Economic Optimization of CO_2 Capture Process Using MEA-MDEA Mixtures

by

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Ir. Dr. Abdul Halim Shah B Maulud)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2014

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.

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(RUTH YONG YAN SHAN)

ABSTRACT

CO_2 emission is the main cause of the greenhouse effect, which consequently leads to the global warming. Most of the CO_2 is emitted through combustion processes, especially from the power plant. However, the combustion facilities are essential for the power plant in order to generate heat and power. Therefore, post combustion of CO_2 capture process is required in order to treat the flue gases before emitting to the atmosphere. This can be done through the process of amine-based absorption in which the MEA-MDEA is the mixed amine-based solvent as it is capable to remove high concentration of CO_2. Nevertheless, amine-based absorption is highly energy intensive due to the thermal energy requirement in regenerating the solvent. Hence, in this project, a simulation model of CO_2 removal is developed using Aspen HYSIS to optimize the process. Subsequently, economic and sensitivity analysis are constructed to evaluate the operating expenditure (OPEX) and capital expenditure (CAPEX) based on the simulation model. It is found that 25 wt% MDEA and 15 wt% MEA is the optimal operating condition that achieve the minimal total cost ($158 mil). From the sensitivity analysis, it showed that utilities cost has the highest sensitivity to the total cost, in other words, utilities cost has a large impact on the total cost. Therefore, in order to minimize the total cost, utilities cost is the most critical factor to be considered.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Carbon dioxide (CO_2) removal from flue gas, synthesis gas (syngas) or natural gas represents an essential process in the industrial applications (Rolker & Seiler, 2011). CO_2 capture process is required for different purposes regarding to the types of industrial process. CO_2 must be removed from natural gas to prevent corrosion of the pipelines and equipments as CO_2 in the presence of water can be highly corrosive. It also reduces the heating value of a natural gas stream and does not meet the end users' sales gas specification (Tan, Lau, Bustam & Shariff, 2012). For syngas, CO_2 is removed in order to synthesis ammonia. On the other hand, flue gas should be treated before venting to the atmosphere as flue gas has high CO_2 content which contributes to global warming.

There are many methods for the CO_2 capture process, such as solvent absorption, solid adsorption, membrane separation, direct conversion and cryogenic fractionation (Movaghanejad & Akbari, 2011). Among these methods, amine-based absorption is the most commonly used and commercially proven technology in the present time. However, this process is highly energy intensive due to the thermal energy requirement needed to regenerate the solvent which affecting the total operating cost significantly (Mores, Rodriguez, Scenna & Mussati, 2012). Apart from the operating cost, CO_2 removal target also depends on the operating parameters of the absorption and regeneration process. Consequently, the optimization of CO_2 capture process is important to determine the best design and operating conditions in order to minimize the total cost.

According to Rodriguez, Mussati & Scenna (2011), parametric analysis using process simulator is one of the most popular approaches to optimize CO_2 capture process. The reason is because of the high cost if the testing is to be done at industrial scale. The process simulators such as Aspen HYSYS, Aspen Plus, TSWEET and iCON have been used for simulation of CO_2 absorption process with various amine-based solvent.

This project will focus on the development of a simulation model of the CO_2 capture process in order to generate an overview of the operational expenditure (OPEX) and capital expenditure (CAPEX). The process will be simulated through HYSIS by using mixed amines which are monoethanolamine-methyldiethanolamine (MEA-MDEA) as the solvent and flue gas as the feed.

1.2 Problem Statement

The main cause of the global warming is greenhouse gases, mainly CO_2, emitted into the environment. As a result, the study of CO_2 capture process has gained widespread interest because this process is crucial in reducing CO_2 emission to the atmosphere. There are many separation techniques to remove CO_2 from the flue gas, but amine-based absorption has been used commercially because absorption is highly effective at various CO_2 concentrations (Mudhasakul, Ku & Douglas, 2013). MEA and MDEA have different CO_2 loading factor, which are 0.5 and 1.0 respectively. Due to this circumstance, different blending proportion will affect the absorption performance and consequently influence the total cost. Thus, minimization of the operating and capital cost becomes the major challenge in the process of CO_2 capture from the flue gas.

Detailed mathematical modeling of the amine-based CO_2 capture process is a complex task because it requires developing accurate and rigorous models to describe all plants equipment, including an absorber, regenerator and heat transfer equipment. Furthermore, the development of a systematic algorithmic procedure to find optimal solutions using realistic cost functions with process simulators is difficult due to the recycle structures in the flow sheet (Rodriguez, Mussati & Scenna, 2011).

Currently, parametric analysis using process simulators is one of the most popular approaches to optimize CO_2 capture process. Thus, this project aims to develop a simulation model of CO_2 capture process, not only to optimize the process, but also helps in optimize the cost.

1.3 Objectives

The objectives of this project are:

- To develop a simulation model of the CO_2 capture process for the purpose of process optimization
- To construct an economic analysis of the CO_2 capture process in terms of operational expenditure (OPEX) and capital expenditure (CAPEX)
- To determine an optimal operating conditions in order to satisfy the CO_2 recovery at minimum total cost

1.4 Scope of Study

This project will evolve on developing a simulation model of CO_2 capture process by using Aspen HYSIS. The simulation model consists of two typical unit operations, namely absorber and regenerator. In the absorber, CO_2 absorption process is carried out. The rich solvent from the absorber will enter the regenerator to strip off the acid gas. After the stripping process, the lean solvent will be regenerated back to the absorber (Nazmul Hasan, 2005; Thitakamol, Veawab & Aroonwilas, 2006). The CO_2 content of the inlet flue gas is 15 mol % and it is targeted to be reduced to around 1 to 2 mol %.

The simulation model can be used to determine the performance of the process. This can be done through the evaluation of several critical parameters such as CO_2 loading, reboiler duty, flow rate of regenerated solvent etc.

Subsequently, the simulation model will be used to develop economic and sensitivity analysis. Economic analysis consists of operating cost and capital cost while sensitivity analysis determines the highest sensitive factor to the total cost. Through this project, an optimal operating condition with a minimal cost is aimed to be achieved. This can be implemented through the simulation model by altering certain operating parameters.

CHAPTER 2

LITERATURE REVIEW

2.1 Properties of Carbon dioxide (CO_2)

Carbon dioxide gas is found in small proportions in the air, which is about 385ppmv. Although it is just a small portion, it is a necessity for the plants to carry out photosynthesis, or else the plants cannot survive. Carbon dioxide is produced through several ways, such as combustion of coal or hydrocarbons, fermentation of liquids and the breathing of humans and animals.

Carbon dioxide comprises two oxygen atoms covalently bonded to a single carbon atom as shown in Figure 1. The molecular shape is linear, and the two C-O bonds are equivalent (116.3pm). It is a gas at standard temperature and pressure.

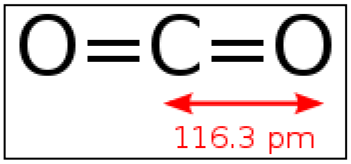

Figure 1: Structural formula of CO_2

The physical properties of carbon dioxide are shown in the Table 1.

Table 1: Physical properties of CO_2

Molecular Weight	44.01 g/mol
Appearance and Odor	Colorless, odorless
Density (at 101.3 kPa)	1562 kg/m^3 at -78.5 °C 1.977 kg/m^3 at 0 °C
Melting Point	−78 °C
Boiling Point	−57 °C
Latent Heat of Fusion (at 101.3 kPa)	-56.6 kJ/mol at 5.2 atm
Latent Heat of Vaporization (at 101.3 kPa)	Sublimes at −146.95 °C
Critical Pressure	7384.77 kPa
Critical Temperature	−31.05 °C

Pure carbon dioxide exhibits triple point behavior dependent on the temperature and pressure, as shown in Figure 2. The triple point is at 5.11 bar and -56.7^{o}C; at this point, carbon dioxide exists in three phases – gas, liquid and solid. Above the critical point (73.8 bar and 31.1^{o}C), the liquid and gas phases cannot exist as separate phases, and liquid phase carbon dioxide develops supercritical properties, where it has some characteristics of a gas and others of a liquid.

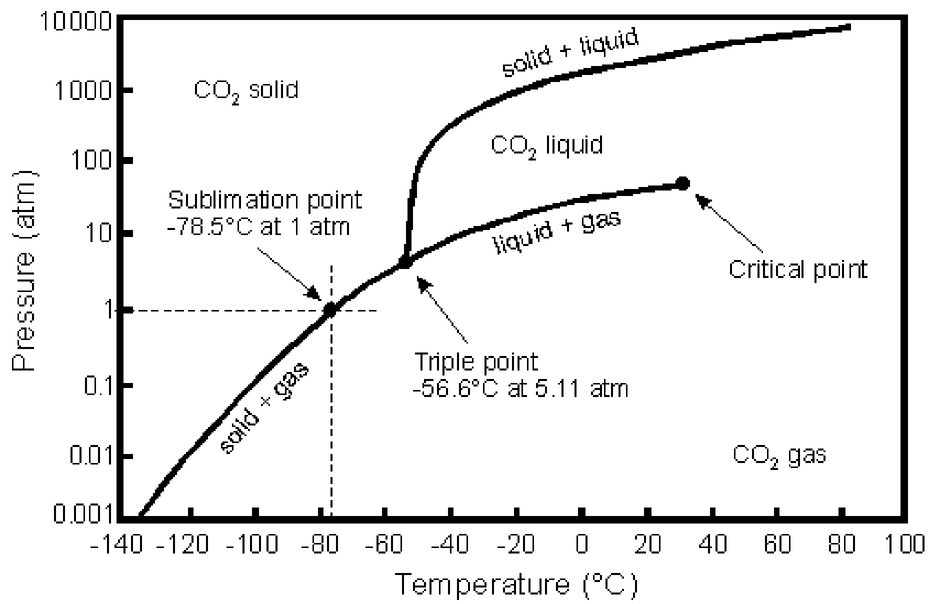

Figure 2: Phase diagram of CO_2 (Global CCS Institute, 2013)

2.2 Uses of Carbon dioxide

Carbon dioxide is widely used commercially. It is used to carbonate soft drinks, beers and wine and to prevent fungal and bacterial growth. It can be used as a cryogenic fluid in chilling or freezing operations, or as dry ice for temperature control during the distribution of foodstuffs. Supercritical carbon dioxide is a good solvent for many organic compounds. It is used to decaffeinate coffee.

In the medical field, carbon dioxide is used as an additive to oxygen as a respiration stimulant to promote deep breathing. It also helps in the operation of artificial organs. In chemicals processing industries, carbon dioxide is used to control reactor temperatures and neutralize alkaline effluents. In supercritical condition, it is used for purifying polymer, animal or plants' fibres (Global CCS Institute, 2013).

In industrial field, carbon dioxide is used in the manufacture of casting molds to enhance their hardness. Apart from that, it is mixed with argon and helps in welding process. The mixture will achieve a higher welding rate and reduce the need for post weld treatment. Dry ice pellets are used to replace sandblasting when removing from surfaces. This can reduce the cost of disposal and cleanup (University Industrial Gases, Inc, 2003).

2.3 Greenhouse Effect

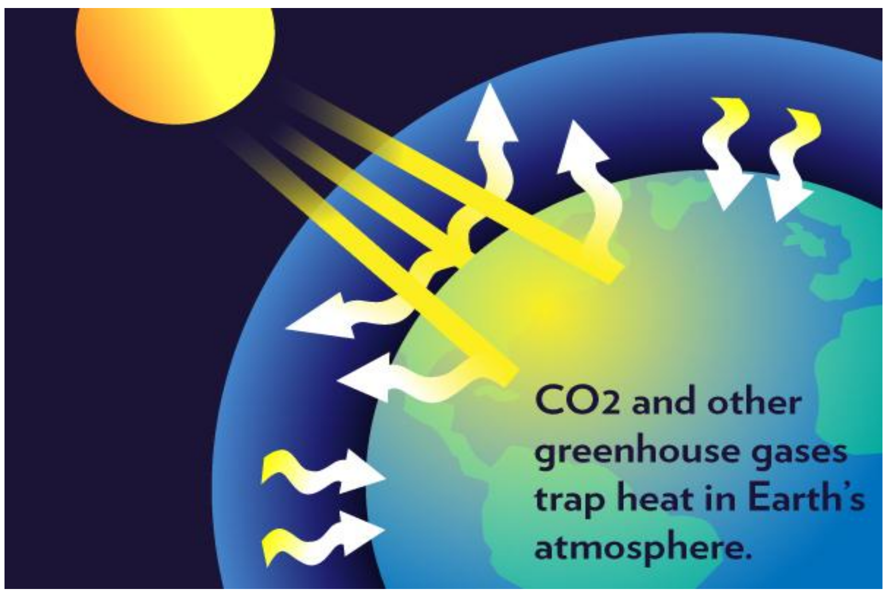

Figure 3: Greenhouse effect

The Sun powers the Earth's climate by radiation of energy. Roughly one-third of the solar energy that reaches the top of the Earth's atmosphere is reflected directly back to the space. The remaining two-third passes through the atmosphere and absorbed by the Earth (Solomon et al, 2007). Greenhouse gases act like a blanket, trapping the heat energy and warming the atmosphere, which in turns warms the Earth's surface. This process is called the greenhouse effect. Without greenhouse gases, the average temperature on the Earth would be 60^{o}F cooler (KQED Education Network).

The major contributors of the greenhouse effect are carbon dioxide and water vapor. These greenhouse gases can be naturally occurring or human-produced. Activities resulting in carbon dioxide emission include deforestation and burning of fossil fuels such as coal, oil and gas in power plants, automobiles and industry.

Therefore, the only way to tackle the problem of greenhouse effect is to reduce the CO_2 emission into the atmosphere.

2.4 Combustion Process

Combustion processes are the major producers of the greenhouse gas, CO_2. Combustion processes are applied in several industries such as power plants, waste incinerators and cement plants. Most of these industries require combustion to generate heat and power for the other subsequent process and this will discharge flue gas. According to Wang, et.al. (2011), power generation from fossil fuel-fired power plants (e.g. coal and natural gas) is the largest source of CO_2 emissions. However, these power plants play a vital role in meeting energy demands.

Flue gases from combustion facilities have a composition very different from air because of high concentrations of the combustion products - water and carbon dioxide (Zevenhoven & Kilpinen, 2001). In addition, the CO_2 concentrations in the atmosphere are rising at approximately 1% per year, which contributes to the climate change. Therefore, the flue gas from the combustion processes must undergo certain treatment before emitting to the atmosphere. This can be done through post combustion of CO_2 capture process.

2.5 CO_2 Capture Process

2.5.1 Gas Absorption

Post combustion capture of CO_2 from flue gases is carried out through gas absorption. According to Cheah (2000), gas absorption is also known as scrubbing whereby the components of a gas mixture are preferentially dissolved in a liquid when they contact to each other. This process is widely used in the industry to remove contaminants or impurities from a gas stream. There are two types of absorption: physical absorption and chemical absorption. Physical absorption does not involve any chemical reaction between solute and solvent while chemical absorption does. In this project, CO_2 will be removed from the flue gas through chemical absorption by using MEA-MDEA as the absorbent.

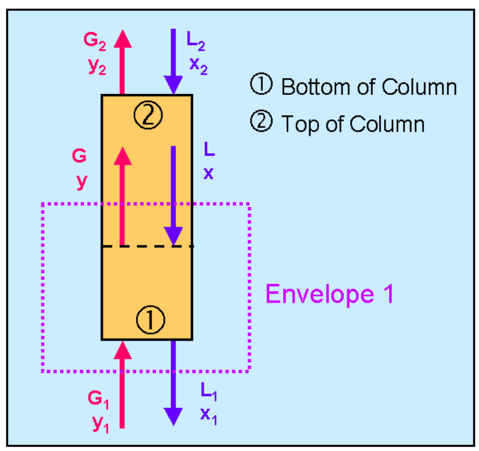

Figure 4: Counter-current gas absorption

Gas absorption is carried out at the absorber counter-currently with the solvent. Counter-current gas absorption occurs when the gas (G) and liquid (L) come into contact in opposite direction as shown in Figure 4. Inside the column, the solute from the gas is absorbed by the liquid. When going up the column, there is a decrease in total gas flow rate and concentration of solute in gas phase (y). At the same time, going down the column, there is an increase in total liquid flow rate and concentration of solute in liquid phase (x) (Cheah, 2000).

2.5.2 Amine-based Solvent

According to Kidnay & Parrish (2006), amines are compounds formed from ammonia (NH_3) by replacing one or more of the hydrogen atoms with another hydrocarbon group. There are three main types of amines, namely primary amines, secondary amines and tertiary amines. Primary amines have only one hydrogen atom being replaced while secondary and tertiary are having two and three hydrogen atoms being replaced respectively. Primary amines are the most reactive, followed by secondary and tertiary amines. Table 2 shows some of the examples of amines.

Table 2: Examples of amines

Amines	Examples
Primary	Monothanolamine (MEA) Diglycolamine (DGA)
Secondary	Diethanolamine (DEA) Diisopropanolamine (DIPA)
Tertiary	Triethanolamine (TEA) Methyldiethanolamine (MDEA)

The differences among the amines are summarized in Table 3.

Table 3: Comparison among amines (Kidnay & Parrish, 2006)

Amines Group	Primary		Secondary	Tertiary
Types of amines	MEA	DGA	DEA	MDEA
Wt% amine	15 to 25	50 to 70	25 to 35	40 to 50
Rich amine acid gas loading (mole acid gas/mole amine)	0.45 to 0.52	0.35 to 0.40	0.43 to 0.73	0.4 to 0.55
Acid gas pickup (mole acid gas/mole amine)	0.33 to 0.40	0.25 to 0.30	0.35 to 0.65	0.2 to 0.55
Lean solvent residual acid gas (mole acid gas/mole amine)	0.12	0.10	0.08	0.005 to 0.01
Heat of reaction of CO_2 (kJ/kg)	1920	1980	1700	1420

In order to minimize the cost of CO_2 capture process, the reduction of energy requirement for regeneration is essential as it contributes to about 70% of the operating cost. Therefore, selection of an effective solvent is very crucial because it will directly affect the regeneration energy requirement. The solvent should have fast reaction kinetics, high absorption capacity and low regeneration energy (Sema et al., 2012). However, there is no solvent that possess all the criteria required.

Primary amines react rapidly with CO_2 which can be shown by the high reaction energy in Table 3. On the other hand, tertiary amine has the lowest reaction energy and high absorption capacity or acid gas pickup. According to Sema et al. (2012), mixed amines system is suggested to optimize the performance and the cost. This can be done by mixing primary (or secondary) amine to tertiary amine. Therefore, in this project, the mixed amines solvent chosen is MEA-MDEA.

2.5.3 CO_2 Capture Process Description

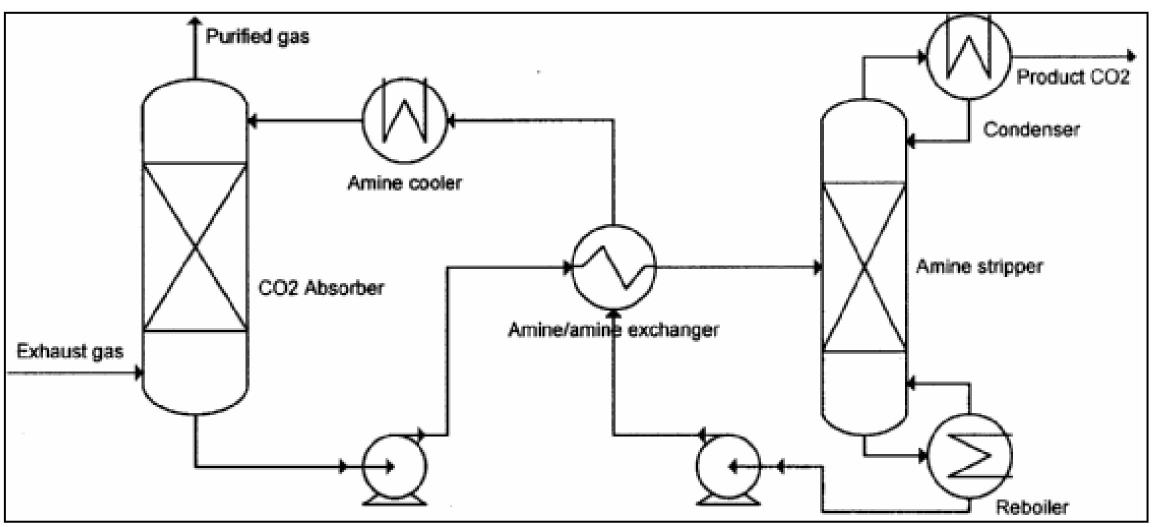

Figure 5: Schematic diagram of the typical amine-based solvent CO_2 capture unit (Oi, 2007)

CO_2 capture process consists of two main sections, an absorber and a regenerator. The absorber is where CO_2 is absorbed into a solvent, while the regenerator is where the absorbed CO_2 is stripped out from the solvent. The flue gas containing CO_2 enters the absorber bottom. At the same time, the lean solvent enters the top of absorber will contact counter-currently with the flue gas and absorbs the CO_2. The treated gas is eventually released from the absorber top to the atmosphere.

The rich solvent containing high content of CO_2 from the bottom of absorber is preheated by a rich-lean heat exchanger before entering the regenerator. When the rich solvent descends in the regenerator, the hot steam, produced from the reboiler, strips the CO_2 out of the rich solvent and forms a mixture with CO_2. After leaving the top of regenerator, the mixture is cooled by a condenser to condense the steam. The reflux drum will then separate the CO_2 and transports it to downstream utilizations and storage. The condensate from the reflux drum is sent back to the regenerator as reflux to maintain the solution concentration.

The hot lean solvent from the regenerator bottom is pumped to the rich-lean heat exchanger for transferring the heat to the rich solvent from absorber. It is further cooled down by the condenser before circulating back to the absorber (Thitakamol, Veawab & Aroonwilas, 2006).

2.6 Cost Mathematical Model

2.6.1 Capital Expenditure (CAPEX)

CAPEX consists of fixed capital and working capital.

According to Sinnott (2005), fixed capital is the total cost of the plant ready for start-up. It includes the cost of:

1. Design, and other engineering and construction supervision.
2. All items of equipment and their installation.
3. All piping, instrumentation and control systems.
4. Buildings and structures.
5. Auxiliary facilities, such as utilities, land and civil engineering work.

Working capital is the additional investment needed to start the plant up and operate it to the point when income is earned. It includes the cost of:

1. Start-up.
2. Initial catalyst charges.
3. Raw materials and intermediates in the process.
4. Finished product inventories.
5. Funds to cover outstanding accounts from customers.

Sinnott (2005) stated that fixed capital estimates for chemical process plants are often based on an estimate of purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost.

Lang Factors

Lang factors can be used to make a quick estimate of preliminary capital cost by applying the equation below (Sinnott, 2005).

$$C_f = f_L C_e \tag{1}$$

where C_f = fixed capital cost,

C_e = the total delivered cost of all the major equipment items,

f_L = the “Lang factor”, which depends on the type of process.

f_L = 3.1 for predominantly solids processing plant

f_L = 4.7 for predominantly fluids processing plant

f_L = 3.6 for a mixed fluids-solids processing plant

Detailed Factorial Estimates

To make a more accurate estimate, the cost factors that are compounded into "Lang factor" are considered individually. The estimation includes the direct-cost items and indirect costs as well. The factors for the fixed capital cost analysis are summarized in Table 4.

Table 4: Typical factors for estimation of fixed capital (Sinnott, 2005)

Item	Process type		
	Fluids	Fluids-solids	Solids
1. Direct cost:			
f_1 Equipment erection	0.40	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
f_6 Utilities	0.50	0.45	0.25
f_7 Storages	0.15	0.20	0.25
f_8 Site development	0.05	0.05	0.05
f_9 Ancillary buildings	0.15	0.20	0.30
2. Indirect cost:			
f_{10} Design and engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10

The total direct cost is calculated by multiplying the total purchased equipment (PCE) by the factor of each item.

$$\textbf{Total direct cost} = \textbf{PCE}\ (\mathbf{1} + \mathbf{f_1} + \cdots + \mathbf{f_9})$$

(2)

Fixed capital cost can be computed by multiplying the factors of indirect cost with the total direct cost.

$$\text{Fixed capital} = \text{Total direct cost}\ (1 + f_{10} + f_{11} + f_{12}) \tag{3}$$

2.6.2 Operating Expenditure (OPEX)

OPEX consists of fixed operating costs and variable costs. Fixed operating costs are the costs that do not vary with production rate while variable costs are dependent on the amount of product produced.

Fixed costs include the cost of:

1. Maintenance (labour and materials).
2. Operating labour.
3. Laboratory costs.
4. Supervision.
5. Plant overheads.
6. Capital charges.
7. Rates (and any other local taxes).
8. Insurance.
9. License fees and royalty payments.

Variable costs include the cost of:

1. Raw materials.
2. Miscellaneous operating materials.
3. Utilities (Services).
4. Shipping and packaging.

The methods to make an approximate estimate of operating costs are summarized in Table 5. Each cost which is listed previously has its own way of estimation.

Table 5: Summary of OPEX estimation (Sinnott, 2005)

Variable costs	**Typical values**
1. Raw materials	from flow sheet
2. Miscellaneous materials	10% of item (5)
3. Utilities	from flow sheet
4. Shipping and packaging	usually negligible
Fixed costs	
5. Maintenance	5-10% of fixed capital
6. Operating labour	from manning activities
7. Laboratory costs	20-23% of item (6)
8. Supervision	20% of item (6)
9. Plant overheads	50% of item (6)
10. Capital charges	10% of fixed capital
11. Insurance	1% of the fixed capital
12. Local taxes	2% of fixed capital
13. Royalties	1% of fixed capital
Additional costs:	
14. Sales expense	add 20-30% to the direct production cost
15. General overheads	
16. Research and development	

Direct production cost can be calculated by the equation below.

$$\text{Direct production cost} = \text{total variable cost} + \text{total fixed cost} \tag{4}$$

Lastly, the total operating cost can be computed by the summation of direct production cost and the additional costs.

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

3.1.1 CO_2 Capture Process Simulation

a. Simulator

In order to achieve the objectives of the project, the most initial activity that has to be carried out is to develop a simulation model of CO_2 capture process. The simulator which will be used to implement the task is Aspen HYSIS.

b. Process scheme

The simulation model of CO_2 capture process is developed by referring to the process flow diagrams from several journals (Ahmed & Ahmad, 2011; Movagharnejad & Akbari, 2011; Oi, 2007). For this project, the simulation model will be similar to the Aspen HYSIS CO_2 removal model as shown in Figure 5 by using MEA-MDEA instead of MEA as the solvent.

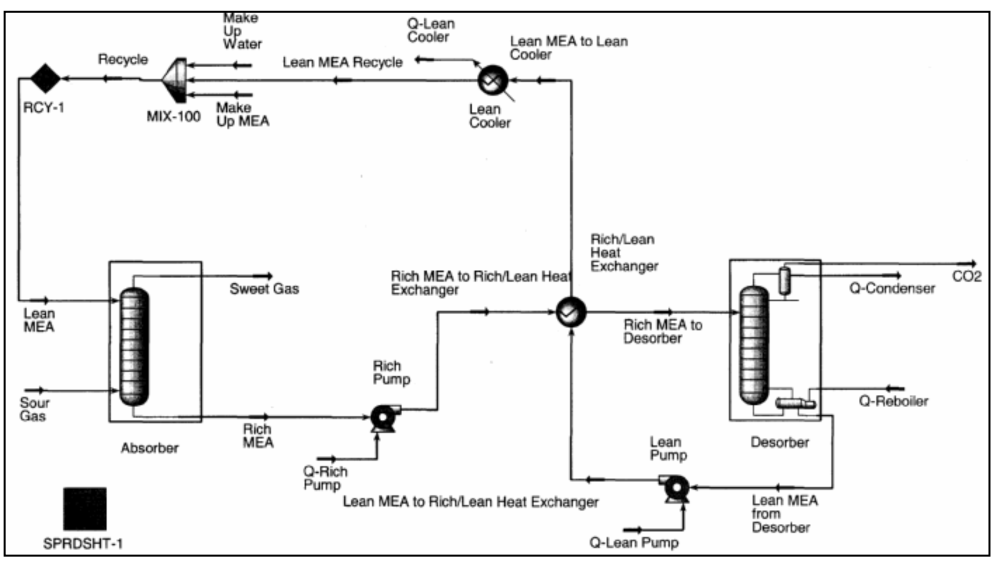

Figure 6: Aspen HYSIS model of CO_2 removal process

c. Property package

In the simulation using Aspen HYSIS, a generalized package for amines called Amines Fluid Package is selected (Ahmed & Ahmad, 2011). Within this package, one of the two models, Kent Eisenberg or Li-Mather, can be used (Oi, 2007). Amines Fluid Package is chosen because MEA-MDEA, an amine-based solvent, is used to absorb CO_2.

d. Components

After the property package is selected, all the components involved are inserted into the model. The list of components is as follows:

i. Carbon dioxide (CO_2)
ii. Water (H_2O)
iii. Nitrogen (N_2)
iv. Oxygen (O_2)
v. Monoethanolamine (MEA)
vi. Methyldiethanolamine (MDEA)

e. Flue gas composition

One of the important parameters that is needed to run the simulation is flue gas composition. The flue gas inlet composition will be as follows:

Table 6: Composition of flue gas (Movagharnejad & Akbari, 2011)

Components	Composition (mol %)
CO_2	15
H_2O	5
N_2	65
O_2	15

Other parameters required are pressure, temperature and mass flow rate of the flue gas. The values of these parameters are inserted at the appropriate fields.

f. Targeted result

The CO_2 capture process simulation will be continuously optimized until the following results are obtained.

Table 7: Targeted result

Parameter	Result
CO_2 content in treated gas (mol%)	< 2
CO_2 recovery (%)	90

g. Fixed variables

In order to achieve the results, there are some parameters that are needed to be fixed during the optimization. The mixtures of MEA and MDEA amines are considered. The total amines concentration assumed is 40 wt% and blending proportions ranging between 40% MDEA (0% MEA) and 40% MEA (0% MDEA). Table 8 shows the model parameter values used for optimization.

Table 8: Model parameter values used for optimization

Stream/Equipment	Parameter	Value
Flue gas	Pressure (bar)	1.5
	Temperature (^oC)	50
	Inlet flue gas flow rate (kmol/h)	40000
Absorber	Number of stages	40
	Pressure (bar)	1.5
	Total pressure drop (bar)	0.5
Regenerator	Condenser	Full reflux
	Number of stages	20
	Feed stage	5
	Total pressure drop (bar)	0.2

3.1.2 Economic Analysis

After the CO_2 capture process simulation is implemented, an economic analysis in terms of OPEX and CAPEX is needed in order to optimize the process with a minimal cost. The economic analysis is started with CAPEX with the following procedure:

1. The material and energy balances are obtained from the simulation model.
2. Major equipment items are sized.
3. Cost of total purchased equipment (PCE) is computed.
4. Direct cost is calculated by using equation (2).
5. Indirect cost is calculated from the direct costs using the equation (3).
6. Fixed capital cost is obtained by adding the direct and indirect cost.
7. The working capital is estimated as a percentage of the fixed capital, around 10-20%.
8. The fixed and working capital are added to get the CAPEX.

After calculating for CAPEX, OPEX can be computed. Below is the procedure to obtain the OPEX:

1. The costs of raw materials and utilities are obtained from literature.
2. Each cost item categorized under the variable and fixed costs is calculated according to Table 3.
3. Direct production cost is calculated using equation (4).
4. OPEX is computed by adding the direct production cost and additional costs.

Having CAPEX and OPEX, total cost can be calculated. The plant life time is assumed to be 15 years.

$$\text{Total cost} = \text{CAPEX} + \text{OPEX (15 years)} \tag{5}$$

3.2 Gantt Chart

The entire project is implemented according to the Gantt chart below. The main tasks in Final Year Project I (FYP I) are preliminary research work, proposal defense and exploration of Aspen HYSIS simulator. This is to prepare for the project execution in Final Year Project II (FYP II). Preliminary research work is essential in order to have a thorough understanding about the project. This is done by studying various journals, articles, books and other available sources. Exploration of Aspen HYSIS simulator is carried out to learn the way of developing a simulation model.

Table 9: FYP I Gantt chart

Project Activities	Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Selection of Project Topic														
Topic Approval														
Preliminary Research Work														
Submission of Extended Proposal						●								
Preparation for Proposal Defence														
Proposal Defence														
Exploration of Aspen HYSIS Simulator														
Submission of Interim Draft Report													●	
Submission of Interim Report														●

In FYP II, the main task is the optimization of the CO_2 capture process in terms of performance and economic. This can be done by running the simulation repeatedly at different operating conditions.

Table 10: FYP II Gantt chart

Project Activities	Week														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Development of Simulation Model & Economic Analysis															
Progress Report								●							
Optimization of CO_2 Capture Process															
Pre-SEDEX															
Draft Report															
Soft-bound Dissertation															
Technical Paper															
Oral Presentation														●	
Hard-bound Dissertation															●

3.3 Tools

To complete the project, there are certain softwares required to aid and assist during the execution of the project.

Table 11: List of software

Software	Function
Aspen HYSIS simulator	To simulate the process unit. To study material and energy balance as well as the properties of the main streams involved in CO_2 capture process. HYSIS can also be used to study the composition of the fluid in the main streams.
Microsoft Excel	To perform economic analysis of CO_2 capture process.
Microsoft Word	For report writing purposes.

CHAPTER 4

RESULTS AND DISCUSSION

As mentioned in Section 1.3, the goal is to simultaneously optimize operating conditions and mixture composition (MEA and MDEA) in order to satisfy the CO_2 recovery (90%) at minimum total cost. The simulation model of CO_2 capture process is developed, as shown in Figure 7.

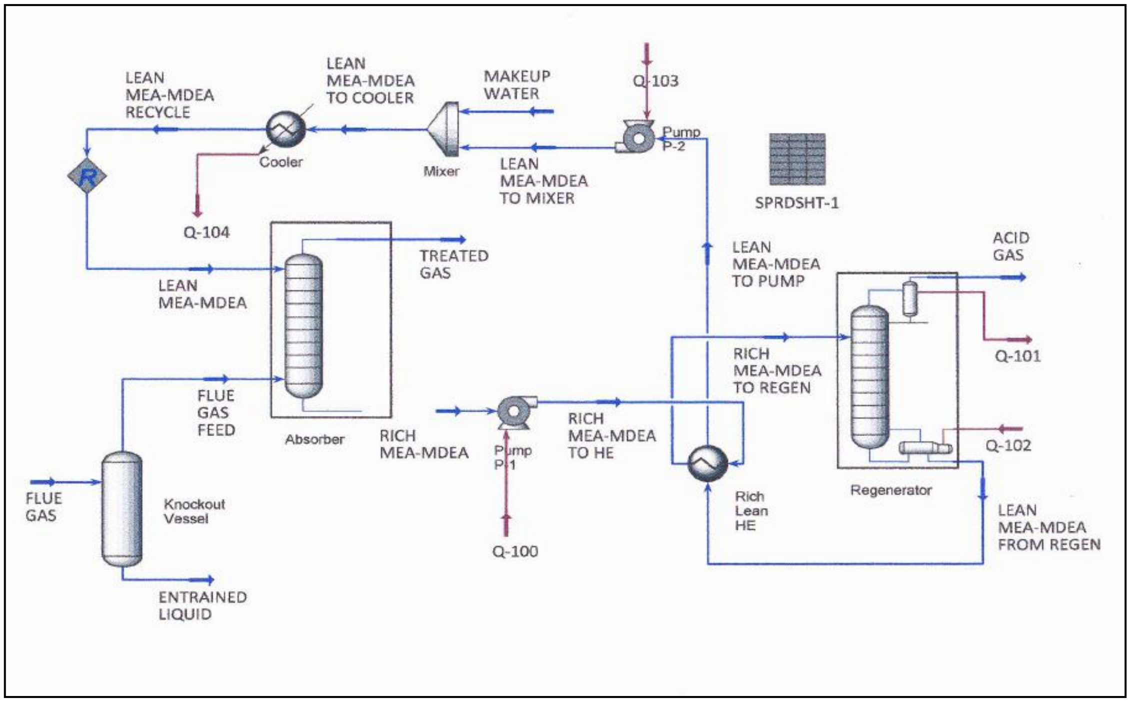

Figure 7: Simulation model of CO_2 capture process

As follows, the numerical results corresponding to the optimal operating conditions of the post combustion CO_2 process are presented and discussed. It should be noted first that all the figures show the optimal values corresponding to the optimal set of solutions achieved by different proportions of amines at 90% CO_2 recovery.

4.1 Optimal Total Cost

Figure 8 illustrates the optimal total cost as a function of MDEA mass fraction in the mixed amine solutions.

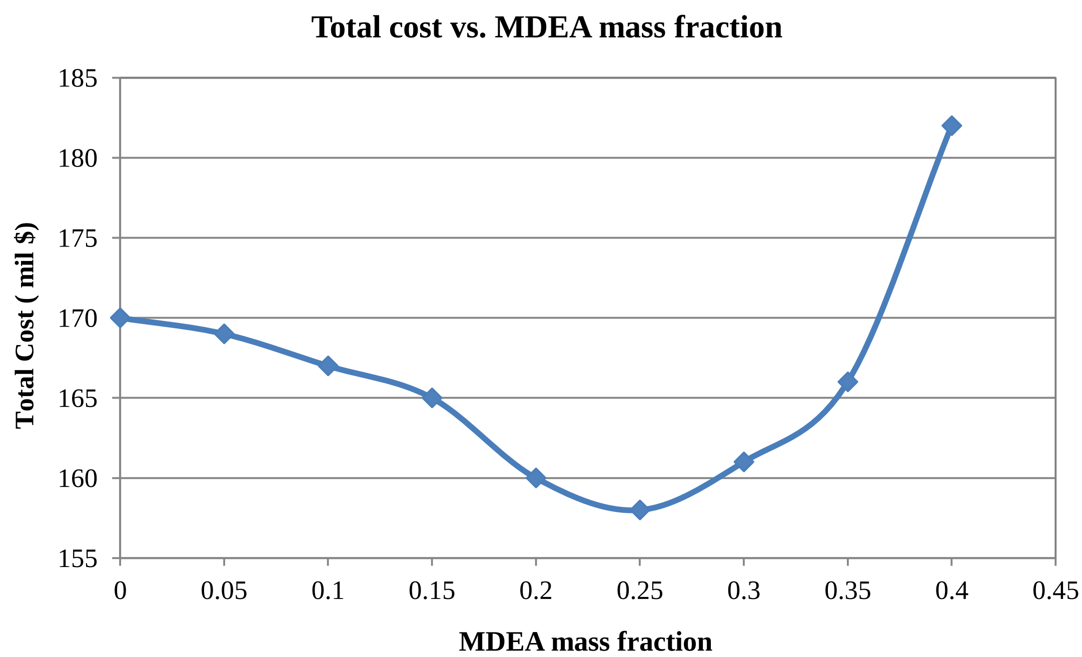

Figure 8: Graph of total cost vs. MDEA mass fraction

The minimum cost is achieved by a mixture with 25 wt% of MDEA and 15 wt% of MEA while the other mixtures with different proportions involve higher total cost. For single MEA amine solution, the total cost is $ 170 million. Lower costs are achieved by increasing the MDEA composition. The lowest total cost ($ 158 million) is reached for a solution containing 25 wt% of MDEA. Beyond that point, the cost increases when the composition of MDEA increases. In other words, any proportion of MDEA that exceeds 25 wt% is not possible to achieve optimal operating conditions to decrease the total cost below $ 158 million.

4.2 Optimal Amine Flow Rates

The amines flow rate is manipulated in order to achieve 90% CO_2 recovery. Other operating parameters are remain constant. Theoretically, higher amines flow rate will absorb more CO_2 from the flue gas. In spite of the amines flow rate, the amines mixture composition is another important factor that governs the CO_2 absorption.

Figure 9 shows the optimal variation of the amine flow rates parametrically on the blended amine proportion.

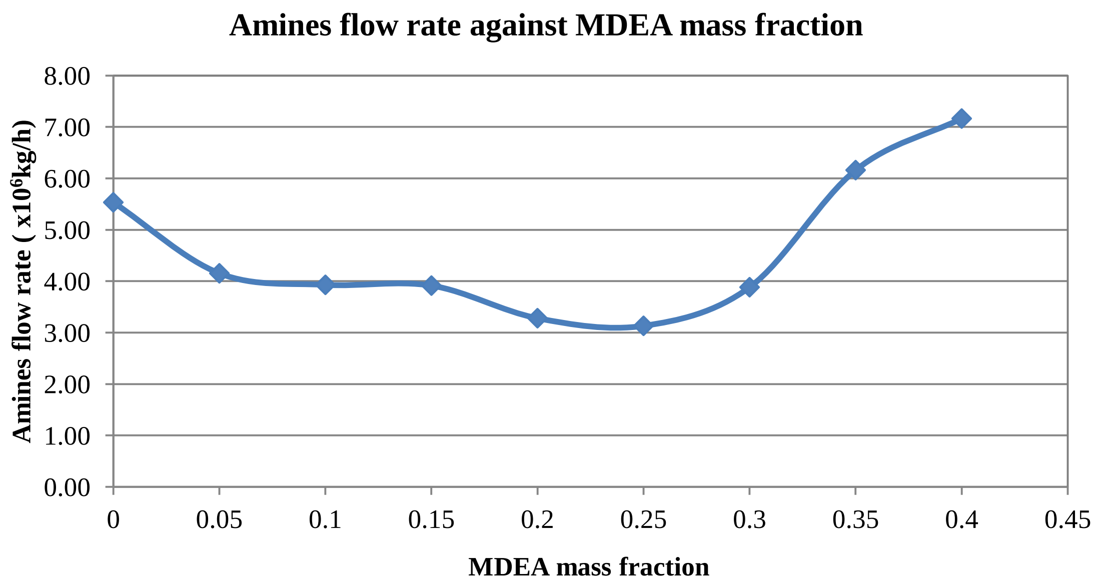

Figure 9: Graph of amines flow rate against MDEA mass fraction

Certainly, primary amines (MEA) have lower CO_2 loading factor than tertiary amines (MDEA). CO_2 loading factor is defined as the ratio between total moles CO_2/total moles amine in the liquid phase. This parameter strongly depends on the types of amine. The CO_2 loading factors of MEA and MDEA are 0.5 and 1.0 respectively. According to Rodriguez et. al. (2011), CO_2 absorption efficiency increases when CO_2 loading decreases. This is because less CO_2 loading leads to an increased thermodynamic driving force for the mass transfer process, which results in reaction kinetics that dominate CO_2 absorption performance.

Based on Figure 9, it is apparent that single MDEA amine solution gives the lowest CO_2 removal efficiency as it requires the highest amines flow rate to achieve 90% CO_2 recovery. This is followed by single MEA amine solution as it has lower absorption capacity. From the results obtained, CO_2 absorption performance is affected by absorption capacity and CO_2 removal efficiency. By comparing both single amine solutions, it is proved that CO_2 removal efficiency is the dominant factor that affect the absorption performance as MDEA which has lower removal efficiency requires more flow rate as compared to MEA which has lower absorption capacity.

Therefore, in order to improve the absorption performance, blending amines solution will give better results as it will improve the absorption capacity and CO_2 removal efficiency at the same time.

4.3 CO_2 Mole Fraction in Treated Gas

Figure 10 shows the graph of CO_2 mole fraction in treated gas against MDEA fraction.

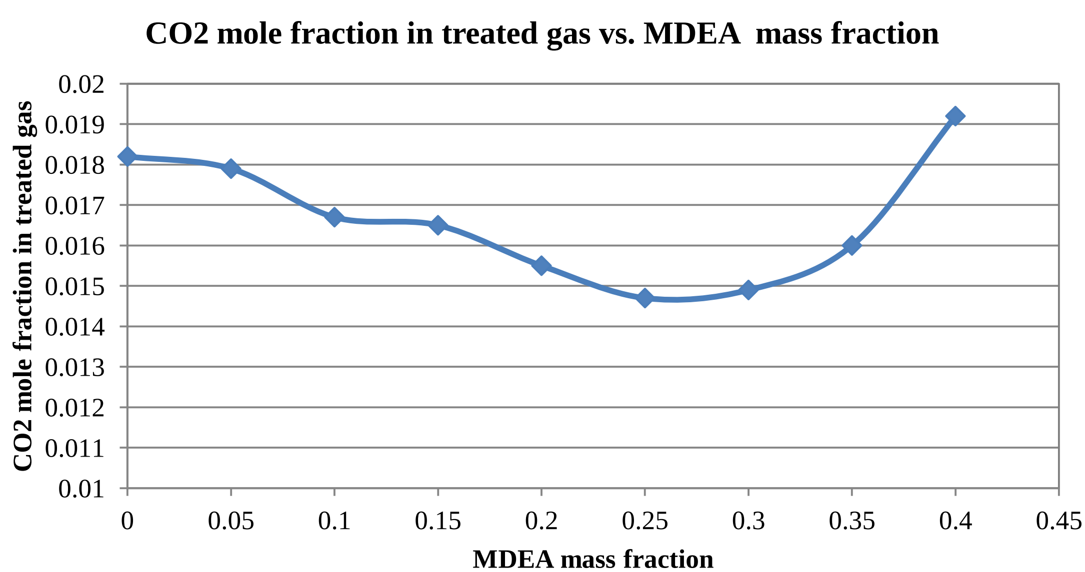

Figure 10: CO_2 mole fraction in treated gas vs. MDEA mass fraction

As mentioned in Section 3.1.1, the process will be optimized until it achieves the CO_2 mole percentage in treated gas which is less than 2%. Based on Figure 10, the treated gas at different amine composition has achieved the targeted CO_2 mole fraction. The minimum CO_2 mole fraction corresponds to a mixture with 25 wt% of MDEA and 15 wt% of MEA.

Single MDEA has highest CO_2 content in the treated gas. This result further proves that lower CO_2 removal efficiency has more significant effect on the absorption performance even though it has larger absorption capacity.

4.4 Optimal Reboiler Heat Duty

Figure 11 illustrates the reboiler heat duty as a function of mixture proportions in the solvent. 1

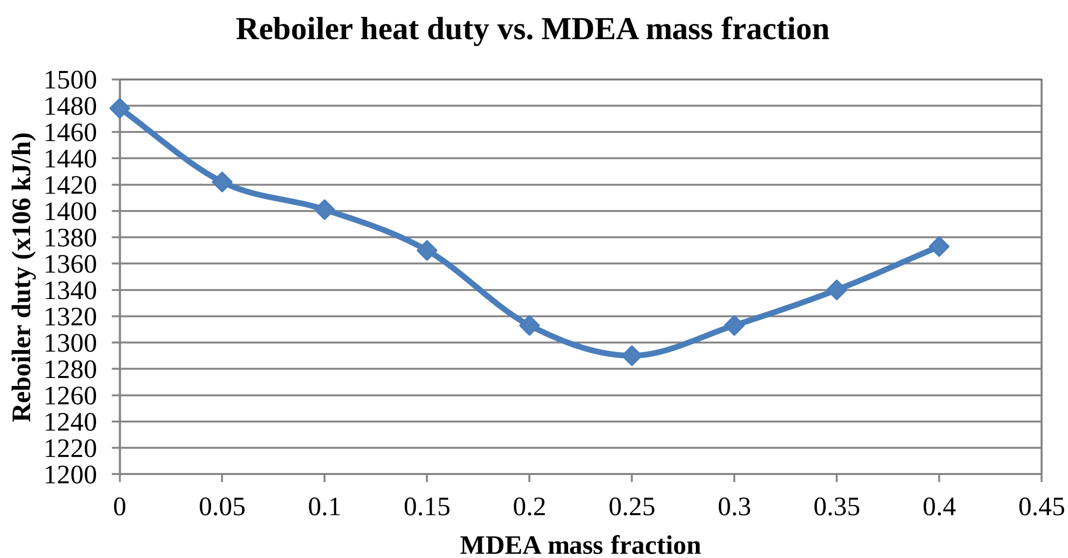

Figure 11: Reboiler heat duty vs. MDEA mass fraction

The minimum reboiler duty is obtained when the solution contains 25 wt% of MDEA and 15 wt% of MEA. Rodriguez et. al. (2011) stated that there are three contributors to the reboiler heat duty: heat of absorption, sensible heat for heating the amine and the latent heat to vaporize water. The reaction between MEA and CO_2 is highly exothermic as compared to MDEA. Hence, more heat is required in the reboiler to regenerate the MEA. Addition of MDEA to the amine solution reduces the reboiler heat duty until the point corresponding to 25 wt% MDEA. When the MDEA proportion exceeds 25 wt%, the reboiler duty increases as the CO_2 content in the rich amines is higher due to lower CO_2 removal efficiency.

4.5 Sensitivity Analysis

Sensitivity analysis is conducted to study the impact of the variations in the values of different input cost to the output total cost. In this case study, the effect of the solvent price, utilities cost and capital investment expenditure are illustrated in the graphs below.

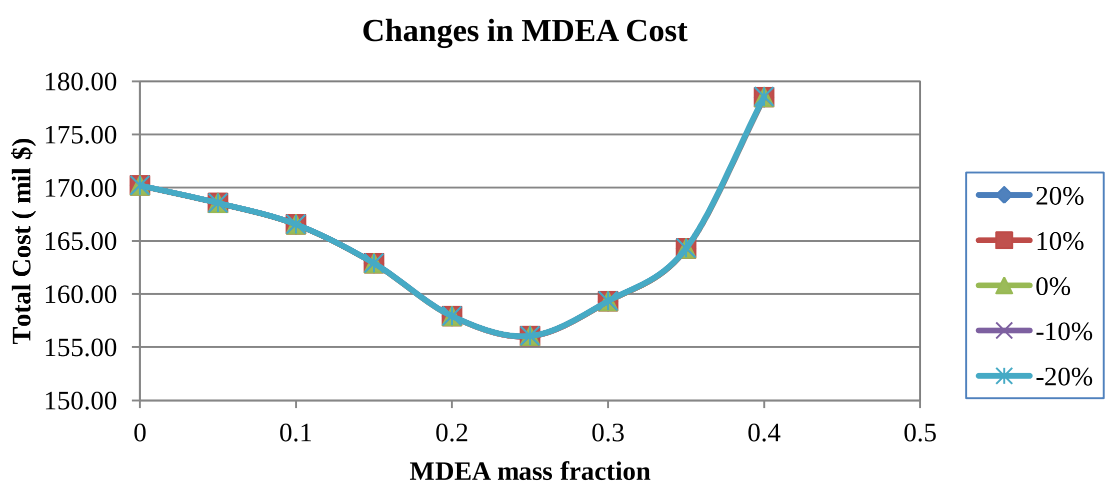

Figure 12: Graph of changes in MDEA cost

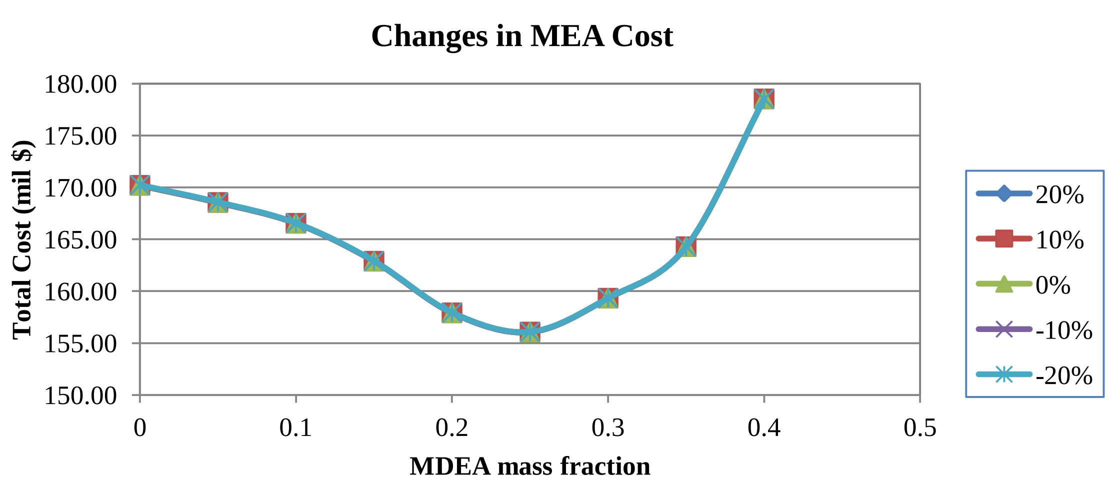

Figure 13: Graph of Changes in MEA cost

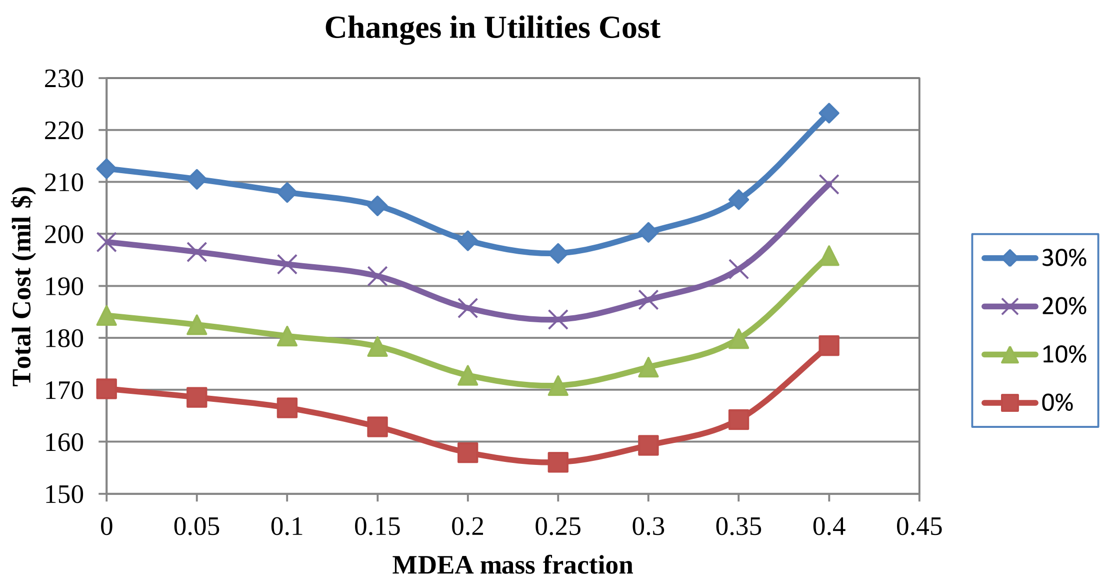

Figure 14: Graph of changes in utilities cost

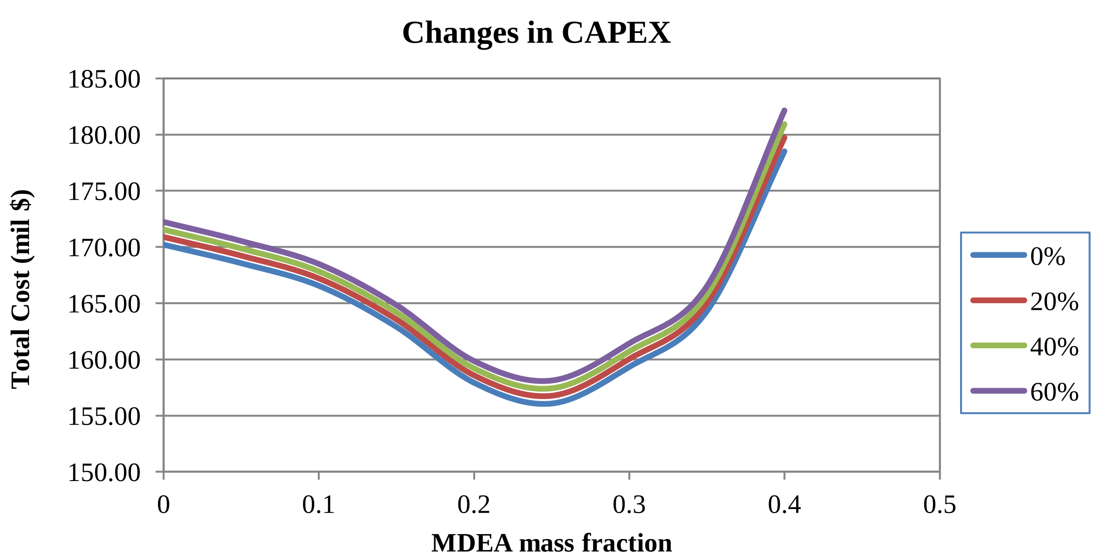

Figure 15: Graph of changes in CAPEX

Based on the graphs, the solvent price does not show any significant impact on the total cost. The total cost does not result in large differences when the cost of MEA or MDEA varies. This indicates that the solvent cost is not the main factor that govern the total cost.

However, utilities cost has the most significant impact on the total cost, followed by the capital investment expenditure (CAPEX). When the utilities cost increases, the total cost increment is large. CAPEX is the intermediate among all the factors, whereby it does causes some changes in the total cost but the increment is not as large as the utilities cost.

Therefore, to minimize the total cost, utilities cost and CAPEX are the most critical factors that need to be reduced.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Relevancy to the Objectives

In this study, post-combustion CO_2 capture process has been investigated. The whole process has been modeled and optimized using a process simulator (HYSYS). It is concluded that optimal values of the parameters follow well-defined trends as a function of MDEA mass fraction in the aqueous blended amine solutions. The blending proportion of the MEA-MDEA mixtures has a strong influence on the CO_2 absorption performance. Specifically, the blending proportion affects the reaction kinetics and CO_2 efficiency, which are found to be the dominant factors of the absorption performance and the total cost. Hence, compared to single amine solutions, blending amines solutions give better results.

Regarding the total cost, a sensitivity analysis has been conducted. It is found that utilities cost and capital expenditure are having significant impact on the total cost. Thus, in order to minimize the total cost, utilities and capital cost have to be more focused. On top of that, both of them are influenced by the absorption performance.

As a conclusion, the objectives of this project are achieved. The optimum operating condition for the CO_2 capture process is the mixture of 25 wt% MDEA and 15 wt% MEA solution, with a minimum cost of $158 million.

5.2 Suggested Future Work for Expansion and Continuation

In future work, CO_2 capture process can be further optimized in order to reduce the utilities cost and CAPEX. The parameters that can be investigated are pressure, temperature, number of stages, type of trays or packing etc. Different solvent mixtures such as DEA-MDEA can be used and compare the absorption performance with the current solvent. Furthermore, simple mathematical model can be proposed to determine optimal process condition, for instance, a model of predicting the solubility of CO_2 in the solvent can be developed.

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APPENDICES

<u>Appendix I: Sample of Calculation of Total Cost (25wt% MDEA and 15 wt% MEA)</u>

1. Capital Expenditures (CAPEX)

1.1 Total purchased equipments (PCE)

a. Absorber

Tray space = 0.5m ; Tray thickness = 0.002m ; Tray diameter = 1.5m

Number of trays, n = 40

$$\text{Height of absorber} = \text{n} \times \text{Tray thickness} + \text{Tray space} \times (\text{n} - 1) = 19.58\text{m}$$

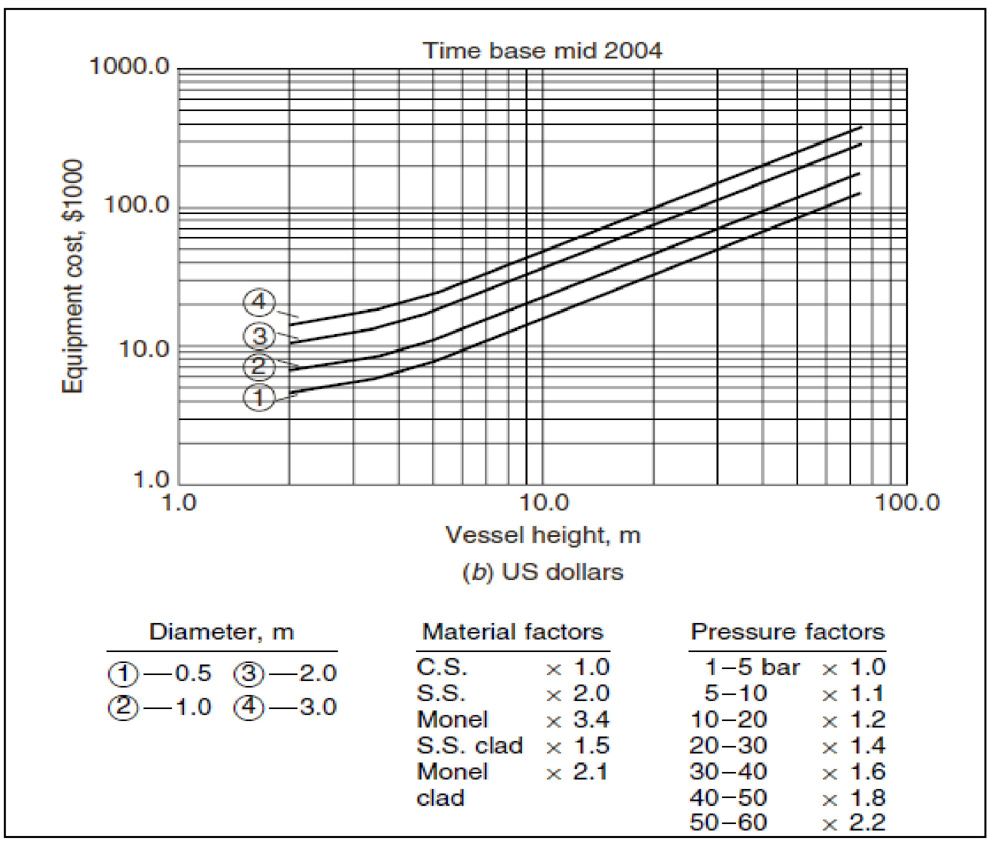


Figure 16: Vertical pressure vessel

Bare vessel cost = $ 60000 (obtained from Figure 12)

Material factor = 1.0 (C.S.) ; Pressure factor = 1.0 (1.5 bar)

$\text{Vessel cost} = \text{bare vessel cost} \times \text{material factor} \times \text{pressure factor} = \$\ 60000$

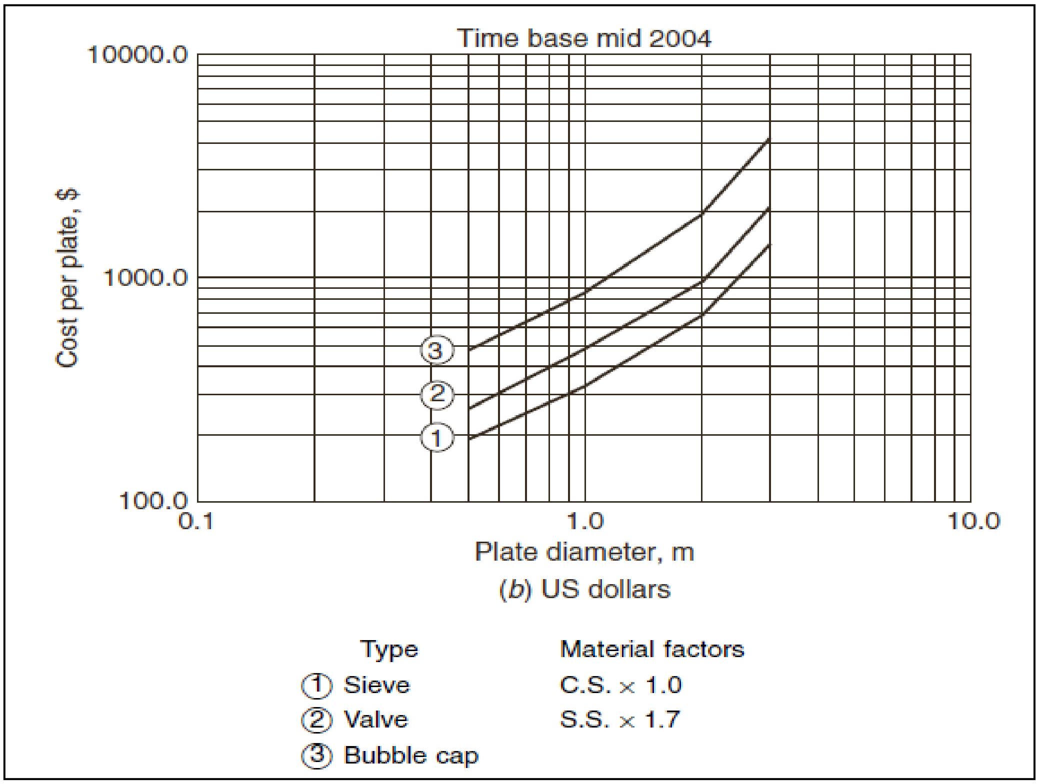


Figure 17: Column plates

Type of trays = Sieve type

Cost per tray = $ 450 (obtained from Figure 13)

Material factor = 1.0 (C.S.)

$\text{Tray cost} = \text{n} \times \text{cost per tray} \times \text{material factor} = \$\ 18000$

$\boldsymbol{\text{Absorber cost} = \text{vessel cost} + \text{tray cost} = \$\ 78000}$

b. Regenerator

Tray space = 0.55m ; Tray thickness = 0.002m ; Tray diameter = 1.5m

Number of trays = 18

$\text{Height of absorber} = \text{n} \times \text{Tray thickness} + \text{Tray space} \times (\text{n} - 1) = 9.4\text{m}$

Bare vessel cost = $ 11500 (obtained from Figure 12)

Material factor = 1.0 (C.S.) ; Pressure factor = 1.0 (1.5 bar)

$\text{Vessel cost} = \text{bare vessel cost} \times \text{material factor} \times \text{pressure factor}$ = $ 11500

Type of trays = Sieve type

Cost per tray = $ 450 (obtained from Figure 13)

Material factor = 1.0 (C.S.)

$\text{Tray cost} = \text{n} \times \text{cost per tray} \times \text{material factor} = \$\ 8100$

$\textbf{Regenerator cost} = \textbf{vessel cost} + \textbf{tray cost} = \$\ \mathbf{19600}$

c. Pump P-1

Volumetric flow rate = 14551 gal/min (obtained from HYSYS)

Type of pump = Vertical axial flow

$\textbf{Pump cost} = \mathbf{0.020(gpm)^{0.78}} = \$\ \mathbf{35326.24}$

d. Pump P-2

Volumetric flow rate = 13094 gal/min (obtained from HYSYS)

Type of pump = Vertical axial flow

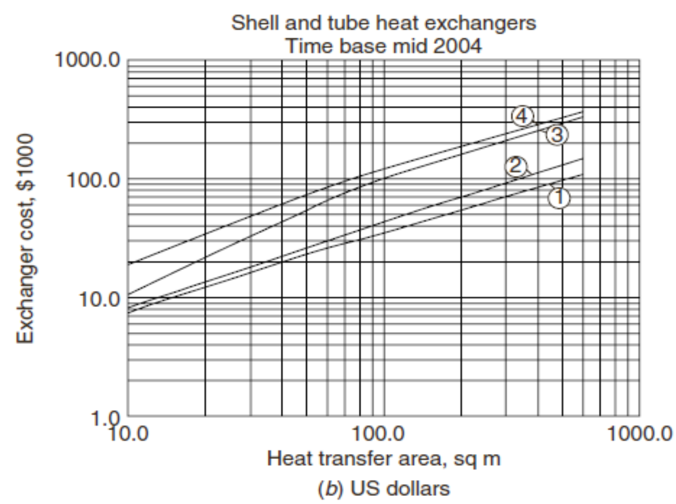
$$\mathbf{Pump\ cost} = \mathbf{0.020(gpm)^{0.78}} = \$\ \mathbf{32534.91}$$

e. Reboiler

UA = 3.6 x 10^5 kJ/h (obtained from HYSYS)

U = 1000 W/m^2.h [Sinnott, 2005]

$$\text{Area, A} = \frac{UA}{U} = 100m^2$$



Materials			Pressure factors		Type factors	
	Shell	Tubes				
1	Carbon steel	Carbon steel	1–10 bar	× 1.0	Floating head	× 1.0
2	C.S.	Brass	10–20	× 1.1	Fixed tube sheet	× 0.8
3	C.S.	Stainless steel	20–30	× 1.25	U tube	× 0.85
4	S.S.	S.S.	30–50	× 1.3	Kettle	× 1.3
			50–70	× 1.5		

Figure 18: Shell and tube heat exchanger

Material = S.S. (shell) ; S.S. (tube)

Bare exchanger cost = \$ 130000 (obtained from Figure 14)

Pressure factor = 1.0 (1.5 bar) ; Type factor = 1.3 (kettle)

$$\mathbf{Reboiler\ cost} = \mathbf{bare\ exchanger\ cost} \times \mathbf{pressure\ factor} \times \mathbf{type\ factor}$$

$$= \$\ \mathbf{169000}$$

f. Condenser

UA = 3.6 x 10^5 kJ/h (obtained from HYSYS)

U = 1000 W/m^2.h [Sinnott, 2005]

$\text{Area, A} = \frac{\text{UA}}{\text{U}} = 100\text{m}^2$

Material = C.S. (shell) ; S.S. (tube)

Bare exchanger cost = $ 100000 (obtained from Figure 14)

Pressure factor = 1.0 (1.5 bar) ; Type factor = 1.0 (floating head)

$\textbf{Condenser cost} = \textbf{bare exchanger cost} \times \textbf{pressure factor} \times \textbf{type factor}$

$= \$\ \mathbf{100000}$

g. Rich-Lean Heat Exchanger

Area, A = 60.32m^2 (obtained from HYSYS)

Material = S.S. (shell) ; S.S. (tube)

Bare exchanger cost = $ 85000 (obtained from Figure 14)

Pressure factor = 1.0 (1.5 bar) ; Type factor = 1.3 (kettle)

Rich-Lean heat exchanger cost

$= \textbf{bare exchanger cost} \times \textbf{pressure factor} \times \textbf{type factor}$

$= \$\ \mathbf{110500}$

h. Amine Cooler

Area, A = 60.33m^2 (obtained from HYSYS)

Material = C.S. (shell) ; S.S. (tube)

Bare exchanger cost = $ 65000 (obtained from Figure 14)

Pressure factor = 1.0 (1.5 bar) ; Type factor = 1.0 (floating head)

Amine cooler cost

$$= \mathbf{bare\ exchanger\ cost} \times \mathbf{pressure\ factor} \times \mathbf{type\ factor}$$

$$= \$\ \mathbf{65000}$$

i. Mixer

Type of mixer = single impeller

Speed = 2 ; a = 8.43, b = -0.088, c = 0.1123

		Single Impeller			Dual Impeller		
		Speed 1	2	3	1	2	3
Carbon steel	a	8.57	8.43	8.31	8.80	8.50	8.43
	b	0.1195	−0.0880	−0.1368	0.1603	0.0257	−0.1981
	c	0.0819	0.1123	0.1015	0.0659	0.0878	0.1239
Type 316	a	8.82	8.55	8.52	9.25	8.82	8.72
	b	0.2474	0.0308	−0.1802	0.2801	0.1235	−0.1225
	c	0.0654	0.0943	0.1158	0.0542	0.0818	0.1075

Speeds 1: 30, 37, and 45 rpm
2: 56, 68, 84, and 100 rpm
3: 125, 155, 190, and 230 rpm

Figure 19: Constants a, b, and c of different types of mixer

Horsepower (HP) = 6.7 HP (assumption)

$$\mathbf{Mixer\ cost} = \mathbf{exp}[\mathbf{a} + \mathbf{b}\ \mathbf{ln\ HP}\ + \mathbf{c}(\mathbf{ln\ HP})^2] = \$\ \mathbf{5819.20}$$

PCE = ∑ Cost of each equipment = $ 615780.35

1.2 Direct and Indirect Cost

Based on Table 4, the factors that will be used for estimation of fixed capital are under "Fluids" category.

$$\text{Total direct cost} = \text{PCE}\,(1 + f_1 + \cdots + f_9) = \$\,2093653.20$$

$$\text{Fixed capital} = \text{Total direct cost}\,(1 + f_{10} + f_{11} + f_{12}) = \$\,3035797.14$$

$$\text{Working capital} = 0.1 \times \text{fixed capital} = \$\,303579.71$$

CAPEX = Fixed capital + Working capital = $ 3339376.86

2. Operating Expenditures (OPEX)

2.1 Variable Costs

a. Raw materials

Table 12: Cost of raw materials

Raw materials	Cost per unit	Amount (m^3)	Total Cost ($/15 yrs)
MEA ($/m3)	1244.32	21.18	79061.31
MDEA ($/m3)	832	35	88059.04

The life time of the raw materials is assumed 5 years. Therefore, in 15 years, the solvent will be replaced 3 times.

$$\text{Total cost } (\$/15\text{ years}) = \text{Amount} \times \text{Cost per unit} \times 3 \text{ times replaced}$$

b. Miscellaneous materials

Refer to Table 5.

$$\text{Miscellaneous materials} = 10\% \text{ of maintenance cost } \times 15 \text{ years}$$
$$= \$3506784.91$$

c. Utilities

Table 13: Cost of utilities

Utilities	Energy (kW)	Cost per unit ($/kW.yr)	Total cost ($/yr)
Hot	3.583×10^{5}	21.7	7.776×10^{6}
Cold	300666.67	2.325	699050

Total utilities cost = ($\$7.776 \times 10^{6}$ + $699050) × 15 years = $127123250

2.2 Fixed costs

a. Maintenance

$$\text{Maintenance cost} = 5\% \text{ of Fixed capital} \times 15 \text{ years} = \$2337856.61$$

b. Operating labour

Operating labour cost is assumed as $468546/year. So, for 15 years, operating labour cost = $7028190

c. Laboratory costs

$$\text{Laboratory cost} = 20\% \text{ of Operating labour} = \$1405638$$

d. Supervision

$$\text{Supervision cost} = 20\% \text{ of Operating labour} = \$1405638$$

e. Plant overheads

$$\text{Plant overheads} = 50\% \text{ of Operating labour} = \$3514095$$

f. Capital charges

$$\text{Capital charges} = 10\% \text{ of Fixed capital} = \$4675713.21/15 \text{ years}$$

g. Insurance

$$\text{Insurance} = 1\% \text{ of Fixed capital} = \$467571.32/15 \text{ years}$$

h. Local taxes

$$\text{Local taxes} = 2\% \text{ of Fixed capital} = \$935142.64/15 \text{ years}$$

i. Royalties

$$\text{Royalties} = 2\% \text{ of Fixed capital} = \$31171.42$$

$$\mathbf{OPEX = Variable\ cost + Fixed\ cost = \$152598171.46}$$