Optimization of CO$_2$ Capture Process with Aqueous Amines Using Response Surface Methodology

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ABSTRACT

Amine is one of candidate solvents that can be used for CO$_2$ recovery from the flue gas by conventional chemical absorption/desorption process. In this work, we analyzed the impact of different amine absorbents and their concentrations, the absorber and stripper column heights and the operating conditions on the cost of CO$_2$ recovery plant for post-combustion CO$_2$ removal. For each amine solvent, the optimum number of stages for the absorber and stripper columns, and the optimum absorbent concentration, i.e., the ones that give the minimum cost for CO$_2$ removed, is determined by response surface optimization. Our results suggest that CO$_2$ recovery with 48 wt% DGA requires the lowest CO$_2$ removal cost of $43.06/\text{ton of CO}_2$ with the following design and operating conditions: a 20-stage absorber column and a 7-stage stripper column, 26 m$^3$/hr of solvent circulation rate, 1903 kW of reboiler duty, and 99°C as the regenerator-inlet temperature.

Keywords: CO$_2$ capture, Amines, Optimization, CO$_2$ removal cost, Response surface methodology

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1. Introduction

Chemical absorption is known as one of the most reliable processes for CO$_2$ recovery from flue gas in post-combustion (Singh et al., 2009). This process is suitable for flue gas with low CO$_2$ concentrations (Mofarahi et al., 2008). During the process, the gas reacts with the solvent via an exothermic reaction in the contactor to form organic compounds (Zare Aliabad, 2009). The most widely used aqueous solvents are alkanolamine (Rinker et al., 2000), of which the primary amines, monoethanolamine (MEA) and diglycolamine (DGA), the secondary amines, diethanolamine (DEA) and diisopropanolamine (DIPA), and the tertiary amines, methyldiethanolamine (MDEA) and triethanolamine (TEA), are the ones that can be used for CO$_2$ removal (Mcketta Jr; Rinker et al., 2000).

There are three main differences in the performances of primary and secondary amines when compared to tertiary amines for the CO$_2$ absorption/desorption process. Primary and secondary amines are very reactive; they form a carbamate by direct reaction with CO$_2$ (Reaction1) and form a bicarbonate ion via hydrolysis. On the other hand, tertiary amines can only form a bicarbonate ion and protonated amine via hydrolysis (Reaction 2) due to their lack of the necessary N-H bond (Rinker et al., 2000). Hydrolysis is slower than the direct reaction. Therefore tertiary amines have low CO$_2$ absorption rates (Rinker et al., 2000).

Primary and secondary amines:

$$\text{CO}_2 + R_1R_2NH \rightleftharpoons R_1R_2NH^+\text{CO}_2^- \text{carbamate} \quad - - - (1)$$

Tertiary amines:

$$\text{CO}_2 + R_1R_2R_3N + \text{H}_2\text{O} \rightleftharpoons R_1R_2R_3N^+ + \text{HCO}_3^- \text{bicarbonate ion} \quad - - - (2)$$

It was suggested that the absorption rate of tertiary amines (MDEA, TEA) can be improved by the addition of a small amount of primary or secondary amines (MEA, DEA) to form a mixture solvent (Abedini et al., 2010; Rangwala et al., 1992; Rivera-Tinoco & Bouallou, 2010). The second difference is the amount of energy necessary for solvent regeneration: primary and secondary amines require high amounts of energy for solvent
regeneration compared to tertiary amines. Last but not least, CO₂ loading capacities of primary and secondary amines, maximum 0.5 mol of CO₂/ mol of amine since they require 2 moles of amine to react with each mol of CO₂, are lower compared to tertiary amines' CO₂ loading capacity, which is close to 1.0 mol of CO₂/ mol of amine (Idem et al., 2005; Rinker et al., 2000).

Currently, the cost of amine-based absorption of CO₂ is relatively high due to high heat duty requirements for the solvent regeneration (Idem et al., 2005; Mofarahi et al., 2008). Given this concern, most of the literature focuses on improving the design of amine absorption/desorption processes and their operating conditions to reduce its cost. For example, Chang and Shih (2005) optimized the design of CO₂ absorption/desorption process which utilizes MEA and DGA/MDEA mixture for CO₂ recovery from coal-fired and natural gas-fired plants flue gases. They compared three different designs: conventional absorption/desorption design, conventional design modified with an absorber intercooler, and a split-flow design. According to their analysis, the cost of CO₂ recovery was reduced 10% with the addition of the intercooler and 26% with the split-flow scheme compared to the removal costs using the conventional design. The cost for the integration of CO₂ capture units into the existing power plants using MEA was estimated by Romeo et al. (2008) for different designs. They considered the addition of a natural gas auxiliary boiler, power plant internal flow streams, and natural gas auxiliary turbine to the CO₂ capture unit to supply energy to the process and to reduce capture cost. They concluded that adding a gas turbine is the optimum design that minimizes the capture cost by reducing the electricity costs (Romeo et al., 2008). Aroonwilas et al. (2007) worked on the integration of CO₂ capture units into the existing coal-fired power plants. Aqueous MEA and blended MEA-MDEA solvents were used both in conventional flow and split flow design schemes. They concluded that CO₂ capture processes using blended amines as solvents with a split flow configuration require less energy. Bernier et al. (2010) developed a multi-objective optimization approach to studying a natural gas combined cycle power plant with CO₂ recovery process using MEA absorption. The objectives were to minimize the cost of electricity and the amount of CO₂ emissions. They suggested increasing absorber cross sectional area and operating close to atmospheric pressures. Bullin et al. (1981) developed a simulation program of amine sweetening plants based on the tray by tray calculations for stripper column. This program was used to study the effects of stripper column stages on the stripping stream rate at the boiler and the circulation rate which are related to the equipment size. They concluded that simulations such as the one developed by the authors should be used to reduce both the capital and the operating costs for amine plants. Halim and Srinivasan (2009) presented a simulation-optimization framework using a jumping gene based multi-objective simulated annealing technique to minimize cost of CO₂ absorption/desorption process. The framework was used to evaluate the CO₂ removal efficiency from the flue gas off of a gas power plant using DEA as the solvent. The trade-off surface of the CO₂ capture efficiency and operating cost was explored. It was reported that the cost would be between $52 and $68 per ton removed CO₂ for 80 - 93% recovery.

A few studies in the literature compared the cost of CO₂ removal using different amine solvents. Chakma et al. (1995) examined the effects of inlet gas composition, feed gas pressure, reboiler energy inputs, and the number of absorber and stripper trays on the cost of CO₂ removal using the following amine solvents: MEA, DEA, DIPA, DGA, MDEA and TEA. The aim was to separate the CO₂ from power plant flue gas with the requirement of minimum 95% CO₂ removal. The results showed that 20 and 30 wt% MEA resulted in the lowest cost of $54.2 and $46.2 per ton CO₂ removed, respectively. Both designs had 15 absorber trays. However, this study did not consider the possible impact of solvent concentrations on the cost. M. Mofarahi et al. (2008) studied the process of CO₂ recovery from flue gas at the atmospheric pressure at various operating conditions: solvent concentration, solvent circulation rate, reboiler and condenser duty, and design parameters: the number of stages in absorber and stripper columns. Aqueous solvents considered in the analysis were DEA, DGA, MDEA, and MEA. The results showed that utilizing DGA as the solvent required the lowest circulation rate and energy consumption in the regenerator at the same operating conditions. This study did not calculate the cost of the CO₂ removal. Although, the cost of CO₂ removal is dependent on the circulation rate and the energy consumption of the regenerator, they are not the only parameters that impact it. In order to obtain the process which will yield the minimum cost of CO₂ removal, all of the design parameters as well as the operating conditions should be considered simultaneously. While many studies exist that examined the impact of several
design parameters and operating conditions on the cost of CO\textsubscript{2} removal, a systematic comparison of the minimum CO\textsubscript{2} removal costs of various amine solvents, both single and blended, is needed to assess the true potential of this technology.

In this paper, a simulation - optimization framework that combines a process simulator with surface response methodology is developed to minimize the cost of CO\textsubscript{2} removal for the amine-based absorption/desorption process. Using this framework, the impact of different amine absorbents and their concentrations on the cost of post-combustion CO\textsubscript{2} removal is analyzed. We used both single and blended aqueous amines in our analysis. The primary amines MEA and DGA, the secondary amine DEA, and the tertiary amines MDEA and TEA were studied as single amines. The mixtures of MEA-MDEA, MEA-TEA, DEA-MDEA and DEA-TEA were studied as blended amines. For each solvent, the parameters considered in the optimization were the number of stages for the absorber and stripper columns, the concentration of the absorbent, the solvent circulation rate, the reboiler duty, and the stripper-inlet temperature.

The details of the framework, the process simulation and the optimization, are introduced in the next section. This is followed by the results and the discussion. Finally, the last section provides conclusions and future directions.

2. Simulation-Optimization Framework

The developed framework combines the process simulation of the amine-based absorption/desorption with the response surface methodology to minimize the cost of CO\textsubscript{2} removal given the feed specifications, the absorbent and the CO\textsubscript{2} purity of the product. In this approach, an optimization module, which searches the decision space systematically utilizing response surface methodology, was implemented in Microsoft Excel Visual Basic for Applications (VBA). The optimization module was coupled with the simulation model developed in Aspen HYSYS. The simulation evaluates the objective function corresponding to the decision variables passed by the optimization module. At the termination of the framework, the number of stages for the absorber and stripper columns, the concentration of the absorbent, the solvent circulation rate, the reboiler duty, and the stripper feed temperature along with the CO\textsubscript{2} removal cost are determined. In what follows, we explain the details of the process simulation and the optimization algorithm.

2.1 Process simulation

In this work, 1365 kg mole/h of gas turbine flue gases at a pressure of 1.1 bar and a temperature of 40°C (Mofarahi et al., 2008) was processed in a conventional amine-based absorption plant for CO\textsubscript{2} recovery. Table 1 summarizes the composition of the flue gases. A schematic diagram of the CO\textsubscript{2} capture plant for the flue gas cleaning is given in Figure 1. The simulation is developed using Aspen HYSYS Version 7.1. The amines property package is used as the thermodynamic model. Li-Mather electrolyte model is selected as the equilibrium model because it gives more reliable results than empirical models, and it is also more suitable for blended amines. A 96 mole% CO\textsubscript{2} purity at the product stream ("CO2 Product" in Figure 1) is specified for all simulations.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>2.44</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>7.28</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>17.00</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>73.28</td>
</tr>
</tbody>
</table>

The sour gas at a slightly higher than the atmospheric pressure is feed to the absorber. The gas flows counter-current to the lean amine solvent. The acid gases are absorbed by the solvent and the sweet gas leaves the column from the top. The rich amine is sent to the pump and then heated through lean/rich amine heat
exchanger. The rich amine is stripped off of its CO$_2$ in the regenerator at a low pressure. The sour gas and some water leave the regenerator through an overhead condenser. The lean amine leaving the bottom of the regenerator passes through the lean/rich amine heat exchanger and mixes with the make-up water and make-up amine. The lean amine is further cooled at a second heat exchanger by cooling water, and then sent back to the absorber.

Figure 1: A schematic diagram of the conventional CO$_2$ capture plant.

It has been shown that there is no cost benefit of operating the absorber at high pressures (Chakma et al., 1995). Therefore, in this work it is assumed that the absorber operates at slightly higher than the atmospheric pressure which is the same as flue gas feed pressure of 1.1 bars. The pressure drops in all equipments and the pipelines are neglected. The pressure of the stripper is fixed at 1.9 bars in order to keep reboiler temperature below 122 °C to avoid the degradation of the amine solvent and to avoid the corrosion in the stripper and the reboiler (Chakma et al., 1995; Romeo et al., 2008).

2.2. Economic evaluation

An economic analysis, including both capital and operating costs, is performed to calculate the CO$_2$ removal cost of the capture process. The analysis involves all major equipment (excluding pumps and piping) costs, utilities cost, and cash flow analysis. The capital cost is estimated using the equations and the data from the capital equipment-costing program (CAPCOST) (Richard Turton, 2003). The data of the purchased cost of equipment are obtained in 2001 (Richard Turton, 2003), and adjusted for inflation by using the values of the Chemical Engineering Plant Cost Index, CEPCI, which was (397) in 2001 and (575.4) in 2008 (Deng & Hägg, 2010).

Assumptions used in the economic analysis are:

- The plant is expected to have a 20 year plant life with no salvage value.
- The CO$_2$ capture plant is an addition to an existing plant.
- The plant operates for 8400 hours 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 15% of the maintenance and repair costs.
- The local taxes and insurance are 4% of the fixed capital investment.
- Each operation slot requires five operators, and the salary per operator is $40,000 a year plus $40,000 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 administrative expenses inflate 3% per year.
- The minimum acceptable rate of return, MARR, is 10%.
- The annual percentage rate of depreciation is for a 7-year recovery period asset using the Modified Accelerated Cost Recovery System (MACRS) method (Max S. Peters, 2003).
- The cost of cooling water, make-up water, saturated steam at 300 kPa, and electricity are $0.05/m$^3$, $0.30/m^3$, $3.00/1000$ kg, $0.07/kW h$, respectively (Max S. Peters, 2003).
- The cost of each make-up amine can be found in Table 2 (Kohl & Nielsen, 1997).

<table>
<thead>
<tr>
<th>Amine solvent</th>
<th>Approximate cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>1.30</td>
</tr>
<tr>
<td>DGA</td>
<td>2.05</td>
</tr>
<tr>
<td>DEA</td>
<td>1.32</td>
</tr>
<tr>
<td>MDEA</td>
<td>3.09</td>
</tr>
<tr>
<td>TEA</td>
<td>1.34</td>
</tr>
</tbody>
</table>

### 2.3 Optimization via Response Surface Methodology

In this paper, the amine based absorber process for CO$_2$ removal using single and blended amines as absorbents is optimized by response surface methodology. The decision variables are the number of stages for the absorber and stripper columns, the concentration of absorbent, the solvent circulation rate, the reboiler duty, and the stripper inlet-temperature. The objective is to minimize CO$_2$ capture cost ($/ton CO$_2$ removal). Response surface methodologies (RSM) utilize the local first- or second-order regression models of the objective function to guide the optimization search by providing a decent direction for the objective function (Montgomery, 2001). The optimization algorithm used in this study utilizes RSM and its details are given in Figure 2. The algorithm is implemented in Microsoft Excel Visual Based for Applications and communicates with the simulation (in Aspen HYSYS) using HYSYS’s automation procedures.

The algorithm includes two main steps. In the first step, the process simulation is run using a full factorial experimental design of the decision variables (a $2^6$ factorial design) and the cost for each run is calculated. The first set of data are set up following the typical operating conditions given in the literature (Aspentech, 2005; Bernier et al., 2010; Freguia & Rochelle, 2003; Mofarahi et al., 2008; Singh et al., 2009; Srinivasan, 2009). The center points of the first data set for each amine solvent are shown in Table 3. The initial concentration of each amine solvent is estimated from the typical ranges of amine concentrations used in the literature (Aspentech, 2005; Mofarahi et al., 2008). The number of absorber stages is set based on the commonly used values in the literature (Srinivasan, 2009; Bernier et al., 2010). The number of stripper stages is assumed to be equal to the number of absorber stages. The solvent circulation rates are estimated according to the finding of Mofarahi et al. (2008). Due to the lack of TEA property data, it is assumed that it exhibits the same properties as MDEA since they are both tertiary amines. The reboiler duty is calculated based on the information of typical duties per gallon of solvent circulation rate (Table 4) obtained from HYSYS manual (Aspentech, 2005). For blended amines, the reboiler duties of the primary or secondary amines are assumed to be the dominant ones. The regenerator-inlet temperature range is 90 °C to 120 °C (Freguia & Rochelle, 2003; Singh et al., 2009).
Prior to regression analysis, the decision variables ($x_i$) are coded to the interval of (-1, 1), which are called coded variables. If $\xi_i$ denotes the natural variable, the relationship between the coded variables and the natural variables are represented by Equation 1.

$$x_i = \frac{\xi_i - \xi_i^0}{\Delta \xi_i} \quad \text{for } i = 1, 2, ..., n \text{ factors}$$ (1)
where $\xi^0_i$ is the natural variable in the center of the domain and $\Delta \xi_i$ is the variation of the natural variable associated to a variation of one unit of the coded variable. It is calculated as $\Delta \xi_i = (\xi^{max}_i - \xi^{min}_i)/2$ (Adamczyk et al., 2008; Montgomery, 2001). The maximum and minimum values of the discrete variables are selected to ensure that the corresponding coded variables used for the $2^6$ factorial design and Box-Behnken design are integer values. Then, the regression analysis is utilized to identify the significant factors that contribute to the CO$_2$ recovery cost.

Table 3: The center points of the initial data set for each amine solvent

<table>
<thead>
<tr>
<th>Amine Conc. (%wt)</th>
<th>Absorber (stages)</th>
<th>Stripper (stages)</th>
<th>Circulation Rate (m$^3$/hr)</th>
<th>Reboiler Duty (kW)</th>
<th>Regenerato r-inlet Temp. (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1˚ or 2˚</td>
<td>3˚</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEA</td>
<td>22</td>
<td>10</td>
<td>10</td>
<td>47</td>
<td>5038</td>
</tr>
<tr>
<td>DGA</td>
<td>60</td>
<td>10</td>
<td>10</td>
<td>31</td>
<td>3925</td>
</tr>
<tr>
<td>DEA</td>
<td>30</td>
<td>10</td>
<td>10</td>
<td>25</td>
<td>2554</td>
</tr>
<tr>
<td>MDEA</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>43</td>
<td>3158</td>
</tr>
<tr>
<td>TEA</td>
<td>-</td>
<td>10</td>
<td>10</td>
<td>43</td>
<td>3158</td>
</tr>
<tr>
<td>Blended MEA - MDEA</td>
<td>20</td>
<td>10</td>
<td>10</td>
<td>47</td>
<td>5038</td>
</tr>
<tr>
<td>Blended MEA - TEA</td>
<td>22</td>
<td>10</td>
<td>10</td>
<td>47</td>
<td>5038</td>
</tr>
<tr>
<td>Blended DEA MDEA</td>
<td>22</td>
<td>10</td>
<td>10</td>
<td>47</td>
<td>3628</td>
</tr>
<tr>
<td>Blended DEA TEA</td>
<td>22</td>
<td>10</td>
<td>10</td>
<td>47</td>
<td>3628</td>
</tr>
</tbody>
</table>

Table 4: Typical duties per gallon of amine solvent

<table>
<thead>
<tr>
<th>Amines</th>
<th>Duty, BTU/US Gallon</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>1200</td>
</tr>
<tr>
<td>DGA</td>
<td>1300</td>
</tr>
<tr>
<td>DEA</td>
<td>1000</td>
</tr>
<tr>
<td>MDEA, TEA</td>
<td>800</td>
</tr>
</tbody>
</table>

In the second step, the process simulation is run according to the Box-Behnken Design (BBD) of the significant variables. The BBD is a class of rotatable or nearly rotatable second-order design which prevents extreme condition experiments since it does not contain the conditions where all factors are at their highest or lowest levels (Ferreira et al., 2007). The outputs of the BBD combined with the full factorial design simulations are used to obtain the first and second order response polyhedrons using all significant variables. One pitfall of using RSM with deterministic simulations is the lack of variation in the results of the replication experiments at the center point; therefore the system does not include a pure experimental error variance to facilitate the switch between the first and the second order models. Instead, we utilized the R-squared and adjusted R-squared statistics in order to assess the fitness of the first and second order response models to the data gathered from the simulation. R-squared statistics (the coefficient of determination) measures how well the regression line fits the data (Amir D. Aczel, 2009). If R-squared statistics is less than 0.5 for the first-order model, the fitness of the model is deemed unacceptable (Amir D. Aczel, 2009; Gary Z. Whitten, 1997).

If it is concluded that the fitness of the first-order model to represent the variation in the data set is acceptable, the method of steepest descent is performed to move the system in the direction of maximum decrease in the objective function. If the first-order model is adequate to represent the effect of decision variables on the objective, this indicates that there is either little or no curvature effect on the objective function, i.e., the
function is monotonically increasing or decreasing with changes in each of the decision variables, therefore the system is still far from the optimum point. Given the fitted first-order model (Equation 2) the step size along the path of steepest descent used is $\Delta x_i = \frac{\beta_i}{\beta_i/\Delta x_j}$ where $\beta_i$ is the largest absolute regression coefficient. The step size is reduced by half until it yielded a reduction in the objective function. Once the lowest cost is reached with the steepest descent, the procedure is repeated using the conditions corresponding to the lowest cost as the center point of the new full factorial design.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i$$

(2)

On the other hand, if it is found that the data set cannot be represented accurately with the first order model according to R-squared statistic, adjusted R-squared statistic is utilized to confirm that quadratic factors have significant effects in the prediction of the response. Adjusted R-squared statistic identifies if an additional independent factor enhances the predictive ability of a model (Ragsdale, 2008). If adjusted R-squared statistic of the second-order model (Equation 3) is higher than the one obtained for the first-order model, it is concluded that the curvature plays a significant role in the prediction of the response. At this point, we utilize the second-order model to find the local minimum CO$_2$ removal cost and the corresponding design and operating conditions.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \epsilon$$

(3)

The nonlinear programming (NLP) model corresponding to this problem is given by:

**Decision variables:** $x_i$ \quad For $i = 1, 2, ..., n$ factors

**MIN:**

$$\beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j$$

(4)

**Subject to:** $-1 \leq x_i \leq 1$ \quad For $i = 1, 2, ..., n$ factors

**3. Results and discussion**

We analyzed the influence of different amine absorbents and their concentrations, the absorber and stripper column heights, and the operating conditions on the cost of the CO$_2$ recovery plant for post-combustion CO$_2$ capture. The CO$_2$ capture cost in this work is calculated by dividing the net present value by the total amount of CO$_2$ captured throughout the lifetime of the plant operation. This calculation yields $/\text{ton}$ of recovered CO$_2$ averaged over the lifetime of the plant.

The results obtained from the steepest descent, the impact of the operating conditions and design parameters, and the sensitivity analysis are discussed in this section.

**3.1 Steepest descent results**

The steepest descent results for each amine solvent are shown in Figure 3. As expected (Figure 3), the cost decreases following each steepest descent step with a decreasing gradient. For example, the cost of CO$_2$ removal using MEA decreases from the first data set (data set1) to data set 2, and so on.
Figure 3: The steepest decent results of single and blended amines

For MEA (Figure 3), it is found that the number of absorber stages has the highest impact on the CO₂ capture costs in the first descent. The direction is along the path of increase in the number of stages. The cost decreases from an average of $58 to $53 per ton CO₂. The amount of CO₂ recovered increases from an average of 84% to 98% recovery. During the second descent, the concentration of the amine solvent becomes the variable with the highest impact on the cost. The cost goes down as the amine solvent concentration decreases. The cost slightly decreases from an average of $53 to $52 per ton of CO₂. The amount of CO₂ recovered decreases to an average of 91%. The increases in the amine concentration and the solvent circulation rate have the highest impacts during the third steepest descent. The amount of CO₂ recovered increases to an average of 96%. Finally, reboiler duty reduction decreases the costs by reducing the energy consumption during solvent regeneration. The amount of CO₂ recovered decreases to an average of 92% with a decrease in the energy consumption.

In the case of DGA as the solvent (Figure 3), the increase in the absorber stages has the highest impact on cost reduction initially. The cost decreases from an average of $51 to $47 per ton of CO₂. The amount of CO₂ recovered increases from an average of 87% to 98% of the total as absorber height increases. Then, the reboiler duty reduction becomes the most significant factor for decreasing costs in the second steepest descent. The amount of CO₂ recovered decreases slightly to an average of 96%. The reboiler duty continues to decrease as the lean amine circulation rate increases sharply during the third steepest descent. The lean amine circulation rate becomes the most important variable in cost reduction and continues to increase in the fourth steepest descent. The increase in the amount of CO₂ recovered is less than 1%.
The reboiler duty has the highest effect on cost both in the fifth and sixth steepest descent cycles. This is because the reboiler duty is adjusted in conjunction with the circulation rate and the regenerator-inlet temperature for reduced energy consumption in the regenerator. The amount of CO$_2$ removed decreases to an average of 95% with an energy requirement reduction.

For DEA (Figure 3), the increases in both the absorber stages and the circulation rate decrease the CO$_2$ removal cost most in the first steepest descent. The amount of CO$_2$ recovery increases significantly from an average of 49% to 83%. The capture costs decrease from an average of $80 to $50 per ton CO$_2$. Then, the number of absorber stages, the DEA concentration, and the reboiler duty are adjusted for reducing cost in the second steepest descent. The amount of CO$_2$ recovery keeps increasing to an average of 89% of the total. The reboiler duty is the only factor that can be reduced in order to decrease cost during the third and fourth steepest descents. Other factors remain the same.

There are only two steepest descents for the process that uses MDEA as the solvent (Figure 3). The number of absorber stages has the highest effect on the costs in the first steepest descent. The number of absorber stages increases dramatically from 10 to 84 stages. The CO$_2$ removal cost decreases from an average of $366 to $116 per ton of CO$_2$ removal. The CO$_2$ recovery increases from an average of 11% to 51%. This is because tertiary amines have very poor CO$_2$ absorption capabilities and therefore require high absorption column heights for high liquid residence times to contact with the flue gas. In the last steepest descent, the decreases in the reboiler duty and the regenerator-inlet temperature result in energy consumption reduction, which in turn reduces the cost. From this analysis, we can see that the important factors for reducing the cost of CO$_2$ capture processes with MDEA are the number of absorber stages, the reboiler duty, and the regenerator-inlet temperature.

For TEA (Figure 3), there is only one steepest descent. The number of absorber stages increases significantly, similar to the case of the MDEA solvent. This is expected because they are both tertiary amines. The cost decreases from an average of $438 to $225 per ton of CO$_2$. The CO$_2$ recovery increases from an average of 9% to 25% of the total. It can be seen that TEA has very poor CO$_2$ absorption capability. The increase in the lean circulation rate, the reduction of the reboiler duty, and the amine concentration, as well as the regenerator-inlet temperature, have minor effects when compared to the number of the absorber stages. The number of stripper stages exhibits a slight effect on the cost.

For the blended amine solvents, MEA-MDEA (Figure 3), increasing the number of absorber stages has the highest impact on cost reduction in the first steepest descent. This behavior is similar to the case of single amines. The cost decreases from an average of $59 to $53 per ton CO$_2$. The amount of CO$_2$ recovered increases from an average of 86% to 98%. During the next descent, the reduction of MEA concentration and the reboiler duty become important determinants for the cost. The CO$_2$ removed slightly decreases to an average of 94%.

Then, decreasing the reboiler duty while increasing the circulation rate results in cost reduction in the third steepest descent. The CO$_2$ removed increases to an average of 97%. The concentration of MEA and the reboiler duty have a high impact and are reduced in order to decrease cost in the fourth steepest descent. All factors are significant, but move at a much slower pace during the last steepest descent.

For blended MEA-TEA solvent systems (Figure 3), the number of absorber stages has the highest impact on cost in the first steepest descent similar to the single amine solvents. The cost decreases from an average of $59 to $53 per ton CO$_2$. The CO$_2$ recovery amount increases from an average of 86% to 99%. Similar to the blended MEA-MDEA solvent case, reduction of MEA concentration plays the most important role in the cost reduction during the second steepest descent. The amount of CO$_2$ recovered decreases to an average of 94%. Then, all factors are adjusted by half a step size (increasing the circulation rate, the MEA concentration, and the number of absorber stages, and reducing the reboiler duty and the regenerator-inlet temperature) during the third steepest descent in order to reduce recovery cost. The amount of CO$_2$ recovered increases to an average of 97%. The reboiler reduction decreases the cost during the fourth steepest descent. As we get closer to the minimum cost, the step sizes in the steepest descent are reduced. However, all factors contribute to the cost reduction during the fifth and the sixth steepest descents. There is an approximate 1% reduction in the costs from the
fourth steepest descent to the sixth steepest descent. The amount of CO₂ recovered decreases to an average of 93% for the last steepest descent.

There are two steepest descents for the blended DEA-MDEA solvent (Figure 3). Increases in the number of absorber stages and the DEA concentration have the highest impact on the CO₂ removal costs during the first descent. The amount of CO₂ recovered increases from 60% to 95% recovery. The CO₂ capture cost decreases from an average of $71 to $49 per ton CO₂.

Then, reductions in the reboiler duty and regenerator-inlet temperature reduce the CO₂ recovery cost during the second descent. The amount of CO₂ removed decreases slightly to 94% of the total.

For blended DEA-TEA (Figure 3), there are also two steepest descents involved. Like blended DEA-MDEA, increases in the number of absorber stages and DEA concentration have the highest impact during the first steepest descent. The costs decrease from an average of $70 to $48 per ton CO₂. The amount of CO₂ recovered increases from an average of 59% to 96%. Then, the reductions of the reboiler duty and the regenerator-inlet temperature have the highest impact during the second steepest descent. The amount of CO₂ recovered decreases slightly to 94% of the total.

The optimum operating conditions, the design parameters, and the cost of CO₂ capture for each amine solution is summarized in Table 5. According to our results, the process that uses MEA requires the highest reboiler duty. This is one of the disadvantages of MEA, i.e., it requires large amounts of energy for solvent regeneration. The removal costs of processes using tertiary amines alone are high, as expected. This is because tertiary amines have poor CO₂ absorption capabilities, and they require high absorber heights to have enough contact time. In the case of the blended amines, adding small amounts of primary or secondary amines into tertiary amines improves the CO₂ absorption rates of the mixture. This finding agrees with the conclusions of Rangwala et al (1992) and Hagewiesche et al (1995). Although the results show that MEA blends require lower reboiler duties than MEA alone, the CO₂ removal rate is lower compared to the MEA only process as well. Therefore, blended amines do not exhibit cost benefits over primary and secondary amines, but only over tertiary amines. Among the studied solvents, the wt% 48DGA with 96% CO₂ recovery results in the lowest CO₂ capture cost due to its high CO₂ absorption capacity and low energy consumption in regeneration.

Table 5: The optimum operating conditions and CO₂ capture costs for amine-based absorption process. Blended 1, 2, 3, and 4 correspond to MEA-MDEA, MEA-TEA, DEA-MDEA, and DEA-TEA blends, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Circulation Rate (m³/hr)</th>
<th>Amine Conc. (wt%)</th>
<th>Absorber (stages)</th>
<th>Stripper (stages)</th>
<th>Reboiler Duty (kW)</th>
<th>Regenerator-Inlet Temp. (°C)</th>
<th>CO₂ capture costs ($/ton CO₂ recovered)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1˚ or 2˚</td>
<td>3˚</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEA</td>
<td>62</td>
<td>14</td>
<td>-</td>
<td>20</td>
<td>9</td>
<td>3848</td>
<td>91</td>
</tr>
<tr>
<td>DGA</td>
<td>26</td>
<td>48</td>
<td>-</td>
<td>20</td>
<td>7</td>
<td>1903</td>
<td>99</td>
</tr>
<tr>
<td>DEA</td>
<td>33</td>
<td>39</td>
<td>-</td>
<td>32</td>
<td>10</td>
<td>2087</td>
<td>104</td>
</tr>
<tr>
<td>MDEA</td>
<td>57</td>
<td>-</td>
<td>31</td>
<td>84</td>
<td>9</td>
<td>2687</td>
<td>100</td>
</tr>
<tr>
<td>TEA</td>
<td>65</td>
<td>-</td>
<td>31</td>
<td>70</td>
<td>9</td>
<td>2720</td>
<td>99</td>
</tr>
<tr>
<td>Blended 1</td>
<td>59</td>
<td>8</td>
<td>13</td>
<td>24</td>
<td>9</td>
<td>3678</td>
<td>93</td>
</tr>
<tr>
<td>Blended 2</td>
<td>62</td>
<td>12</td>
<td>17</td>
<td>21</td>
<td>9</td>
<td>3681</td>
<td>92</td>
</tr>
<tr>
<td>Blended 3</td>
<td>48</td>
<td>32</td>
<td>22</td>
<td>27</td>
<td>9</td>
<td>2687</td>
<td>98</td>
</tr>
<tr>
<td>Blended 4</td>
<td>47</td>
<td>33</td>
<td>25</td>
<td>27</td>
<td>9</td>
<td>2668</td>
<td>98</td>
</tr>
</tbody>
</table>

3.2 Impact of operating conditions and design parameters

The impacts of operating conditions and design parameters on the CO₂ capture costs for all solvents except MDEA and TEA are shown in Figure 4. The diagrams for MDEA and TEA can be found in Appendices A. This
diagram is provided separately because the CO₂ capture cost of the processes using tertiary amines are very high compared to the cost obtained by primary and secondary amines. The plots represent average costs at the lower, middle, and upper levels of the decision variables for each data set.

3.2.1. The number of absorber stages

The number of absorber stages has a significant impact on the CO₂ capture cost. The cost decreases as the number of absorber stages increases up to around 20 stages for all solvents. The increase in absorber height increases liquid residence time in the column, which increases the CO₂ loading and hence the CO₂ recovery. However, increasing the column height also increases the capital cost and after around 20 stages the increase in the CO₂ recovery is not enough to offset the increases in the capital cost.

3.2.2. Solvent circulation rate

The cost of CO₂ removal goes down as the solvent circulation rate increases for all solvents except DGA. This is because DGA has very high acid gas-carrying capacity, which results in lower circulation rates. In other words, solvents with low carrying capacities require higher circulation rates. The solvent circulation rate impacts both the amount of CO₂ recovered and the capital cost. An increase in the solvent circulation rate
increases the amount of CO$_2$ removed but also contributes to the capital cost, therefore increasing the circulation rate above 50-60 m$^3$/h would not decrease the cost of CO$_2$ removal.

3.2.3. Reboiler duty

The CO$_2$ removal cost decreases as reboiler duty decreases for all absorbents. Decreasing the reboiler duty reduces the energy consumption in the regenerator, which in turn reduces operating costs. It can be seen from Figure 4 that decreasing the reboiler duty below around 2000 kW may increase the CO$_2$ removal cost.

3.2.4. Solvent concentration

For single and blended amines, the cost decreases with decreasing solvent concentration of primary amines (MEA and DGA). For secondary amines, for example for DEA, the cost decreases as the solvent concentration increases. This is because the CO$_2$ absorption capacities of MEA and DGA are better than that of DEA’s. The concentration of tertiary amines has negligible impact on the CO$_2$ capture cost.

3.2.5. The number of stripper stages

The number of stripper stages impacts the cost of CO$_2$ removal much less significantly compared to the number of absorber stages. The cost decreases slightly as the number of stripper stages decreases.

3.2.6. Stripper inlet-temperature

In general, the stripper inlet-temperature slightly affects the CO$_2$ capture cost. The cost tends to decrease as the temperature decreases for all absorbents.

3.3 Preliminary sensitivity analysis

This section presents our preliminary analysis of the effect of amine prices and feed composition fluctuations on the CO$_2$ capture cost. The amine-based absorption using DGA as the solvent was chosen as our case study because it yields the lowest CO$_2$ capture cost among all of the studied solvents. To illustrate the influence of amine price fluctuations, a sensitivity analysis has been performed utilizing five different amine price conditions. Table 6 gives a summary of optimal operating conditions, design parameters and the minimum CO$_2$ capture costs of these amine prices. In Table 6, the base case results are highlighted in bold.

<table>
<thead>
<tr>
<th>DGA Prices ($/kg)</th>
<th>Circulation Rate (m$^3$/hr)</th>
<th>Concentration (wt %)</th>
<th>Absorber (stages)</th>
<th>Stripper (stages)</th>
<th>Reboiler Duty (kW)</th>
<th>Regenerator-Inlet Temp. (°C)</th>
<th>CO$_2$ capture costs ($/ ton CO$_2$ recovered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.82</td>
<td>20</td>
<td>58</td>
<td>18</td>
<td>11</td>
<td>1575</td>
<td>103</td>
<td>41.43 ± 0.03</td>
</tr>
<tr>
<td>1.64</td>
<td>27</td>
<td>52</td>
<td>20</td>
<td>9</td>
<td>1928</td>
<td>98</td>
<td>42.55 ± 0.08</td>
</tr>
<tr>
<td><strong>2.05</strong></td>
<td><strong>26</strong></td>
<td><strong>48</strong></td>
<td><strong>20</strong></td>
<td><strong>7</strong></td>
<td><strong>1903</strong></td>
<td><strong>99</strong></td>
<td><strong>42.67 ± 0.08</strong></td>
</tr>
<tr>
<td>2.87</td>
<td>26</td>
<td>41</td>
<td>22</td>
<td>10</td>
<td>1920</td>
<td>95</td>
<td>43.25 ± 0.04</td>
</tr>
<tr>
<td>4.10</td>
<td>30</td>
<td>43</td>
<td>20</td>
<td>9</td>
<td>2190</td>
<td>99</td>
<td>44.72 ± 0.10</td>
</tr>
</tbody>
</table>

The results show that the minimum CO$_2$ capture cost increases slightly (less than 1%) from $43.06 to $43.32 per ton of CO$_2$ removed when the amine price increases by 40%. With a dramatic twofold increase in the amine prices, the CO$_2$ capture cost increases by only 4.2%. A 20% and 60% decrease in the amine price compared to the base case results in 0.6% and 3.6% decrease in the CO$_2$ removal cost, respectively. Therefore, we can conclude that the cost of CO$_2$ capture is insensitive to fluctuations in amine prices. However, it should be noted that there is a slight increase in the suggested absorber and stripper stages (Table 6). Furthermore, the CO$_2$ capture cost of our base case suggested design was estimated with the five amine prices given in Table 6. The
base case design CO2 capture cost with each amine price was within 2% of the CO2 capture cost of the optimum design suggested for the corresponding amine price.

In the analysis of the influence of feed composition fluctuations on the results, the feed composition of the gas turbine flue gas was varied between 2 and 3% CO2 mole fraction. This is the typical CO2 composition at the exit of the gas turbines as sources of flue gas. The summary of the CO2 capture costs and the optimal operating conditions, and the design parameters for different CO2 compositions are shown in Table 7.

Table 7: The optimum operating conditions and CO2 capture costs for different feed compositions.

<table>
<thead>
<tr>
<th>CO2 mole fraction (mole%)</th>
<th>Circulation Rate (m3/hr)</th>
<th>Concentration (%wt)</th>
<th>Absorber (stages)</th>
<th>Stripper (stages)</th>
<th>Reboiler Duty (kW)</th>
<th>Regenerator-Inlet Temp. (˚C)</th>
<th>CO2 capture costs ($/ ton CO2 recovered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>17</td>
<td>49</td>
<td>21</td>
<td>9</td>
<td>1548</td>
<td>98</td>
<td>NLP 51.32 ± 0.09</td>
</tr>
<tr>
<td>2.44</td>
<td>26</td>
<td>48</td>
<td>20</td>
<td>7</td>
<td>1903</td>
<td>99</td>
<td>HYSYS 42.67 ± 0.08</td>
</tr>
<tr>
<td>3.00</td>
<td>31</td>
<td>50</td>
<td>19</td>
<td>9</td>
<td>2376</td>
<td>98</td>
<td></td>
</tr>
</tbody>
</table>

The results show that the CO2 capture cost shows an inversely almost linear dependency on the CO2 composition of the flue gas (Table 7). The cost increases by 17% as the CO2 composition increases by 22% from 2 mole% to 2.44 mole%. In the case of 50% CO2 mole fraction increase from 2 mole% to 3 mole%, the cost increases by 30%. A close investigation of the suggested operating and design conditions for each CO2 composition (Table 7) shows that the changes in the CO2 composition significantly impacts the amine circulation rate and reboiler duty, however does not change the number of absorber and stripper stages and the rest of the operating conditions significantly. Therefore, based on these preliminary results the process design seems not sensitive to the CO2 composition for the gas turbine flue gas. In general, a higher CO2 mole fraction in the feed results in higher CO2 capture amounts and results in lower capture costs.

4. Conclusion

Amine absorption is preferred for CO2 recovery of flue gas with low CO2 concentration. In this paper, we presented an optimization approach for the amine absorption process. The approach utilized a simulation - optimization framework that combines process simulator with the response surface methodologies. Using the proposed approach, we analyzed the impacts of the absorber and stripper column heights, the concentration of amine solvents, and operating condition on the CO2 removal cost of amine based CO2 recovery processes with various amine solvents. The results show that the absorber height, solvent circulation rate and reboiler duty have the highest impacts on the cost while the stripper height and the regenerator-inlet temperature does not show significant effects. The addition of primary or secondary amines to tertiary amines improves the CO2 absorption capacity of the mixture. Among the solvents of this study, the 48 %wt DGA with 96% CO2 removal amount was found to be the lowest cost process due to its high CO2 absorption capability and low energy consumption.

A preliminary sensitivity analysis was carried out during this study. For future work, a systematic sensitivity analysis of the impact of different model parameters on the CO2 capture cost will be performed. It should be noted that the solution obtained using surface response approaches does not guarantee global optimality and it is highly dependent on the initial data set. Our future work will focus on finding global optimum to this problem. Unfortunately, the applicability of rigorous first-principle models this process is limited due to the complexity of the amine property equations. As a remedy, we will investigate the abilities of neural networks to represent these relationships in the optimization problem.

Acknowledgements

The financial support from the University of Tulsa is greatly acknowledged.
References


Appendix A: The impacts of operating and design parameters on the CO$_2$ capture cost for MDEA and TEA