

Amines' effect on CO₂ removal efficiency

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Abstract:

Efficient CO₂ mitigation techniques will become increasingly demanding due to environmental issues. There are many sources which release CO₂ and combustion of fossil fuel plays the major role. Coal fired power plants are the most prominent CO₂ emitting source today. The main purpose of this study is to understand the solvent's effect on CO₂ removal efficiency for power plant flue gas treating. Four different types of solvents are taken into consideration. MEA, Diethanolamine (DEA), Diglycolamine (DGA) and Methyldiethanolamine (MDEA) are applied as solvent for capturing processes. A coal fired flue gas removal process is implemented in to Aspen Plus. The solvent strength and lean loading are considered as most relevant factors for analyzing. With the variation of these factors, efficiency of CO₂ removal from power plant flue gas is examined for different solvents. The four different solvents have unique optimum conditions such as; concentration, lean loading and solvent temperature, for highest removal efficiency. The suitable concentrations for MEA, DEA and MDEA are normally around 20-30wt%, however, DGA can be used as higher concentration solvent for CO₂ removal. MDEA has low heat of regeneration and maximum loading capacity as well as less corrosive effect than MEA.

Keywords

Solvent properties, simulations, CO₂ removal efficiency, temperature Profiles

1. Introduction

Carbon dioxide (CO₂) emission from electric power generating sector can be accomplished by three different methods. The pre combustion CO₂ capture, carbon is removed from the fuel prior to combustion, Oxy fuel combustion, coal is combusted with oxygen instead of air and finally, post combustion capture, where fossil fuel is combusted to produce energy, and in the end, CO₂ is removed from the flue gas [1].

The partial pressure of CO₂ in the flue gas stream is low. Therefore, technologies driven by high partial pressures, such as physical solvents or membrane

separation are not efficient for post combustion CO₂ capture. The most suitable method is the chemical absorption process with amine based solvents. There are different types of amines available and some of them are categorized as primary amines (MEA, DGA), secondary amines (DEA), tertiary amines (MDEA, TEA), hindered amines (AMP) and cyclic amines (Piperazine). Primary amines are formed when one of three hydrogen atoms in ammonia is replaced by alkyl group. Secondary amines are formed when two hydrogen atoms are substituted by two alkyl groups and tertiary amines are formed with three alkyl groups combined with nitrogen. Cyclic amines are formed with 3-member ring called aziridine or 6-member ring piperidine. Hindered amines are arising with amine functional group surrounded by a crowded steric environment. Alkanolamines consist of both hydroxyl groups (-OH-) and amino groups (-NH₂). The hydroxyl part helps to reduce vapor pressure and increase solubility of water while the amino group provides the required alkalinity in solution to perform reactions with acid gases [2].

In this study four different amine's effect on CO₂ removal efficiency is considered. These amines are Monoethanolamine (MEA), Diethanolamine (DEA), Diglycolamine (DGA) and Methyldiethanolamine (MDEA). Basic information about these amines is given in Table 1.

Table 1. Properties of Amines [2]

Amine	MEA	DEA	DGA	MDEA
Chemical formula	C ₂ H ₇ NO	C ₄ H ₁₁ NO ₂	C ₂ H ₁₁ NO ₂	C ₅ H ₁₃ NO ₂
Amines category	Primary	Secondary	Primary	Tertiary
Molecular weight [g/mol]	61.08	105.14	105.14	119.163
Density [g/cm ³]	1.012	1.090	1.06	1.043
Boiling point[°C]	170	217	223	247

The amines are categorized as primary, secondary and tertiary according to the number of organic groups attached to the alkaline nitrogen atom [3]. Typically primary and secondary amines form carbamate species while reacting with CO₂.

2. Model Development

The main objective of this study is to compare the different kind of amine's effect on CO₂ capturing process. The model is implemented in Aspen Plus with Electrolyte NRTL property method. The 500MW coal fired power plant flue gas stream data is used for simulations with the parameters and kinetic data given in literatures [4], [5]. The explanation used for parameter calculation, process flow diagram and flue gas stream data related to implemented model is discussed in this section.

There are several models involve with calculating parameters in Electrolyte NRTL property method. In vapor phase fugacity coefficient and density, it use Redlich-Kwong equation of state and calculating enthalpy, entropy and Gibbs energy use ideal gas heat capacity together with Redlich-Kwong equation of state. Similar to that in liquid phase, calculating fugacity coefficient and Gibbs free energy, it uses extended Antoine vapor pressure and Henry's constants.

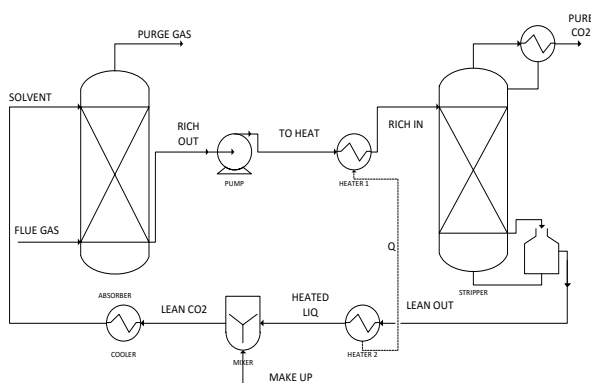


Figure 1. Process flow diagram

A simplified process flow diagram of an implemented model which employs CO₂ capture by absorption / stripping with an aqueous solvent is shown in Figure 1. Flue gas with CO₂, H₂S and other components is introduced at the bottom of the absorber, where it flows upwards and counter currently contacts with the aqueous amine solution which is introduced at the top of the absorber. The absorber inlet streams are operated at 40°C and pressure inside the absorber maintained around 1 bar with 0.1 bar pressure drop. The amine solution is pumped through the heater where its temperature is raised by heat releasing from the lean amine stream. Subsequently, the heated rich amine stream at 115°C is supplied to the stripper at the top where it counter currently contacts steam around 120°C temperature. Stripper is operating around 2 bar pressure with 0.1 pressure drop throughout the column. The re-boiler

supplies the energy necessary to regenerate the amine solution and to separate acid gases that leave through the column top. The lean acid gas is then pumped through the heater unit to cool down the temperature which finally is recycled back to the absorber unit after adding the makeup stream.

Flue gas stream data for the four different models are given in the Table 2 [3], and the same flue gas condition is used for each model. Parameters and constants related to packed section is taken from the Stichlmair et al [6].

Table 2. Coal fired power plant flue gas data

Parameter	Value
Flow Rate (tones/ hour)	2424.4
Pressure (bar)	1.1
Temperature (°C)	40
Major components (mol %)	Composition
H ₂ O	8.18
N ₂	72.86
CO ₂	13.58
O ₂	3.54
H ₂ S	0.05

3. Simulation Studies

This section is divided into four different sub sections for each solvent.

3.1. MEA

Figure 2 and 3 represent the MEA concentration and lean loading effect on removal efficiency. On the other hand, the liquid phase mole fraction variation with CO₂ loading in the absorber bottom outlet stream is shown in Figure 4.

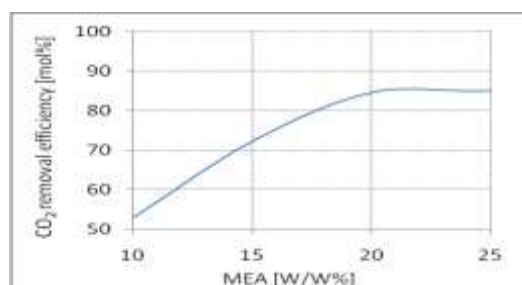


Figure 2. Removal efficiency variation with MEA concentration (25% lean loaded MEA at 40°C)

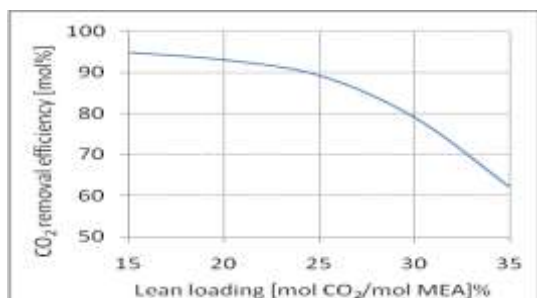


Figure 3. CO₂ removal efficiency variation with lean loading (25w/w% MEA at 40°C)

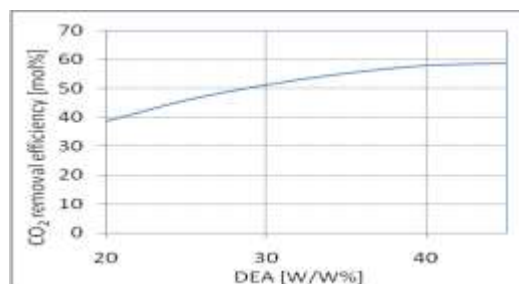


Figure 5. Removal efficiency variation with DEA concentration (25% lean loaded DEA at 40°C)

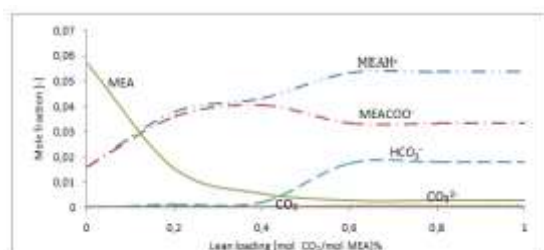


Figure 4. Liquid phase composition of a 25w/w% MEA solution loaded with CO₂ at 40°C

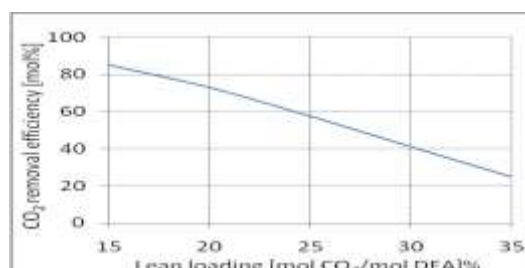


Figure 6. CO₂ removal efficiency variation with lean loading (40w/w% DEA at 40°C)

The CO₂ removal efficiency rapidly increases with MEA concentration, but maximum efficiency according to the range of this study is obtained between 20-25% MEA concentrations (Figure 2). This is because of the increased capture capacity with amine concentration. When the lean loading of MEA solvent is increased from 15 to 35% [mol CO₂/mol MEA], efficiency of the removal process is drastically decreasing (Figure 3). The capacity of the solvent for CO₂ absorption decreases with the increase of lean loading, hence efficiency of the CO₂ removal is decreasing [7]. The bulk concentrations in liquid phase with CO₂ loading is illustrated in Figure 4 which shows stable liquid phase concentrations after 0.6 loading.

3.2. DEA

Similar attempt in this section as for MEA is made to check the removal efficiency of DEA upon concentration and lean loading variation of DEA (Figure 5 and 6).

Figure 5 shows the DEA concentration effect on removal efficiency. Comparison of it against MEA plot suggests that the efficiency is lower than that of MEA system. Maximum efficiency of 58% in this case is achieved at 45[W/W%] concentrations. CO₂ removal efficiency variation with lean loading is given in Figure 6 and maximum efficiency reached, in the range tested, is 84% at 15% [mol CO₂/mol MEA] lean loading. The mole fraction variation in liquid phase with CO₂ loading in the absorber bottom outlet stream is explained by Figure 7. It is almost similar to MEA plot (Figure 4), when analyzed at 40°C.

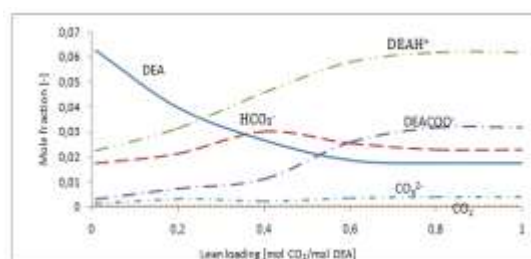


Figure 7. Liquid phase composition of a 40w/w% DEA solution loaded with CO₂ at 40°C.

3.3. DGA

Figure 8 represents the removal efficiency variation with DGA concentration. Similar to DEA, efficiency is less compared to the MEA system and

maximum efficiency in the range of varied during this work is achieved around 90% at 50 [w/w%] concentrations. CO₂ removal efficiency variation with lean loading given in Figure 9 showing that maximum efficiency observed about 98% at 15% [mol CO₂/mol MEA] lean loading. Figure 10 is mole fractions in liquid phase for the DGA analysis.

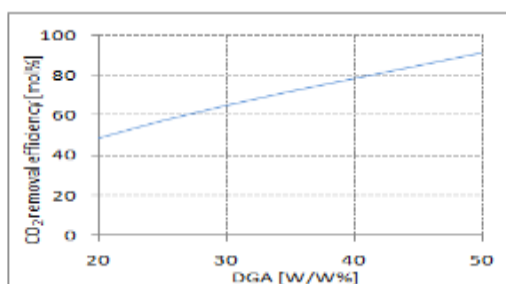


Figure 8. Removal efficiency variation with DGA concentration (25% lean loaded DEA at 40°C)

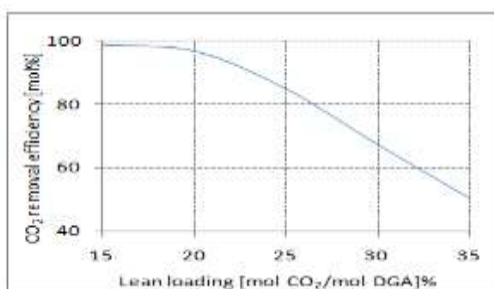


Figure 9. CO₂ removal efficiency variation with lean loading (45w/w% DGA at 40°C)

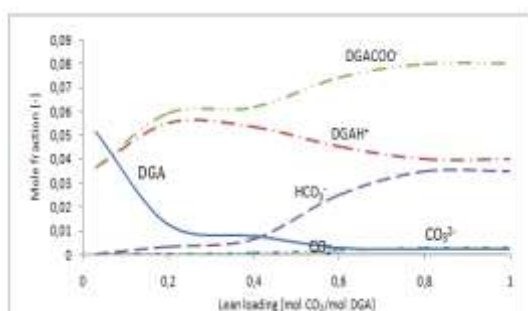


Figure 10. Liquid phase composition of a 45w/w% DGA solution loaded with CO₂ at 40°C

3.4. MDEA

MEA and DEA are the widely applicable and preferred alkanolamine for gas treating applications. However, recently MDEA has been used as an alternative to MEA and DEA in certain gas purification applications. It is used in bulk CO₂

removal applications due to low heat of regeneration [8].

Figure 11 represents the variation of removal efficiency with MDEA concentration. However, efficiency is very low compared to the MEA, DEA and DGA systems and maximum efficiency achieved around 16% at 7% [w/w%] concentrations. CO₂ removal efficiency variation with lean loading is given in Figure 12 and maximum efficiency of 17% is obtained at 15[mol CO₂/mol MEA] % lean loading for the range studied in this work. Mole fraction variation is given in Figure 13 for liquid phase.

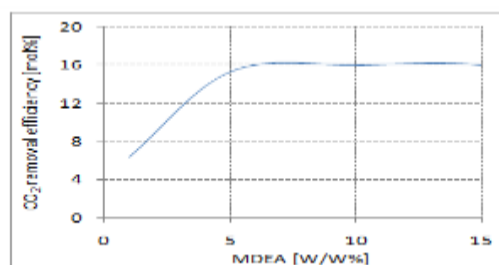


Figure 11. Removal efficiency variation with MDEA concentration (20% lean loaded MDEA at 40°C)

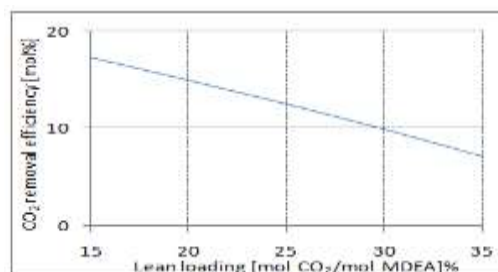


Figure 12. CO₂ removal efficiency variation with lean loading (15w/w% MDEA at 40°C)

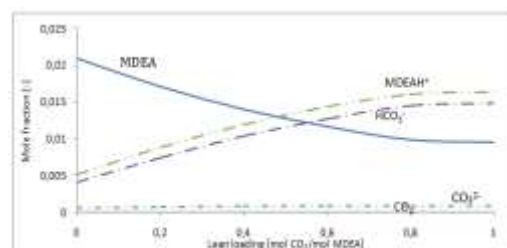


Figure 13. Liquid phase composition of a 15w/w% MDEA solution loaded with CO₂ at 40°C

MDEA has a low heat of regeneration, and maximum loading capacity as well as it is less corrosive than MEA. The drawback of pure MDEA, on the other hand, is it has low reaction capability with CO₂ directly due to lack of N-H bond, which required forming carbamate ion with CO₂ [9].

Chakravarty et al. [10] indicated that adding a small amount of primary or secondary amines, such as MEA or DEA, to the aqueous MDEA can enhance the absorption rate of CO₂. The use of blended amines for absorption of CO₂ from flue gas streams has received considerable attention because of the potential for low energy requirements for regeneration, high CO₂ absorption capacity, good chemical stability, and acceptable rate of CO₂ absorption.

4. Conclusion

The CO₂ removal efficiency rapidly increases as the amine concentration increases. The maximum efficiencies, in the range tested, are listed for different amines, see Table 3. Increasing efficiency is obtained because of increased capture capacity with amine concentration.

Table 3. Maximum CO₂ removal efficiency at optimum concentration according to the range of present study

Parameter	MEA	DEA	DGA	MDEA
Efficiency [mol%]	85	58	90	16
Concentration [%]	22	45	50	7

Efficiency of MDEA is very low compared to the MEA, DEA and DGA systems and maximum efficiency achieved around 16% at 7[w/w%] concentrations. Pure MDEA does not react with CO₂ directly due to lack of N-H bond, which is required to form carbamate ion with CO₂.

When the lean loading of MEA solvent is increased, efficiency of the removal process decreases drastically. The capacity of the solvent for CO₂ absorption decreases with the increase of lean loading, hence efficiency of the CO₂ removal is decreasing.

5. References

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