Modelling and Simulation Study of CO₂ Capturing Process in Coal Fired Power Plant using Various Amine Solvents

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Abstract

In the present world, Scientists are very much concern on to reduce the concentration level of carbon dioxide in environment to save the world. In the present work, the CO₂ capturing efficiencies of three different amine solvents were analyzed. The selected solvents were mono-ethanol amine (MEA), solvent containing mixture of methyl diethanol amine (MDEA) and piperazine (PZ) called activated -MDEA and aqueous ammonia (NH₃) solution. Rigorous simulation method was considered in the current study. The effects of different key parameters for different solvents on the CO₂ removal efficiency were analyzed. Packing height, solvent temperature and absorber height were the significant influential parameters for MEA system whereas for activated-MDEA (a-MDEA), those are the ratio of the solvent to feed quantity and the mixed solvent PZ concentration level. For aqueous NH₃ solution, absorber and stripper’s temperature, CO₂ loading, concentration of NH₃, height of the absorber, lean and rich solvent flow rate, boil up ratio, regeneration energy, temperature of the condenser, and duty of the reboiler were considered. The comparative study showed that MEA process recovered the maximum CO₂ from flue gas. But it was suffered by the maximum regeneration duty. a-MDEA with PZ recovered 91% CO₂. Overall, technically, a-MDEA was the best choice as solvent. Compared to a-MDEA and MEA, aqueous ammonia was identified as more propitious and environment friendly solvent due to its satisfactory performance and easy availability.

Keywords: Modelling; CO₂; Power Plant; Amines
| Abbreviations | Definition       |
|--------------|-----------------|
| MEA          | monoethanolamine|
| MDEA         | methyldiethanolamine|
| PZ           | piperazine      |
| DEA          | Diethanolamine  |
| DIPA         | Diisopropylamine|
| PCC          | Post Combustion Capture |
1. Introduction

Carbon dioxide capture is one of the major concerns among scientists. The captured CO₂ is converted to value added products through many innovative techniques like artificial photosynthesis, etc. It is also used for the production of green steel. Waste CO₂ in huge quantity is available in coal-fired power plants as flue gas. In situ capture of CO₂ from a flue gas is a promising technology to reduce and control the emission of CO₂ from fossil fuels. But it has a drawback of high energy consumption. Popular Post Combustion Capture (PCC) technique can easily be fitted into an existing power station with minimal modification. It is also used in cement, steel and lime manufacturing industries with ease [1, 2]. In research level, other technically feasible techniques such as chilled ammonia process, cryogenics, physical adsorption and membrane separation are explored, but they are yet to be commercialized. An alternative like Chemical absorption is widely used technique for the effective removal of CO₂ economically [3].

The selection of appropriate solvent is the key challenge for capturing CO₂ using absorption technology [4]. Amines especially alkanol amines which contains both amine (-NH₂, -NHR, -NR₂) and hydroxyl (-OH) functional groups can be used to capture carbon dioxide. Among amines, tertiary amines such as MDEA are the least but primary amines such as MEA-mono-ethanolamine are the most reactive. Stable carbamates and bicarbonates are formed due to reaction of amines with CO₂. Thus, amines are preferred to capture CO₂ [5].

The chemistry of the of the CO₂ absorption process is discussed in many published documents. Using the same process chemistry, designing a large scale removal of CO₂ by absorbing them in different amine solutions is very crucial. This has encouraged authors to simulate the absorption process for identifying the better process operating conditions with best solvent. Aspen plus tools are used for the simulation purpose. The main objective of the current research work is to identify the best solvent among MEA, a-MDEA, and aqueous solution of NH₃ through parameter sensitivity analysis by varying single process parameter at a time keeping others fixed.

The work basically consists of two sections. Development of an Aspen property package is first crucial step adopted in the present study. Data for various parameters related to thermodynamic property and chemical reactions were taken from literature. After developing the property package, a simulation model of the process for Carbon dioxide capture is then selected. The second section of the work involved the estimation of the effect of different operating parameters, size of absorber, CO₂ loading, temperature of the condenser, etc. on the CO₂ concentration in the leaving stream, CO₂ recovery efficiency etc.

2. Development of the overall process flow diagram

The developed process flow sheet for CO₂ capture process is presented in Fig. 1. The overall process basically consists of an absorber and stripper and an in-between heat exchanger connecting both of them. The flue gas, after being cooled and desulphurized, enters the absorber from bottom. From the top of the absorber the lean solvent (amine) enters, and flue gas enters the bottom of the column. The amine solution becomes heavy after absorbing CO₂ from the flue gas and then moves down to enter stripping column through a heat exchanger. In the stripper, CO₂ is stripped from the amine solution. The lean amine stream called Lean-out from the stripper bottom is further recycled to the absorber after passing through the above stated heat exchanger. For the downstream utilisation, CO₂ collected here is transported to storage sites. The operating pressure in both the columns are kept at ambient pressure for reducing the temperature of the regenerator; in turn, it helps to reduce heat duty of whole plant [6, 7].

![Fig. 1 Simplified flow sheet of the CO₂ capture system.](image)

3. Selection of Mass Transfer and Thermodynamics Models
Process modelling with mass transfer, heat transfer and the reactions are considered in the present study to simulate the real life behaviour of the discussed CO₂ capture process. Both the equilibrium-based model (RadFrac) and non-equilibrium rate-based model (RateFrac) available in Aspen are tested. RateFrac is used to show the effects of operating parameters on the target parameters. The flow model is considered as counter-current. The Redlich–Kwong equation of state and the Electrolyte-NRTL method are used for determining the properties of the vapour phase and liquid phase respectively. Overall, the flow sheet is solved by dynamic simulator to achieve the steady state outputs which are depicted here.

4. Specification of Process Data

The concentration of CO₂ is typically in the range of 12-14% for a coal fired power plant. On the basis of approach to flooding, the sizes of the columns are decided. 70% flooding approach is considered to assure smooth functioning of the system even for a sudden change in operating conditions. The flue gas flow-rate from a power plant of 500 MW capacity is 2200 tons/hr. The specified other input data are listed in Table 1.

| Parameter | Value |
|-----------|-------|
| Flow Rate | 2200 tons/hr |
| Pressure  | 101 kPa |
| Temperature | 50 °C |
| Volume Fraction of Flue Gas | |
| Nitrogen | 75.73 % |
| Carbon Dioxide | 12.43 % |
| Water | 11.84 % |
| Column Internal Diameter | 0.427 m |
| Packing Height | 6.1 m |
| Packing Size | 0.0381 m |
| Packing Specific Area (Absorber) | 145 m²/m³ |
| Packing Specific Area (Regenerator) | 420 m²/m³ |
| Cross Heat Exchanger Area | 7 m² |
| Volume of Reboiler | 1 m³ |
| Volume of Condenser | 2 m³ |

4. Results and Discussions

The current simulation study includes the analysis of the effect of different amine based solvents (MEA, Mixer of Piperazine and MDEA and Ammonia solution) on the absorption of CO₂ from flue gas. The following sections discuss the analysis of the achieved simulation results for individual cases.

4.1 Results and Discussions for Absorption by MEA

4.1.1 Effect of specified percentage removal of CO₂ on reboiler duty

The study depicts that the reboiler duty increase with increase in the percentage recovery of CO₂. A sharp increase occurs when the capture percentage approaches 95%. This happens due to increase of solvent load in the column in turn in the reboiler.

4.1.2 Effect of solvent temperature on reboiler duty

Theoretically, the driving force for absorption increases with the decrease of the temperature of absorber. However, with declining the temperature, the rate of the reaction and diffusive mass transfer decrease too. Simulations are carried out at solvent temperatures of 20, 30 and 40 °C. It shows almost invariant reboiler duty with the solvent temperature. Hence, it can be concluded that the performance of the system is independent of the temperature of the solvent.

4.1.3 Effect of absorber height on reboiler duty

To determine the effect of absorber height on the reboiler duty, the height is varied by keeping the column diameter constant. It shows that with the rise of the absorber height, the rich-out stream loading increases and thus, the reboiler duty decreases. However, the increase of pressure drop in the absorber with the absorber height leads to an undesirable increase in the capital cost of the absorber. Hence, the feasible column height should be determined doing economy analysis of the process with the help of some optimization routines.

4.2 Results and Discussions for Absorption by Aqueous Solution MDEA and Piperazine (a-MDEA)

Although less reactive to CO₂, MDEA (Methyl di-ethanol amine) is a good option for absorbing carbon dioxide from flue gas because of its low corrosive nature, environmental friendliness, high loading capacity, resistance to thermal and oxidative degradation, and low heat of regeneration, over other amines. Thus, piperazine (PZ) having high reactivity with CO₂ is added in aqueous solution of MDEA with compositions of 45 wt% MDEA and 5 wt% PZ. In a-MDEA (activated-MDEA), PZ enhances the activity of MDEA during reaction with CO₂. Further, in a-MDEA, MDEA keeps its original merits like chemical
stability and requiring a low heat of regeneration intact [8]. Thus, the mixed MDEA and PZ amine solvent has turned out as the most promising solvents for processes to capture CO₂.

### 4.2.1 Effect of piperazine (PZ) concentration on the CO₂ recovery in absorber

The variations of CO₂ recovery from the absorber due to change of the piperazine concentration are analysed at the solvent to feed ratio of 2.5. It is depicted in Fig. 2. It illustrates a significant effect of the PZ concentration on the exit concentration of CO₂ from the absorber. Fig. 2 also shows a linear rise of the CO₂ recovery due to change of PZ concentration from 0 wt % to 4 wt % and almost constant recovery at higher piperazine concentrations. The figure further shows a rise of recovery percentage of CO₂ by 10% for each 1 wt % increase of PZ concentration in the solvent. Present study also shows that the maximum recovery achieved by MDEA alone i.e. without the addition of PZ is only 57%. Hence, alone MDEA is incapable to remove CO₂ from flue gas causing a rejection of large quantity of CO₂ into atmosphere.

![Fig. 2 Effect of PZ conc. in solvent in CO₂ recovery % in the absorber for S/F= 2.5](image)

### 4.2.2 Effect of PZ concentration on reboiler duty per captured CO₂ in the stripper

Fig. 3 shows the variation of reboiler duty per captured CO₂ with the piperazine (PZ) concentration at the considered ratio of feed to solvent flow ratio (2.5). It shows a rising trend of reboiler duty with increasing the PZ concentration after some initial lag. Whereas, MDEA as a pure solvent develops low heat of regeneration and thus incapable to absorb CO₂ without addition of PZ into it.

![Fig. 3 Effect of PZ conc. in solvent on the reboiler duty per captured CO₂ of the stripper at S/F=2.5](image)

### 4.3 Results and Discussions with Aqueous NH₃ Solution

The main disadvantage of the above stated two solvents are their low reactivity with CO₂. But in comparison to MEA and α-MDEA, aqueous ammonia possesses high CO₂ loading capacity, no degradation of the absorbent and less consumptions of energy. Moreover, it can produce value-added chemicals such as ammonium sulphate and ammonium nitrate along with capturing simultaneously all CO₂, SO₂ and NOx present in the flue gas and [9]. Therefore, aqueous ammonia can safely be
considered as the most favourable solvent for the large scale CO₂ capturing process. The effects of the concentration of NH₃ and temperature of the lean solvent on the removal efficiency of CO₂ has been carried out by Chen [10] in a continuous absorption system. At high NH₃ concentration, the CO₂ removal efficiency may reach up to 90%.

4.3.1 Effect of absorber height

The residence time of both the lean solvent and flue gas rises proportionately with the size of the absorber. As a result, with the height of the absorber, the CO₂ removal efficiency (Fig. 4) and its loading in the rich solvent (Fig. 5) increases. Thus, the corresponding regeneration energy decreases. Both the figures confirm asymptotic nature of the curves especially for larger diameter column. The optimum column height beyond which the dependent variables in the figures become independent increases with the diameter of the column. It may be due to the lower mixing of the gas and solvent at lower column diameter.

![Fig. 4 Effects of the size of absorber on the CO₂ removal efficiency](image1)

![Fig. 5 Effects of the size of absorber on the CO₂ loading of rich solvent](image2)

4.3.2 Effect of the NH₃ concentration in the lean solvent

According to Fig. 6, NH₃ concentration in the exit flue gas increases monotonically and with the increase of NH₃ concentration in the lean solvent, the CO₂ removal efficiency rises asymptotically. This rapid increase of CO₂ removal is stabilised after the NH₃ concentration becomes 3 mol/L. As shown in Fig. 7, ammonia concentration in the reboiler increases with increase in the feed NH₃ concentration. The boiling point of solution in the reboiler decreases, and thus, a declining trend of reboiler duty with NH₃ concentration in the lean solvent is observed. Fig. 7 also shows the appearance of the maximum CO₂ removal rate at 3 mol/L of NH₃ concentration. Below it, the lower removal rate of CO₂ occurs due to unavailability of sufficient NH₃ to react with the absorbed CO₂ in the absorption column. Above 3 mol/L, the declining trend of the removal rate of CO₂ happens because of the releasing of excess NH₃ along with CO₂ in the CO₂ outlet stream.
4.3.3 Effects of flow rate of the Lean solvent

The effects of Lean-in flow rate on the ammonia gas concentration at the exit of the absorber and also on the carbon dioxide removal efficiency are graphically presented in Fig. 8. The figure illustrates clearly that the concentration of NH$_3$ remains almost invariant to the change of the flow rate of the lean solvent (Lean-in) but the increase of the removal efficiency of CO$_2$ is very rapid (the increasing trend is linear). The invariant nature of the NH$_3$ concentration profile and monotonic increasing nature of CO$_2$ removal are due to use of lesser quantity of ammonia than its saturation level by CO$_2$ gas. In Fig. 9, at constant boil-up ratio, both the reboiler duty and CO$_2$ output rate from the regenerator (stripper here) rise up almost linearly with the flow rate of the Lean-in stream. The increasing trend of the CO$_2$ removal rate is due to the availability of higher quantity of NH$_3$ to react with fixed amount of CO$_2$ molecules. The increasing trend of the reboiler duty appears because of increasing liquid load in the reboiler at higher Lean-in flow rate. It can thus be concluded that with the increase in Lean-in flow rate, carbon dioxide absorption is improved but alongside it also increases the requirement of the regeneration heat.
4.3.4 Effect of CO$_2$ loading of the Lean solvent (Lean-in)

Sometime the Lean-in stream may contain CO$_2$ along with NH$_3$. Analysis of the effect of loading of CO$_2$ in the Lean-in stream on the system outputs is performed in this section. Fig. 10 confirms that both the concentration of NH$_3$ in the exit flue gas stream and removal efficiency of CO$_2$ in the absorption process decrease linearly with increasing CO$_2$ loading of the Lean-in stream. Use of lesser quantity of NH$_3$ is responsible for the declining trend of the mentioned NH$_3$ concentration and also the CO$_2$ removal efficiency due to leaving of the unreacted CO$_2$ from the system. There is a linear increase of CO$_2$ output rate with the increase of the CO$_2$ loading because of the same reason (Fig. 11). The small decrease of the reboiler duty in the figure occurs owing to increase of the aqueous solution sensible heat in the reboiler in presence of higher amount of water. According to the figure, the optimum CO$_2$ loading of the Lean-in stream is 0.235.
4.3.4 Analysis of CO₂ regeneration process

The regeneration or stripping process plays a crucial role for making the process more efficient by recycling the used aqueous solution of ammonia in the Lean-in stream. In the following sub-section the behaviour of the regeneration process is analysed.

(i) Effect of boil-up ratio on the CO₂ regeneration process

The purpose of using reboiler is to remove soluble CO₂ from the reboiler stream to increase the concentration of NH₃ in the same stream. To achieve it, the reboil ratio increases gradually. The effect is illustrated in Fig. 12. It shows an expected increasing trend of both the CO₂ out flow rate and the concentration of NH₃ for initial increase of the boilup ratio. The NH₃ concentration in the bottom stream of stripper reaches asymptotically almost the inlet NH₃ flow rate in the Lean-in stream. But CO₂ output rate from top of the stripper passes through a maxima and then decreases with further increase of the reboil ratio. The decreasing trend of CO₂ flow rate is due to increasing loss of water vapour along with the CO₂ in the CO₂ out stream.
(ii) **Effect of Rich-in stream temperature on regeneration process of CO₂**

The effect of Reach-in stream temperature on the NH₃ and CO₂ output rates from the stripper is discussed here. The effects are illustrated in Fig. 13. As temperature increases, the absorption capacity of Lean-in stream decreases which is also confirmed from Fig. 14. It also causes the loss of more NH₃ in the CO₂ out stream. Thus CO₂ in the CO₂ out stream and NH₃ in Lean-out stream declines with rising the temperature of the Lean-in stream. In Fig. 15, the variations of the reboiler duty (supplied total energy to the reboiler) and Regeneration energy (defined as the ratio of total energy supplied to the reboiler and CO₂ desorption rate) are presented. As temperature of the Rich-in stream increases, the temperature level of the reboiler liquid increases. It results in the less power consumption in the reboiler at higher temperature of the Lean-in stream. In contrary, the regeneration energy gradually increases with increasing the Lean-in temperature. It occurs due to decrease of the CO₂ output rate (Fig. 13) with the mentioned temperature.
(iii) Effect of the temperature of the condenser on the CO\textsubscript{2} regeneration process

The condenser temperature may also affect the performance of the stripper’s behaviours. Increase of both CO\textsubscript{2} and NH\textsubscript{3} removal rate are expected to occur with rising the temperature of the condenser. The same is observed in Fig. 16. Loss of NH\textsubscript{3} gas in the CO\textsubscript{2}-out stream at greater extent is responsible for increasing trend of concentration profile of NH\textsubscript{3} as shown in Fig. 17. The effect of the temperature of the condenser on the regeneration energy and reboiler duty is similar to the effect of Lean-in stream temperature on them ((Fig. 15).
4.4. Comparison Among Solvents

Analysis and comparison of four important property parameters is performed for the three different solvents- a-MDEA, MEA, and NH$_3$ solution to select the best solvent. These are height of packing, CO$_2$ capture percentage, CO$_2$ loading and Regeneration Energy (heat supplied to the Reboiler per kg of captured CO$_2$). According to the analysis, NH$_3$ solution has the lowest capturing capacity (90%) followed by activated MDEA (91%) and then MEA (95%). A disadvantage of using MEA is that it requires very high heats of regeneration of 4600 kJ/kg of CO$_2$ although it has very high capturing percentage. NH$_3$ solution also has high regeneration energy (4100 kJ/kg of CO$_2$). Activated MDEA is identified as a better option with 91% CO$_2$ capture percentage and 3750 kJ/kg of CO$_2$ as the heat of regeneration if these two parameter are taken into account for the selection of the best solvent. However, CO$_2$ loading in the Lean-out stream in case of activated MDEA is quite low which is half of the loading of MEA and NH$_3$ solution. Moreover, activated MDEA requires a huge quantity of packing material which is evident from the packing height of 24.1m, 4 to 5 m more than the other two solvents. Because of these two major drawbacks, activated MDEA is not considered suitable for capturing CO$_2$. So, the final selection of the most suitable solvent for capturing CO$_2$ relies on the cost analysis which is suggested as future work.

5. Conclusions

The CO$_2$ capture from a flue gas meets some key challenges to reduce the energy consumption for a fixed CO$_2$ emission target and to identify an appropriate amine solvent. Analysis of the relative superiority of three different amine solvents namely aqueous ammonia solution, a mixed solvent made of MDEA and piperazine (PZ), called a-MDEA and MEA was performed. Effect of different system parameters like packing height, solvent flow rate, concentration of PZ and NH$_3$ in the Lean-in stream and its temperature, CO$_2$ loading of the Lean-in stream and boilup ratio on the performance in terms of the controlling
parameters like CO₂ output rate, NH₃ concentration in the CO₂ output stream, reboiler and regeneration duty etc. are analysed in detail. CO₂ output rate has been increased with increasing the concentration of PZ in MDEA and NH₃ in aqueous solution. A little decreasing trend of reboiler duty has occurred with increasing the NH₃ concentration, where as an increasing trend of the regeneration energy has happened with increasing the PZ concentration in MDEA. A larger effect of packing height on the CO₂ removal efficiency using aqueous NH₃ as the solvent has been observed for larger diameter column. Flow rate of the aqueous solution of NH₃ has minimal effect on the CO₂ removal efficiency, while it affects largely the CO₂ output rate and reboiler duty. In the solvent recovery or stripping section, the condenser temperature has varied substantially the CO₂ output rate, NH₃ output rate, reboiler duty and regeneration energy. Similar variations are also noticed while boil up ratio has been varied.

The comparative study showed that the MEA process has recovered the maximum CO₂ from flue gas. But it simultaneously is suffered by the maximum regeneration duty. MDEA with PZ has recovered 91% CO₂ which is less than the recovery capacity of MDA. But a-MDEA has produced the lowest regeneration energy. Overall, technically, a-MDEA is the best choice for recovering CO₂. But owing to PZ, a-MDEA is costly solvent. Thus, compared to a-MDEA and MEA, aqueous ammonia has been identified as more promising and environment friendly solvent due to its satisfactory performance and easy availability. The suitable inner diameter and the height of packing of the absorber have been identified as 12m and 20m, respectively.
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