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The Study of CO_2 Removal by Aqueous Solution of Methyldiethanolamine through Absorption Process

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Abstract

The removal of carbon dioxide from flue gases of power plant to meet their discharge limits in atmosphere is usually achieved by chemical absorption in aqueous solutions of alkanolamines.

In this paper, a tertiary amine, (N-methyldiethanolamine- MDEA) was investigated for CO_2 absorption process in a laboratory-scale packed column. The effects of initial CO_2 concentration, the height of column packing and the liquid–gas (L_0/G_0) ratio on the absorption process and on CO_2 recovery rate were analyzed.

Key words: *CO_2 removal, N-methyldiethanolamine, absorption***,** *experimental study.*

Introduction

Climate change is caused directly or indirectly by human activities that can alters the composition of the global atmosphere and which were added to natural climate variability observed over the comparable periods. The majority of the world scientific community agrees that climate change can already be seen due to human activities that produce the greenhouse gases emissions. The use of hard coal to produce energy leads to a specific CO_2 emission which means more climate pollution [10].

Besides the energy sector some energy intensive industries are responsible for significant CO_2 emissions. Manufacture of raw materials such as chemicals, petrochemicals, iron and steel, cement, paper and aluminum requires significant consumption of electricity, heat and steam [7]. There are a number of industrial activities that generate streams of flue gases with very high concentrations of CO_2 (e.g. natural gas processing plants and ammonia, and hydrogen production plants) [6].

The global challenges on the issues of energy and greenhouse gas emissions, innovative ideas as well as revolutionary approaches require long-term solutions.

There are four technical options for CO_2 control broadly defined as:

- the selection of energy sources;
- increasing energy efficiency;
- implementing the concept of CO_2 capture and storage (CCS);
- utilisation of CO_2.

Carbon capture and storage (CCS) is a potentially technology in reducing greenhouse gas emissions, while allowing the continued use of fossil fuels.

The CO_2 capture can be divided into three categories [2]:

- post-combustion processes for power station coal;
- pre-combustion processes for gasification and reforming;
- oxyfuel processes.

Some of pros and cons of each of these technologies capture are shown in Table 1.

Table 1. The pros and cons of capture technologies [9].

Capture technology	Pros	Cons
Post - combustion capture	Supplimentary removal of NO_X and SO_X polutants	Energy penalty due to solvent regeneration process Solvent loss
Pre-combustion capture	Low emissions	Cooling of flue gas is necessary before CO_2 capture
Oxyfuel combustion capture	Absence of nitrogen eliminates NOx emissions Absence of nitrogen provides low volume of gases and reduced size of entire process, also.	High energy consumption for air separation Burning in pure oxygen is complicated.

Although the concept of CO_2 capture from flue gases is developed especially for the production of energy (power plants), still post combustion capture through chemical absorption could be applied to almost all industrial processes [5]. However, specific capture technologies could provide more effective alternatives. A summary of the assumptions made about the possible capture options in three major industries are shown in Table 2.

Table 2. Summary of capture options for other emission sources (excluding energy sector) [12].

Source type	Flue gas flow targeted	CO_2 concentration in the flue gas (% by volume)	Capture technology	Cost / tonne CO_2 captured	Recovery rate (% of total CO_2 emissions from installations)
Petroleum refinery	Furnaces and boilers	3-13	Oxyfuel combustion	~30	65
	Combined heat and power (CHP) and Catalytic Cracking (CC) plants		Post-combustion capture	~45	80
Integrated steelmaking facilities	Furnaces	20	Gas recirculation from the top of the furnace	~20	70
Cement plants	Precalcination	14-33	Oxyfuel combustion	~34	50
			Post-combustion capture	~60	80

In this work, we investigated the CO_2 absorption process in a laboratory-scale packed column using 45 wt% MDEA in aqueous solution. The effects of CO_2 input concentration, the height of column packing and the liquid–gas (L_0/G_0) ratio on the absorption process and on CO_2 recovery rate were analyzed. It has to be mentioned that all experiments were carried out under identical operating conditions (temperature was kept constant at 30°C and pressure equal to atmospheric pressure).

Experimental Studies

The experiment of CO_2 absorption by aqueous N-methyldiethanolamine (MDEA) was carried out using air as CO_2 gas source. MDEA can be used in aqueous solutions at a concentration of above 50-55 by weight. The main advantages of MDEA are: less corrosion, very low vapor pressure, negligible loss by evaporation and low degradation rate. Most of all, the heat of reaction of CO_2 with MDEA is much less than monoethanolamine (MEA) or diethanolamine (DEA), and therefore its regeneration cost is much lower [3]. A major disadvantage is the slow kinetics of CO_2 absorption in aqueous MDEA [11]. This can be compensated by increasing the number of trays or the height of absorption and regeneration columns [14, 15].

Materials

The N-methyldiethanolamine used for the preparation of the aqueous solutions had a purity >99% and it was purchased from Sigma -Aldrich. MDEA was used without any additional purification. All solutions were prepared with demineralised water. Aqueous solution of MDEA was prepared by weighing out the requisite amount of amine using Mettler Toledo mass balance with ±0.01% accuracy.

The purity of carbon dioxide was more than 99.8% (Linde Gas Romania).

Experimental procedure

A schematic drawing of the experimental set-up is shown in Figure 1. It consists of an absorber, a liquid supply, a gas supply, and a gas sampling part.

The absorption column is a vertical glass tube filled with polypropylene rings (Winston rings), constituting the packing. Inside diameter of the column is equal to 0.045 m and the useful height of the contactor is 0.30 m in first set of experiments and 1.00 m in the second set. Further experimental details are given in [8]. The absorbent, namely aqueous MDEA (45 wt%), and a peristaltic pump is used to feed the absorption solution to the top contactor.

The gas phase is a synthetic mixtures prepared by a flow of air generated by compressor, in which CO_2 released from the gas supply is added to obtain the desired concentration. The experiments reported were carried out at 10 vol% CO_2 (in range of CO_2 in flue gases from fossil fuel combustion in a power plant) and 20 vol% CO_2 (in range of CO_2 in flue gas from cement plant). The gas mixture contacts counter-currently the liquid flowing on the packing rings. The gas flow rates are metered by the two flow meters. Sampling of gas simultaneously at the input and the output of the column is performed continuously by a CO_2 gas analyzer (Vaisala CO_2 Meter, measuring range 0-20 vol%). The gas feed temperature and pressure was continuously controlled. Temperature was kept constant at 30°C and pressure was equal to atmospheric.

The absorption rate was determined for various total liquid flow rate and two different packing heights. The operating conditions are summarized in Table 3.

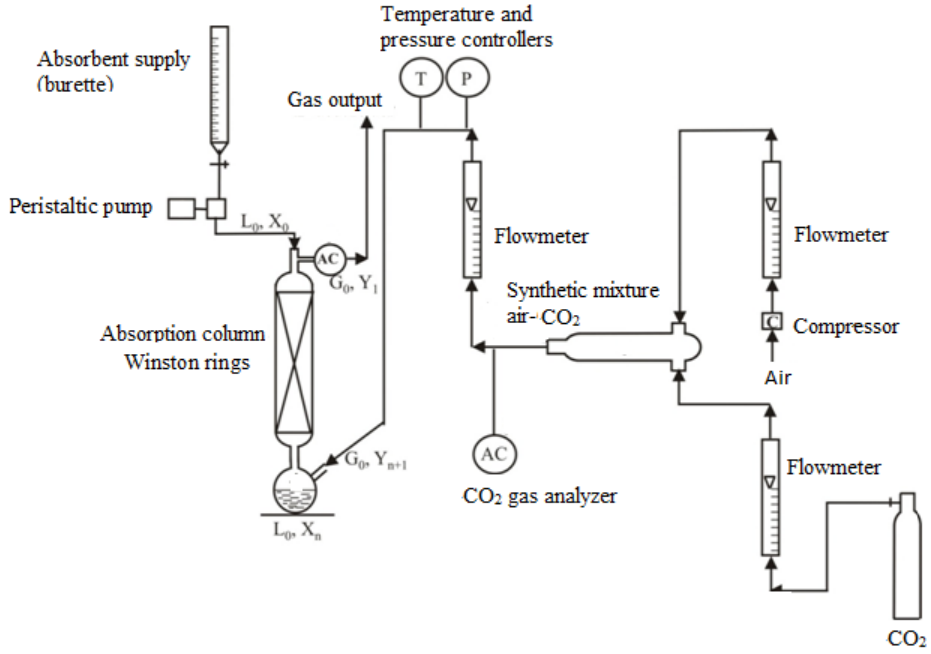

Fig.1. Schematic diagram of the experimental apparatus with the gas-liquid contactor.

Table 3. Operating conditions of absorption test runs.

Absorber height of 0.30 m		
Air flow rate, liter/h	Input CO_2 concentration, vol%	Liquid flow rate, cm^3/min
18	10,1	9
18	20	9
Absorber height of 1.00 m		
Air flow rate, liter/h	Input CO_2 concentration, vol%	Liquid flow rate, cm^3/min
18	10	9
18	20	5
		9
		15

Modeling of absorption performances

The experiments carried out with the apparatus showed in Figure 1 have as firstly purpose the providing of CO_2 concentrations in the flows at the ends of absorption column. For gas flows, these were calculated as molar ratio denoted Y_{n+1} for bottom and Y_1 for top of column, respectively. The input/output concentrations of CO_2 were measured as vol% (or mol%) by the Vaisala Meter devices.

$$\text{Yn+1 or Y1}=\frac{\text{mol\% CO2}}{\text{100-mol\% CO2}} \tag{1}$$

The molar flow rate of absorbed CO_2 was calculated as:

$$G_{CO_2}^{R} = G_0(Y_{n+1} - Y_1) \tag{2}$$

The amine molar flow denoted L_0 was calculated based on the total liquid flow rate expressed in cm^3 /min or liter/h by means of the density of the aqueous amine solution, MDEA concentration and its molecular weight. The liquid–gas (L_0/G_0) ratio is a key parameter for the chemical absorption process in a packed column. To investigate the effects of L_0/G_0 ratio on the absorption process, we varied the flow rate of the aqueous solution of MDEA while keeping the flow rate of air constant.

For liquid flows at the ends of absorption column, the CO_2 loadings were adopted as molar ratio, also. At the top column, this was assigned us zero value because the lean amine flow was not recirculated from a stripping column. The CO_2 loading i.e. moles CO_2 absorbed per mol of MDEA was calculated as:

$$X_n = \frac{G^R_{CO_2}}{L_0} \tag{3}$$

Finally, the recovery rate of CO_2 was calculated as follows:

$$\varphi = \frac{Y_{n+1} - Y_1}{Y_{n+1}} \cdot 100 \tag{4}$$

Results and Discussions

The first runs of the CO_2 absorption experiments were carried out in the column with packing height of 0.30 m. Table 4 presents the main experimental values related to this first case.

Table 4. Experimental values of CO_2 absorption in 45 wt% MDEA aqueous solution. Packing height 0.30 m

Volumetric air flow rate, liter/h at 20ºC	18.00	18.00
CO_2 input concentration, %vol.	10.10	20.00
CO_2 outlet concentration, %vol.	7.05	9.20
Y_{n+1}, moles CO_2/mol air	0.112	0.250
Y_1, moles CO_2/mol air	0.0758	0.101
Molar air flow rate Go, mol/h	0.749	0.749
Volumetric flow rate of lean amine solution, cm^3/min	9.00	9.00
Volumetric flow rate of lean amine solution, cm^3/h	540.00	540.00
Density of aqueous MDEA at 30ºC, g/cm^3 [4]	1.03664	1.03664
Mass flow rate of lean amine solution, g/h	559.79	559.79
Molecular weight of MDEA, g/mol	119.17	119.17
Mass flow rate of MDEA, g/h	251.90	251.90
Molar flow rate of MDEA, mol/h	2.11	2.11
Molar liquid–gas (L_0/G_0) ratio, moles MDEA/mol air	2.82	2.82
Molar flow rate of absorbed CO_2, mol/h	0.0273	0.111
CO_2 loading, Xn, moles CO_2/mol MDEA	0.0129	0.0527
Recovery rate of CO_2,%	32.49	59.47

As it can be seen in Table 4, at the constant molar liquid–gas (L_0/G_0) ratio, by doubling the input concentration of CO_2 it was obtained an increase in CO_2 loading and an increasing in recovery rate of CO_2. This shows that MDEA absorbent has a good absorption capacity at high concentration of CO_2 in gas flow. In fact, this behavior was expected due to the reaction mechanism that allows loading of 1 mole CO_2 per mol MDEA [16]. It is well known that in a tertiary amine, the nitrogen atom is bonded to three hydrocarbon groups and no hydrogen atoms

and is reacted with CO_2 to form bicarbonate [1, 13]. As the carbamation reaction cannot take place like in primary and secondary amines, the absorption rate of MDEA with CO_2 is quite low.

To increase the recovery rate of CO_2 in aqueous solutions of MDEA, in fact to increase the reaction rate of CO_2, one way is to increase the absorption column height. In order to prove the effect of increasing the height of the column on the absorption, all experiments are repeated on a column of 1.00 m. Main experimental results are presented in Table 5.

Table 5. Experimental values of CO_2 absorption in 45 wt% MDEA aqueous solution. Packing height 1.00 m

Volumetric air flow rate, liter/h at 20ºC	18.00	18.00	18.00	18.00
CO_2 input concentration, %vol.	10.10	20.00	20.00	20.00
CO_2 outlet concentration, %vol.	3.30	5.60	6.00	5.10
Y_{n+1}, moles CO_2/mol air	0.112	0.25	0.25	0.25
Y_1, moles CO_2/mol air	0.0341	0.0593	0.0638	0.0537
Molar air flow rate Go, mol/h	0.749	0.749	0.7490	0.7490
Volumetric flow rate of lean amine solution, cm^3/min	9.00	9.00	5.00	15.00
Volumetric flow rate of lean amine solution, cm^3/h	540.00	540.00	300.00	900.00
Density of aqueous MDEA at 30ºC, g/cm^3 [4]	1.03664	1.03664	1.03664	1.03664
Mass flow rate of lean amine solution, g/h	559.79	559.79	310.99	932.98
Molecular weight of MDEA, g/mol	119.17	119.17	119.17	119.17
Mass flow rate of MDEA, g/h	251.90	251.90	139.95	419.84
Molar flow rate of MDEA, mol/h	2.11	2.11	1.17	3.52
Molar liquid–gas (L_0/G_0) ratio, moles MDEA/mol air	2.82	2.82	1.57	4.70
Molar flow rate of absorbed CO_2, mol/h	0.0586	0.143	0.139	0.147
CO_2 loading, Xn, moles CO_2/mol MDEA	0.0277	0.0676	0.119	0.0417
Recovery rate of CO_2,%	69.62	76.27	74.47	78.50

Comparing the data from Table 4 with those of Table 5, it is found that by increasing the height of the column from 0.30 m to 1.00 m (for the same input concentration of CO_2 and the same the liquid–gas (L_0/G_0) ratio) it were obtained higher loadings in rich MDEA and an increase of recovery rate, also. These findings prove the beneficial effect of increasing the column height over absorption efficiency. Data from Table 4 shows that the absorption performances are insignificant influenced by increasing the flow rate of absorbent (for the same initial CO_2 concentration).

Conclusions and Perspectives

The present experimental investigation is a comparative study of absorption performance of CO_2 absorption in aqueous solution of 45 wt% MDEA through chemical absorption process in a packed column with two different heights of 0.3 m and 1.00 m. Absorption study is performed on the temperature of 30ºC, nearly atmospheric pressure and initial CO_2 concentration of 10 vol% and 20 vol%. It is observed from the experimental findings that the CO_2 loading in absorbent increases with increasing the initial concentration of CO_2 from 10 to 20 wt% (at the constant liquid–gas (L_0/G_0) ratio) and these prove the good absorption capacity of MDEA. But, the percentage of CO_2 absorbed during absorption process is limited around the value of 76% even with increasing of packing height from 0.3 m to 1.00 m (at the constant ratio of absorbent). Experimental data show that by increasing the liquid–gas (L_0/G_0) ratio (at initial CO_2 concentration constant i.e. 20 vol%) the percentage of CO_2 absorbed increase very slightly.

Hence, it is concluded from the experimental observations that the aqueous solution of 45 wt% MDEA is a proper absorbent towards CO_2 gas capture from flue gas, but the absorptive performances, particularly rate of reaction, can be improved by increasing the height of the absorber column only to attain a moderate recovery rate. A recovery rate to 90% can be obtained by blending MDEA with an accelerator such as piperazine PZ.

In order to be able to simulate this gas treatment process in a wider range of practical industrial operating conditions, the effects of temperature and of absorbent blends could be investigated. In our future work we intend to test other amine types, such as blended amine solutions (for example N-methyldiethanolamine and piperazine) under different concentrations in aqueous solutions, or other amine activators (for example piperidine), or to test sterically hindered amine.

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Studiul eliminării CO_2 prin absorbţie în soluţii apoase de metildietanolamină

Rezumat

Eliminarea dioxidului de carbon din gazele de ardere ale termocentralelor, pentru a respecta limitele de evacuare în atmosferă, se realizează de obicei prin absorbție chimică în soluții apoase de alcanolamine.

În această lucrare, o amină terțiară, cum ar fi, metildietanolamina a fost investigată în procesul de absorbție a CO_2 într-o coloană cu umplutură, la scară de laborator. Au fost analizate efectele concentrației de intrare a CO_2, a înălțimii de umplutură a coloanei și a raportului gaz/ lichid (L_0 / G_0), raportul asupra procesului de absorbție și asupra gradului de recuperare a CO_2.