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TECHNICAL ASSESSMENT OF CO_2 CAPTURE USING ALKANOLAMINES SOLUTIONS

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ABSTRACT: The most promising technology for carbon dioxide removal from coal and natural gas fired power plant flue gases at large scale applications is based on gas – liquid absorption. This paper evaluates the carbon dioxide absorption at low CO_2 partial pressures from flue gases by post-combustion using aqueous solution of alkanolamines e.g., monoethanolamine, diethanolamine, triethanolamine, methyldiethanolamine and diisopropanolamine. The aim of the present paper is to evaluate and compare the energy penalty involved by carbon capture technology using alkanolamines through the following technical coefficients: power consumption, heating agent and cooling agent consumptions. The CO_2 absorption modelling and simulation work described in this paper was developed in ChemCAD software.

Keywords: *CO_2 Absorption and Desorption, Alkanolamines, Technical Assessment, Carbon Capture and Storage (CCS)*

INTRODUCTION

The most alarming global environmental problems of today are the increase of global temperature and the climate changes. These problems are most likely caused by the increasing atmospheric carbon dioxide concentration due to the burning of fossil fuels from human activity.

Given the advantages of fossil fuels, such as their availability, relatively low cost, and the existing infrastructure for delivery and distribution, they play a major role in the worldwide energy production for at least the next 75 years. On the other hand, combustion of fossil fuels such as coal and natural gas are main sources of CO_2 emissions that, according to the Intergovernmental Panel on Climate Change (IPCC), constitute a major man-made contribution to global warming of our planet.[1]

A significant reduction of greenhouse gas emissions (mainly CO_2) resulting from fossil fuels can only be obtained by increasing the efficiency of power plants and production processes, and decreasing the energy demand,

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combined with CO_2 capture and long term storage (CCS). CO_2 capture and storage is a modern technology approach trying to mitigate the contribution of greenhouse gas emissions resulted from the fossil fuels usage to global warming, based on capturing the carbon dioxide from large point sources such as fossil fuel power plants. The carbon dioxide is then permanently stored away from the atmosphere in suitable geological formations or used for Enhanced Oil Recovery (EOR).[2]

There are three main CO_2 capture techniques generated from the combustion of fossil fuels: post-combustion capture, pre-combustion capture and oxy-fuel combustion.[3] Several possible ways of CO_2 capture technology such as absorption, adsorption, membranes or other physical and biological separation methods are shown in Figure 1.

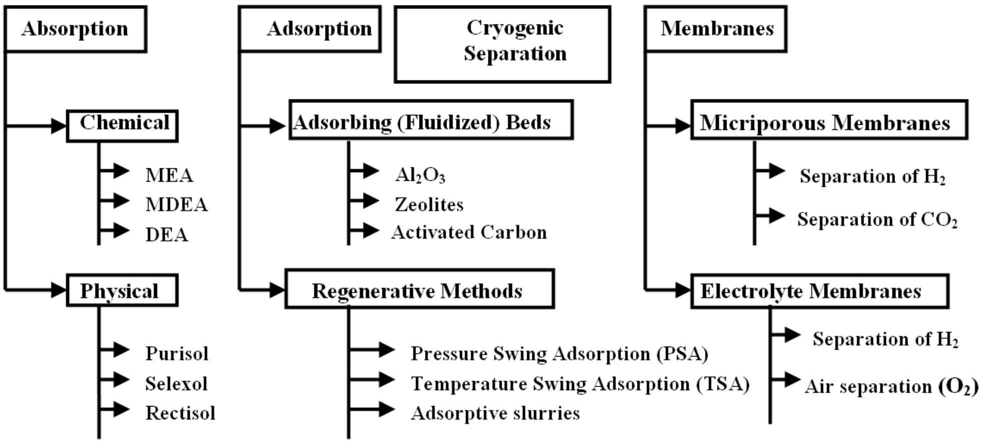

Figure 1. Carbon dioxide capture technologies[4]

Carbon dioxide capture by gas - liquid absorption is one of the common industrial technologies today and, in many cases, has been observed to be the most viable solution, compared to the other processes that are available. However, technological improvements are necessary to reduce the high capital cost and energy requirements of the absorption process. It is expected that process design innovation or the use of better solvents can reduce the capital and energy costs significantly.[5]

As it can be noticed from Figure 1, CO_2 absorption can be divided into chemical absorption (mainly used in post-combustion capture technique) and physical absorption (used in pre-combustion capture technique). In the case of pre-combustion capture technique, where CO_2 partial pressure is relatively high (over 15 bar) and CO_2 concentration is around 40%, it is recommended to use physical solvents containing for instance methanol (Rectisol® process) or dimethyl ethers of polyethylene (Selexol®). In the case of post-combustion capture technique, where CO_2 partial pressure is close to atmospheric pressure and CO_2 concentrations are relatively low e.g., 4-8% vol. in natural gas-fired and 12-15% vol. in coal-fired power plants. It is recommended that chemical solvents such as aqueous solutions of alkanolamines, sodium hydroxide (NaOH) or ammonia (NH_3) to be used. No matter what solvent is used for CO_2 capture, the electric power, the heat (steam) and the cooling duties that are required for the capture process are very important aspects that must be considered. From the point of view of electric power consumption, in case of chemical solvents usage, the solvent flow rate is lower than in the case of physical solvents, which means a lower electric power consumption for solvent circulation. The situation is totally reversed for heat consumption; the chemical solvents require much more heat for regeneration than physical solvents due to the chemical reactions involved. These issues require a careful integration analysis in terms of heat and electric power for the CO_2 capture plant. [6]

This paper is focused on post-combustion CO_2 capture by gas – liquid absorption using aqueous alkanolamines because this technology has the highest potential to be implemented on a large scale for CO_2 capture from flue gases (e.g., power generation sector) in the next decade.

It is very important that as a result of the reaction between the CO_2 and solvent, the resulted compounds to be stable enough so that they do not decompose in CO_2 in the absorption column, but can decompose easily in the desorption column with minimal thermal energy consumption. It is also important that the solvent has low volatility in order to avoid losing it with the stream that leaves the absorption column. Considering these circumstances, a comparison between the solvents used for CO_2 absorption: aqueous sodium hydroxide (very strong base), ammonia (too volatile) and alkanolamines (middle alkalinity and low volatility) was made with the conclusion that the most convenient solvents are the alkanolamines. As a result, they were chosen for technical assessment in this paper (quantification of energy penalties involved by carbon capture).[7]

In the present paper are analyzed and compared for the first time the technical coefficients in terms of energy consumption (power, heating duty and cooling duty consumption) of carbon dioxide absorption using five different alkanolamines (monoethanolamine - MEA, diethanolamine - DEA, triethanolamine - TEA, diisopropanolamine - DIPA and methyldiethanolamine - MDEA). The quantification of CO_2 capture energy demand is crucial for the successful implementation of carbon capture and storage technologies in real applications (e.g., in the power generation sector).

RESULTS AND DISCUSSION

Post-combustion CO_2 capture using alkanolamines

The removal of CO_2 by absorption in alkanolamines is widely used in chemical industry (e.g., ammonia synthesis). This process is based on the reversible chemical absorption of CO_2 using an acid - base reaction in an absorption - desorption loop. In the absorber (relatively low temperature and/or high pressure) the acidic gases are absorbed, while in the desorber the loaded solvent is regenerated (elevated temperatures and/or reduced pressure). The alkanolamines that are the most used for this process are: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA) and diisopropanolamine (DIPA).

The absorption of CO_2 into an alkanolamine solution is a reaction between a weak acid and a weak base, where both are weak electrolytes. The weak electrolytes partially dissociate in aqueous solution. The chemical equilibrium is achieved in liquid phase when CO_2 is absorbed in an aqueous solution of primary or secondary alkanolamines such as MEA ($NH_2CH_2CH_2OH$), DEA ($NH(CH_2CH_2OH)_2$), DIPA ($NH(CH(CH_3)_2)_2$). The equilibrium is described by the following equations where R_2N is an alkyl- or alkanolamine and R can represent an alkyl, alkanol group or hydrogen:

Water dissociation: $2H_2O \Leftrightarrow H_3O^+ + OH^-$ (1.1)

CO_2 dissociation: $CO_2 + 2H_2O \Leftrightarrow H_3O^+ + HCO_3^-$ (1.2)

Carbonate dissociation: $HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$ (1.3)

Amine dissociation: $R_2NH_2^+ + H_2O \Leftrightarrow H_3O^+ + R_2NH$ (1.4)

Carbamate reversion: $R_2NCOO^- + H_2O \Leftrightarrow R_2NH + HCO_3^-$ (1.5)

The reaction of CO_2 with primary or secondary alkanolamines (like monoethanolamine or diethanolamine) can be approximated by a single chemical reaction as follow:

$$2RNH_2 + CO_2 \rightarrow RNHCOO^- + RNH_3^+ \tag{1.6}$$

The above equation implies that all absorbed CO_2 reacts with the alkanolamine to form carbamate. Equation (1.6) neglects the presence of bicarbonate (HCO_3^-), hydroxide (OH^-), and carbonate (CO_3^{2-}) ions. The concentration of these ions will be very small in the region of loading. This is of interest to CO_2 capture from fossil fuels burning power plants using a primary or secondary alkanolamine since the area of interest is where the fast carbamate reaction is dominant.

For aqueous solutions of tertiary alkanolamines such as MDEA ($CH_3N\ (C_2H_4OH)_2$) or TEA ($N(CH_2CH_2OH)_3$) equation (1.5) can be neglected since no stable carbamates are formed, thus the main reaction for carbon dioxide absorption process is:

$$RNH_2 + CO_2(aq.) + H_2O \rightarrow RNH_3^+ + HCO_3^- \qquad (1.7)$$

Carbamate is the main product for the reaction of CO_2 with primary and secondary alkanolamines. For aqueous solutions of tertiary alkanolamine, the carbamate stability is low and there, for the main reaction product, is bicarbonate, as seen in equation (1.7). [3, 8]

Results of post-combustion CO_2 capture

The carbon dioxide absorption process was modelled and simulated using the AMINE model from the ChemCAD software. The CO_2 absorption simulation results using various alkanolamines are presented in Table 1.

Table 1. Simulation results

	Case 1	**Case 2**	**Case 3**	**Case 4**	**Case 5**
Absorbent	MEA	DEA	TEA	DIPA	MDEA
Absorbent mass flow (kg/h)	$29 \cdot 10^5$	$37 \cdot 10^5$	$5 \cdot 10^8$	$5 \cdot 10^8$	$82 \cdot 10^5$
Initial CO_2 mass flow (kg/h)	$3.67 \cdot 10^5$	$3.67 \cdot 10^5$	$3.67 \cdot 10^5$	$3.67 \cdot 10^5$	$3.67 \cdot 10^5$
Final CO_2 mass flow to storage (kg/h)	$3.32 \cdot 10^5$	$3.33 \cdot 10^5$	$2.65 \cdot 10^5$	$2.65 \cdot 10^5$	$3.32 \cdot 10^5$
CO_2 removal ratio (%)	90.48	90.63	72.12	72.23	90.61
Power required (MW_e)	28.02	28.49	-27.23	14.56	28.02
Heating agent duty (MW_{th})	$1.27 \cdot 10^3$	$0.25 \cdot 10^3$	$4.90 \cdot 10^3$	$142 \cdot 10^3$	$0.21 \cdot 10^3$
Cooling agent duty (MW_{th})	$1.35 \cdot 10^3$	$0.29 \cdot 10^3$	$5.06 \cdot 10^3$	$12.80 \cdot 10^3$	$0.28 \cdot 10^3$

As it can be noticed from Table 1, a capture rate of around 90% in most alkanolamines was obtained. This capture rate was calculated reporting the final mass flow CO_2 to the initial mass flow CO_2. Having these results from Table 2 and using the equations below, the technical coefficient for CO_2 absorption in alkanolamines solution was calculated.

$$Power_{required}\ (MW) = \sum(Ep_{pump}) + \sum(Ep_{compressor}) + \sum(Ep_{engine\ turbine})\ (MW) \qquad (1.8)$$

$$Heating\ agent_{required}\ (MW) = \sum(reboiler\ heating\ required)\ (MW) \qquad (1.9)$$

$$Cooling\ agent_{required}\ (MW) = \sum(heat\ exchanger\ agent)\ (MW) \qquad (1.10)$$

$$X_{coefficient}\ (MWh/kg_{CO2\ captured}) = X_{required}\ (MW)/Final\ CO_2\ captured\ (kg/h) \qquad (1.11)$$

where: X can be electric power (Ep), heating or cooling duties.

Table 3 shows that the best value in all three technical coefficients for CO_2 absorption is the tertiary amine MDEA (methyldiethanolamine). Since this amine is less alkaline than the other four amines, it can be used in a higher concentration (~50%), therefore has a better reactivity.

Table 2. Technical coefficient for CO_2 absorption in alkanolamines solution

Alkanolamine	Energy coefficient (MWh/kg $_{CO2}$)	Heating agent coefficient (MWh/kg $_{CO2}$)	Cooling agent coefficient (MWh/kg $_{CO2}$)
MEA	$8.63 \cdot 10^{-5}$	$3.82 \cdot 10^{-3}$	$4.06 \cdot 10^{-3}$
DEA	$8.62 \cdot 10^{-5}$	$0.81 \cdot 10^{-3}$	$0.83 \cdot 10^{-3}$
TEA	$10.28 \cdot 10^{-5}$	$18.50 \cdot 10^{-3}$	$19.12 \cdot 10^{-3}$
DIPA	$5.49 \cdot 10^{-5}$	$47.75 \cdot 10^{-3}$	$48.32 \cdot 10^{-3}$
MDEA	$\mathbf{8.57 \cdot 10^{-5}}$	$\mathbf{0.75 \cdot 10^{-3}}$	$\mathbf{0.80 \cdot 10^{-3}}$

Another advantage of the methyldiethanolamine is that MDEA does not form carbonates with CO_2, has high resistance to degradation, does not cause corrosion and presents low environmental toxicity.

CONCLUSIONS

Chemical absorption by using alkanolamines solutions is presently considered the most practical and economical method to separate CO_2 from flue gases generated by power sector at near atmospheric pressure. Various solvents are used for the recovery of CO_2 from these gases. The disadvantages of the majority of solvents are that they degrade in the process (thermal degradation, oxidation, forming stable salts with SO_x and NO_x, corrosion etc.), in addition, the desorption process for solvent regeneration requires a great deal of energy in form of heat. If more energy is required for desorption, the total energy demand of the process per unit CO_2 produced will be increasing.

The present paper was devoted to the evaluation of carbon dioxide capture using post-combustion methods and quantification of energy related coefficients (power consumption coefficient, heating agent coefficient, cooling agent coefficient) for CO_2 absorption in five different alkanolamines solution (monoethanolamine, diethanolamine, triethanolamine, methyldiethanolamine and diisopropanolamine). The paper also evaluates the performance of these five alkanolamines.

As it can be seen in the previous paragraph the best alkanolamine for CO_2 absorption is methyldiethanolamine. This tertiary amine can be used in a higher concentration (30-50%) than the other four alkanolamines, it does not form carbonates with CO_2, has high resistance to degradation, it does not cause corrosion and presents low toxicity.

EXPERIMENTAL SECTION

The above paragraph specifies many CO_2 capture techniques, but the present section only deals with the post-combustion capture technique by absorption. The CO_2 is captured from the flue gas after the gasification of coal in a coal power plant.

The CO_2 post-combustion process by absorption technology described in the present paper was modelled and simulated using the AMINE database model from the ChemCAD software. In ChemCAD AMINE model uses the Kent-Eisenberg method. This method is a simplified way to model the reactions (and phase equilibria) in a gas sweetening system. The model can be used in a system where water with one amine is used to treat gas with carbon dioxide, sulfuric acid, and/or ammonia.

For post-combustion capture technique, the CO_2 capture plants that use as solvent alkanolamines consists of an absorption column, a desorption column, drops separators, heat exchangers and stages compressors. A schematic diagram of the equipment used in this work is shown in Figure 2.

Absorption takes place at temperature of about 30 - 45℃ and a pressure around to atmospheric (about 1.05 bar). The purified gas, obtained at the top of the absorption column, contains a very small amount of unabsorbed CO_2 (less than 1 % vol.). The rich CO_2 amines solutions obtained at the bottom of the absorption column is sent to the desorption column for solvent regeneration. Contrasting the absorption process, the desorption process takes place at a higher temperature and lower pressure. The rich CO_2 amine stream is compressed using a pump and then is heated to about 100 - 120℃ temperature using a heat exchanger and afterwards is sent to the desorption column. The solvent regeneration is done by using a low pressure stream of 2 bar. The top stream is cooled and is sent to a drop separator from where the water is recovered at the bottom and the rich CO_2 gas (more than 90 % CO_2 vol.) is recovered at the top. The rich CO_2 gas obtained is sent to the compression unit, which has 4 compression stages with intercoolers. In the first stage the gas is compressed from 1.98 to about 6 bar; then the pressure is further increased in the second stage from 6 to 18 bar; the third stage the pressure reached 54 bar and last the final pressure is 122 bar. This stage compression method was chosen in order to avoid the overheating of the compressor and to allow the intermediate cooling of the compressed gas. After each cooler a drop separator is added in order to removes the water drops that could condense. The compressed CO_2 stream at 122 bar will be sent at the storage sites (geological storage like saline aquifers or used for Enhanced Oil Recovery - EOR).

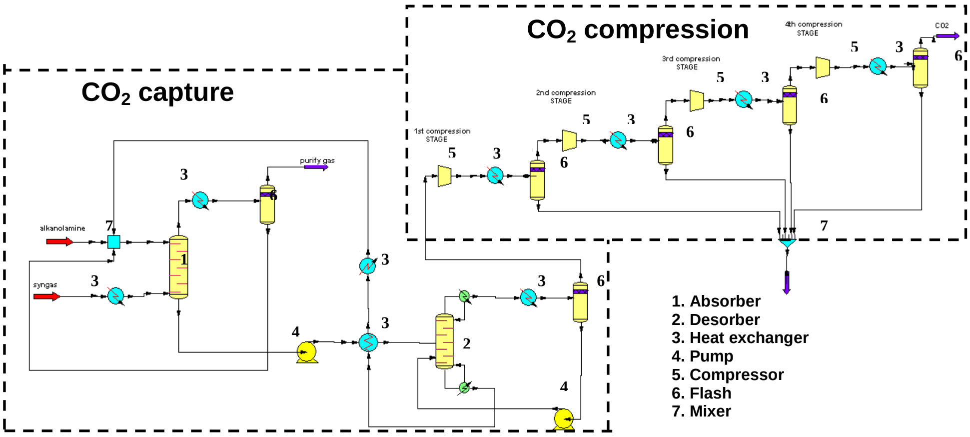

Figure 2. Carbon dioxide capture plant

The carbon dioxide absorption process was modelled and simulated using the AMINE model from the ChemCAD software. Other sub-systems of the plant and their design assumptions used in the mathematical modelling and simulation are presented in Table 3.

Table 3. Main design assumptions

Stream/Unit	**Parameters**
Flue gas	Pressure: 1.05 bar Temperature: 40 ℃ Composition (gas % vol.): 12.04 % O_2; 74.13 % N_2; 8.40 % CO_2; 4.52 % H_20; 0.91% Ar
Absorption column	Absorbent: alkanolamine Absorbent feed temperature: 40 ℃ Absorbent feed pressure: 1.05 bar Absorbent feed concentration (wt %): 30% MEA (case 1); 30% DEA (case2); 30% TEA (case 3); 30% DIPA (case 4); 50% MDEA (case 5)
Heat exchangers	ΔT_{min} =10℃ Pressure drop: 1% of inlet pressure
Desorption column	Pressure: 2 bar Temperature: 105 ℃
CO_2 compression	Delivery pressure: 122 bar Compressor efficiency: 85%
Captured CO_2 stream	H_2O limit concentration: <500 ppm CO_2 capture rate: >90%

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