the temperature of the lean amine stream, the CO₂ absorption rate, CO₂ removal rate and reboiler duty reduce when the temperature rises. In contrast, increasing concentration of MDEA in the lean amine solution has raised the CO₂ absorption rate, CO₂ removal rate and reboiler duty.

According to the comparative study that has been made, all the new configurations of the removal system cannot satisfy the objective of the problem. All the options cannot reduce the energy requirement of the reboiler. The amount of the CO_2 which is being removed from the feed gas also cannot be increased. Besides, the usage of the hydraulic turbine cannot generate much power as expected from the theory. The usage of the valve, heater and flash tank also cannot assist the removal system to reduce the energy requirement.

5.2 Recommendation

For further research, changes on pressure drop inside the absorber column can be made to observe the effect on the absorption rate of CO₂ and also reboiler duty. The analysis on the structural or design changes such as the different placement of the reboiler and condenser of the desorber also can be performed to observe the effect of the changes to the absorption rate and energy requirement.

In addition, more modifications on the CO₂ separation system should be made. For example; different design of the system by using simple flashing with multiple stages or usage of pump after the first hydraulic turbine to increase the pressure before it enters the second hydraulic turbine.

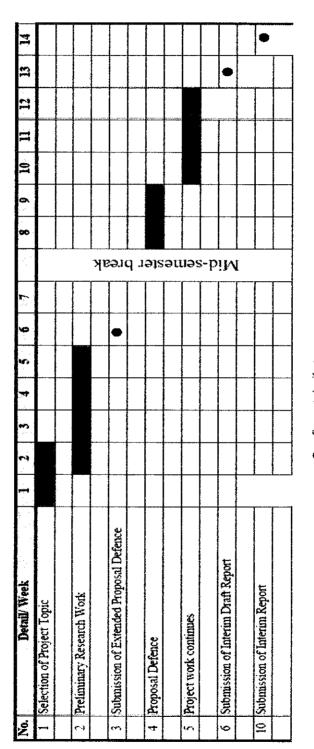
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APPENDICES

Timelines for FYP 1



Suggested milestone
 Process

Figure 26: Gantt chart for FYP1 (January 2012)

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Figure 27: Gantt chart for FYP2 (May 2012)

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3.3 Key MilestoneActivities							WEEK	WEEK NUMBER	IBER						
	7	2	3	4	S	9	7		œ	6	10	11	12	13	14
Topic selection															
Research about topic															
Literature review															
Base case simulation															
Simulation on different operating parameters															
Analysis on absorption rate															
Analysis on CO ₂ ventilation rate															
Analysis on reboiler duty															
Compilation of results									-						

						표	FINAL YEAR PROJECT 2	AR PR	DIECT	2					
Activites							WEEK	WEEK NUMBER	BER						
	-	2	က	4	5	9	7		ö	6	10	11	12	13	14
Simulation on different arrangement of system															
- usage of hydraulic turbine					-										
- number of flashing stage						1	:								
- usage of pump															
- usage of heater															
Analysis on the energy performance		·													
Optimization of the system									·						
Data analysis and report															

Figure 28: Key Milestone

Table 5: Simulation data at different pressure (T=60°C)

				Pressure o	f of lean am	Pressure of of lean amine stream (kg/cm2g)	(kg/cm2g)			
(kg/hr)	10	20	20.4	30	40	50	09	70	80	06
feed gas	11552.31	11552.31	11,14,57,34	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31
lean amine 2	219.7714	219.7714 219.7714	7600 972	219.7714	219.7714	219.7714	219.7714	219.7714	219.7714	219.7714
rich amine	8517.018	8501.136	657.8588	8485.138	8467.971	8451.891	8435.81	8419.759	8403.739	8387.745
treated gas 3	3255.068	3270.95	1000	3286.948	3304.114	3320.195	3336.276	3352.327	3368.346	3384.341
CO ₂ vent	8292.65	8277.266	8275 \$86	8261.78	8245.145	8229.56	8213.991	8198.432	8182.897	8167.39
total inlet	11772.09	11772.09	1.1768,32	11772.09	11772.09	11772:09	11772.09	11772.09	11772.09	11772.09
total outlet 1	11772.09	11772.09	11,768,32	11772.09	11772.09	11772.09	11772.09	11772.09	11772.09	11772.09
Absorption rate (%)	72.35	72.21	17.21	72.08	71.93	71.80	71.66	71.52	71.39	71.25
CO2 ventilation rate										
(%)	71.78	71.65	71.63	71.52	71.37	71.24	71.10	70.97	70.83	70.70
	3852510	3849771	3847443	3847114	3844151	3841372	3838587	3835805	3833027	3830247
Reboiler duty (kJ/h)	9	3	- 2	5	80	5	0	Ö	8	80
Reboiler duty (MW)	10.70	10.69	10.69	10.69	10.68	10.67	10.66	10.66	10.65	10.64

Table 6: Simulation data at different temperature (P=20.4 kg/cm²g)

					Pressure ≈ 2	Pressure ≈ 20.4 kg/cm²g				
mass flow of CO2				Tempera	ture of of le	Temperature of of lean amine stream (°C)	eam (°C)			
(kg/hr)	50	55	9	65	70	75	80	85	90	45
feed gas	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31	11552.31
lean amine	208.1961	227.2498	220,0817	213.4142	231.1896	236.6101	209.471	206.79	227.262	220.3758
rich amine	8969.27	8739.997	8502.057	8270.396	8049.06	7808:073	7525.333	7222.655	6917.539	9224.976
treated gas	2791.241	3039.567	3270.339	3495.332	3734,443	3980.851	4236.452	4536.449	4862.037	2547.714
CO2 vent	8745.241	8518.838	8278.76	8045.056	7826.521	7586,165	7303.706	7002.505	6695,985	9001.671
Absorption rate (%)	76.27	74.20	72.22	70.29	68.31	66.23	63.98	61.42	58.72	78.36
CO2 ventilation rate (%)	75.70	73.74	71.66	69.64	67.75	65.67	63.22	60.62	57.96	77.92
	3914562	3881476	3851044	3821409	3788984	3755625	3716794	3673938	3634147	3948470
Reboiler duty (kJ/h)	0	2	2	3	0	5	7	6	7	4
Reboiler duty (MW)	10.87	10.78	10.70	10.62	10.52	10.43	10.32	10.21	10.09	10.97

Table 7: Simulation data at different concentration of MDEA ($T=60^{9}C$, $P=20.4 \text{ kg/cm}^2g$)

(ad/ad) COO to male areas			Co	Concentration of MDEA (wt %)	of MDEA (wt	(%		
inass now of COZ (ng/iii)	10	15	20	25	30	35	9	45
feed gas	11552.31	11552.31	11552.31	11552.31	11552.31	11552:31	10552.31	11552.31
lean amine	0.00	654.51	564.28	418.64	291.03	187.68	216.01	269.49
rich amine	404.64	7729.71	8134.40	8193.61	8127.03	7991.05	8498,26	8964.67
treated gas	11147.67	4477.11	3982.19	3777.35	3716.32	3748.95	3270.07	2857.12
CO2 vent	404.64	7058.00	7554.45	7767.01	7828.71	7786.71	8275.34	8684.86
total inlet	11552.31	12206.82	12116.60	11970.95	11843.34	11740.00	11768.32	11821.80
total outlet	11552.31	12206.82	12116.60	11970.95	11843.34	11740.00	11,768.32	11821.80
Absorption rate (%)	3.50	63.32	67.13	68.45	68.62	68.07	72.21	75.83
CO2 ventilation rate (%)	3.50	61.10	62.39	67.23	67.77	67.40	71.63	75.18
Reboiler duty (kJ/h)	26528356	34221126	35430647	36365750	37007825	37449452	38474432	39455315
Reboiler duty (MW)	7.37	9.51	9.84	10.10	10.28	10.40	10.69	10.96

ENERGY CONSERVATION STUDY IN MDEA-BASED CO₂ REMOVAL SYSTEM

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Abstract: Energy requirement of CO₂ removal section in Ammonia Plant is extremely large and costly. Numerous developments have been done so that it is more energy efficient and affordable; for instance absorption of CO2 in an amine based solution. A simplified carbon dioxide removal system using MDEA solution has been simulated with the Aspen HYSYS software. **Analysis** ОП the operating parameters such as the absorption temperature and pressure, and also the concentration of MDEA in lean amine solution have been performed to study the effect of operating parameters changes absorption rate of carbon dioxide, reboiler and CO₂ ventilation rate. comparative study on the structural changes of the absorption system also has been carried out to observe the energy performance of the system which apparently can reduce the capital investment if optimization of the energy requirement can be accomplished. Subsequently, new configurations of the CO₂ removal system including usage of hydraulic turbine in the system do not contribute much in reducing energy requirement of the system. Hence, the energy cost could not be reduced much.

Keywords: CO₂ removal system, MDEA, HYSYS simulation, absorption, hydraulic turbine, energy conservation

I. INTRODUCTION

Carbon dioxide emission has become the center of attention of the world today as CO₂ contributes in global warming and greenhouse

effect. In ammonia synthesis, CO₂ is an undesirable constituent in the synthesis gas because it poisons the ammonia synthesis catalysts in the reactor. Carbon dioxide content in the synthesis gas must be reduced to 5 to 10 part per million (ppm) by volume [1]. There are several of technologies used to remove CO2 from the synthesis gas including chemical solvent absorption [2], adsorption [3], biological fixation [4], and membrane separation [5]. Among the broad variety of techniques for CO2 separation, absorption is the best process to separate CO2 from the synthesis gas. Absorption process is divided into two categories; physical absorption [2] and chemical absorption [6]. Present day, the most preferred solution in alkanoamines process is activated methyldiethanolamine (MDEA).

The hydraulic turbine has been developed since ancient Greece and used until now [7]. Hydraulic turbine transfers the energy from a flowing fluid to a rotating shaft [8]. Hydraulic turbine has a row of blades fitted to the rotating shaft or rotating plate. When passing the turbine, the flowing fluid mostly water will strikes the blades and makes the shaft to rotate. The velocity and pressure of the liquid reduce as the fluid flows through the hydraulic turbine. These result in the development of torque and rotation of turbine shaft.

There are different forms of hydraulic turbines used in the industry, depending on the operational requirements. Each type of hydraulic turbine has their specific use which can provide the optimum output. Hydraulic turbines can be classified into two categories which are based on flow path and pressure change. Based on the flow path of the liquid, hydraulic turbine can be categorized into three types [8]; axial flow hydraulic turbine [9], radial flow hydraulic turbines and mixed flow hydraulic turbine. Impulse turbine and reaction

turbine are hydraulic turbines which operate based on the pressure change.

II. BACKGROUND STUDY

The selection and design of carbon dioxide removal system was the most difficult engineering job of the Phulpur Expansion Project (PEP) [10]. PEP is a repeat of Aonla Expansion Project (AEP). The new ammonia plant was consuming higher energy per ton of ammonia as compared to the design value and the carbon dioxide removal system was identified as one of the higher energy consuming areas.

The most actual method for carbon dioxide removal is by absorption in an amine based solvent [11]. Two major criteria must be considered to choose the adequate amine solution [12]; the absorption performance and the energy requirement for the solvent regeneration. Different types of amines can also be mixed in order to combine the specific advantages of each type of amines and obtain the highest absorption rate [13] [14] [15].

The simplest and most used amine for the removal these days is MDEA [11]. In alkanoamine technology, usage of activated amine solutions which consist of a conventional amine doped with small amounts of an accelerator or activator has been developed [16]. Activator is used to enhance the overall CO₂ absorption rate. Piperazine (PZ) is one activator that has been the focus of many researchers. The piperazine has been mixed with MDEA and MEA [16] [17] to observe the effect of PZ on the absorption and desorption rate of CO₂ Besides, aqueous ammonia also has been used as the solvent to absorb CO₂ [18] [19].

Carbon dioxide removal by absorption using MDEA solution is highly energy intensive. Studies have been done to perform some analysis on the system to improve the performance and reduce the energy consumption. Process simulation tool for instance Aspen HYSYS has been used to evaluate such processes as it is hard to do observation on the current operating plant [11]. An important advantage of using Aspen HYSYS is it has an Amine Property Package which comprised of two models; Kent Eisenberg and Li-Mather.

Based on simulation of carbon dioxide removal with an aqueous MEA solution [11] [20] [21], changing some of the important parameters can give effect to the process. For Selexol® process used in Integrated Gasification Combined Cycle (IGCC) power plant, packing and height of absorber and desorber can affect the reboiler duty [22].

However, stripping section still requires a lot of energy to make sure the regeneration of MDEA solution happens effectively. Amine solution that is regenerated by flashing results in large energy savings compared to stripping [23]. This is proved by the first triethanolamine (TEA) wash plant operation commenced in Ludwigshafen, West Germany in 1966.

III. METHODOLOGY

3.1 Aspen HYSYS Process Simulation Tool

The simulation study for the carbon dioxide removal system using MDEA has been done via Aspen HYSYS process simulation tool.

3.2 Aspen HYSYS Input Data

All the data and information used for the system are taken from the existing ammonia plant. The following table shows the information used for the system:

Table 1: Operating parameters for CO₂ removal process

Operating parameter	Value
Feed gas inlet temperature (°C)	45
Feed gas inlet pressure (kg/cm ² g)	20.4
Feed gas molar flow rate (Nm ³ /h)	142 459
Lean amine inlet temperature (°C)	60
Lean amine inlet pressure (kg/cm²g)	20.4
Lean amine mass flow rate (kg/hr)	236 001

Concentration of MDEA (wt %)	40
Composition of feed gas (mol %)	
Hydrogen (H ₂)	67.91
Nitrogen (N ₂)	0.14
Carbon monoxide (CO)	22.93
Carbon dioxide (CO ₂)	4.13
Methane (CH ₄)	4.43
Water (H₂O)	0.46

3.3 Description of Process Equipment

For the CO₂ removal units the following is a brief description of the major equipment necessary for successful of amine unit.

The absorber lets counter-current flow of lean amine solution from the top and feed gas from the bottom. The rich amine is flowing to the bottom while the treated gas is collected at the top for further reaction to produce ammonia. The rich/lean amine heat exchanger is a heat conservation equipment where rich amine solution being heated by the hot lean amine solution from. The rich amine flows into stripping unit to separate CO2 from the amine solution. Separated CO2 is collected at the top of the column while lean amine solvent from the reboiler is further cool through a cooler before entering the absorber again. The centrifugal pump is installed to maintain the recycle lean solvent at the desired operating pressure of the absorber.

3.4 Aspen HYSYS Simulation Procedure

The first step in doing HYSYS simulation is to select the correct fluid package. In this work, Amine Fluid Package with Kent-Eisenberg thermodynamic model is selected. The component selection window is opened by selecting view in the component-list as in the following figure:

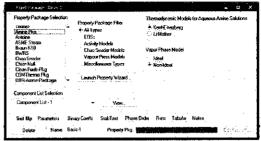


Figure 1: Fluid package basis

Figure 2 shows dialog window is used for components selection:

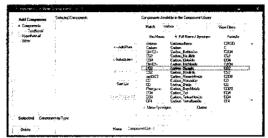


Figure 2: Component selection window

After selecting the component of the fluid, the simulation environment can be activated where the process flow diagram is built. Stream specifications are made for lean amine and feed gas inlet temperature, pressure and flow rate. The compositions of the inlet streams are also specified. Other streams specifications made are tube and shell pressure drop for the heat exchanger, stages of the absorber and desorber, outlet temperature of CO₂ vent streams, outlet pressure of pump and outlet temperature of the cooler.

One of the rigorous tasks is the convergence of the absorber and desorber. The temperature of the top and bottom of the column was specified and run, as in Figure 3. The desorber is converged by specifying the condenser temperature, distillate rate and reflux rate, as in Figure 7.

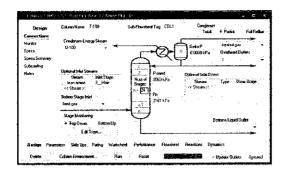


Figure 3: Converged window of the absorber column

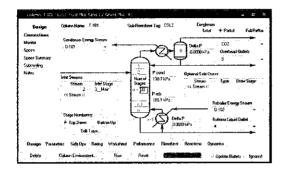


Figure 4: Converged window for desorber unit

A complete amine simulation for the base case is established. Then, a few changes have been done to the arrangement of the system. Hydraulic turbine has been used to convert the energy from the high pressure rich amine solution into electrical power. However, there is no turbine in the simulation tool, Aspen HYSYS. Hence, expander has been used to replace the hydraulic turbine usage. Different in pressure has to be set to get a converge expander but there will be error stating that there is liquid in the stream as expander is used for gas stream. Then, separation of CO₂ from the solution is done using flash drum or separator.

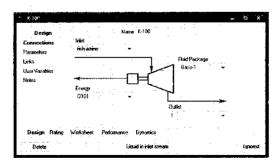


Figure 5: Expander (hydraulic turbine)

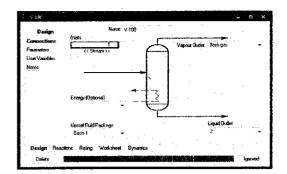


Figure 6: Separator (flash tank)

IV. RESULT AND DISCUSSION

4.1 Base case simulation

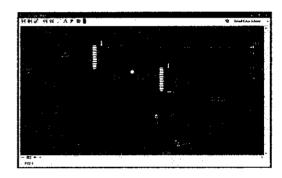


Figure 7: Complete simulation unit

Figure 7 clearly shows the simulation of the base case as per data from existing ammonia plant. To simulate the base case problem, the property package, Amine Package has been chosen. It is preferred as the process uses MDEA as the solvent to separate the carbon dioxide (CO₂) from the feed gas. According to the base case simulation, there are about 11, 552 kg/hr of CO₂ in the feed gas that has to be removed through the absorption process. Via absorption system that uses absorber and desorber as the main equipments, 8278.8 kg/hr of CO2 has successfully being removed from the feed gas. However, the desorber that functions to separate the CO₂ from the rich amine solution requires about 10, 700 kW (10.7 MW) of energy to operate the boiler. It is a large value and has to be reduced to minimize the operating cost and save the energy. In order to do that, operating parameters have been changed to examine the effect of the adjustment to the reboiler duty and at

the same time the CO₂ absorption and removal rate. Besides, modifications on the current carbon dioxide removal system also have been done to observe any changes of the type of equipment used and equipment arrangement to the amount of CO₂ removed and the energy requirement for the reboiler.

4.2 Effect of changing operating parameters to the absorption rate and the reboiler duty

One of the aim of the study is to investigate the effect of changing the operating parameters on the CO₂ removal system using the process program HYSYS. Operating simulation parameters that have been tested are the pressure and temperature of the lean amine stream as it is the stream that can be manipulated to get desired amount of CO₂ that can be removed. Concentration of the MDEA in the solution also has been changed to study the effect of different solvent concentration on the absorption rate of the CO_2 .

4.2.1 Pressure of lean amine stream

The simulation result, Figure 8 shows the effect of changing the pressure of the lean amine stream on the absorption rate at different lean amine temperature while other parameters are remained constant. The CO₂ absorption rate decreases when increasing the pressure of lean amine stream. The trend is same for all temperatures. The highest absorption rate, 76.40% is achieved at 50°C and 10 kg/cm²g.

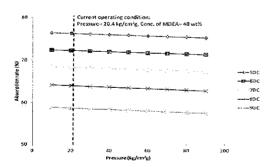


Figure 8: The effect of different lean amine pressure upon the CO2 absorption rate at different temperature

In Figure 9, increasing lean amine pressure has lead to the decreasing in reboiler duty which

is good for the system but at the same time decreases the CO_2 ventilation rate which is not preferrable. The highest CO_2 ventilation rate is 71.78% with 10.70 MW energy requirement.

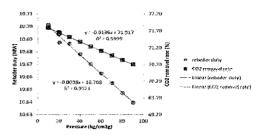


Figure 9: The effect of different lean amine pressure upon the reboiler duty and CO₂ ventilation rate

Figure 10 shows the correlation between the reboiler duty and CO_2 removal rate at different pressure of lean amine stream. It can be concluded that CO_2 ventilation rate is increasing linearly with increament of reboiler duty. There is a point wich disturbing the relationship and it can be considered as error from the process simulation.

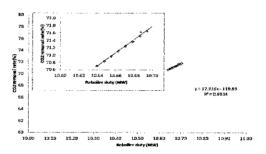


Figure 10: Correlation between reboiler duty and CO2 removal rate at different pressure of lean amine stream

4.2.2 Temperature of lean amine stream

Figure 11 shows the effect of different lean amine temperature upon the absorption rate of CO₂ at different lean amine pressure. Limitation of the cooler usage (before lean amine solution fed up into absorber from desorber) has restricted the study of the temperature effect as the lean amine temperature only can be changed in range of 45°C - 90°C only. From the figure, it can be

concluded that increasing temperature will decrease the absorption rate of CO₂.

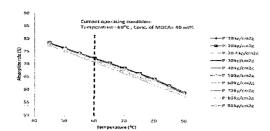


Figure 11: The effect of different lean amine temperature upon the absorption rate at different pressure

In Figure 12, it can be seen that increasing lean amine temperature led to decreasing reboiler duty and also CO_2 ventilation rate. Reboiler duty is at lowest value (10.09 MW) when the temperature is at $90^{\circ}C$.

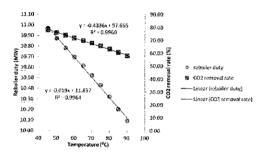


Figure 12: The effect of different lean amine temperature upon reboiler duty and CO₂ ventilation rate

4.2.3 Concentration of MDEA (wt %)

Figure 13 shows the effect of different concentration of MDEA (wt %) in the lean amine solution upon the absorption rate at current operating pressure (20.4 kg/cm²g). The absorption rate increases when the concentration of MDEA increases. However, there is limitation on concentration of MDEA used as using Amine Fluid Package; the system can only be converged if the range of the MDEA's concentration is in between 10-50 wt%. The figure also shows that the highest absorption rate which is 75.83% can be obtained when using 45 wt% of MDEA in the solution.

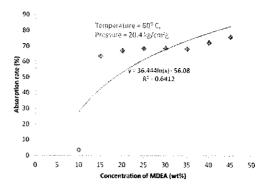


Figure 13: The effect of different concentration of amine solution upon the absorption rate at different pressure

Figure 14 shows the effect of different concentration of MDEA in amine solution upon reboiler duty and CO₂ ventilation rate. Increasing the concentration of MDEA has increased the reboiler duty and CO₂ ventilation rate. For current operation (40 wt% MDEA), the system is already vented huge amount of CO₂ but also consume large amount of energy for the reboiler operation at the desorber unit.

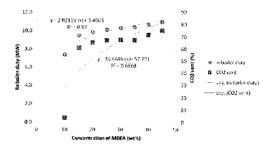


Figure 14: The effect of different concentration of amine solution upon reboiler duty and CO₂ ventilation rate

4.3 Comparative study

Comparative study has been done to observe the effect of different arrangement of the CO₂ separation system to the energy performance and amount of CO₂ being removed from the system. All changes are compared to base case simulation.

4.3.1 Usage of Two Hydraulic Turbine and Flash Tanks

According to BASF TEA wash process flow diagram [23], hydraulic turbines were used in the system. Hydraulic turbine can transfer the energy

from a flowing fluid to a rotating shaft and producing the electrical power. For this problem, the rich amine solution that is going out from the absorber has potential to generate energy as the absorber column is operated at high pressure. Therefore, hydraulic turbine is used to generate energy from the solution as shown in the following figure:

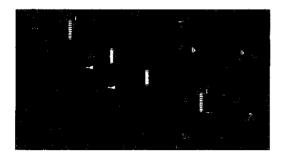


Figure 15: Usage of Hydraulic Turbine and flash tanks

Based on the simulation, power generated from the turbine is extremely small. The highest total power generated from the hydraulic turbines is 47.189 kW which is only 0.5% from the energy requirement of the reboiler in the base case. This means that the usage of the hydraulic turbine is not effective in the problem.

The possible cause of the small amount of power generated from the turbine is because the limitation of the software Aspen HYSYS. There is no specific equipment of hydraulic turbine in the software. Hence, instead of turbine, expander is used to represent the turbine. However, expander or commonly known as gas turbine is used for gas flow; rich amine solution is liquid solution, therefore the model that specifically designed for gas purpose is not applicable for liquid problem. The enthalpy calculated by the model is different from the actual enthalpy. Besides, energy produced basically depends on temperature. pressure. volume and compressibility of the fluid. Supposedly for large pressure difference, the temperature difference also should be large. Nevertheless, in the case, the difference of the temperature is tremendously small. Thus, the power generated is small.

4.3.2 Usage of Multiple Hydraulic Turbines and Flash Tanks

Instead of using two hydraulic turbines, other configurations using different number of

hydraulic turbines also are simulated to observe the power generated by the turbines as shown in the following figure:

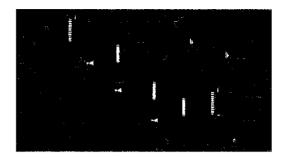


Figure 16: Usage of 3 hydraulic turbines and 3 flash tanks

It is clearly shown that the highest power generated is when using 1 hydraulic turbine. With 51.96 kW of power generated, total CO2 that is successfully being separated is about 109.7615 kg/hr. However, compared to base case simulation the amount of power generated is extremely small and cannot accommodate the energy requirement by the reboiler.

4.3.3 Usage of flash tanks and valves

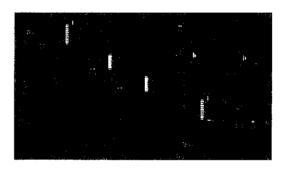


Figure 17: Usage of valves and flash tanks

Instead of using hydraulic turbine, valve is used to reduce the pressure of the rich amine solution. However, there is no power generated if using the valve. A valve is a device that regulates, directs or controls the flow of fluid by opening, closing or partially obstructing various passageways manually or automatically. Only 100.94 kg/hr of CO₂ is being separated during flashing the solution. This is extremely small if compared to the total CO₂ that has to be removed. The reason of the small amount of the CO₂ separated is possibly because of no temperature difference in the rich amine solution stream.

Separation needs changes in temperature and pressure to make sure the separation process takes place effectively. In addition, using the arrangement as shown in Figure 17, the reboiler duty of the desorber increases to 20, 490 kW which is unacceptable as it increases the energy requirement of the system. Therefore, this arrangement is not applicable for the problem.

4.3.4 Usage of flash tanks, heaters and valves

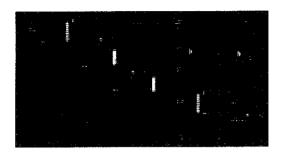


Figure 18: Usage of valves, heaters and flash tanks

Upgrading the simulation in Figure 17, heaters have been added before the separator to increase the temperature of the stream. Adding the heaters increase the amount of CO₂ that is being separated during flashing process which is 6483.655 kg/hr. The reboiler duty also decreases from 10, 700 kW to 9839 kW. However, extra energy (18, 500 kW) is required when using the heater because the heater is operated with the aid of hot utility such as steam. Therefore, this configuration is not preferable.

4.3.5 Usage of hydraulic turbine and make up water stream



Figure 19: Usage of hydraulic turbine and make up water stream

Figure 19 shows different configuration where there is no desorber used in the system. The new

configuration uses 2 hydraulic turbines, 2 heaters and 2 flash tanks to separate the CO2 from the rich amine stream. After going through second flash tank, the amount of water decreases as it goes out with the CO2 in the gas stream. Therefore, make up water stream is added to top up the amount of water so that the concentration of water in the lean amine solution is 60 wt%. According to the configuration, there is about 7078.8 kg/hr of CO₂ being removed from the system and 623.11 kW of power generated by the hydraulic turbines. However, the energy requirement has increased to 27, 327 kW which is from the base case simulation. Consequently, this configuration is not preferable as it cannot achieve the objective of the study.

V. CONCLUSION

Based on the study that had been done, Aspen HYSYS process simulation tool has successfully simulated the chosen base case simulation. The analysis on CO₂ absorption rate, CO₂ removal rate and reboiler duty when changing the operating parameters of the system also have been carried out. It can be concluded that when increasing the pressure of the lean amine stream, the CO2 absorption rate and CO2 removal rate decrease. The reboiler duty also decreases when the pressure increases. Similar with the temperature of the lean amine stream, the CO₂ absorption rate, CO₂ removal rate and reboiler duty reduce when the temperature rises. In contrast, increasing concentration of MDEA in the lean amine solution has raised the CO2 absorption rate, CO2 removal rate and reboiler duty. According to the comparative study that has been made, all the new configurations of the removal system cannot satisfy the objective of the problem. All the options cannot reduce the energy requirement of the reboiler. The amount of the CO2 which is being removed from the feed gas also cannot be increased. Besides, the usage of the hydraulic turbine cannot generate much power as expected from the theory. The usage of the valve, heater and flash tank also cannot assist the removal system to reduce the energy requirement.

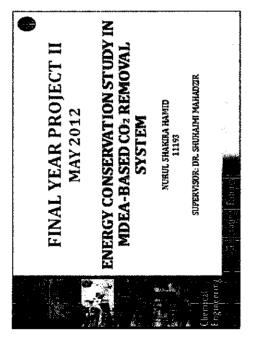
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Results & Discussions

Recommendation

Conclusion

Literaturereview

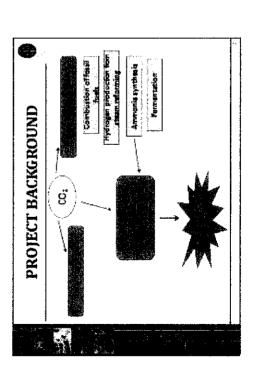
Methodology

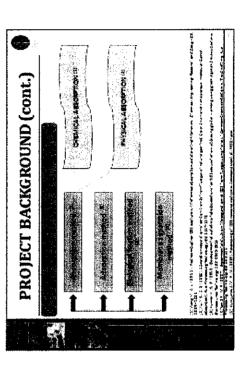
Scope of study

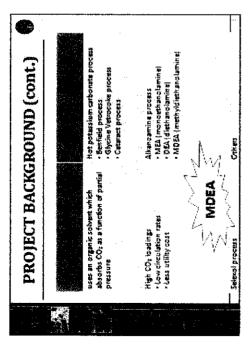
Objective

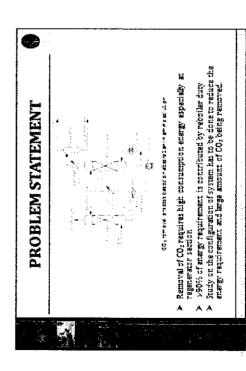
OUTLINE

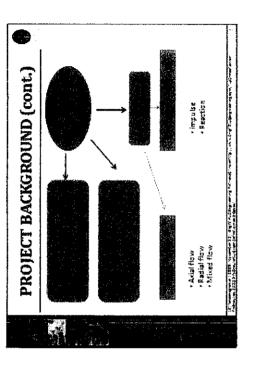
Project background
 Problem statement











OBJECTIVE

 To simulate chosen CO₂ removal system case using Aspen HYSYS

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- To perform analysis on the CO₂ absorption rate, CO₂ removal rate and reboiler duty when changing the operating parameters, pressure, temperature and concentration
- To study different configuration of the removal system on the energy requirement and amount of CO₂ which is removed from the synthesis gas

SCOPE OF STUDY

Conducting simulation study of CO; removal system using Aspen HYSYS under different operating condition and structural changes such as:

- pressure of lean amine stream
- · remperature of lean amine stream
- concentration of amine in the solution.
- Canducting study on the effects of the different system configuration on the absorption rate and energy requirement

.

LITERATURE REVIEW



- Lars (2007) says that the most actual method for carbon dioxide removal is by absorption in an antine based solvent followed by description $\pi_{\rm c}$.
- According to Dubois (2011), two major criteria must be considered to choose the adequate amine solution $|\mathcal{P}_i|$
 - the absorption performance
- the energy requirement for the solvent regeneration

. 17 January (n. 1921). New Sammedynn 1521 was absorbed to the constitution of the con

LITERATURE REVIEW (cont.)



- The simplest and most used amine for the removal these days is methyldiethanolamine (MDEA). .
- The advantages of using MDEA are: .
- High solution concentration (up to 50 to 55 wt%)

- Low corrosion seen at high solution loadings

- High acid gas loading

- Jerry et al. (1596); "** has explored the use of MDEA and mixtures of
antines for bulk CO; removal. It has been proved that MDEA can be used
quite advertageously for bulk CO? removal and the performance is often
very sensitive to the operating parameters such as less amine
empleasure.

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-Hargalapuly et al. (2012)¹¹¹ have done a pilot plant study of four new solvents for post conduction carbon dissible capture by reactive description. The results are being compared to MEA.

- CO, explure on monoethenolamine (PEA) is one of the most mature chamical absorption methods of post-cambustion technologies 100

- · Slow degradation rates
 - Lower heats of reaction
- Low vapor pressure and solution losses.

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The different types of amines can also be mixed in order to combine the specific advantages of each type of amines and obtain the highest absorption rate.

LITERATURE REVIEW (cont.)



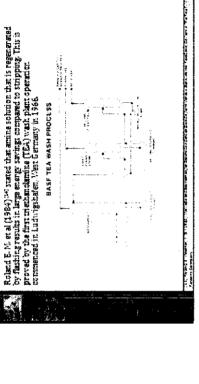
LITERATURE REVIEW (cont.)

Based on simulation of carbon disoxice removal with an aqueous MEA, solution done by Lars (2007) % changing some of the important parameters can give effect to the process

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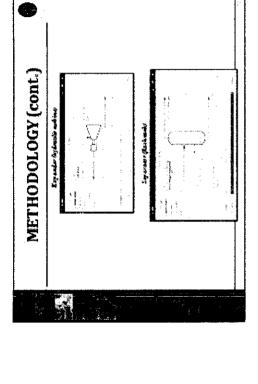
- 18 (Sec.) 18.16 装灶 :X 85 a a 3 ¥ 4 METHODOLOGY (cont.) Aspen MYSYS Input Data Branch States Geregoran energias April 1980 and the second second second second Ceresnale de Cou The state of the s Fredge volpefgungs North (1)、中心ののできるとなるのでは、内臓を持ち The second A so of the particulation 古典の事務を持たる 770.000.00 Section 2

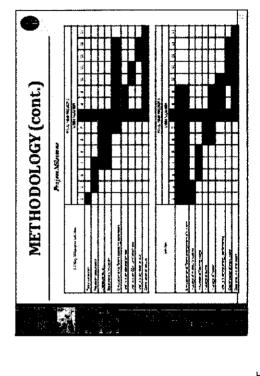
METHODOLOGY

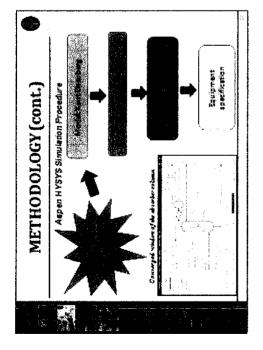
The simulation study for the carbon dioxide removal system using MDEA has been done via Aspen H1515 process simulation tool.

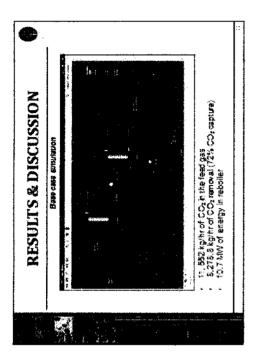
Aspen HYSYS is a market-leading process modeling tool for conceptual design, optimization, hishess planning asset management and performance monitoring for oil and gas production, gas processing, petroleum retining and air separation industries.

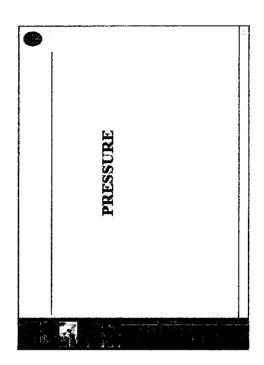
- Features of Aspen HYSIS:
 - 695y to u se
- easy to train
- best in dass physical properties method and data
- -bas comprehensive ilorary of unit operation models
 -introduce the novel approach of steady state and dynamic simulations in the same platform.

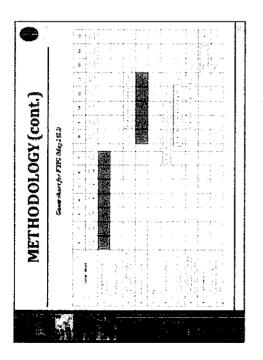


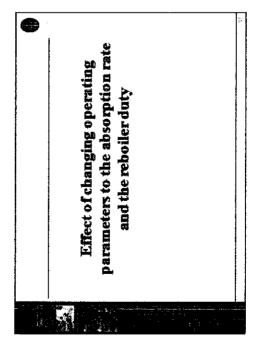




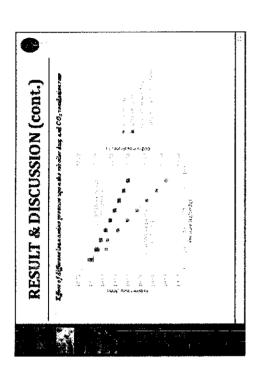


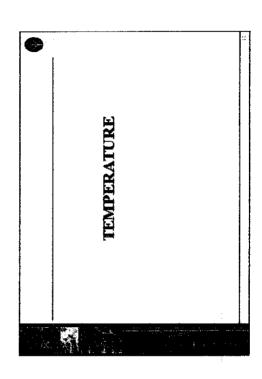


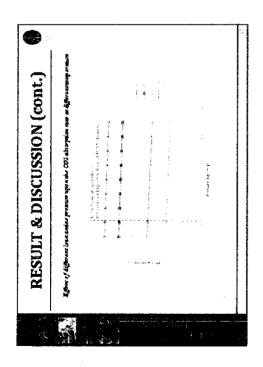


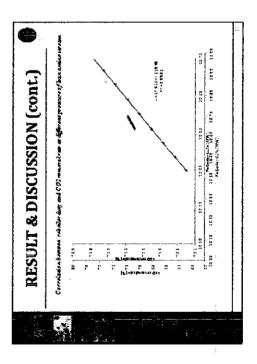


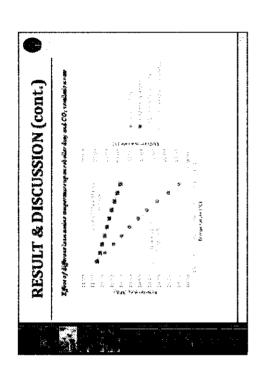


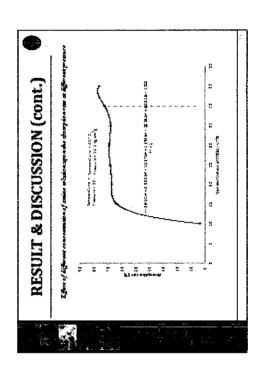


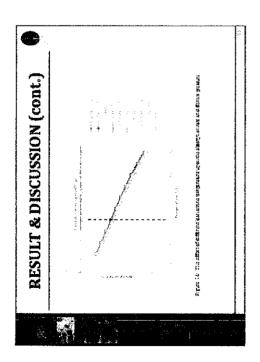


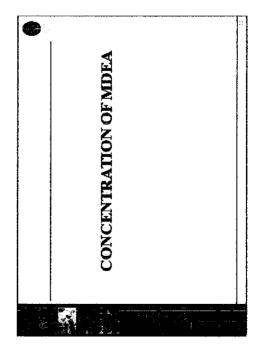


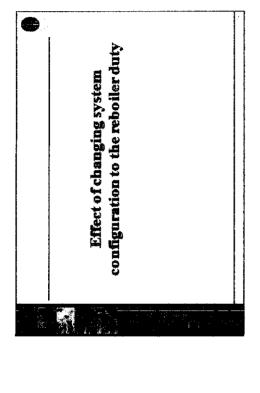


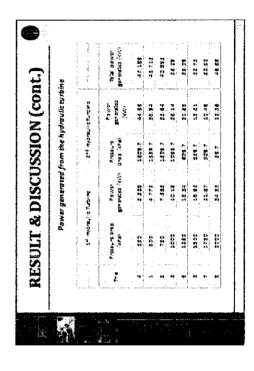


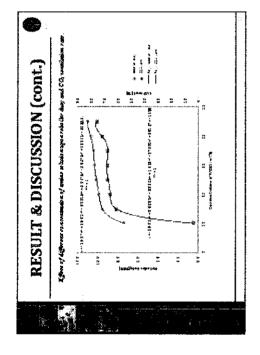


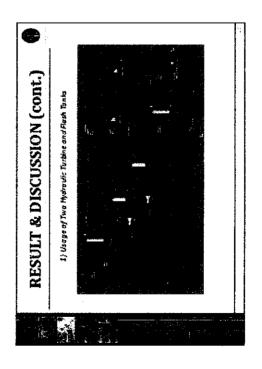


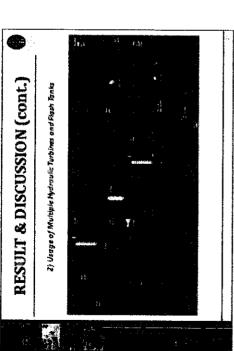












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RESULT & DISCUSSION (cont.)

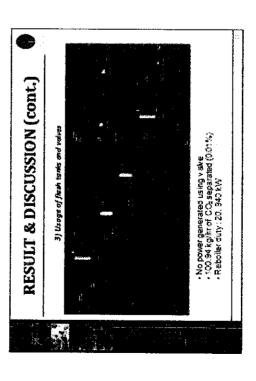
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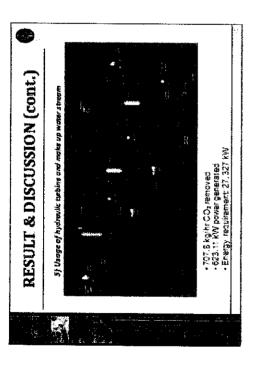






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- 6, 483,655 kg/hr CO, separated • Reboiler duty: 3, 839 kW • Extra energy required: 18, 500 kW



RECOMMENDATION

- Changes on pressure drop inside the absorber column.
- Analysis on the structural or design changes
 different placement of the reboiler and condenser of the desorber
- CO; separation system
- different design of the system by using simple flashing with multiple stages
- usage of pump after the first hydraulic unfone to increase the pressure before it enters the second hydraulic unfone.

CONCLUSIONS

- A selected CO₂ removal system has been simulated on Aspen HYSTS.
- Analysis on the CO, aboseption rate. CO, removal rate and reboiler duy when changing the operating parameters; pressure, temperature and conventration has been performed.
- -Co, sisorgman ress. Co, removal ress and rebailer dary decrease whan minesting the pressure and rempleceure of the leanaring access.
 - Arrestemple consequention of MDPA is the leanaring solution has increased the U.S.
 - stoopphorese. Co, removal over and repolate lang.
- Different configuration of the removal system on the energy requirement and amount of CGs which is removed from the synthesis gas has been studied.
 - All this spirans cannot reduce the aneaty requirement of the reducier.
 Amount of the TD, which is being removed from the field gas also cannot be increased.
- nernessy - Gaggs of the hydraulic tarbans zannor ganarara much power se supermedhom the shoopy

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THANK YOU