Economic Analysis of CO_2 DEA-MDEA Removal System

By

CHUA WEE KHENG
(SID: 11913)

Supervisor:
IR. DR. ABDUL HALIM SHAH MAULUD

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

SEPTEMBER 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar,
31750 Tronoh,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

____

(**IR. DR. ABDUL HALIM SHAH MAULUD)**

UNIVERSITY TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

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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(**CHUA WEE KHENG**)

ABSTRACT

Removal of CO_2 using aqueous amine systems is one of the popular methods in treating flue gas. Aqueous amines are organic solvents that selectively remove CO_2 gas from waste stream. Various types of amines are often used together in a blend of mixture to maximize their advantages. This paper aims to conduct a sensitivity analysis on how changes in the market price of one type of amine in an amine mixture will affect the overall cost of flue gas treatment. It is an extension of the work done by Rodrigues (2011), who optimized the post-combustion CO_2 capture using an amine mixture consisting of Methyldiethanolamine (MDEA) and Diethanolamine (DEA). Rodriguez has successfully determined the mass fraction of the MDEA-DEA in an amine mixture that will achieve a CO_2 removal target with minimal cost. In this paper, 95% removal target data will be used as a basis. This paper further Rodriguez's work by adding the dimension of sensitivity analysis to the cost optimization. The market price of the 2 amine solvents is expressed as a price ratio to yield a single value to work with. The investigation is carried out using HYSIS simulation software, in which the fluid package Amine Property Package is used with Li-Mather as the model. A simplified process flow sheet of the CO_2 amine system is simulated which involve two major equipment: the absorber and regenerator. The simulation shows the minimum solvent flow rate to achieve the 95% CO_2 removal target, amount of flue gas removed by the solvent, and the energy of regeneration of the recycled solvent. In addition to that, by using the initial cost function described by Rodriguez (2011), several other models of the minimum cost function that incorporated the MDEA-DEA price ratio can be created and the sensitivity analysis for each model can be investigated. The most feasible model to describe how the changes in market price will affect the minimum cost is selected. The result shows that an economic analysis with much useful information can be interpreted from the selected cost function.

ACKNOWLEDGEMENTS

My most heart-felt gratitude to the following people for contributing towards the success of my Final Year Project and dissertation:

-----Supervisor: Ir. Dr. Abdul Halim Shah Maulud----

Thank you for your invaluable guidance and teachings thorough the two semesters. You have taken meticulous care to ensure that I have fully understood the project scopes and always set me on the right path when I encountered a road block or hurdle in the project. Your time and dedication is much appreciated.

-----FYP Coordinators: Dr Nurhayati Mellon and Pn Asna M Zain----

Thank you for coordinating the Final Year Research for the whole Chemical Engineering Department and ensuring a smooth flow and communication channel between the students and their respective coordinators. The various seminars and briefings organized have been helpful.

-----Internal and External Examiners----

Thank you for providing thoughtful comments and advices that is imperative in improving my project. An added dimension of input from other field of expertise is much needed to gain a better insight and useful perspectives to enhance my thinking and understanding of the project.

-----Lab technicians and Chemical Department staff----

Thank you for providing endless support and help to the students. Without the staff and technicians working behind the scenes to keep the lab equipment and computers in working conditions, students would have not successfully completed their project in time.

-----Family and friends----

Thank you to my beloved family members and my close friends for the 24/7 moral support when I am working on my project. They can be counted on for being there when I am going through a rough time. They have also provided additional advices that help improves the non-technical aspects of the project.

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CHAPTER 1

PROJECT BACKGROUND

1.1 INTRODUCTION

Recent years have seen the development of carbon capture and storage technology as the world move towards green technology and more eco-friendly industrial processes. Many developed countries have since pledged to reduce their carbon footprints by cutting CO_2 emissions. The European Union, for example, has targeted to reduce CO_2 emission by 30% by the year 2020. With global CO_2 emissions at approximately 35 billion tons and rising, the world need to sought effective measures to reduce CO_2 emission. Malaysia, as a developing country should keep abreast with the carbon capture developments as our country can be a big industrial player globally.

Various methods to scrub CO_2 from flue gas exist, and they can generally be classified as using physical solvent or chemical solvent. Physical solvents like Methanol and Polyethylene Glycol are suitable for gas purifications at high pressure but not practical when partial pressure is low or gas stream contains high amount of hydrocarbon. Chemical solvents, while being more versatile because it removes CO_2 via chemical reactions, can be corrosive and requires a regeneration unit. (Burr B. & Lyddon L.) Newer technologies exist such as membrane technology but can be expensive. Thus, it can be seen that various methods are suitable for different applications.

For chemical solvent, using aqueous amine solutions to strip CO_2 form flue gas is still a popular method widely used today in many flue gas treatment plants as it is reliable and efficient. (Rodriguez 2011). This paper will focus on the using amine system to remove CO_2. Amines system has been in general use since the 1960's and 1970's according to Polasek (1994). Before the 1970's, monoethanolamine (MEA) was the first amine to be considered in a sour gas treatment process. After that, diethanolamine (DEA) became more favored as it yield more benefits compared to MEA, which one of them is DEA is less corrosive compared to MEA. In the years that followed, several more amines have been added to the family of amines for gas sweetening such as MDEA, DGA, and mixed amines. Meanwhile, piperazine, used as an additive to amine solvents, has first been in used during the 1980s, where a US patent introduced its use with MDEA (Optimized Gas Treating, Inc, 2008). Therefore, piperazine can be considered a newer class of amines. The article from Optimized Gas Treating, Inc (2008) shows the effectiveness of piperazine in improving CO_2 removal efficiency. In fact, over the years amine system treatment has been widely investigated and there is an abundance of their performance data for both conventional amines and newer class of amines.

1.2 PROBLEM STATEMENT

In his journal, Rodrigues (2011) has done extensive work to calculate the cost to remove CO_2 from of flue gas using DEA-MDEA mixture. A cost model is successfully developed with the specific cost ($/ton of flue gas) versus the MDEA mass fraction. This is done for 80%, 85%, 90% and 95% CO_2 removal.

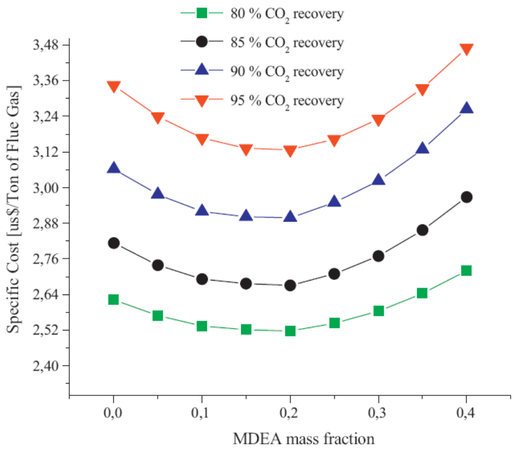


Figure 1.1: Specific Cost ($/ton of flue gas) versus MDEA mass fraction

From Figure 1.1, the amount of MDEA mass fraction to use that incurs a minimum is determined to be at 0.2 MDEA mass fraction, followed by 0.2 DEA and 0.6 water. From the 95% CO_2 removal, the graph shows the minimum cost is $3.18 per ton of flue gas. As a side note, one ton of flue gas consists of 4% CO_2 according to the composition. Hence, if one wish to express the cost in $/ton CO_2 removed, it will be $79.5/ton of CO_2. Nevertheless, in this report the cost will be expressed in 4/ton flue gas.

The problem from the above analysis is that it fails to take into account the amine price sensitivity analysis. The market price of amine, subjected to market demand and supply, is not constant and will change, which subsequently affect the cost of flue gas treatment. If the market price of MDEA increases by for example 50%, will using 0.2 mass fraction MDEA still yield the minimum cost? How much will the minimum cost change, and to what extend should the MDEA mass fraction be reduced are also some of the results we are interested to find out. Because MDEA is used as a mixture with DEA, the change in price of DEA can also shift the minimum cost. Therefore, an assessment will be required to evaluate whether the present amine system is still economical or a new mixture will be more cost saving hence a better alternative.

1.3 OBJECTIVE AND SCOPE OF STUDY

The objectives in this project are:

1) To develop several cost models of Specific Cost (\$/ton of CO_2) versus MDEA mass fraction by fitting the price ratio of MDEA to DEA into an initial cost function. The initial cost function is of quadratic nature with a global minimum.
2) To perform sensitivity analysis using the price ratio term that has been fitted into the proposed cost models.

The scope of amine solvents studied here are DEA and MDEA. The amine are mixed with a significant proportion of water to reduce its corrosiveness because "operating the process beyond a typical concentration can cause a significant increase in the system corrosiveness". Hence, our amine mixture consists of 40% MDEA-DEA and 60% water, which is in compliance with the typical operating range. The MDEA-DEA composition complements each other. If mass fraction of MDEA is 0.1, DEA would be 0.3 for instance. Because we are only studying the sensitivity analysis for the price change in amines, the total capital cost of the plant remain fixed thorough the analysis. It is targeted to remove 95% of CO_2 from the flue gas. The sensitivity analysis is investigated up to 60% change in the price of both MDEA and DEA.

1.4 RELEVANCY AND FEASIBILITY OF STUDY

As with all engineering applications, besides being physically realizable, the economic feasibility must also be considered in real situations. This will provide benefits not only economically but also optimize usage and prevent wastage of resources. Future engineers must also be able to make proper judgments on the feasibility of a project not only based on technicality but an overall economic analysis as well. Hence, this project is well-suited for this purpose because we can gain exposure towards optimization.

As for the feasibility, this project will not incur any significant cost as UTP computer labs are well-equipped with the HYSYS software needed to simulate the gas sweetening plant. Microsoft Excel is also easily available in every computer. The project activities are spread out neatly with a suitable timeframe assigned to each task as seen from the Gantt Chart attached in the Appendix section. Hence, this project is feasible within the available resources and time.

CHAPTER 2

LITERATURE REVIEW

The beginning part of the literature review will introduce various types of amine and elaborate on their properties and characteristics. The amine gas sweetening plant is reviewed after that followed by the economic data of various amine solvents.

2.1 TYPES OF AMINE SOLVENTS

Many types of amine solvents exist that are used to remove carbon dioxide from flue gas. Table 2.1 gives an overview of the chemical structure of the wide range of amines conventionally used and their chemical formula.

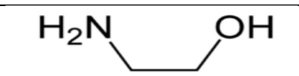
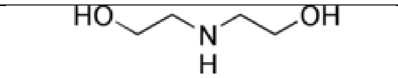
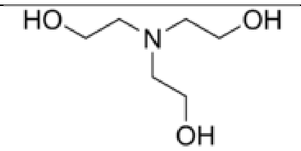
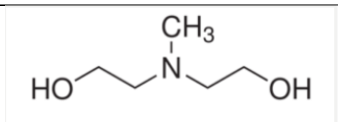
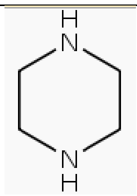
Name	Chemical structure	Formula	Boiling point
MEA, Monoethanolamine		C_2H_7NO	170^oC
DEA, diethanolamine		$C_4H_{11}NO_2$	271^oC
TEA, triethanolamine		$C_6H_{15}NO_3$	335^oC
MDEA, methyldiethanolamine		$C_5H_{13}NO_2$	247^oC
PZ, Piperazine		$C_4H_{10}N_2$	146^oC

Table 2.1: Types of amine used in carbon dioxide absorption

Different types of amines exhibit different properties while reacting with CO_2. At room temperature, most of the amines exist in liquid state. They are soluble in water, although the solubility decreases as the hydrocarbon chain attached to the molecules gets longer. Amines are further classified into primary, secondary, and tertiary amines based on the number of alkyl group, R, (C_2H_4OH) that replaces the hydrogen atoms in an ammonia molecule (which originally has 3 atoms attached to it, NH_3). For example, a primary amine will have the formula RNH_2, while tertiary amines have the formula R_3N. All amines have the characteristic pungent smell of decaying matter and are flammable at high temperature.

2.2 REACTIONS OF AMINE SOLVENTS

Primary and secondary amines react with CO_2 to form carbamate ions. Besides that, reaction of piperazine and CO_2 also yields carbamate ions as shown:

$H_2O + 2MEA + CO_2 \leftrightarrow MEACOO^-$ (carbamate ion) + $MEAH^+$ (protonated amine)

$H_2O + 2DEA + CO_2 \leftrightarrow DEACOO^- + DEAH^+$

$H_2O + PZ + CO_2 \leftrightarrow PZCOO^- + H^+$

The reactions are highly exothermic and fast, but the heat required to regenerate the amines is also greater, therefore requiring an increased cost. Theoretically, primary and secondary amines have a CO_2 loading factor of 0.5mol CO_2/mol amine (Rodriguez et al., 2011).

For tertiary amines, they react with CO_2 to produce bicarbonate ion as shown:

$H_2O + MDEA + CO_2 \leftrightarrow HCO_3^-$ (bicarbonate ion) + $MDEAH^+$ (protonated amine)

$H_2O + TEA + CO_2 \leftrightarrow HCO_3^-$ (bicarbonate ion) + $TEAH^+$ (protonated amine)

The reaction is slower compared to primary and secondary amine, therefore requiring higher residence time to achieve the desired CO_2 removal. Despite that, it requires a lower heat requirement to regenerate the amine solvent and has a higher loading factor which is 1 mol CO_2/mol amine (Kundu et al., 2006). Figure 2.1 depicts the CO_2 loading versus the rate of absorption for both classes of amine:

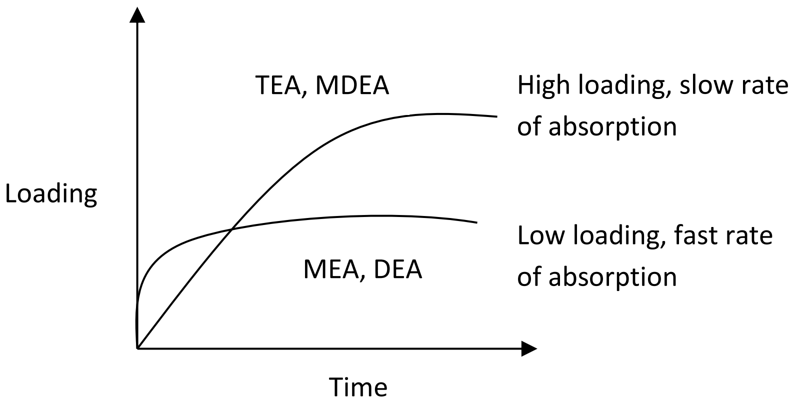


Figure 2.1: CO_2 loading versus rate of absorption for amine systems

Therefore, we can observe that both classes of amines have their distinctive advantages and disadvantages over one another. It is thus important to find an optimal between them that will maximize the benefits from both components while minimizing the disadvantages.

2.3 PROCESS FLOW SHEET OF A GAS SWEETENING PLANT

The treatment of flue gas removes acidic compounds such as CO_2 and H_2S that are known as 'sour gases'. Therefore, the exiting gas stream becomes clean and less harmless, which is how the term 'gas sweetening' originate. Figure 2.2 shows a process flow sheet of a typical amine gas treatment plant.

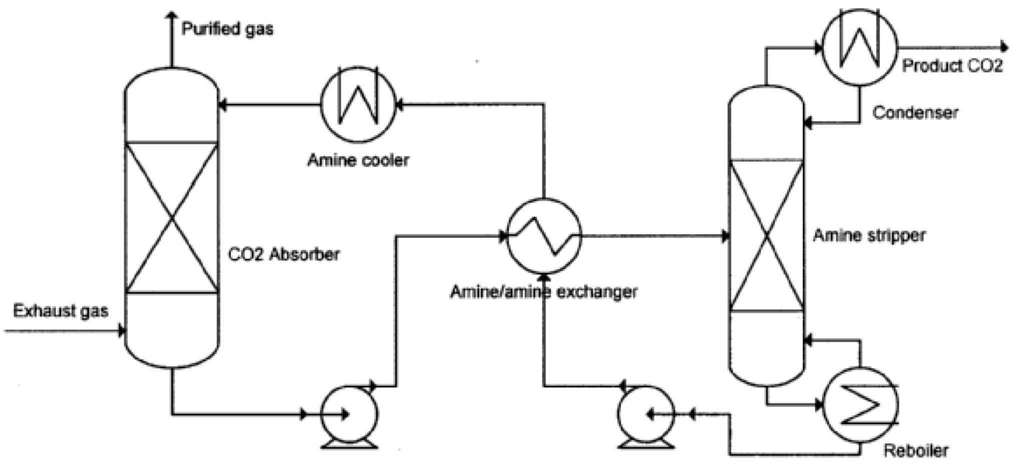


Figure 2.2: Process flow sheet of an amine gas treatment plant (Lars E.O. (2007))

The main equipment involved are the absorber and regenerator unit, which can be also described as a stripper unit. Sour gas enters the absorber from below while lean amine from the top is contacted with the sour gas. Sour gas is absorbed by the amine liquid. The rich amine carrying the acidic gas (CO_2 and H_2S) is sent to the regenerator unit which strips the amine of its acidic gas. The acidic gas will leave at the top and is purged from the regenerator unit. Meanwhile, the lean amine, with acidic gas removed from it, will go to the bottom of the regenerator and is recycled back to the absorber unit, ready to repeat the whole gas treatment process. Typical operating range for the absorber is 35-50^{o}C and 5 atm to make it favorable for acidic gas to react with amines at low temperature and high pressure. The inverse can be observed at the regenerator unit, which utilizes high temperature (115-126^{o}C) and low pressure (1.7 atm) to induce desorption of acidic gas from the amine solvents.

2.4 MOLAR COMPOSTION OF FLUE GAS

The molar composition of flue gas from a gas turbine is shown in Table 2.2: (Nuchitprasittichai, A., & Cremaschi, S. (2011).

Component	**Mol %**
CO_2	2.44
H_2O	7.28
O_2	17.00
N_2	73.28

Table 2.2: Molar composition of gas turbine flue gas

Different industrial processes will have flue gas of different compositions. Despite the variations, most flue gas compositions will have nitrogen as the bulk component (>70%), while CO_2 only comprises of 2-10% of the composition in the flue gas. In large molar flow rate, the amount of CO_2 in the flue gas will become significant regardless of its low percentage.

2.5 COST OF AMINE SOLVENTS

The cost of some typical amine solvents are listed in Table 2.3. Assumptions used for the economic analysis is also shown. According to Nuchitprasittichai (2011), the cost data is estimated using the capital equipment costing program (CAPCOST) and are adjusted using the values of Chemical Engineering Plant Cost Index (CEPCI).

Amine solvent	**Approximate cost ($/kg)**
MEA	1.30
DEA	1.32
MDEA	3.09
TEA	1.34
Piperazine	2.20

Table 2.3: Cost of amine solvents

For piperazine, the price is estimated from AliBaba.com, which is online global trade website for many industrial chemicals.

To perform the economic analysis on the overall plant cost, the following assumptions made are: The assumptions are based on the literature by Nuchitprasittichai, A., & Cremaschi, S. (2011).

- The plant is expected to have a 20 year plant life with no salvage value.
- The plant operates for 8400 hour per year.
- The working costs are 15% of the fixed capital investment.
- The maintenance and repair costs are 5% of the fixed capital investment.
- The operating supplies costs are 155 of the maintenance and repair costs.
- The local taxes and insurance are 4% of the fixed capital investment.
- Each operation slot requires 5 operators, and salary per operator is $40000 a year plus $40000 a year benefit.
- The laboratory charges are 15% of the labor costs.
- The plant overhead costs are 60% of labor costs.
- The administrative expenses are 50% of labor costs.
- The labor costs, the maintenance and repairs, laboratory charges, and the administrative expenses inflate 3% per year.
- The minimum acceptable rate of return, MARR is 10%

- The cost of cooling water, make-up water, saturated steam at 300kPa , and electicity are \$0.05/m^3, \$0.30/m^3, \$3.00/1000kg, \$0.07/kWh, respectively.

It must be noted that this set of economic data is only for reference to give a "feel" of how our plant operates. In this project, we assume that capital cost of a plant is fixed because we our scope of interest is only on the cost of amines at various price ratio.

In calculating the minimum cost of CO_2 removal (\$/ton flue gas), Rodriguez (2011) estimated the total annual cost by the following formula:

$$TAC = TAOC + (TIC \times CRF \times \emptyset)$$

Where:

TAOC refers to the total annual operating cost,

TIC is the total investment cost,

CRF is the capital recovery factor,

$\emptyset$ is the maintenance factor.

The equation is used to generate the cost function of the specific cost of CO_2 removal (\$/kg flue gas) at different CO_2 removal target shown later in the next chapter.

CHAPTER 3

METHODOLOGY

3.1 PROJECT ACTIVITIES

As with many tasks, this project must follow certain procedures and activities in order to meet its objectives in the end. The activities needed to be carried out are mainly:

1. Define the underlying problem (problem statement) and determine the objectives
2. Conduct thorough literature review and investigation on project background
3. Determine the suitable methods to execute the project that will achieve the set objectives
4. Set up the parameters and design the experiment. For a simulation project, objective function must be set and its constraints must be known
5. Obtain the results and document them.
6. Interpret obtained results followed by discussion and report writing.
7. Conclusion, whether objectives are met.

While the activities above are generally done in order, they can be revisited and repeated if the situation requires it. For example, while interpreting the results, more literature review can be conducted again if the results require new information to justify them.

3.2 KEY MILESTONES

The key milestones for Final Year Project II are shown below. Activities and deadlines set in the Gann Chart should take close consideration of these milestones.

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report									●							
3	Project Work Continues																
4	Pre-EDX								Mid-Semester Break				●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone

Process

Table 3.1: Key Milestones for FYPII

3.3 GANN CHART FOR FYPII

The Gann Chart is a personalized timetable that provides more details of each activity that needs to be carried out. It met the requirements of the key milestone.

		Week															
No	Milestones	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Recap FYP I, meeting with SV								Mid Sem Break								
2	HYSYS simulation to obtain cost function																
3	Excel cost fitting and modelling																
4	Submission of Progress Report																
5	Rectifying the cost models																
6	More detailed modelling																
7	Pre-EDX																
8	Submission of Draft Report																
9	Submission of Dissertation (soft bound)																
10	Submission of Technical Paper																
11	Oral Presentation																
12	Submission of Progress Dissertation (Hard Bound)																

Table 3.2: Gann Chart for FYPII

3.4 TOOLS

HYSYS and Microsoft Excel are the software used in this project. The main reference used here for our basis is Rodriguez (2011). He has studied the optimization of post-combustion CO_2 process using DEA-MDEA mixtures. Therefore, our scope will be confined to these two amines. There are two methodologies for this project as explained below:

3.4.1 HYSYS SIMULATION

An amine gas sweetening plant is simulated with an absorber unit and regenerator unit as shown in Figure 3.1. From the simulation, much important information can be obtained, and we are mainly interested in the flow rate of amine solvent needed to achieve a 95% CO_2 removal target based on the MDEA and DEA mass fraction. Furthermore, HYSYS will also indicate the energy for reboiler and condenser in the regenerator. The flow rate of amine and the energy of regeneration will become the basis (the manipulated variables) to calculate the amine cost.

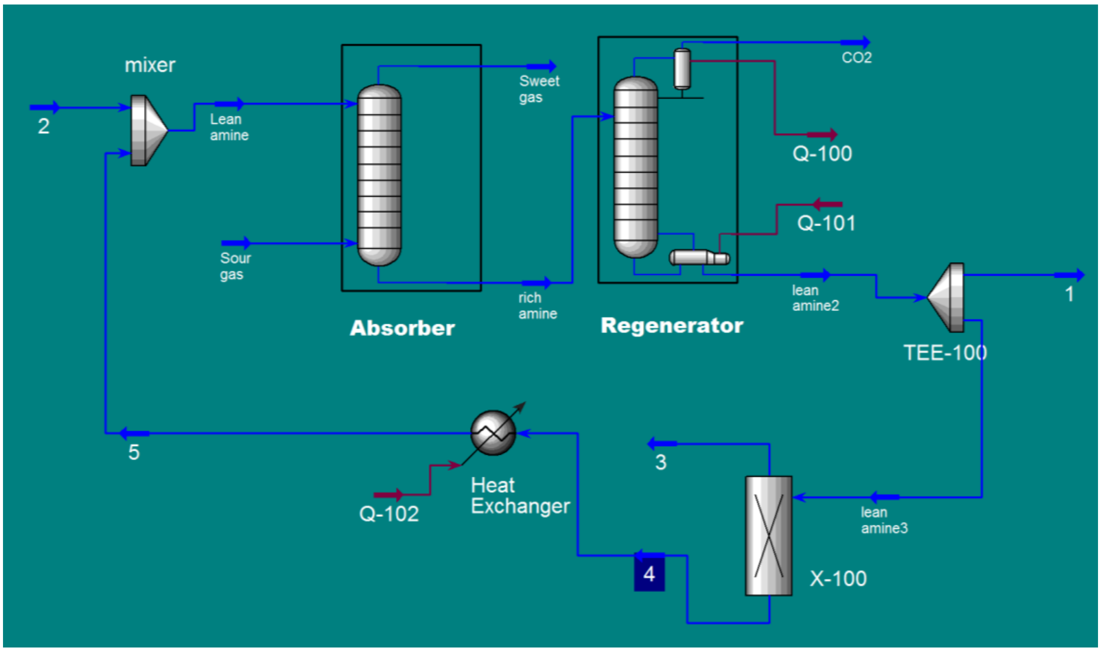


Figure 3.1: Simulation of amine gas sweetening plant using HYSYS

Meanwhile, equipment sizing and operating conditions are fixed thorough to maintain a fixed capital cost as mentioned previously. The parameters are:

Flue gas flow rate and composition

Halim (2008) investigated a simulation-optimization framework to capture CO_2 from a gas power plant. Table 3.3 shows the composition of the flue gas used, which we use as a basis in HYSYS. This is different than the composition used for Rodriguez (2011) to prove the reproducibility of the results using other case studies.

	Operating Value
Flue gas rate (kmol/h)	59,000
N_2 (mol%)	69.96
CO_2 (mol%)	9.74
O_2 (mol%)	13.79
H_2O (mol%)	6.51
Gas temperature (°C)	55
Gas pressure (kPa)	110

Table 3.3: Flue gas composition and flow rate

Amine Solvent Flow Rate

4 mixtures of amine solvent is investigated which consist of MDEA and DEA in different proportion with a total of 0.4 mass fraction but with the same mass fraction of 0.6 of water for all mixture. This is shown in Table 3.4. Water exists in larger proportion because pure and concentrated amine is corrosive.

Amine	DEA mass fraction	MDEAmass fraction	Water mass fraction
A	0.10	0.30	0.60
B	0.15	0.25	0.60
C	0.20	0.20	0.60
D	0.25	0.15	0.60

Table 3.4: Compositions of 4 amine mixture

The absorber

An absorber of 20 stages is used with an operating pressure of 500 kPa. The dimensions are also shown in Figure 3.2.

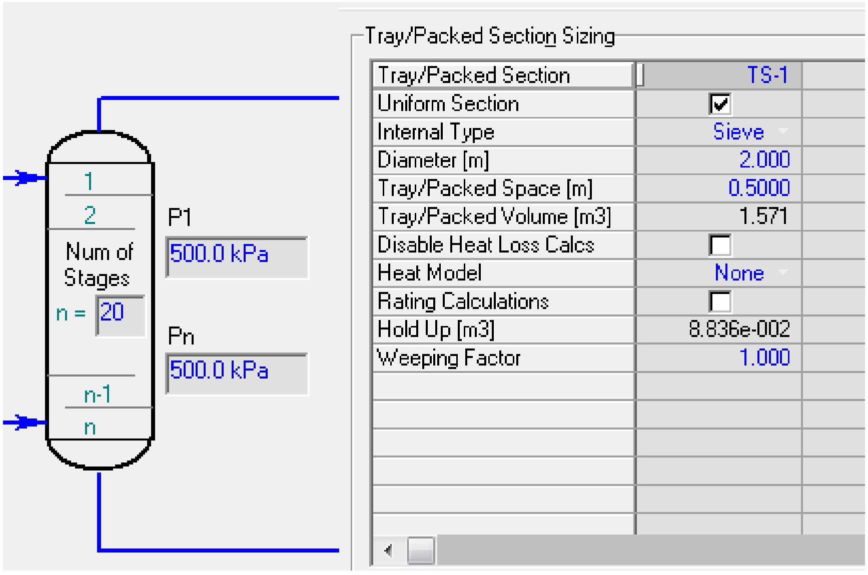


Figure 3.2: Specifications of the absorber unit in HYSYS

The regenerator

The regenerator consists of 30 stages and operates at 130kPa. The dimensions are also shown below Figure 3.3.

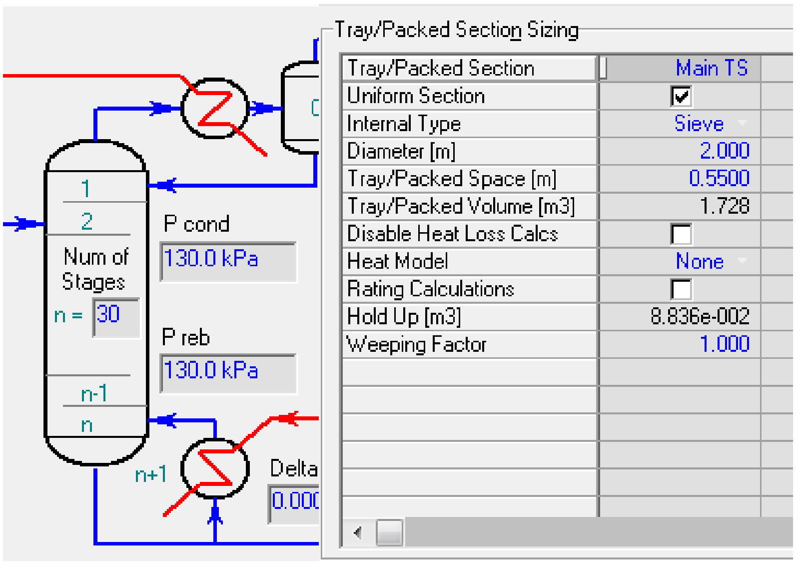


Figure 3.3: Specifications of the regenerator unit in HYSYS

3.4.2 DEVELOPING COST MODELS USING EXCEL

HYSYS is an attempt to prove that the minimum cost lies near 0.2 mass fraction of MDEA. Meanwhile, the initial cost function can also be obtained from an available cost function in the literature. Rodriguez (2011) has plotted the specific cost per ton of flue gas versus MDEA mass fraction in a DEA-MDEA amine mixture.

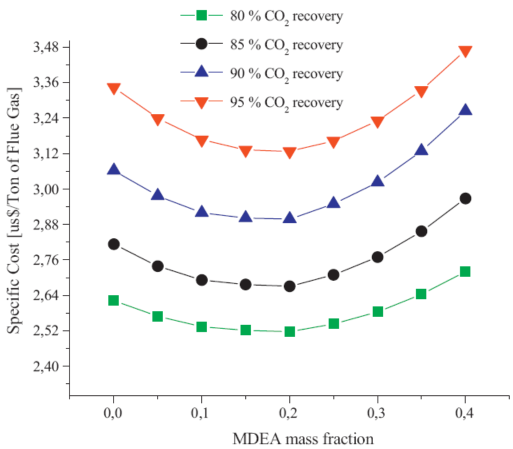


Figure 3.4: Specific cost versus MDEA mass fraction in a DEA-MDEA amine mixture.

From Figure 3.4, a mass fraction of 20% DEA and 20% MDEA blend in 60% water will yield the minimum cost. The minimum point is the same regardless of CO_2 removal target. We will select the curve at 95% CO_2 removal as our initial cost function. Each data point is read from the curve and the graph is re-plotted in excel. Because the curve is a polynomial function, Excel can be asked to produce the equation for the cost function.

MDEA mass fraction	cost $/ton flue gas
0	3.34
0.05	3.25
0.1	3.18
0.15	3.14
0.2	3.14
0.25	3.18
0.3	3.24
0.35	3.34
0.4	3.48

Table 3.5: Data points based on 95% CO_2 removal

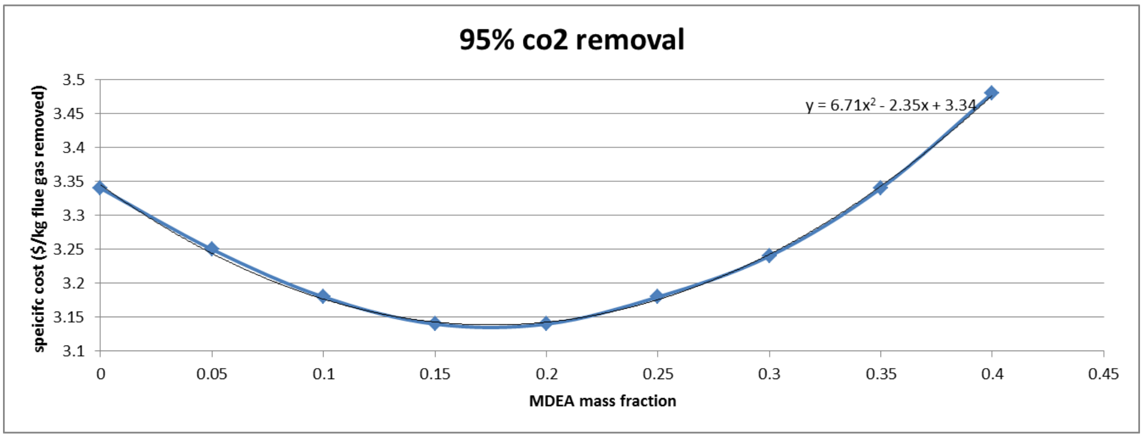


Figure 3.5: 95% CO_2 removal plotted on excel

From graph plotted, the cost function equation is:

$$y = 6.71x^2 - 2.35x + 3.34$$

Our literature review earlier has stated that the price of MDEA/kg is \$3.09 while DEA is \$1.32/kg, therefore the price ratio of MDEA to DEA is 3.09/1.32 = 2.34

Knowing the price ratio, we can incorporate this value into the original cost function by substituting it into any terms in the equation and multiplied it by a certain factor so the same coefficient is returned. The term "x" is still the MDEA mass fraction. Using this method, we managed to add a price sensitivity component in the cost function. Many possible cost functions can be developed. In our project, 4 cost models are proposed here..

Model 1:

$$Cost = (price\ ratio)(factor)x^2 - 2.35x + 3.34$$

Model 2**:**

$$Cost = 6.71x^2 - (fator)(price\ ratio)x + 3.34$$

Model 3**:**

$$Cost = 6.71x^2 - 2.35x + price\ ratio(factor)$$

Model 4**:**

$$Cost = (price\ ratio)(factor)x^2 - 2.35x + price\ ratio(factor)$$

The changes in the market price of MDEA and DEA are calculated in excel and its subsequent effect to the price ratio is shown in Table 3.6 and Table 3.7.

Change in MDEA price		MDEA price	
% change		$/kg	price ratio (MDEA to DEA)
-60%	0.4	1.24	0.94
-50%	0.5	1.55	1.17
-40%	0.6	1.85	1.40
-30%	0.7	2.16	1.64
-20%	0.8	2.47	1.87
-10%	0.9	2.78	2.11
0%	1	3.09	2.34
10%	1.1	3.40	2.58
20%	1.2	3.71	2.81
30%	1.3	4.02	3.04
40%	1.4	4.33	3.28
50%	1.5	4.64	3.51
60%	1.6	4.94	3.75

Table 3.6: Changes in price of MDEA and its effect on the price ratio. (DEA=$1.32)

Change in DEA price		DEA price	
% change		$/kg	price ratio (DEA to MDEA)
-60%	0.4	0.53	0.17
-50%	0.5	0.66	0.21
-40%	0.6	0.79	0.26
-30%	0.7	0.92	0.30
-20%	0.8	1.06	0.34
-10%	0.9	1.19	0.38
0%	1	1.32	0.43
10%	1.1	1.45	0.47
20%	1.2	1.58	0.51
30%	1.3	1.72	0.56
40%	1.4	1.85	0.60
50%	1.5	1.98	0.64
60%	1.6	2.11	0.68

Table 3.7: Changes in price of DEA and its effect on the price ratio. (MDEA=$3.09)

The ‘factor’ in the cost model is a value that returns the coefficient of its term to the original value in the cost function. For example, the coefficient of the first term in the cost function is 6.71. For model 1, the original price ratio is 2.34 in the first term. Therefore, to comply with the original cost function, it is multiplied with a factor of 2.8675 which maintains the coefficient at 6.71. The factor remains constant at 2.8675, while the price ratio changes during the sensitivity analysis, which will affect the cost function. For each price ratio, we can generate a new cost function. A graph of minimum cost versus % change in amine price can then be plotted. In addition, all the adjusted cost function can be plotted together to better see where the minimum point shifts.

The price ratio shown in Table 3.6 is used for Model 1 and Model 3. However, for Model 2, the price ratio is a negative term. Due to this, when the price ratio increases (MDEA becomes more expensive), the cost decreases. This does not make sense because the cost should increase when the MDEA becomes more expensive. Therefore, to correct this, the price ratio is inversed. The new price ratio will be expressed as DEA to MDEA instead of the previous MDEA to DEA, as shown in Table 3.7. By doing so, when MDEA becomes more expensive, the cost will be higher because the price ratio becomes smaller.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 HYSYS SIMULATION

HYSYS is used to simulate the amine plant using the operating parameters described earlier in Chapter 3, Methodology. Four different mixture compositions are compared. The minimum flow rate of each amine mixture required to achieve the 95% CO_2 removal is obtained and exported to Microsoft Excel.

CO_2 in sour gas (kmol/hr)	5900
Removal target (95% CO_2)	5605

Mass Fraction						
DEA	MDEA	water	flow rate (kmol/hr)	kg/kmol	DEA (kg/hr)	MDEA (kg/hr)
0.25	0.15	0.6	390000	27.07	2639325	1583595
0.2	0.2	0.6	500000	27.11	2711000	2711000
0.15	0.25	0.6	850000	27.15	3461625	5769375
0.1	0.3	0.6	1800000	27.19	4894200	14682600

Table 4.1: MDEA and DEA mass flow rate to achieve 95% CO_2 removal

Residence time is calculated based on the whole plant volume of $124.89m^3$. This is shown in Table 4.2. Knowing the residence time allows us to determine the total amount of amine used in kg. All tables shown after this are continuation from the Table 4.1.

DEA flow rate (m3/hr)	MDEA flow rate (m3/hr)	total flow rate (m3/hr)	total flow rate (m3/s)	residence time s	DEA used (kg)	MDEA used (kg)
2405.94804	1525.621387	3931.569427	1.092102619	114.3573853	83840.64057	50304.38434
2471.285324	2611.753372	5083.038695	1.411955193	88.45181533	66609.13093	66609.13093
3155.53783	5558.16474	8713.70257	2.420472936	51.59735444	49614.08113	82690.13521
4461.440292	14145.08671	18606.527	5.168479721	24.16377866	32850.65709	98551.97127

Table 4.2: Amount of MDEA and DEA based on residence time

The price of DEA is 1.32 $/kg while the MDEA is $3.09/kg. The total cost of amine can be calculated for each composition. Because MDEA is more expensive than DEA, the result shows that increasing the use of MDEA in the composition will increase the total amine cost.

DEA cost ($)	MDEA cost ($)	Total amine cost ($)
110669.65	155440.55	266110.19
87924.05	205822.21	293746.27
65490.59	255512.52	321003.10
43362.87	304525.59	347888.46

Table 4.3 Total amine cost ($) based on different amine composition

Subsequently, we can obtain the reboiler and condenser energy from HYSYS, thus the energy cost can also be calculated. The energy price, determined earlier from literature review, is $0.07 kWh. It is shown that increasing the MDEA mass fraction will decrease the energy cost. This is in agreement with the earlier explanation in literature review that says DEA is more energy-intensive and requires more energy to regenerate the solvent.

Reboiler energy (kW)	Condenser energy (kW)	total energy (kW)	energy cost ($)
1.136E+07	1.020E+07	2.156E+07	47937.45
1.162E+07	1.020E+07	2.182E+07	37527.18
1.245E+07	1.020E+07	2.265E+07	22724.33
1.471E+07	1.020E+07	2.491E+07	11701.91

Table 4.4 Total energy cost ($) based on different amine composition

Therefore, a trade-off exists in the amount of MDEA and DEA. Using more MDEA will increase total amine cost while saving on energy cost. Meanwhile, using more DEA will increase energy cost though it will save on amine cost. This is shown in the table 4.5.

Mass Fraction			Total amine cost ($)	energy cost ($)
DEA	MDEA	water		
0.25	0.15	0.6	266,110.19	47,937.45
0.2	0.2	0.6	293,746.27	37,527.18
0.15	0.25	0.6	321,003.10	22,724.33
0.1	0.3	0.6	347,888.46	11,701.91

Table 4.5 Total energy cost versus total energy cost

The total cost is the sum of amine cost and energy cost. It is shown in Table 4.6 that despite the trade-off, the total cost is increasing linearly as MDEA increases. This is not the desired U-shaped curve that we seek in an optimization problem. This error arises because our simulation is oversimplified. More parameters should be considered, although at the moment detailed cost modeling involving highly complex mathematical models are beyond our scope in this project.

Despite the result not yielding a suitable cost function for our sensitivity analysis, HYSYS has successfully proven that there is a trade–off between the amine cost and energy cost when using MDEA and DEA amine mixture.

Mass Fraction			Total amine cost ($)	energy cost ($)	total cost ($)
DEA	MDEA	water			
0.25	0.15	0.6	266,110.19	47,937.45	314,047.64
0.2	0.2	0.6	293,746.27	37,527.18	331,273.45
0.15	0.25	0.6	321,003.10	22,724.33	343,727.44
0.1	0.3	0.6	347,888.46	11,701.91	359,590.37

Table 4.6 Total Cost of CO_2 removal

4.2 EXCEL FITTING AND MODELLING

From Chapter 3, Methodology, the initial cost function is:

$$y = 6.71x^2 - 2.35x + 3.34$$

while the 4 proposed cost models are:

Model 1:

$$Cost = (price\ ratio)(factor)x^2 - 2.35x + 3.34$$

Model 2**:**

$$Cost = 6.71x^2 - (fator)(price\ ratio)x + 3.34$$

Model 3**:**

$$Cost = 6.71x^2 - 2.35x + price\ ratio(factor)$$

Model 4**:**

$$Cost = (price\ ratio)(factor)x^2 - 2.35x + price\ ratio(factor)$$

A sample calculation is shown to better explain how the sensitivity analysis is determined.

MODEL 1:

$$Cost = (price\ ratio)(factor)x^2 - 2.35x + 3.34$$

Factor= 2.8675

From table 9 in methodology, if there is no price change, price ratio = 2.34 which gives:

$$Cost = (2.34)(2.8675)x^2 - 2.35x + 3.34$$

$$Cost = 6.71x^2 - 2.35x + 3.34$$

Min point on graph: x = 0.18, cost = $3.13

The above equation is same as the original cost function.

If MDEA market price changes, the price ratio will change. Referring to Table 9 again, let's use price ratio = 0.94 which is at 60% MDEA price reduction:

$$Cost = (0.94)(2.8675)x^2 - 2.35x + 3.34$$

$$Cost = 2.70x^2 - 2.35x + 3.34$$

Min point on graph: x = 0.44, cost = $2.83

Therefore, the minimum point has shifted from 0.18 to 0.44, indicating that more MDEA can be used because of the price drop. The above steps are repeated for other price ratio and soon we can obtain the minimum cost for each case. This is shown in Table 4.7 at the following page, where the 1^{st} column is the MDEA % price change, followed by the MDEA-DEA price ratio, minimum CO_2 removal cost at that particular price ratio, MDEA mass fraction, and % change in CO_2 removal cost.

MDEA % p. c	p.r	Min Cost	MDEA m.f	% chage in cost
-60%	0.94	2.83	0.44	-9.78%
-40%	1.4	3.00	0.29	-4.41%
-20%	1.87	3.08	0.22	-1.65%
0%	2.34	3.13	0.18	0.00%
20%	2.81	3.17	0.15	1.10%
40%	3.28	3.19	0.12	1.88%
60%	3.75	3.21	0.11	2.47%

Table 4.7: Sensitivity analysis for MDEA price (Model 1)

A graph can plotted based on Table 4.7.

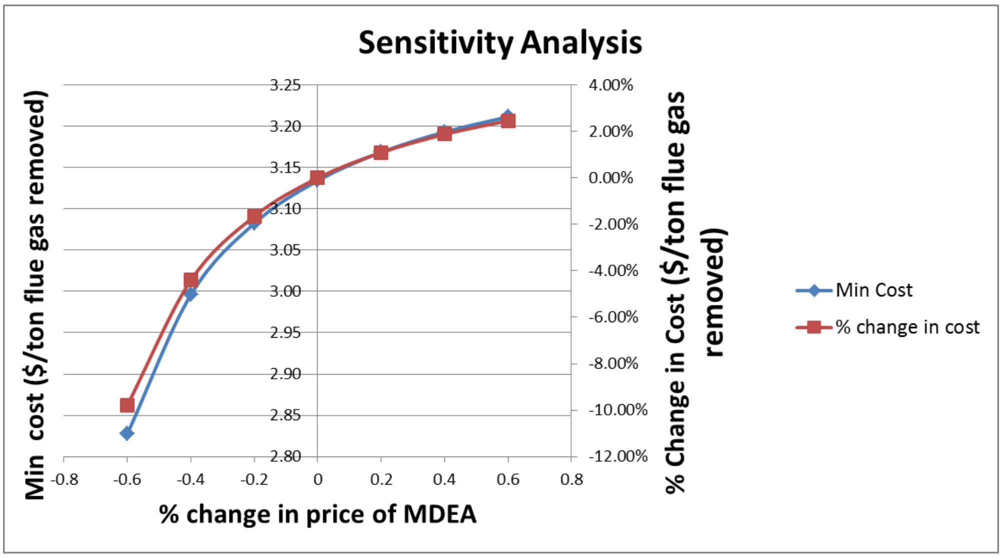


Figure 4.1: Min Cost of CO_2 removal and the % change versus % change in MDEA price (Model 1)

From on Figure 4.1, it is observed that when there is an increase in market price, the cost of CO_2 removal is only slightly affected. A 60% increase in price of MDEA increases the minimum CO_2 removal cost by 4%. On the other hand, if the market price decreases, the cost is observed to fall sharply. A 60% decrease in the price of MDEA decreases the minimum CO_2 removal cost by nearly 10%. These 2 observations are desirable traits in an amine mixture because it has potential for huge savings and is unlikely to be affected much by price hike.

Likewise, knowing all the adjusted cost functions, a graph can be plotted to compare all the cost functions of each price ratio. This is shown in Figure 4.2.

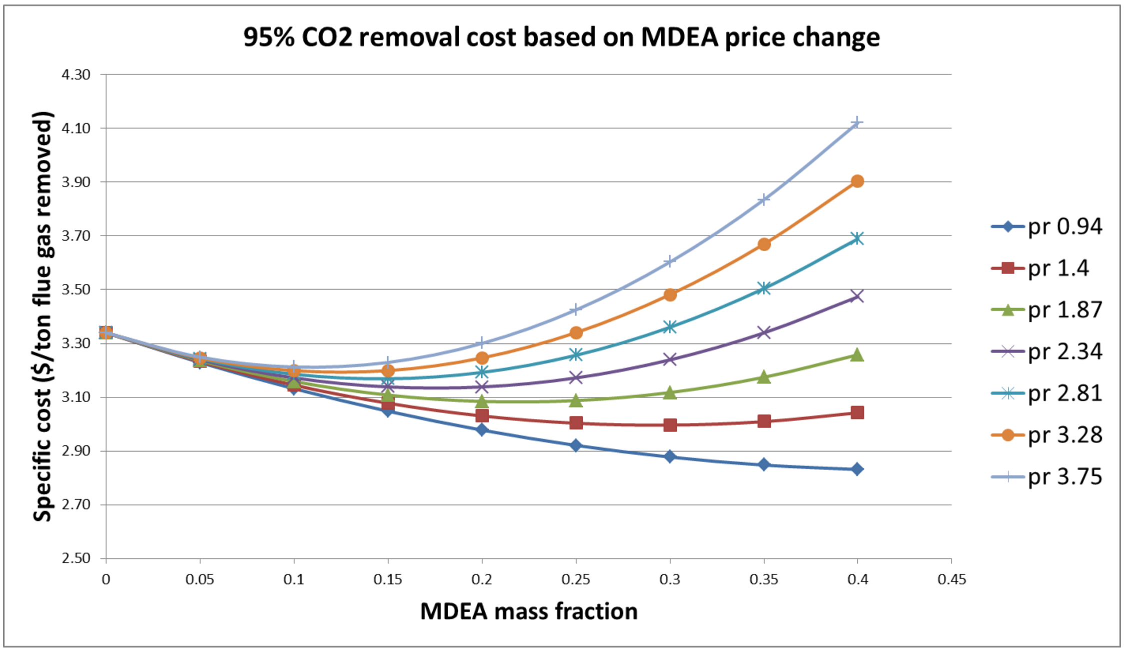


Figure 4.2: Graph of cost functions for MDEA price change (Model 1)

Figure 4.2 shows that while Model 1 does seem to describe the sensitivity behavior quite adequately, it does have its limitations. At x= 0 (no MDEA in mixture), all the cost functions seem to initiate from the same point at cost= $3.34/ton flue gas. This means that if the amine solvent consists purely of DEA, then the cost of CO_2 removal must be $3.34, no matter what the price of DEA. Obviously, this cannot be true. This model is only valid when the price of MDEA price changes and DEA remains fixed. The limitation arises because at x=0, price ratio is cancelled from the equation, leaving only intercept value.

MODEL 2

An almost similar trend can be observed for Model 2:

$$Cost = 6.71x^2 - (5.50)(price\ ratio)x + 3.34$$

The sensitivity analysis is shown in Table 4.8 and Figure 4.3. This model shows that CO_2 removal cost will change by 34.57% when MDEA price decreases by 60% whereas when the MDEA increases by 60%, the removal cost only changes by 4%. This trend is almost similar to Model 1, with the only difference is that the price drops more steeply. This is because in Model 1, the price ratio is multiplied with the MDEA mass fraction to the power of 2, therefore the effect of change is reduced. For Model 2, it is simply multiplied with the mass fraction, therefore any change in price ratio becomes more significant.

MDEA % p.c	p.r	min cost	MDEA m.f	% change cost
-60%	1.07	2.05	0.44	-34.57%
-40%	0.71	2.77	0.29	-11.49%
-20%	0.53	3.02	0.22	-3.46%
0%	0.43	3.13	0.18	0.00%
20%	0.36	3.19	0.15	1.99%
40%	0.31	3.23	0.13	3.20%
60%	0.27	3.26	0.11	4.03%

Table 4.8: Sensitivity analysis for MDEA price (Model 2)

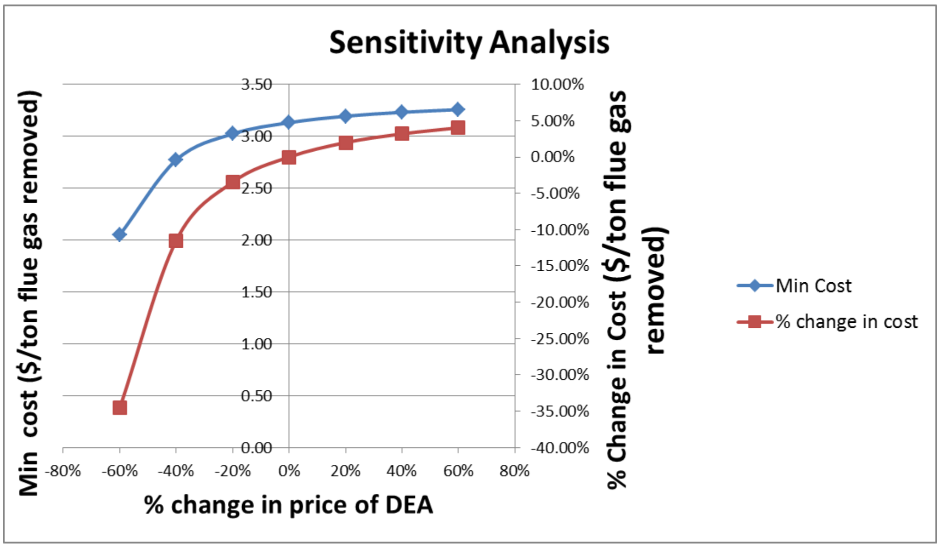


Figure 4.3: Min Cost of CO_2 removal and the % change versus % change in MDEA price (Model 2)

The cost function at each price ratio is also shown in Figure 4.4:

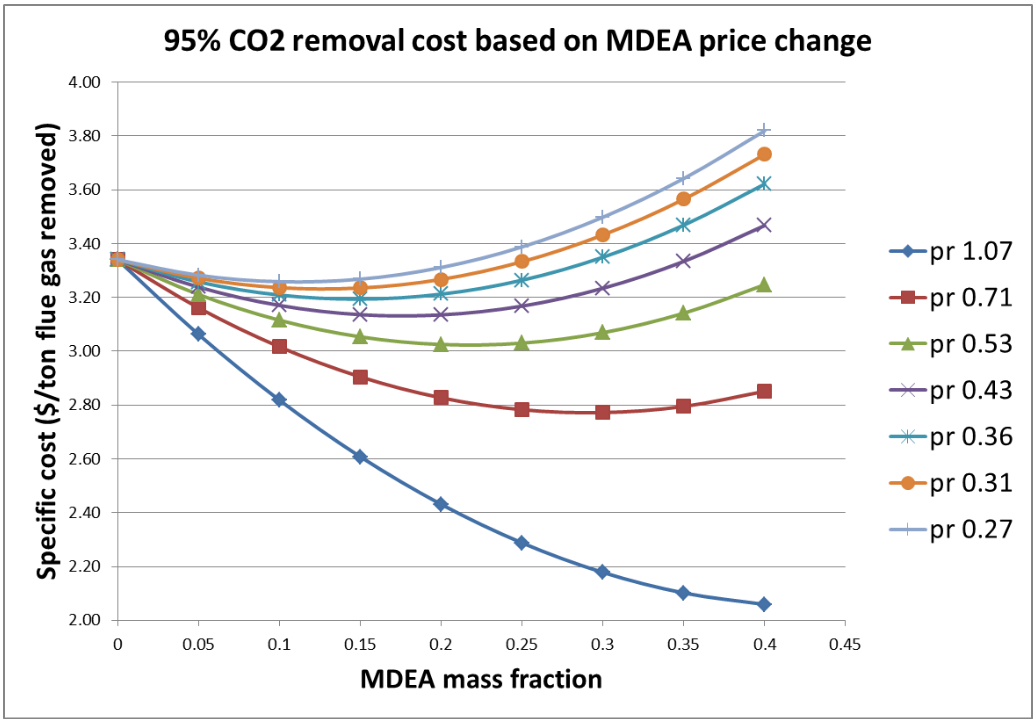


Figure 4.4: Graph of cost functions for MDEA price change (Model 2)

It can be observed that Model 2 from Figure 4.4 also has the same limitations as Model 1. At MDEA mass fraction = 0, the value converge to the intercept value of the cost function.

MODEL 3

For Model 3**:**

$$Cost = 6.71x^2 - 2.35x + price\ ratio(1.43)$$

Figure 4.5 shows the sensitivity analysis for Model 3.

From the sensitivity analysis, the minimum cost changes almost linearly with the change in price in both directions (increase and decrease in prices). When the price of MDEA increases by 60%, the minimum removal cost increases by 64.21%. Likewise, when the price decreases by 60%, the removal cost decreases by 63.76%, which is almost similar. The change is linear because each price ratio is multiplied with a constant value= 1.43.

MDEA % p.c	p.r	min cost	chemical ratio	% change cost
-60%	0.94	1.14	0.18	-63.76%
-40%	1.4	1.79	0.18	-42.81%
-20%	1.87	2.46	0.18	-21.40%
0%	2.34	3.13	0.18	0.00%
20%	2.81	3.80	0.18	21.40%
40%	3.28	4.47	0.18	42.81%
60%	3.75	5.14	0.18	64.21%

Table 4.9: Sensitivity analysis for MDEA price (Model 3)

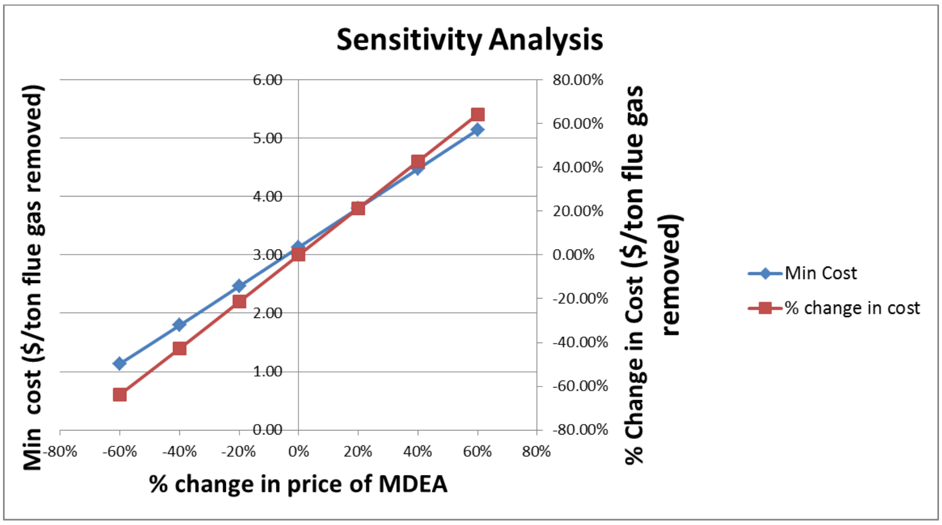


Figure 4.5: Min Cost of CO_2 removal and the % change versus % change in MDEA price (Model 3)

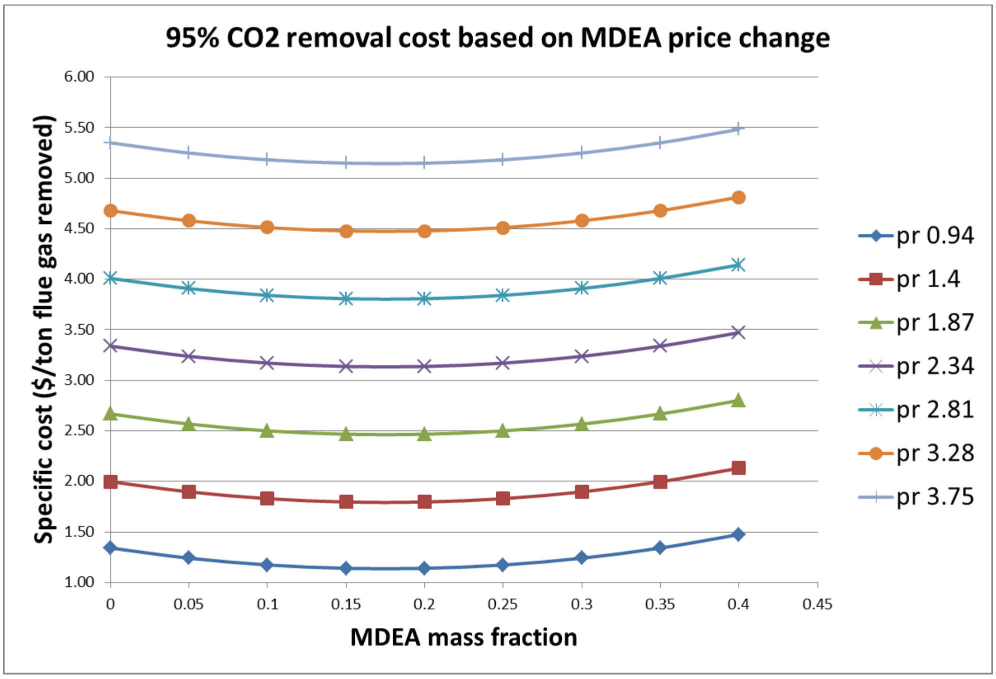


Figure 4.6: Graph of cost functions for MDEA price change (Model 3)

Meanwhile, the cost functions graph shows a tidier trend without the limitations of Model 1 and Model 2. Figure 4.6 shows that the higher price of MDEA (which means higher price ratio of MDEA to DEA), the higher the removal cost, which is sensible. Unfortunately, Model 3 also has its own limitation. For every price ratio, the minimum point is always at x=0.18, no matter how much the price of MDEA changes, which cannot be true. This limitation occurs because price ratio is expressed in the intercept term, therefore only affecting the y-intercept value when the price ratio changes, while "x" remains unaffected.

<u>MODEL 4:</u>

$$Cost = 2.87(price\ ratio)x^2 - 2.35x + price\ ratio(1.43)$$

Model 4 differs from other models because it considers the price ratio to exist in 2 terms of the cost function. The minimum cost at each price ratio is calculated and the sensitivity analysis is plotted in Table 4.10.

MDEA % p.c	p.r	min cost	MDEA m.f	% change cost
-60%	0.94	0.83	0.44	-73.49%
-40%	1.40	1.66	0.29	-47.20%
-20%	1.87	2.42	0.22	-23.05%
0%	2.34	3.14	0.17	0.00%
20%	2.81	3.85	0.15	22.50%
40%	3.28	4.54	0.12	44.68%
60%	3.75	5.23	0.11	66.66%

Table 4.10: Sensitivity analysis for MDEA price (Model 4)

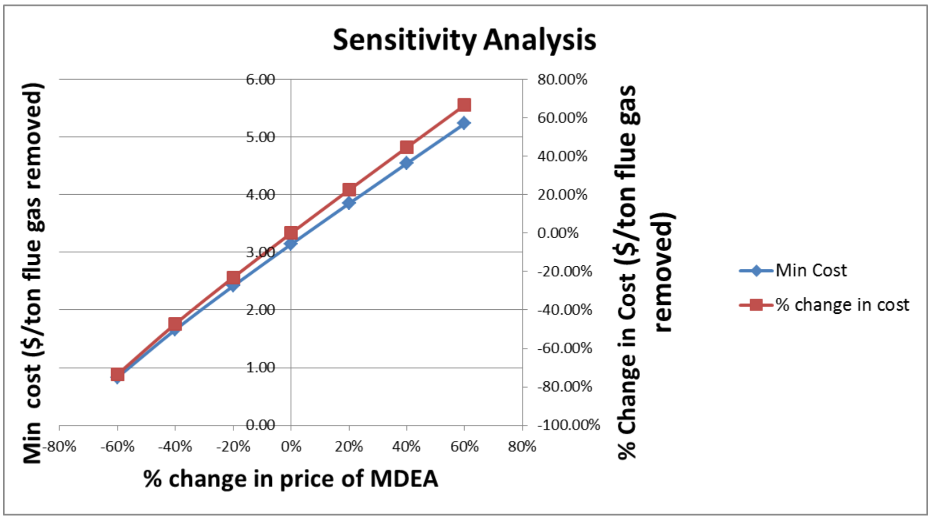


Figure 4.7: Min Cost of CO_2 removal and the % change versus % change in MDEA price (Model 4)

The sensitivity analysis of Model 4 shows that the removal cost of CO_2 is very sensitive towards the change of price of MDEA. A 60% increase in MDEA price can increase the removal cost up to 73.49%, while a 60% decrease will also reduce the cost sharply down to 66.67%. Model 4 show a greater sensitivity compared to the previous models because it has two price ratio factor in the cost model, which means greater change in the whole cost function compared to having only one price ratio factor is the cost function.

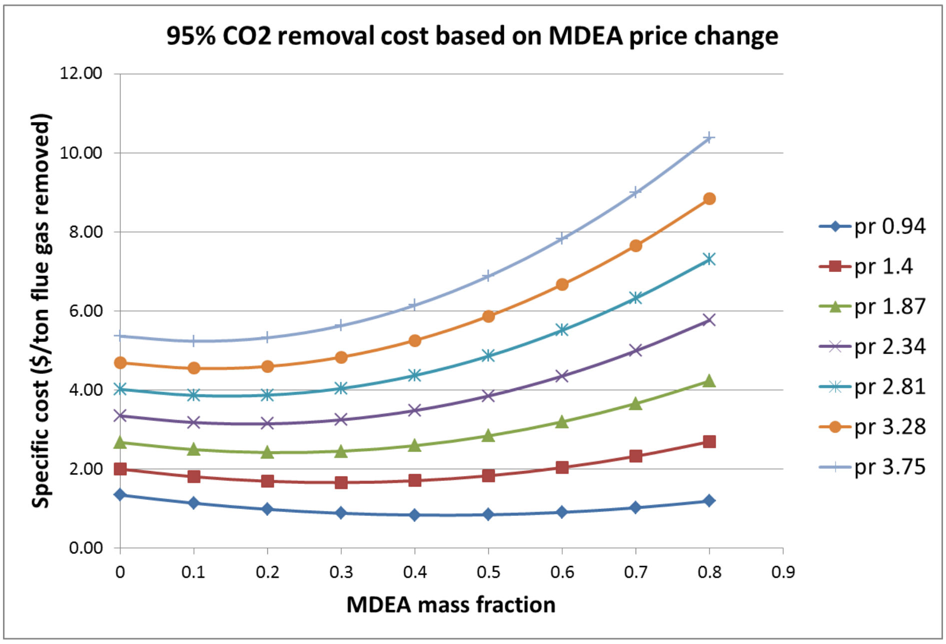


Figure 4.8: Graph of cost functions for MDEA price change (Model 4)

Figure 4.8 shows the cost function at each price ratio for Model 4. It can be seen that by including the price ratio in 2 terms of the cost function, we have successfully overcome the limitations of the previous model. The price ratio at the 1st term will give shift the minimum point for each different price ratio, while the price ratio at the 3rd term (intercept) will give varying minimum CO_2 removal cost at MDEA mass fraction = 0, which remove the limitation that causes all the minimum cost to converge shown in Model 1 and 2.

Analysis of Most Feasible Model

Based on the above justifications, we have decided that Model 4 is the most feasible cost model to represent how the change in market price of amines will affect the CO_2 removal cost. We performed a more in-depth analysis on Model 4, by determining the effect price change of DEA and also derive useful cost information from the cost function graph.

Figure 4.9 shows the minimum CO_2 removal cost and MDEA mass fraction at the minimum removal cost plotted against the price ratio of MDEA and DEA.

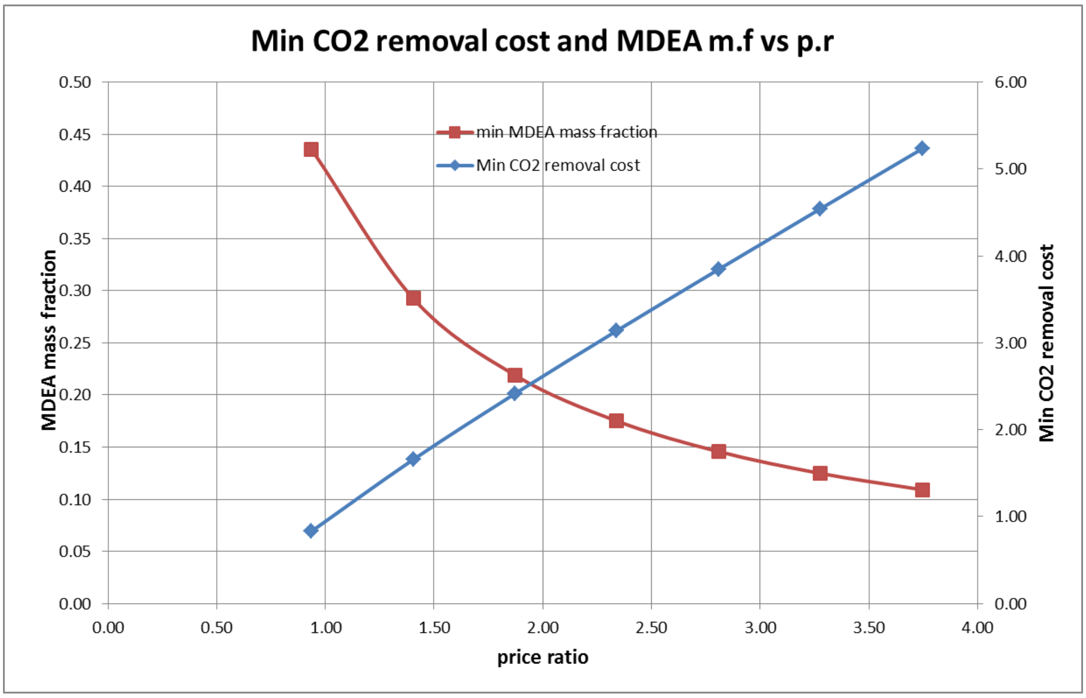


Figure 4.9: Minimum CO_2 removal cost and its MDEA mass fraction versus the price ratio of MDEA-DEA

It is observed that when the price ratio of MDEA-DEA increases, the minimum CO_2 removal cost increases. For example, at the original price ratio of 2.34, it is possible to remove CO_2 at \$3.14 /ton flue gas. But as MDEA becomes more expensive, for instance at a price ratio of 3.50, the only minimum possible cost to remove CO_2 is now \$4.80/ton flue gas based on the chart. On the other hand, the MDEA mass fraction to be used to achieve the minimum cost decreases. The two trends show that it is recommended to use less MDEA mass fraction when the MDEA price increases, because using it in excess will increase the CO_2 removal cost.

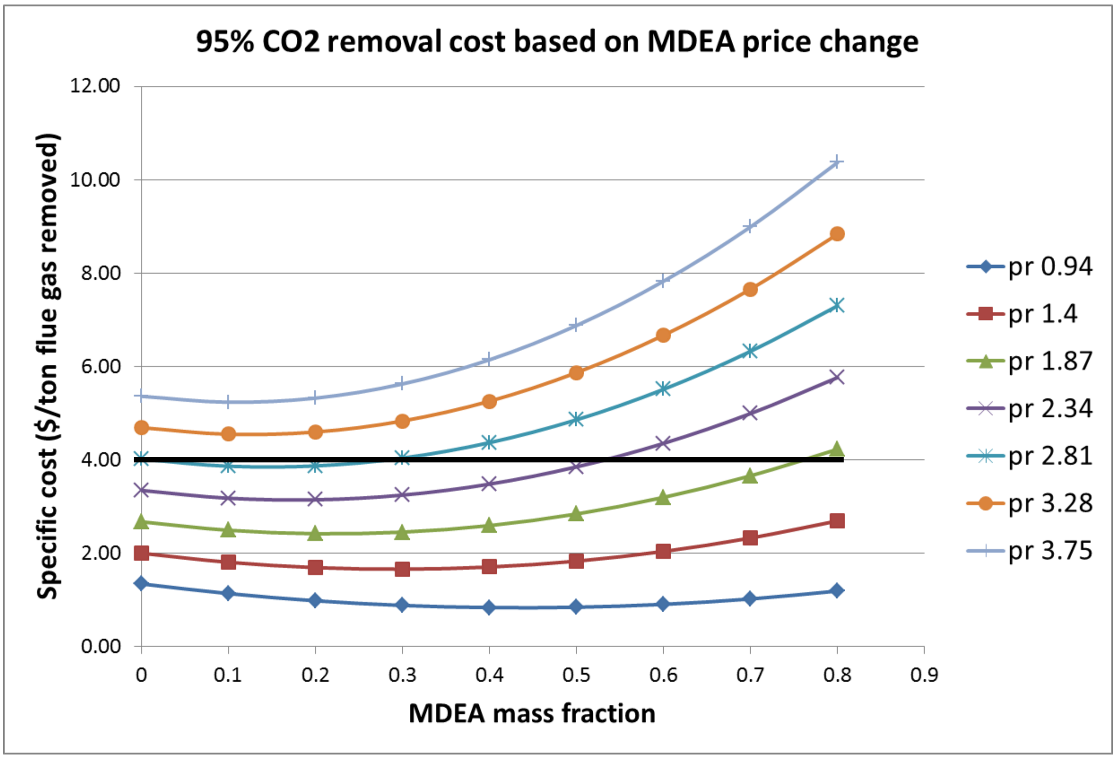


Figure 4.10: *Intersected cost function at removal cost of \$4/ton flu gas*

From Figure 4.10, using the cost function graph, we can also derive some useful information about the recommended amine usage and its cost. For example, if a plant wishes to maintain its CO_2 removal cost below \$4.00/ton flue gas, Figure 4.10 shows that the highest possible price ratio limit to maintain the cost at \$4 is 2.81. Beyond that, the cost will exceed \$4 no matter what fraction of MDEA is used. By drawing a line at y-axis = \$4.00, we can see that there is also a limit on the 3 price ratio of 2.81, 2.34, and 1.87. At price ratio 2.81, using an MDEA mass fraction of more than 0.3 will cause the cost to exceed \$4.00. Naturally, for price ratio of 1.87, because MDEA is cheaper, the MDEA mass fraction limit to use can be higher. In this case, we can use up to 0.76 MDEA mass fraction before the cost exceeds $4.00. But due to the constraint of maximum 40% MDEA as mentioned in our project objectives and scope, the line only intersects at price ratio of 2.81. The MDEA mass fraction is limited to 0.3.

<u>DEA price change</u>

Previous analysis focused on the price change of MDEA and its effect on the CO_2 removal cost. For Model 4 to be feasible, it must also take into account the price of DEA. Table 4.11 shows the price change of DEA and its effect on the MDEA-DEA price ratio.

Change in DEA price		DEA price	
% change		$/kg	price ratio (MDEA to DEA)
-60%	0.4	0.53	5.85
-50%	0.5	0.66	4.68
-40%	0.6	0.79	3.90
-30%	0.7	0.92	3.34
-20%	0.8	1.06	2.93
-10%	0.9	1.19	2.60
0%	1	1.32	2.34
10%	1.1	1.45	2.13
20%	1.2	1.58	1.95
30%	1.3	1.72	1.80
40%	1.4	1.85	1.67
50%	1.5	1.98	1.56
60%	1.6	2.11	1.46

Table 4.11 Changes in price of DEA and its effect on the price ratio. (MDEA=$3.09)

The sensitivity analysis is conducted and the results are shown in the Table 4.12:

DEA % p.c	p.r	min cost	MDEA m.f	% change cost
-60%	5.85	8.27	0.07	163.79%
-40%	3.90	5.44	0.11	73.67%
-20%	2.93	4.01	0.14	27.95%
0%	2.34	3.13	0.18	0.00%
20%	1.95	2.54	0.21	-19.07%
40%	1.67	2.10	0.25	-33.07%
60%	1.46	1.76	0.28	-43.90%

Table 4.12: Sensitivity analysis for DEA price (Model 4)

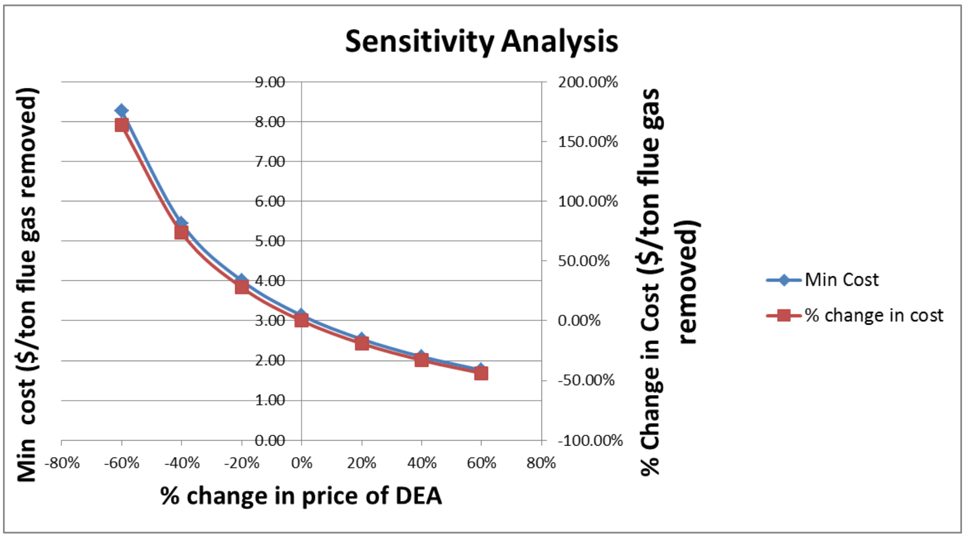


Figure 4.11: Min Cost of CO_2 removal and the % change versus % change in DEA price (Model 4)

Figure 4.11 shows that when an increase in DEA price actually decreases the CO_2 removal cost and vice versa. This seems counter-intuitive, but using a high amount of DEA increases the duty of the reboiler and condenser in the regeneration prcoess, therefore inflating the cost. Hence, when DEA price increases, MDEA mass fraction to be used increases, when means less DEA used since they complement each other to make up 40% amine, and therefore this translates to lower removal cost. The sensitivity analysis shows that the CO_2 removal cost is very sensitive towards DEA price change, reaching a 164% increase for a 60% reduction in DEA price, which is more than double the original removal cost.

Figure 4.12 below shows the cost function at each price ratio for DEA price change. The CO_2 removal cost can go up to $8.27/ton flue gas at a price ratio of 5.85 (60% price reduction of DEA), and the MDEA mass fraction and minimum cost is 0.07, which mean (0.40 – 0.07 = 0.33 DEA mass fraction). This proves that although DEA may be a lot cheaper than MDEA, it is very energy intensive and requires a huge operating cost if used in high amount.

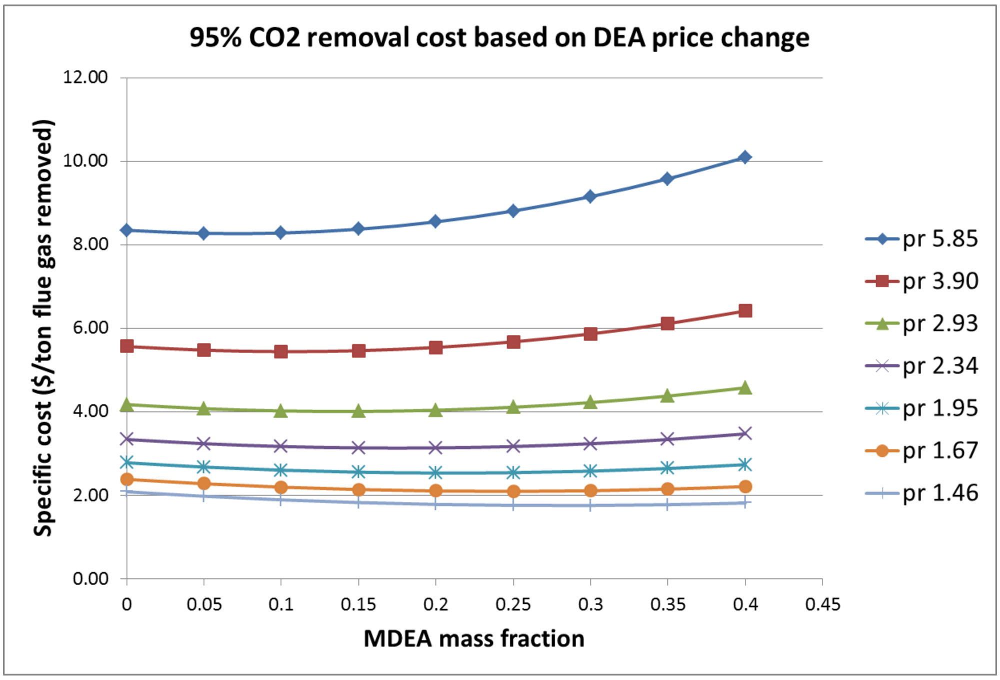


Figure 4.12: Graph of cost functions for DEA price change (Model 4)

CHAPTER 5:

CONCLUSION AND RECOMMENDATION

In conclusion, we have successfully fit the price ratio of MDEA-DEA into an original cost function and developed a few cost models based on the price ratio to describe how changes in market price of amine will affect the CO_2 removal cost. Initially, the original cost function is validated using HYSYS, which does not successfully replicate the cost function but nevertheless able to prove that a trade-off exists in using MDEA and DEA mixture. Total amine cost increases when MDEA is used in higher mass fraction while total energy cost increases when DEA is used in higher mass fraction. We proceed to the price ratio fitting, where 4 models are developed based on the original cost function. Model 1 and Model 2 suffered from a limitation that causes the cost at each price ratio to converge to one value at MDEA mass fraction = 0. Meanwhile, Model 3 has the same MDEA mass fraction at every minimum CO_2 removal cost. Model 4 that considers the price ratio on two terms seems to be the most feasible model so far by eliminating the limitations of Model 1, 2, and 3. Using the fitted models, we also investigate the sensitivity analysis of the price change. Based on Model 4, the cost of CO_2 removal is very sensitive to amine price change, reaching a value of 73.5% for MDEA and 164% for DEA by a 60% increase in price. By analyzing the graph of cost function at each price ratio, we managed to interpret useful information for economic decisions. Thus, we have achieved all our objectives in this project.

Nevertheless, there can still be recommendations for room of improvements. Detailed analysis of the cost function must be conducted to determine what exactly makes up the component of the cost function. Only then we can incorporate the price ratio more accurately and realistically into the cost models. The parameters must also be investigated thoroughly for HYSYS simulation to avoid oversimplification. Model 4 should also validated since it shows the most promising and feasible trend. These are some of the future work to be looked into to develop a more practical and accurate cost model.

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