Synthesis and selection of new amine absorbents for CO₂ capture

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Abstract
This work focuses on synthesizing and selecting hindered new amine absorbents to reduce the regeneration energy cost for CO₂ capture. To achieve this target we investigated 34 amine based CO₂ absorbents (10 secondary and 24 tertiary) with systematic modification of their chemical structures. Performances evaluations of these absorbents in aqueous solutions were carried out based on their CO₂ absorption rate, absorption capacity and heat of reaction measurements. Particular attention was paid to absorbents with a potential for high absorption rate and low heats of reaction. The results were then compared with conventional absorbents AMP and MDEA which were chosen as the base case for all comparisons. We found five secondary and eight tertiary amine absorbents with advantages of high absorption rate and low heats of reaction compared with AMP and MDEA. Absorbents higher absorption rate and lower reaction heat characteristics will reduce the regeneration energy cost of CO₂ during solvent stripping.

Keywords: amine absorbent, CO₂ capture, absorption-regeneration, reaction rate, heat of reaction

1. Introduction
Carbon dioxide is known as a representative greenhouse gas that causes global warming. To prevent global warming by the greenhouse gas effect CO₂ capture and storage is essential. As for the capture technologies, a chemical absorption process is promising because it can be easily and practically made for large-scale CO₂ point sources. Furthermore, in the currently used systems more than half of the capture cost is caused by the absorbent regeneration. In order to make it practical in the near future, it is essential to reduce the absorbent regeneration cost by developing new absorbents. To achieve this target, we focused on the development of unique amine based CO₂ absorbents which have a low heat of reaction, a fast absorption rate and a high capacity for carbon dioxide.

Previously we developed several cost saving new absorbents for CO₂ capture [1-3]. They were evaluated on their CO₂ loading capacity, heats of reaction and absorption rates by comparison to MEA and MDEA. Those results showed that there is a structure-performance relationship between amino alcohols and CO₂ capture performance. The relationship between CO₂ absorption rate and heat of reaction, as determined experimentally, for a primary (Monoethanolamine, MEA), and 2-amino-2-methyl-1-propanol, (AMP) a secondary (Diethanolamine, DEA) and a tertiary (Methyldiethanolamine, MDEA) alkanolamine are shown in Figure 1. It is apparent from Figure 1 that the heat of reaction and absorption rate of alkanolamines is dependent on the nitrogen substituent feature as MEA reacts faster than AMP, then DEA and MDEA. It also shows hindered amines such as AMP and MDEA requires less reaction heat and low rates of absorption compared with unhindered amine MEA. Our research target was thus to
increase the absorption rate and decrease the heat of reaction for hindered secondary and tertiary amines compared with conventional amines AMP and MDEA.

2. Experimental, Absorbent Selection Methodology, Results and Discussion

The hindered amino alcohols have been synthesized based on an approach of rational molecular design and synthesis. Five secondary and two tertiary hindered amino alcohols were synthesized in our laboratory. The rest amines were purchased from Sigma Aldrich chemical Co. and Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. To select unique absorbents from the above mentioned amines three fundamental experiments were performed in our laboratory to evaluate their CO2 capture performance. They were screening tests, vapor-liquid equilibrium tests and heat of reaction measurements. Through these experiments solvent characteristics such as absorption-regeneration rate, saturated CO2 loading, absorption capacity, cyclic CO2 loading, and heat of reaction were obtained. Parallel solubility studies of conventional alkanolamines were also conducted at the same conditions for comparisons.

We have investigated 34 amine based CO2 absorbents (10 secondary and 24 tertiary) with systematic modification of their chemical structures by an appropriate placement of substituent functional groups especially the alkyl functions (e.g. methyl, ethyl, isopropyl, isobutyl, secondary butyl etc.), relative to the position of the amino group. We found five secondary and eight tertiary alkanol amines with higher CO2 absorption rates and lower heat of reaction compared with conventional absorbents AMP and MDEA, as shown in Figure 1. As mentioned in Figure 1, the absorbents of low heat of reaction usually had the feature of low CO2 absorption rate. However, our investigated several amino alcohols show opposite trend. Although several absorbents do not show improved activity when compared with the conventional amine absorbents, some useful information has been obtained to understand structure–activity relationships.

3. Conclusions

We demonstrated that by way of rational molecular design and placement of functional groups, hindered amino alcohols for promoting CO2 capture can be developed. It has been shown that the placement of functional groups within the amino alcohols affects the performance of the amino alcohols in CO2 capture. Thus, there is a structure-performance relationship between amino alcohols and CO2 capture performance. Out of 34 amines tested five secondary and eight tertiary were found higher CO2 absorption rates and lower heat of reaction compared with conventional absorbents AMP and MDEA. Absorbents higher CO2 absorption rate and lower heat energy consumption characteristics will reduce the regeneration energy cost of CO2 during solvent stripping. Finally, this can lead to a lower cost for CO2 capture.

References