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Synthesis and selection of hindered new amine absorbents for CO$_2$ capture

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Abstract

This work focuses on synthesizing and selecting hindered new amine absorbents to reduce the regeneration energy cost for CO$_2$ capture. To achieve this target we synthesized seven secondary and two tertiary amine based CO$_2$ absorbents with systematic modification of their chemical structures by an appropriate placement of substituent functional groups especially the alkyl functions (e.g. methyl, isopropyl, isobutyl, secondary butyl etc.), relative to the position of the amino group. Performances evaluations of these new absorbents in aqueous solutions were carried out based on their CO$_2$ 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 for the synthesized amino alcohols were then compared with conventional absorbents AMP and MDEA which were chosen as the base case for all comparisons. We found three high performance absorbents with advantages of high absorption rate and low heats of reaction compared with AMP and MDEA. Absorbents higher CO$_2$ absorption rate and lower heat energy consumption characteristics will reduce the regeneration energy cost of CO$_2$ during stripping.
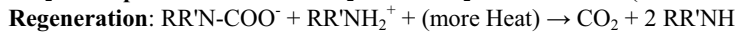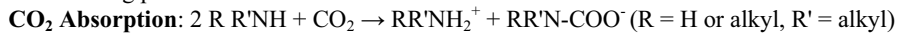
1. Introduction

Human activities contribute to climate change particularly the burning of fossil fuels, causes emissions of CO$_2$, the main gas commonly referred to as 'greenhouse' gas causing global warming. To prevent global warming by the greenhouse effect it is crucial to develop energy saving absorbents for capturing and separating CO$_2$ from its large point sources [1]. CO$_2$ capture by chemical absorption using an aqueous solution of amine based absorbents is a common industrial process and has, in many cases, been found to be the most viable solution compared with other processes [2]. 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 amine absorbents. To achieve this target, we focused on the development of
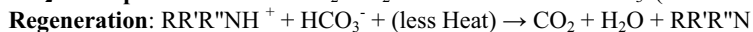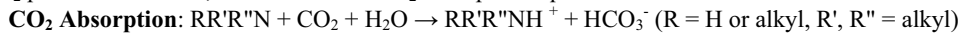
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unique amine based CO_2 absorbents which have a low heat of reaction, a fast absorption rate and a high capacity for carbon dioxide. During chemical absorption process the acid gas is absorbed into the solution at lower temperatures and regenerates from the solution by heating to higher temperatures. The process chemistry is complex, but main reactions taking place are

CO_2 Absorption: $2\ R\ R'NH + CO_2 \rightarrow RR'NH_2^+ + RR'N\text{-}COO^-$ (R = H or alkyl, R' = alkyl)

Regeneration: $RR'N\text{-}COO^- + RR'NH_2^+ + (\text{more Heat}) \rightarrow CO_2 + 2\ RR'NH$

An 'unhindered' amine forms a weakly bonded intermediate called 'carbamate' that is fairly stable. Only half a mole of CO_2 is absorbed per mole of amine, as shown in the CO_2 absorption equation above. On application of heat, this carbamate dissociates to give back CO_2 and amine absorbent, as shown in the second equation above. Since the carbamate formed during absorption is quite stable, it takes lot of heat energy to break the bonds and to regenerate the absorbent. For other 'hindered' amines (*e.g.,* where R is a bulky group), the carbamate formed is not stable, and an alternate reaction leads to formation of bicarbonate ions and hence a higher theoretical capacity of one mole of CO_2 per mole of amine, as shown in the CO_2 absorption equation below

CO_2 Absorption: $RR'R''N + CO_2 + H_2O \rightarrow RR'R''NH^+ + HCO_3^-$ (R = H or alkyl, R', R'' = alkyl)

Regeneration: $RR'R''NH^+ + HCO_3^- + (\text{less Heat}) \rightarrow CO_2 + H_2O + RR'R''N$

The regeneration of these amines requires lesser amount of heat energy as compared with unhindered amines. Low rates of CO_2 absorption, however, make hindered amines difficult to use for removing CO_2 gas. In order to resolve the above mentioned limitations formulated solvents consists of amine blends and some chemical additives are receiving considerable attention. The advantages derived from amine blends are also limited to commercially available individual amines. The aforementioned facts motivate us to synthesis hindered secondary and tertiary alkanolamine based CO_2 absorbents that have a low heat of reaction and a fast absorption rate.

2. Research Target

In the previous studies, commercially available amine absorbents were broadly investigated by a number of researchers. For example, the relation between absorption/desorption rates and amine structure was investigated from the screening tests (Bonenfaout et al., 2003) [3]. Measurements of vapor-liquid equilibrium (VLE) of amine solvent and heat of reaction were also studied (Jou et al., 1994, Mathonat et al., 1998, Mimura et al., 2005) [4-6]. Recently, a new class of amines referred to as sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP), and 2-Piperidineethanol (2-PPE) have been proposed as commercially attractive new solvents for acid gas treating over commercial amines such as monoethanolamine (MEA), diethanolamine (DEA), 2-(ethylamino)ethanol, (EAE), and *N*-methyldiethanolamine (MDEA) [7-8]. There is very little information available regarding synthesized new amines or amino alcohols. Recently, new types of amino alcohols were synthesized by Maneeintr et al [9] was applied to promote CO_2 capture performance.
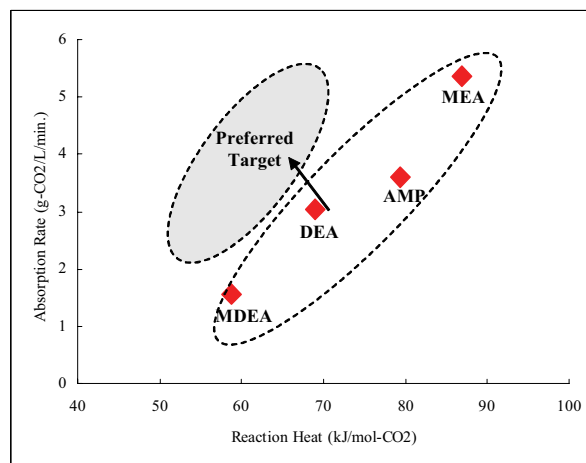

Figure 1. The trade-off between reaction heat and CO_2 absorption rate

Development of new absorbents is an ongoing specific research task of the RITE projects. Past research of our group has developed several cost saving new absorbents for CO_2 capture [10-11]. They were evaluated on their CO_2 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 CO_2 capture performance. The relationship between CO_2 absorption rate and heat of reaction, as determined experimentally, for a primary MEA and AMP, a secondary DEA and a tertiary MDEA alkanolamines 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. Figure 1 also shows hindered amines such as AMP and MDEA requires less heat energy and low rates of CO_2 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.

3. Experimental, Absorbent Selection Methodology, Results and Discussion

3.1. Experimental

Chemicals

All conventional amines (MEA, AMP, DEA and MDEA) were purchased from Sigma Aldrich chemical Co. and Tokyo Kasei Kogyo Co. Ltd. and were used without any further purification. The hindered new amino alcohols were synthesized in our laboratory by the alkylation reaction of amines and their corresponding alkylhalides. Synthesized amines purity and structure determination were established by GC and NMR spectroscopy. For all amines a 30wt% aqueous solution was used for the screening test, vapor-liquid equilibrium test and heat of reaction measurements.

3-2 Absorbents selection methodology, Results and Discussion

Synthesis and selection of new absorbents is very laborious. A tremendous amount of experimental work has to be done on characterizing the new solvents with respect to different properties. The hindered amino alcohols have been synthesized based on an approach of rational molecular design and synthesis. This involved a systematic tuning of their chemical structures by an appropriate placement of substituent functional groups, especially the alkyl function (e.g. methyl, isopropyl, isobutyl, secondary butyl etc.), relative to the position of the amino group. Some of the resulting amino alcohols were 2-N-methylamino-2-methyl-1-propanol (MAMP), 2-N-ethylamino-2-methyl-1-propanol (EAMP), 2-(isopropylamino)ethanol (IPAE), 2-(isobutylamino)ethanol (IBAE), 2-(secondarybutyamino)ethanol (SBAE), 2-(isopropyl)diethanolamine (IPDEA) and 1-Methyl-2-piperidineethanol (1M-2PPE) are listed in Table 1 and their chemical structures are shown in Figure 2. These new amino alcohols were designed to promote CO_2 capture performance and to study the effect of such placement of functional groups on the performance of the amino alcohols for CO_2 capture.

Table 1 Investigated amine absorbents

Conventional amine absorbents	Synthesized amine absorbents
1. 2-aminoethanol (MEA)	**5**. 2-N-methylamino-2-methyl-1-propanol (MAMP)
2. 2-amino-2-methyl-1-propanol (AMP)	**6**. 2-N-ethylamino-2-methyl-1-propanol (EAMP)
3. Diethaholamine (DEA)	**7**. 2-(isopropylamino)ethanol (IPAE)
4. Methyldiethanolamine (MDEA)	**8**. 2-(isobutylamino)ethanol (IBAE)
	9. 2-(secondarybutyamino)ethanol (SBAE)
	10. 2-(isopropyl)diethanolamine (IPDEA)
	11. 1-Methyl-2-piperidineethanol (1M-2PPE)

To select unique absorbents from the above mentioned amines three fundamental experiments were performed in our laboratory to evaluate their CO_2 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, capacity of CO_2 capture, and heat of reaction were obtained. A parallel solubility study of conventional alkanolamines were also conducted at the same conditions for comparison of their performance in terms of absorption rate, absorption capacity and reaction heat. The details of these tests will be described in the following paragraphs.
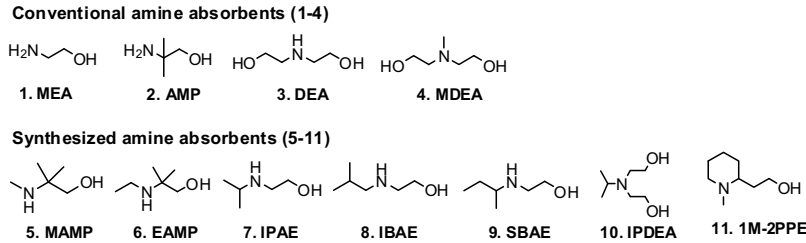
Conventional amine absorbents (1-4)

1. MEA　　**2. AMP**　　**3. DEA**　　**4. MDEA**

Synthesized amine absorbents (5-11)

5. MAMP　**6. EAMP**　**7. IPAE**　**8. IBAE**　**9. SBAE**　**10. IPDEA**　**11. 1M-2PPE**

Figure 2. Investigated amine absorbents and their chemical structures

Screening

The goal of screening test was to clarify the initial reactivity of absorbents with CO_2. Figure 3 demonstrate the schematic diagram of the experimental apparatus. The equipment designed to operate at atmospheric pressure and temperatures up to 100 °C consists of six bubble absorbers. Firstly, a 250ml glass scrubbing bottle filled with 50 ml of a 30wt% screening solvent was placed in the water bath controlled at 40 °C. A 20% CO_2 gas balanced with N_2 was then supplied to the bottle at a flow rate of 700ml/min. After 60 minutes of CO_2 absorption, the bottle was moved to the other water bath which was controlled at 70 °C and CO_2 was regenerated from the solvent for 60 minutes. The flow rate and CO_2 concentration of the feed gas were constant for the absorption and regeneration tests. During the test, the outlet gas from the reactor was analyzed with a carbon dioxide analyzer (VA-3001, HORIBA). The CO_2 loading and absorption/regeneration rates with time were estimated from the measured CO_2 concentration. The reproducibility of the experiments was checked, and the error in all of the experimental measurements was found to be less than 3%.

CO_2 absorption and regeneration of the four conventional amine absorbents (**1-4**) and the seven newly synthesized amine absorbents (**5-11**) were measured. Figure 4 expresses the typical example of screening tests. The saturation is reached for all compounds within the experimental time frame (one hour), enables a comparison of rates of absorption and saturation values. The absorption rates of all tested amines were calculated from 50% saturated CO_2 loading (absorption curves approach linearity in this range). The screening test provided a saturated CO_2 loading capacities and absorption/desorption rates of amines during a chemical absorption process. The relative performances of all amines are shown in Table 2 where AMP and MDEA are regarded as a reference absorbent for performance comparison.
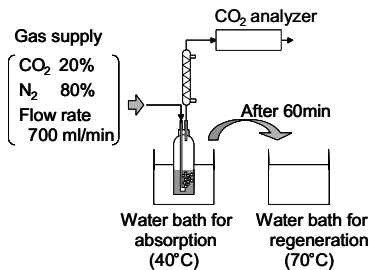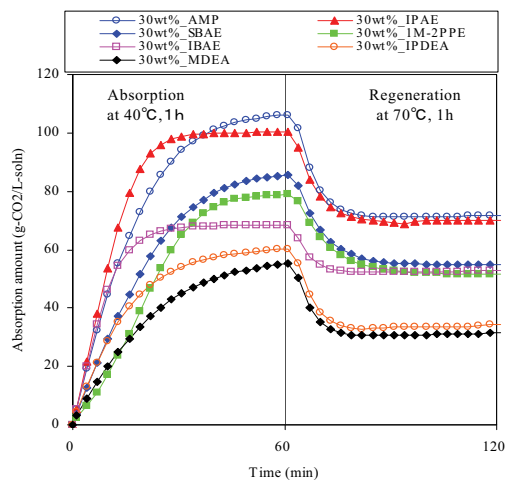
Figure 3. Schematic diagram of screening test apparatus

Figure 4. Typical examples of screening tests

Figure 4 demonstrate the saturated CO_2 loading and absorption rate of IPAE and 1M-2PPE were much higher than AMP and MDEA respectively. In case of developing new absorbents we thus focused on the absorbents that outperformed than AMP and MDEA in screening tests. Table 2 shows the experimental results of all screening amines with regards to their absorption rates, saturated CO_2 loading and absorption capacities. Table 2 and Figure 4 clearly show that the absorption rates of synthetic secondary amine IPAE and IBAE are higher than the absorption rate of AMP (unhindered MEA doesn't considered for comparison). Similar effect was also observed in case of synthetic tertiary amine IPDEA and 1M-2PPE in comparison to MDEA shown in Table 2 and Figure 4. In addition synthetic amines also present reasonable CO_2 absorption capacity entry **7**, **9**, **10** and **11** (Table 2) in comparison to AMP and MDEA. The slow absorption rate of the *N*-substituted, α-dimethylated amines MAMP and EAMP relative to AMP indicates that the presence of three bulky alkyl groups around the reaction site causes too much of a physical barrier thus greatly decreasing the reaction rate. Screening results provided clear trends concerning the structural effects of hindered amine absorbents. Methyl, Isopropyl and Isobutyl groups were found to be the most suitable substituted functional groups for the enhancement of initial absorption rate and capacity. From the screening test results several amine absorbents with high CO_2 absorption rates and capacities compared to AMP and MDEA were selected for vapor-liquid equilibrium test.

Table 2. Experimental results for screening and heat of reaction tests

Amine Absorbents	Absorbents 30wt% aqueous solutions	Absorption rate [a] g-CO_2/L-soln./min	Absorption amount [b] g-CO_2/L-soln.	Regeneration amount [c] g-CO_2/L-soln.	Absorption capacity [d] g-CO_2/L-soln.	Reaction Heat [e] kJ/mol-CO_2
1	MEA	5.39	117	108	9	86.9
2	AMP	3.69	106	71	35	79.4
3	DEA	3.04	69	53	16	68.9
4	MDEA	1.56	55	31	24	58.8
5	MAMP	1.53	86	77	9	-
6	EAMP	1.47	86	79	7	-
7	IPAE	5.21	100	69	31	63.5
8	IBAE	4.66	69	52	17	62.8
9	SBAE	2.51	86	55	31	67.4
10	IPDEA	2.43	60	33	27	59.7
11	1M-2PPE	2.65	79	51	28	56.4

[a] Absorption rate calculated at 50% of total CO_2 loading, [b] Maximum CO_2 loading at 40℃, 1h, [c] Maximum regeneration at 70℃, 1h, [d] Difference of CO_2 loading between (40℃~70℃), [e] Reaction heat measured between α = (0.4 ~ 0.6) mol-CO_2/mol-amine at 40℃

Vapor-liquid equilibrium (VLE)

Figure 5 shows the experimental apparatus used for vapor-liquid equilibrium tests which contained a 700-cm^3 crstal glass cylindrical vessel (autoclave), a water-saturator, an electric heater, a mechanical stirrer, a condenser and a CO_2 analyzer. It was designed to operate at temperatures up to 200 ℃ and pressures up to 1 MPa. Tests were conducted between 40 ℃ and 120 ℃. Before starting the experiment the apparatus was purged with N_2. During the experiment the autoclave was filled with a test solvent and heated with an electric heater. The gas which was controlled to a specific CO_2 concentration was then supplied to the autoclave after flowing through a water-saturator. The equilibrium was determined when the CO_2 analyzer indicated a constant CO_2 concentration in the outlet gas. This typically took 2 to 3 hours. To analyze the equilibrium condition the CO_2 concentration in both gas and liquid phase was measured. The CO_2 partial pressure was derived from the temperature, total pressure and the measured CO_2 concentration. For the liquid phase a sample was drawn from the autoclave and the amount of absorbed CO_2 was measured with a Total Organic Carbon analyzer (TOC-VCH, Shimadzu).

Solvents that showed superior performance from screening tests were selected for the evaluation of their vapor-liquid equilibrium property. Figure 6 express the typical example of vapor-liquid equilibrium tests for conventional amino alcohols MEA, MDEA and synthetic amino alcohols IPAE and 1M-2PPE. The effective CO_2 loading of all the chosen absorbents are shown in Table 3. The effective CO_2 loading is the difference between absorber and

regeneration conditions of the CO_2 capture system. The effective CO_2 loading, is a key index that determines the net cyclic capacity in the CO_2 capture system.
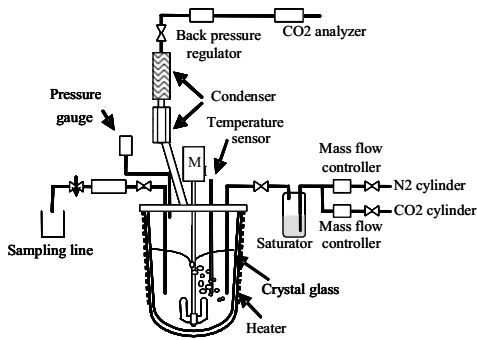

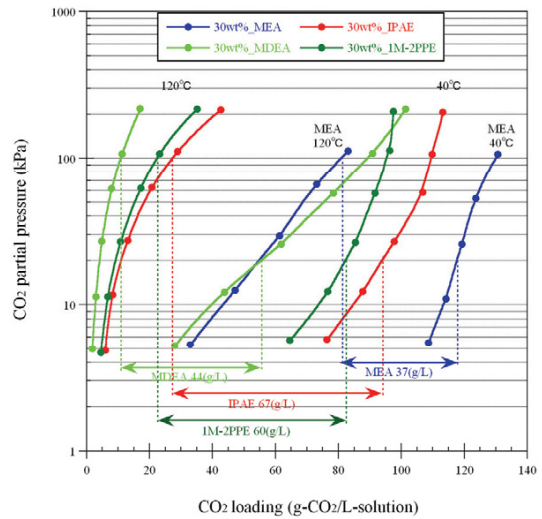Figure 5. Experimental apparatus used for vapor-liquid equilibrium tests

Figure 6. Typical examples of vapor-liquid equilibrium (VLE) tests

The experimental results of the selected four new absorbents compared to conventional amines at various conditions are presented in Table 3. Data from Table 3 shows that conventional absorbents AMP and hindered new absorbents IPAE and 1M-2PPE have good VLE property. This means, these three absorbents absorb more CO_2 and release more CO_2 off at high temperature. Good VLE property will reduce liquid flow rate and steam required for CO_2 recovery. This advantage can result in lowering the cost for gas treating process thereby making it more economically feasible.

Table 3. Experimental results for VLE tests

Amine Absorbents	Absorbents 30wt% aqueous solutions	CO_2 Loading (g-CO_2/L-soln.)		Effective CO_2 loading[c] g-CO_2/Lsoln.
		Absorber condition[a]	Regeneration condition[b]	
1	MEA	117.4	80.2	37.2
2	AMP	107.7	27.2	80.5
3	DEA	67.8	25.9	41.9
4	MDEA	55.0	11.1	43.9
7	IPAE	93.9	27.2	66.7
8	IBAE	70.6	23.3	47.3
10	IPDEA	56.7	11.1	45.6
11	1M-2PPE	82.2	22.2	60.0

[a] Temperature 40℃, CO_2 partial pressure 20kPa, [b] Temperature 120℃, CO_2 partial pressure 100kPa,

[c] Difference of CO_2 loading between 40℃ (20kPa) and 120℃ (100kPa) under equilibrium condition

Heat of Reaction

The heat of reaction for selected absorbents was measured with a Differential Reaction Calorimeter (DRC, SETARAM) as shown in Figure 7. This instrument works on the simple principle of differential thermal analysis which continuously measures the difference in temperature ΔT between a sample reactor and a reference reactor. The amount of absorbed CO_2 in the solvent was then measured with a Total Organic Carbon analyzer. To calculate

the heat of reaction the total generated heat was divided by the increase in CO_2 in the solvent during CO_2 injection. The solvent volume was 150ml and the injected gas was 100% CO_2.
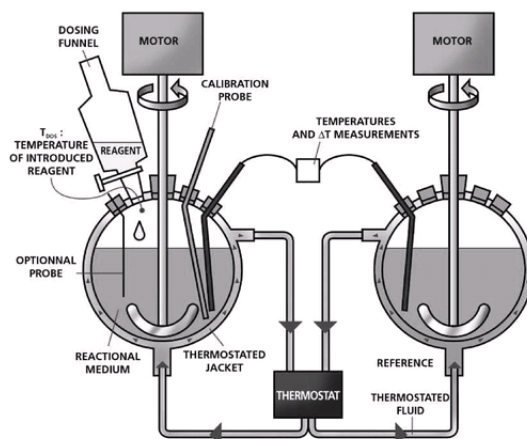

Figure 7. Experimental apparatus for heat of reaction measurements (SETARAM, DRC)
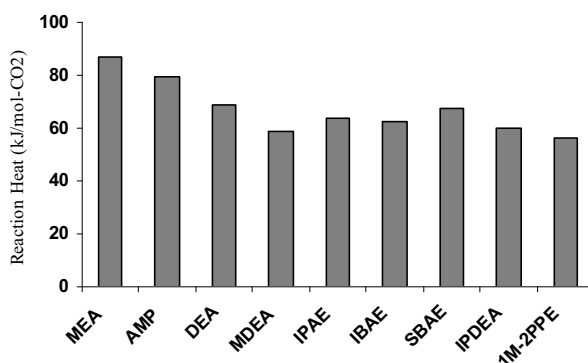

Figure 8. Experimental results for the heat of reaction tests

We selected nine test absorbents (four conventional and five synthetic amines) for the heat of reaction measurements. The results are presented in Figure 8 and Table 2. The general order of heat of reaction for conventional amines became primary>secondary>tertiary as expected from previous measurements (Figure 1). Table 2 also shows that the heat of reaction for synthesized amino alcohols provide much lower reaction heat than that of the conventional amine. Synthetic secondary amine compared with AMP, the heats of reaction as follows, AMP>SBAE>IPAE, IBAE and that for tertiary amines were: MDEA, IPDEA>1M-2PPE.

Figure 9 shows the relationship between heat of reaction and CO_2 absorption rate between conventional amines and synthesized amino alcohols. As mentioned in Figure 1, there was a trade-off relationship between heat of reaction and absorption rate for primary, secondary and tertiary amines. That is, the absorbents of low heat of reaction usually had the feature of low CO_2 absorption rate. However, the results in this study showed that IPAE, IBAE, IPDEA and 1M-2PPE solvents were plotted at outside of the trade-off relationship formed by the conventional amine absorbents. Namely, IPAE, IBAE and 1M-2PPE solvents had a unique performance that they had a feature of a low heat of reaction and kept a moderately high absorption rate.
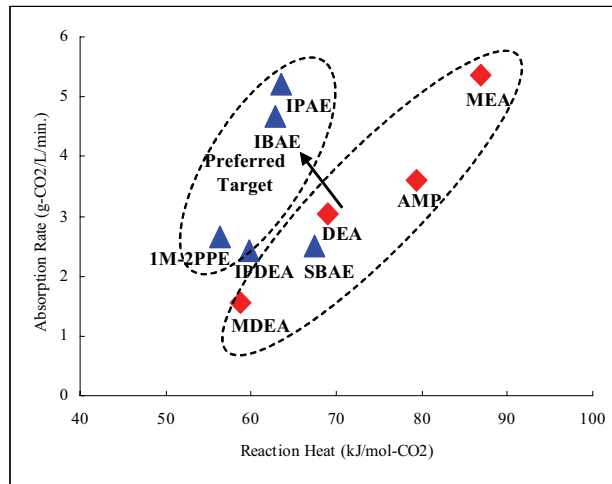
Figure 9. Performance comparisons between conventional amines and synthesized new amines

4. Conclusions

We demonstrated that by way of rational molecular design and placement of functional groups, hindered amino alcohols for promoting CO_2 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 CO_2 capture. Thus, there is a structure-performance relationship between amino alcohols and CO_2 capture performance. We have investigated seven hindered secondary and two tertiary alkanol amine based CO_2 absorbents with different chemical structures and found two secondary (IPAE and IBAE) and two tertiary (1M-2PPE and IPDEA) alkanol amines with higher CO_2 absorption rates and lower heat of absorption than the conventional absorbents AMP and MDEA. In addition new absorbents have reasonable performance in terms of cyclic capacities. Absorbents higher CO_2 absorption rate and lower heat energy consumption characteristics will reduce the regeneration energy cost of CO_2 during stripping. Finally, this can lead to a lower cost for CO_2 capture.

Acknowledgements

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