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Carbon dioxide chemical absorption using methylpiperidines aqueous solutions

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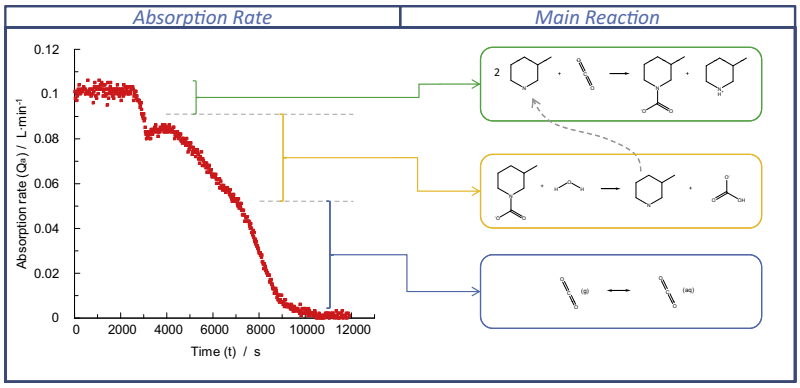
HIGHLIGHTS

- A methyl group placed away the N group shows the better behavior.
- 3-Methylpiperidine reaches better regeneration results than monoethanolamine.
- 3-Methylpiperidine is a suitable solvent for carbon dioxide chemical absorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Present research work has centered on the improvement of carbon dioxide chemical absorption with piperidine aqueous solutions changing the solvent to reach better solvent characteristics and avoid certain negative items such as high toxicity and corrosion. This aim will be obtained by using solvents with an additional methyl group in the molecule in different parts of piperidine, and analyzing the effect upon carbon dioxide absorption behavior. The carbon dioxide absorption rate has been analyzed under different operation conditions (gas flow-rate and amine concentration) and type of solvent using a semicontinuous gas-liquid contactor (batch for liquid phase and continuous for gas phase). Also carbon dioxide loading was determined for each solvent in relation with reaction mechanism between carbon dioxide and each amine. The regeneration process was carried out for the best solvent using a treatment with calcium hydroxide avoiding the high temperatures in stripping methodology reaching better results that the best available technique.

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1. Introduction

Carbon dioxide capture or separation processes are being the aim of different research studies trying the intensification of the overall operation and these works have involved different research fields. One of them is centered on the development of new more efficient solvents that improve the overall process of carbon dioxide separation [1,2]. The searched improvements are related with different aspects mainly based on: higher reaction rate, higher carbon dioxide loading, lower equipment corrosion, lower solvent degradation and lower cost of solvent regeneration. Different researchers have proposed, in the last few years, new solvents

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based on the development of molecules different than conventional ones [3], mixtures of amines [4] or ionic liquids [5], but the improvements are not very important and some types of these solvents showed negative characteristics such as high viscosity (for instance for ionic liquids due to the formation of hydrogen bonding networks that decrease mass transfer rate), toxicity (for instance monoethanolamine and piperazine have shown important toxicity degrees) and high degradation rate (for instance aqueous solutions of monoethanolamine and N,N-diethylethanolamine show high degradation rates) [6,7].

Included in the research field based on the development of new solvents that intensificate the carbon dioxide separation by chemical absorption process, previous results of our research team concluded that solvents based on certain cyclic amines such as pirrolidine and piperidine [8,9] enhance carbon dioxide capture rate in comparison with aqueous solutions of monoethanolamine and other commonly used alkanolamines. One of the reasons that show these cyclic amines solvents as an interesting option is the high reaction rate with a different reaction order [9]. This fact increases the reaction rate and enhances carbon dioxide mass transfer phenomenon. Both piperidine and pirrolidine showed a similar behavior regarding chemical kinetics and absorption rate. The analysis of the reaction mechanism [8] allowed to conclude that carbamate stability is lower than conventional alkanolamine-based solvents producing bicarbonate ion as main reaction product due to carbamate hydrolysis. This last reaction is produced in an important degree reaching carbon dioxide loadings near to 1 mol CO_2·mol amine^{-1} because the reaction stoichiometry to produce bicarbonate ion is more favorable 1:1 (carbon dioxide:amine) in comparison with carbamate production (1:2).

Some research studies centered on the development of chemical solvents have concluded that sterically hindered amines can be consider as suitable solvents to carry out this type of separation [10,11] with better overall results than the conventional and linear alkanolamines. These conclusions are based on the fact that this type of amines can improve the process taking into account the overall results of absorption and regeneration. These solvents reduce the amount of carbamate in the reaction products allowing to reach a higher carbon dioxide loading and better regeneration characteristics. But generally these suitable characteristics in sterically hindered amines are reached at the expense of a lost in carbon dioxide capture rate caused by a decrease in the chemical kinetic that affects negatively in the overall process of mass transfer and chemical reaction.

Present work proposes alternatives to commonly used amines at industrial level trying to improve the overall process and specific items: reaction rate, carbon dioxide loading, absorption rate and regeneration degree. To reach these aims several methylpiperidines have been used in aqueous solutions as solvents in the carbon dioxide chemical absorption in a bubble column reactor.

2. Materials and methods

2.1. Materials

Carbon dioxide was supplied by Praxair with a purity of 99.998% and piperidine, N-methylpiperidine, 2-methylpiperidine, 3-methylpiperidine and 4-methylpiperidine were supplied by Alfa Aesar with purities of >99%, 99%,>98%, 98% and >98% respectively. Aqueous solutions of these amines were used to chemically absorbs the carbon dioxide. These solutions were prepared on mass with double distilled water. The reagent used in the regeneration processes was calcium hydroxide supplied by Merck with a purity >96%.

2.2. Absorption studies

Carbon dioxide absorption experiments were carried out using a square bubble column reactor (side length = 4 cm and height = 65 cm) made in poly(methyl methacrylate) (PMMA), and using a liquid phase volume of 0.9 L. The gas phase (pure carbon dioxide) was fed to the contactor through a five-hole sparger built in Teflon®. The inlet and outlet gas flow-rate were controlled and measured with two mass flow controllers (Alicat Scientific MC-5SLMP-D). The mass flow controllers were calibrated for the used gas flow-rate and pressures ranges by the supplier. Flow Vision SC software package (Alicat Scientific) was used to control the flowmeters and to record the carbon dioxide outlet flow-rate during the experiments. The amount of carbon dioxide transferred to liquid phase throughout time has been calculated as the difference between inlet and outlet gas mass flow-rates. The pressure drop was measured between the column inlet and outlet, using a Testo 512 digital manometer. The working regime was continuous in relation to the gas phase and batch regarding the absorbent liquid one. The effects of some experimental variables were analyzed in this work and the experimental ranges for gas flow rate and amine concentration were: $0.1\ L{\cdot}min^{-1} < Q_G < 0.5\ L{\cdot}min^{-1}$; $0.1\ mol{\cdot}L^{-1} < C_B < 0.5\ mol{\cdot}L^{-1}$.

2.3. Regeneration process

The experimental technique consists on a treatment with a stochiometric amount of calcium hydroxide in suspension calculated from absorption experiments. During this operation different reactions take place to regenerate the chemical solvent: the deprotonation of amine is produced and the bicarbonate is transformed in carbonate ion. This fact causes the removal of carbon dioxide chemically absorbed by the precipitation of calcium carbonate. After the filtration process, a clear amine solution was obtained to reuse again in the chemical absorption process.

3. Results and discussion

Present work tries to increase the research in the field of the development of new chemical solvents for carbon dioxide separation and more specifically in the use piperidine-based solvents taken into account the suitable behavior of this amine in previous works and also avoiding the negative characteristics mainly centered on toxicity and corrosion.

3.1. Tertiary methylpiperidine solvent

Fig. 1 shows a first comparison between aqueous solutions of piperidine and N-methylpiperidine on the basis of carbon dioxide absorption rate. The experimental data indicate that the behaviors are different though the molecules only differ in the presence of a methyl group. But the presence of this substituent causes a change in the type of amino group (a tertiary amine). The presence of a tertiary amino center [12] causes significant changes in the absorption behavior in comparison with primary and secondary amines. The observed behavior in Fig. 1 shows a high decrease in carbon dioxide absorption rate mainly in the period corresponding to low carbon dioxide loadings. This behavior is in agreement with previous studies that have analyzed different tertiary amines and the corresponding reaction mechanism that shows differences with primary and secondary amines though the main reaction product will be the same [13,14]. In general the reaction mechanism for tertiary amines involves a low reaction rate and this fact affects upon the overall carbon dioxide absorption process because the driving force decreases for this type of solvents.

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