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Analysis of the Regeneration of Monoethanolamine Aqueous Solutions by Microwave Irradiation

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Abstract

Even if numerous studies were published over the last decades about the CO_2 capture process by aqueous amine solutions, only one paper was found so far in the literature concerning the use of microwave (MW) to regenerate the spent solutions. The present work was then performed to investigate the regeneration efficiency of MEA aqueous solutions by MW while testing various amine concentrations including the well-known 30 wt%. Stripped CO_2 quantities were compared to the MW energy absorbed by the solution to find the optimal regeneration conditions. The heating rate of solutions by MW was found to be influenced by their heat capacity and viscosity, two parameters with opposing effects giving rise to a maximal heating rate around 50-60 wt% MEA. By performing absorption and regeneration cycles, the cyclic CO_2 capacity of each solution was found and compared to the amount of MW energy absorbed by the solution during the stripping step. The lowest energy per mole of stripped CO_2 ratio was found for the 50 wt% MEA solution which is 30 % lower than the value found for the benchmark 30 wt% MEA.

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Keywords: Monoethanolamine aqueous solutions, Microwave heating; Regeneration optimization; Energy efficiency.

1. Introduction

Post-combustion carbon dioxide (CO_2) capture from fossil fuel-fired power plants using chemical absorption with aqueous alkanolamine solutions is today's best available technology [1] and monoethanolamine (MEA) has been considered for many decades as the benchmark amine for this process. According to Rochelle [2], amine scrubbing will probably remain the dominating technology for CO_2 capture up to 2030. This cyclic process consists of CO_2

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absorption and desorption typically performed in two packed columns [3]. The CO_2 contained in the flue gas is absorbed by the solution in the first column then the rich solvent is sent to desorption unit where it is heated to strip the CO_2. The lean solvent could be sent back for absorption while the CO_2 is compressed and transported for further use or storage.

However, the main drawbacks of this amine-based CO_2 capture process arise from the large equipment size [4] and the high energy consumption for the desorption step usually carried out around 120-140 °C which accounts for around 70% of the overall operating cost [5, 6]. Up to date, solutions to these problems were mainly focussed on the development of *(i)* more efficient gas-liquid contactor devices (such as rotating bed or membrane contactors) [7, 8] or *(ii)* new low-energy-requiring solvents (such as thermomorphic biphasic solvents or sterically hindered amines) [9, 10]. Here, we investigate one new possibility that is the use of microwave (MW) irradiation as an alternative energy-efficient approach to the conventional thermal heating to recover CO_2 from rich amine solutions.

Theoretically, MW heating is based on the ability of molecules with a dipole moment to absorb microwave energy and effectively convert it into heat. Two constants are essentially involved: the dielectric constant (ε') which is a measure of the substance's ability to store electric energy, and the dielectric loss factor (ε'') which is a measure of the substance efficiency to convert electromagnetic energy into heat [11, 12]. These constants are function of the MW frequency, the temperature and the molecule chemical interactions inside the solution [13].

As MW heating occurs through direct molecular interactions with the electromagnetic radiation, the main advantages of MW are an instantaneous and volumetric heating without the heat transfer restrictions associated with conventional conductive or convective heating. In the last decades, MW heating applications have been largely reviewed [12, 14-16] and despite the above-mentioned advantages, only one very recent research paper [17] has been published concerning MW use for CO_2 stripping from a spent 30 wt% MEA aqueous solution. That study showed that MW can regenerate the solution more quickly than with conventional heating and at low temperatures (70–90 °C), potentially reducing overall process costs.

There is clearly a lack of research about the use of MW to recover CO_2 from rich amine aqueous solutions. The present work was then performed to investigate the regeneration efficiency of MEA aqueous solutions by MW while testing various amine concentrations including the well-known 30 wt%. Stripped CO_2 quantities were compared to the MW energy absorbed by the solutions to find the optimal regeneration conditions. At our knowledge, such study is lacking from the literature and is primordial to assess the efficiency of MW heating for the regeneration of rich amine solutions and to optimize this process.

2. Experimental

2.1. Reagents

In this work, aqueous amine solutions were prepared by gravimetric method using distilled water and MEA (CAS No. 141-43-5). The amine (from Sigma-Aldrich UK) had a minimum purity of 98 % and was used without further purification. A Sartorius ED224S balance with a precision of $\pm 1\times10^{-4}$ g was used to prepare the solutions and it was calculated that the uncertainty of the reported concentrations was less than 0.1 wt%. Gases used for absorption and desorption experiments (CO_2 and N_2) were of commercial grade with a minimum purity of 99.99% (Linde Group UK).

2.2. Microwave generator setup

As a complete description of the MW regeneration setup can be found elsewhere [17], only a brief description will be given here. MW regeneration of the CO_2-loaded aqueous MEA solutions were performed with a device composed of a microwave magnetron operating at 2.45 GHz with a maximum output power of 1.2 kW controlled by an Alter SM445 power supply. A single mode waveguide directed the microwave energy towards respectively: *(i)* a dual-directional coupler (GAE Inc., GA310x) to measure the forward and reflected MW power flow, *(ii)* a resonant cavity where the sample could be placed, and *(iii)* a sliding short circuit (Sairem) to reflect the MW wave at normal incidence.

In the sample cavity, 5 ml of the solution could be contained in a cylindrical quartz reactor (which is transparent to MW) which has an outside diameter of 17 mm and a thickness of 1.5 mm. The temperature of the solution was

measured at the center of the liquid bulk every second with an optical fiber thermometer (Opsens OTG-MPK8) suited for use with amine solutions and MW irradiation. Gases were fed via two mass flow controllers (Brooks Instruments GF-Series, 0-400 ml/min N_2, 0-100 ml/min CO_2) and bubbled at the bottom of the solution through a small quartz tube. The outlet gas stream of the reactor passed successively through a cold trap, a humidity meter, a non-dispersive infrared (NDIR) CO_2 sensor (COZIR-W-100) and finally a flow meter (Brooks Instruments SLA5860, 0-500 mL/min) before exiting through an exhaust line. All experiments were performed at atmospheric pressure and to avoid unexpected CO_2 absorption by the solution, all gas lines were purged with N_2 before and between experimental runs.

2.3. Absorption and regeneration procedures

In order to obtain CO_2-loaded aqueous MEA solutions to perform the regeneration, CO_2 absorption was first accomplished by feeding the quartz vial with a binary gas mixture of 20% CO_2 and 80% N_2 which was bubbled through the 5 mL MEA solution at a total flow rate of 100 mL/min for 20 minutes and ambient temperature. The outlet CO_2 flow rate was calculated by multiplying the CO_2 sensor and flow meter readings. A blank absorption run was performed with an empty reactor to allow the absorbed quantity of CO_2 to be calculated by integrating the difference between the blank and sample CO_2 outlet flow rates.

Once a loaded MEA solution was obtained, the MW regeneration step could be performed. N_2 flow rate was first set at 100 ml/min to purge the gas line from CO_2 and then acted as a sweeping gas. The MW source was turned on for 10 min at an initial power of 100 W to heat the solution from ambient to the desired regeneration temperature and then the power was manually reduced and controlled to maintain a constant temperature. After these 10 min, MW was turned off and the solution was allowed to cool down for 10 min. The amount of stripped CO_2 was determined by direct integration of the outlet CO_2 flow rate.

3. Results and Discussion

3.1. Effect of MEA concentration on MW regeneration

3.1.1. Heating profile

Before performing the regeneration of CO_2-loaded MEA solutions, fresh solutions were first used in order to gauge their behaviour to microwave heating. This preliminary work allowed us to select an adequate initial MW heating power of 100 W which was sufficient to heat the solutions in a short time frame (less than 1 min) but not too high to avoid large temperature overshoot of the selected temperature set point. Several MEA concentrations were tested and results can be seen in Fig. 1 along with the heating curve of pure water.

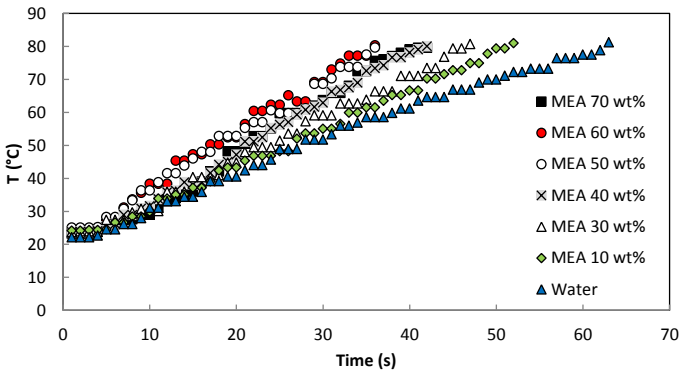

Fig. 1. Heating profile for various fresh MEA solutions with MW power of 100 W.

From this figure, it is first possible to see that the heating rate increases with MEA concentration but up to 50 wt%

MEA. The 60 wt% MEA solution has a similar heating profile than the 50 wt% one and the 70 wt% MEA solution take even longer time to reach 80°C. The heating rates can be partly explained be the heat capacity of each solution. Data reported in the literature [18] show that the heat capacity of MEA solution decreases continuously with an increase in concentration at a given temperature (e.g. 4.19, 3.76, 3.43 and 3.14 J/g.K for water, and 30, 50 and 70 wt% MEA respectively at 25°C). Therefore, the heating rates should increase continuously in the same way with MEA concentration, which is true up to 50 wt% but not for higher values.

One possible explanation for the different behaviour at higher concentrations may come from the viscosity of the solution that significantly increases above 50 wt% (e.g. 0.89, 2.48, 5.51, 12.46 mPa.s for water and 30, 50 and 70 wt% MEA respectively at 25°C) [19]. According to Salvi et al. [20], molecules in highly viscous media have a slower response to the oscillating MW electric field so they have a slower heating rate. A maximal heating rate can then be explained to be around 50-60 wt% MEA based on the opposite effect of the solution heat capacity and solution viscosity. From a process point of view, this maximal heating rate is interesting as if the solution take less time to reach its temperature set point, less MW energy is required.

3.1.2. Cyclic absorption and desorption experiments

To evaluate the efficiency of MW for the regeneration of CO_2-loaded MEA solutions, cyclic absorption and regeneration experiments were performed as would occur in the industrial CO_2 capture process. Same conditions were applied for all the solutions, i.e. a 20-minute absorption step at ambient temperature followed by 10 minutes of MW irradiation at 80°C and a 10 min cool-down step. Absorption and regeneration cycles were accomplished until the absorbed amount of CO_2 in the absorption step was the same as the stripped amount during regeneration. It took usually 2 to 3 cycles to achieve. An example of the absorption and regeneration cycles for the 10 wt% MEA solution can be found in Fig. 2 (a) and (b) respectively.

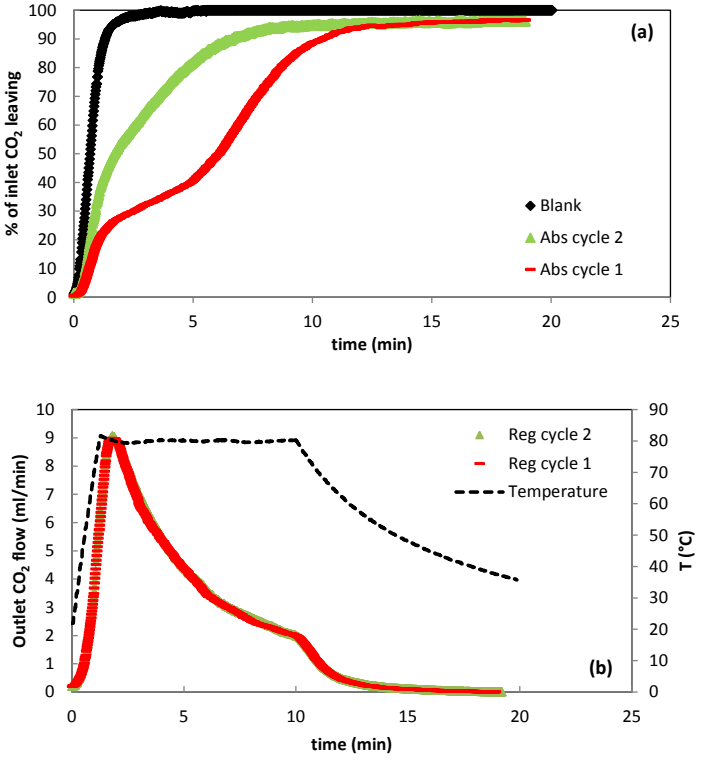

Fig. 2. (a) absorption curves; (b) regeneration curves of a 10 wt% MEA solution.

On Fig. 2 (a), concerning the CO_2 absorption, it is possible to see as expected that during the first cycle, much more CO_2 was absorbed than during the second cycle. The area between the blank and the first absorption curves is bigger. This can be explained by the fact that at the beginning of the second cycle, there was already some CO_2 inside the solution so less CO_2 could be absorbed before the solution reached a near equilibrium (after around 12 min). Here two cycles were enough to show in Fig. 2 (b) that the stripped amount of CO_2 was the same at each regeneration step (overlapping of the two curves) making possible the determination of the cyclic capacity that is the amount of CO_2 absorbed and desorbed at each cycle. It is also possible to see that it took around 72 sec for the 10 wt% MEA CO_2-loaded solution to reach 80°C in comparison to 52 sec for the fresh solution (see Figure 1). This increase of time may be explained by some MW energy reversing the CO_2 reaction instead of heating the solution.

Similar results were obtained for the other MEA concentrations at the exception of the 70 wt% MEA where a suspension of bicarbonate salt appeared during the absorption steps. As the presence of solid could be a problem in an industrial CO_2 capture process (pipe clogging, equipment erosion, etc.), this MEA concentration was discarded from further analysis.

3.1.3. MW energy efficiency

As explained in *Section 2.2*., the MW setup allowed with the dual-directional coupler to determine the quantity of energy absorbed by the solution during MW regeneration steps. It should be mentioned that the desorption energy measured during the regenerations were divided by the energy measured by the benchmark 30 wt% MEA and reported in Table 1. This division was done as it is known in the literature [21] that the MW desorption energy measured for small scale volumes (as 5 ml in this work) overestimate the real energy consumption and cannot be used directly. These data, divided by the CO_2 cyclic capacity could be used as a good tool to optimize the regeneration process by determining the conditions were the amount of energy per mole of stripped CO_2 is the lowest.

Table 1. Energy consumption for different aqueous MEA solutions.

MEA concentration (wt%)	Rich loading	Cyclic capacity (mol CO_2)	Desorption energy	Energy/CO_2 (mol^{-1})
10	0.56	0.0019	1.10	580
30	0.52	0.0030	1.00	333
40	0.49	0.0034	0.93	275
50	0.47	0.0036	0.84	234
60	0.41	0.0026	0.67	257

From Table 1, some trends can be observed. First, the rich loading achieved during the cycling absorption-regeneration process decreased with the increase of MEA concentration as expected and reported in the literature [22]. This shows that even if there are more amine molecules in a given volume at higher concentrations, these amines are less effective individually to absorb CO_2. Besides, the cyclic CO_2 capacity generally increased with the amine concentration as the absolute amount of absorbed CO_2 increased with the MEA concentration. However, the value at 60 wt% is significantly lower than at 50 wt%. Data analysis revealed that the CO_2 desorption with the 60 wt% loaded solution is much slower than with lower concentrations maybe due to the high viscosity of the solution as explained earlier in *Section 3.1.1*.

Finally, taking into consideration the energy absorbed by the solutions and the amount of CO_2 desorbed, the lowest ratio, which is 30 % lower than for 30 wt% MEA, it appeared that 50 wt% MEA is the optimal concentration for the CO_2 capture process with MW regeneration under the tested conditions in this work.

4. Conclusions

Even if numerous studies were published over the last decades in the literature about the CO_2 capture process by aqueous amine solutions, only one paper was found so far concerning the use of microwave to regenerate the spent solutions indicating that is still much to learn about this new regeneration technique. In this work, we showed that the MEA concentration influenced significantly the cycling absorption-MW regeneration process. The heating rate of

solutions by MW was found to be influenced by their heat capacity and viscosity, two parameters with opposing effects giving rise to a maximal heating rate around 50-60 wt% MEA. By performing absorption and regeneration cycles, the cyclic CO_2 capacity of each solution was found and compared to the amount of MW energy absorbed by the solution during the stripping step. The lowest energy per mole of stripped CO_2 ratio was found for the 50 wt% MEA solution which is 30 % lower than the value found for the benchmark 30 wt% MEA. This indicated that the 50 wt% MEA solution may potentially be used to reduce the energy consumption in an industrial CO_2 capture process using MW for regenerating the solutions.

It is unquestionable that the MW regeneration process of spent aqueous amine solutions can be further understand, harnessed and optimized. In addition to the amine concentration, other parameters like the regeneration time and temperature, the MW power intensity or the CO_2 loading inside the solution may influence the MW regeneration efficiency. Evaluation of these parameters is currently in progress in our laboratory and will be reported in an upcoming publication.

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