

Low-energy-consumption and environmentally friendly CO₂ capture via blending alcohols into amine solution

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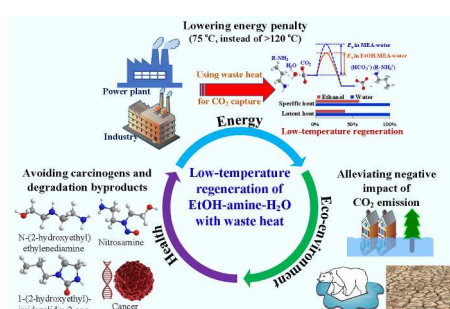
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HIGHLIGHTS

- Alcohols-amines-water significantly increase the CO₂ desorption rates.
- Ethanol increases the cyclic CO₂ capture capacity by 6.8 times at 75 °C.
- Addition of ethanol can change the reaction pathway.
- Low temperature CO₂ desorption can effectively prevent amines from degradation.
- This technology can utilize low-temperature waste heat for CO₂ capture.

GRAPHICAL ABSTRACT



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ABSTRACT

The conventional regeneration processes for aqueous amine-based sorbents require high regeneration temperature and are very energy intensive. In this work, a low-temperature and energy-saving CO₂ capture technology has been successfully developed by using alcohols-amines-water mixtures as sorbents. The addition of certain amounts of alcohols [especially ethanol (EtOH)] to amines can significantly increase the CO₂ desorption rates and cyclic CO₂ capture capacities in comparison with those of monoethanolamine-water, diethanolamine-water, and methyldiethanolamine-water systems. The sorbent containing 40 wt% EtOH, 20 wt% monoethanolamine (MEA), and 20 wt% H₂O can increase cyclic CO₂ capture capacity by 6.8 times and a maximum improvement of 236 times in CO₂ desorption rate at 75 °C, which makes the use of the low-temperature waste heat in power plants for CO₂ capture or self-supported CO₂ capture in power plants possible. To the best of authors' knowledge, this is the first time that Raman and Fourier transform infrared spectroscopy characterizations have been used to confirm that ethanol in EtOH-MEA-H₂O can change the reaction pathway by forming C₂H₅OCO₂⁻ instead of HCO₃⁻, which is difficult to decompose. In addition, the experimental results confirm that the new technology can significantly avoid amine degradation – a common challenge of the state-of-the-art CO₂ capture technologies. Therefore, the new CO₂ capture technology is promising from the perspectives of energy saving and environmental protection.

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1. Introduction

The continuous increase in atmospheric CO₂ concentration that could be the cause of noticeable climate changes has drawn significant attention [1,2]. What should people do with the potentially environmentally non-friendly force? The CO₂ capture, utilization, and storage (CCUS) process is one of the most promising approaches to reduce the CO₂ emissions [3–8], and amine-based scrubbing is the state-of-the-art capture technology [7–9]. However, two vital shortcomings of state-of-the-art technology are its high-energy consumption [10–12] and secondary environmental pollutions resulting from the degradation of amines. The latter could potentially result in health and ecosystem damages. For example, conventional post-combustion CO₂ capture technology could reduce the overall energy efficiencies of thermal power plants from ~45% to ~35%, a significant energy penalty for both energy industries and eventually a large financial burden for consumer [12,13]. Also, the health issue or cancers potentially resulting from the emission of the volatile byproduct from amine degradation cannot be neglected when CO₂ capture is widely applied in the world [14,15]. Therefore, the development of new CO₂ capture technology to overcome the two large challenges is imperative [16–19].

Accordingly, various new technologies including blends of amines [20–24], catalytic regeneration [16,25–28], biphasic solvents [29–33], and electrochemically mediated amine regeneration [18] have been developed. However, there is a long way to go for the CO₂ capture technologies to be applicable in power industries.

Any novel but practical sorption-based CO₂ capture technologies should have two factors considered. One of them is fast CO₂ sorption and desorption rates even at low temperatures, especially CO₂ desorption rate, and the other one is the use of a large amount of low-temperature heat in power plants by significantly lowering CO₂ desorption temperature. One of the methods for significantly increasing the CO₂ desorption rate is to lower H₂O usage in the CO₂ capture system. However, the strategy slows CO₂ sorption. Thus, the effective method for resolving the dilemma is to partly replace H₂O with other solvents. Barzagli et al. investigated the low-temperature regeneration of blends of 2-amino-2methyl-1-propanol, alkanolamine, and non-aqueous solvents [34]. A non-aqueous absorbent of piperazine in diethylene glycol has been proposed by Yu et al. for CO₂ capture with reduced regeneration energy [35]. Lin et al. reported that a piperazine/diethylenetriamine/methanol/water blend could have a good regeneration efficiency at 80 °C with a low energy penalty [36]. Novek et al. used aqueous ammonia and organic solvents to realize low temperature (68 °C) regeneration of sorbent for CO₂ capture [37]. Yu et al. studied the regeneration of MEA in methanol at temperatures below 100 °C [38]. Guo et al. reported that the regeneration of nonaqueous amine-based absorbents at 100 °C could achieve ~50% reduction of regeneration energy [39]. However, the low-temperature (especially < 80 °C) regeneration of amine-based sorbent is still challenging.

The consequence of CO₂ desorption at low temperature can lead to the realization of using low-temperature waste heats in power plants, natural integration of simultaneous consideration of the above-mentioned two factors, and realization of environmentally benign and cost-saving CO₂ capture operation. According to Gingerich et al., there were about 18.9 billion GJ_{th} of waste heat discharged by the thermal power plants in the U.S. in 2012 [40]. The waste heat with a weighted average temperature of 88.6 °C even accounts for more than 68% of the total energy generated by the thermal power plants [37,40]. Also, a huge amount of other low-grade industrial waste heat is available for potential utilization [41,42]. Unfortunately, the conventional amine scrubbing technology requiring as high as ~120 °C for sorbent regeneration cannot utilize these large and valuable waste heat. To further advance the progress in lowering energy penalty and preventing secondary environmental emission, a low-temperature (< 80 °C) CO₂ capture technology with the characteristic of considering both factors is

Table 1

Effect of different alcohols on CO₂ capture with MEA-based sorbents.

MEA solvents	CO ₂ loading after abs. step ^a	CO ₂ loading after des. step ^a	CO ₂ capture capacity ^a
MEA-H ₂ O	0.484	0.465	0.0188
EtOH-MEA-H ₂ O ^b	0.499	0.352	0.1468
Isopropanol-MEA-H ₂ O ^b	0.501	0.376	0.1249
Butanol-MEA-H ₂ O ^b	0.488	0.445	0.0433

^a mol CO₂ mol⁻¹ MEA.

^b 40 wt% alcohols.

developed in this research by using alcohols-amines-water mixtures as sorbents. This work not only provides a promising method for the low-temperature regeneration of amine-based sorbent but also opens a new avenue for reducing energy penalty of CO₂ capture through using waste heat as the energy source for sorbent regeneration.

2. Experiment

2.1. Materials

Monoethanolamine (Sigma-Aldrich, ≥ 99.0%), diethanolamine (Sigma-Aldrich, ≥ 99.0%), methyl diethanolamine (Sigma-Aldrich, ≥ 99%), sodium bicarbonate (Fisher Scientific, ACS grade), and ethanol (Decon Laboratories, USP grade) were used without further purification in this work. 100 g liquid amine solution was prepared by mixing amine with certain amounts of deionized water and EtOH. The typical compositions of the EtOH, MEA, and H₂O in EtOH-MEA-H₂O (EMH) sorbent were 20 wt%, 40 wt%, and 40 wt%, respectively, while the corresponding compositions MEA and H₂O in MEA-H₂O (MH) sorbents were 20 wt% and 80 wt%.

CO₂ (99.99%), O₂ (99.999%), and N₂ (99.999%) gas were purchased from US Welding Inc. A simulated flue gas with 10 vol% CO₂, 10 vol% O₂, and 80 vol% N₂ was prepared by mixing individual gases from their corresponding cylinders. A Parker mass flow controller (Model 201) was used to control the gas flow from each gas cylinder.

2.2. CO₂ capture experiments

CO₂ capture tests were performed using a setup as shown in Fig. S1. 100 g of 20 wt% amine-based sorbents were evaluated using a 200 ml batch reactor with a magnetic stirrer. Tests with and without the additions of EtOH were performed to evaluate the effect of EtOH. All CO₂ absorption tests were performed at 25 °C and under local atmospheric pressure (78 kPa, Laramie, WY). A stirring rate of 600 rpm was used for all CO₂ absorption and desorption tests. The simulated flue gas (10 vol % CO₂, 10 vol% O₂, and 80 vol% N₂) with a flow of 500 ml/min was employed for all the CO₂ absorption tests. The gas was bubbled into the prepared sorbent via a muffler (< 100 μm). The CO₂ concentration of outlet gas was measured by an online non-dispersion infrared gas analyzer from California Analytical Instruments and recorded per second with a data recorder. The quantities of CO₂ sorbed under various conditions were obtained by integrating the recorded CO₂ absorption profiles. The absorption times for the fresh 20 wt% amine-based sorbent and the cyclic sorbents were 5400 s and 1800 s, respectively.

The CO₂ desorption experiments were performed by heating the spent sorbents to ~75 °C without introduction of the carrier gas into the reactor. A 500 ml/min of N₂ was used to mix with desorbed CO₂ gas exiting the reactor and then the mixture gas was analyzed by the online gas analyzer. The measured CO₂ concentration of the mixed gas was recorded by the data recorder. The cooling liquid from a cooling unit with its temperature being set as -1 °C was used to condense vapors in the condenser. The time for the desorption step was 30 min. The following cyclic test was started after the sorbent was cooled to 25 °C.

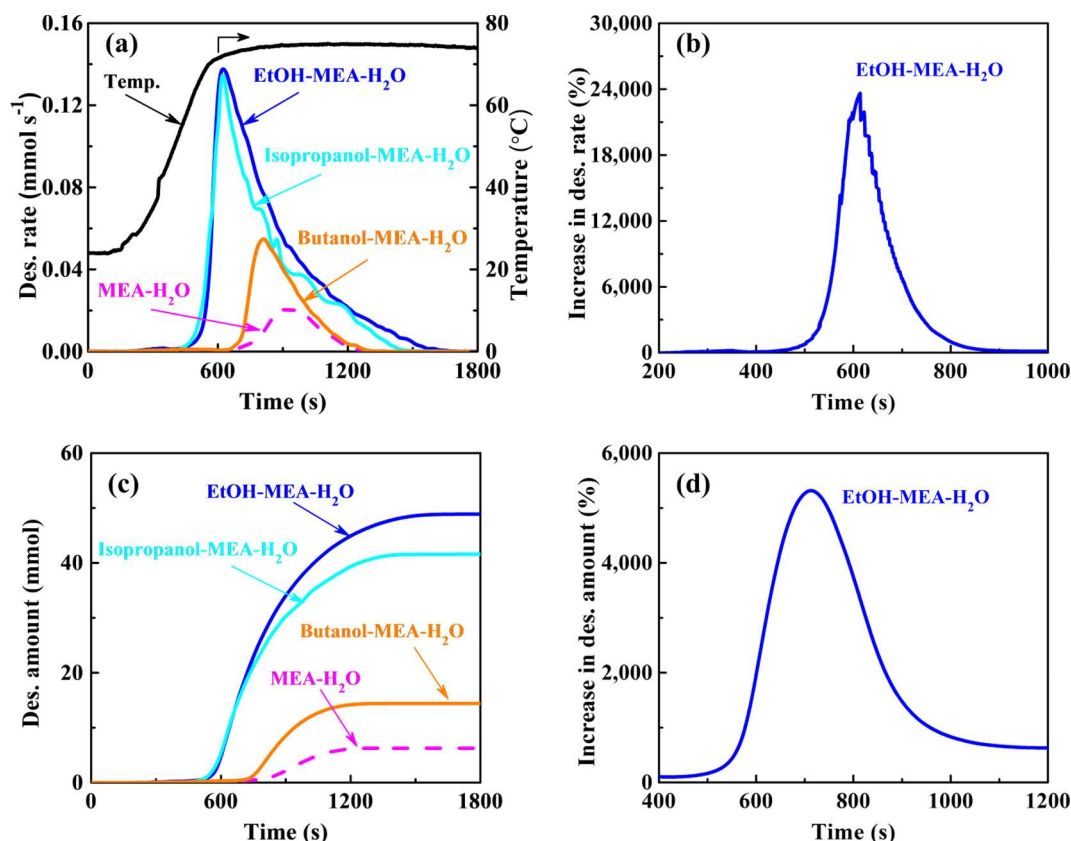


Fig. 1. Effect of different alcohols on CO₂ desorption from spent MEA. (a) The rates of CO₂ desorption from spent MEA sorbent without and with the presence of 40 wt% alcohols. (b) The increases in CO₂ desorption rate due to the presence of 40 wt% EtOH. (c) Effects of alcohols on the quantities of desorbed CO₂. (d) The increases in CO₂ desorption amount due to the presence of 40 wt% EtOH.

2.3. Thermal degradation experiments

The 20 ml of 20 wt% MEA solutions with and without EtOH loaded with 0.4 mol of CO₂ per mole of amine were introduced into a 200 ml Teflon-lined stainless-steel autoclave. The autoclave containing EMH solution was put into an oven maintained at 80 °C for 120 h, while the autoclave containing MH solution was put into an oven maintained at 80 °C or 125 °C for 120 h. The solutions after degradation test were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

2.4. Analytical methods

An Advantage 785 Raman Spectrometer (758 nm laser and up to 60 mW radiation power) were used for Raman spectrum studies. The sorbent samples with different desorption time were prepared by taking ~1 ml solutions with a dropper at the different time and then transferring solutions into clear shell vials for further measurements. 5 wt% NaHCO₃–H₂O–EtOH mixtures were prepared by mixing NaHCO₃ with certain amounts of deionized water first and then adding the required amount of EtOH into the mixtures. Thermo/Nicolet Magna-IR 760 Spectrometer was used to collect Fourier transform infrared (FT-IR) spectroscopy of fresh and spent sorbents as well as the liquid of 5 wt% NaHCO₃–H₂O–EtOH mixtures with various EtOH amount. GC analysis was carried out on an Agilent 7890A GC system with an auto sampler, flame ionization detection (FID) detector, and HP-5 column (30 m, 0.32 mm i.d., 0.25 µm film thickness). The samples were diluted to 1/10 in EtOH before the analysis. GC–MS analysis was performed on an Agilent 7890B GC system with an auto sampler, Agilent 2977B MSA mass spectrometer, and DB-XLB column (30 m, 0.25 mm i.d., 0.1 µm film thickness).

3. Results and discussion

3.1. Effect of different alcohols on CO₂ capture

CO₂ capture experiments with 100 g sorbents containing 20 wt% amines were performed using the setup as shown in Fig. S1. The CO₂ sorption and desorption with and without uses of EtOH, isopropanol, and butanol were conducted to evaluate the effect of alcohols on the CO₂ capture performances of 20 wt% MEA based sorbents. Table 1 summarizes the CO₂ loadings under the conditions of 5400 s of absorption and 1800 s of desorption as well as the cyclic CO₂ capture capacities of MEA sorbents. The CO₂ loading of MH sorbent after the absorption step is 0.484 mol CO₂ mol⁻¹ MEA. As shown in Table 1, alcohols-MEA-H₂O sorbents with 40 wt% of EtOH, isopropanol, and butanol all show slightly increased amounts of CO₂ absorption within the same time – 5400 s. The CO₂ desorption experiments were conducted by heating the spent MEA sorbents to the desired desorption temperature (~75 °C). The MH sorbent only shows a cyclic CO₂ capture capacity of 0.0188 mol CO₂ mol⁻¹ MEA, an indication of the poor regeneration ability of MH sorbent at such a low temperature. However, alcohols-MEA-H₂O sorbents show excellent CO₂ desorption capacities under the same temperature. Among them is EMH sorbent that desorbs as high as 0.1468 mol CO₂ mol⁻¹ MEA, an increase by 6.8 times in comparison to that of MH. It should be noted that this desorption capacity is already similar to 0.18 mol CO₂ mol⁻¹ MEA achieved by the practical implication of aqueous MEA sorbent regeneration under high temperatures [43–45]. While, the performances of the sorbents with 40 wt% isopropanol and 40 wt% butanol are 5.6 and 1.3 times better than that of MH, respectively. These results clearly demonstrate that the addition of alcohols, especially EtOH, to MEA can significantly improve the CO₂ desorption of MEA based sorbents.

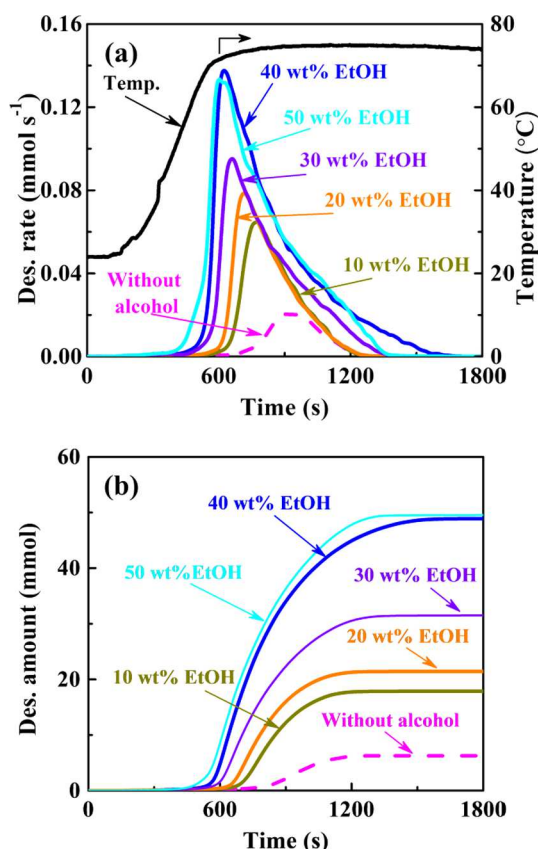


Fig. 2. Effect of the EtOH concentration on CO₂ desorption from spent MEA. (a) The rates of CO₂ desorption from spent MEA sorbent with different EtOH concentrations. (b) Effects of EtOH concentration on the quantities of desorbed CO₂.

Table 2

Effect of the presence of 40 wt% EtOH on different amines for their CO₂ capture capacities.

20 wt% amine solvents	CO ₂ loading after abs. step ^a	CO ₂ loading after des. step ^a	CO ₂ capture capacity ^a
MEA-H ₂ O	0.484	0.465	0.0188
EtOH-MEA-H ₂ O ^b	0.499	0.352	0.1468
DEA-H ₂ O	0.531	0.458	0.0726
EtOH-DEA-H ₂ O ^b	0.491	0.173	0.3184
MDEA-H ₂ O	0.398	0.385	0.0131
EtOH-MDEA-H ₂ O ^b	0.365	0.159	0.2061

^a mol CO₂ mol⁻¹ MEA.

^b 40 wt% EtOH.

Although the quantity of CO₂ desorbed is important, CO₂ desorption rate reflecting the CO₂ desorption kinetics is more important to the application of the sorption based CO₂ capture technology. Fig. 1a shows the changes in the rates of CO₂ desorption from the spent 20 wt% MEA sorbents with and without 40 wt% alcohols with time. It is obvious that the additions of EtOH, isopropanol, and butanol lead to great improvement in CO₂ desorption. While the spent MH sorbent maximally desorbs CO₂ with the rate of 0.0213 mmol/s at 928 s, the CO₂ desorption rate of the spent EMH sorbent reaches 0.137 mmol/s at as early as 622 s. The maximum CO₂ desorption rates of the spent isopropanol-MEA-H₂O and butanol-MEA-H₂O sorbents are 0.135 and 0.0548 mmol/s, respectively. Fig. 1b presents the percentage increase of CO₂ desorption rate due to the addition of 40 wt% EtOH with time. Remarkably, the increase of CO₂ desorption rate can be as high as 236 times at 614 s. Therefore, EtOH can significantly enhance CO₂ desorption at a low desorption temperature, making the regeneration of MEA based sorbent

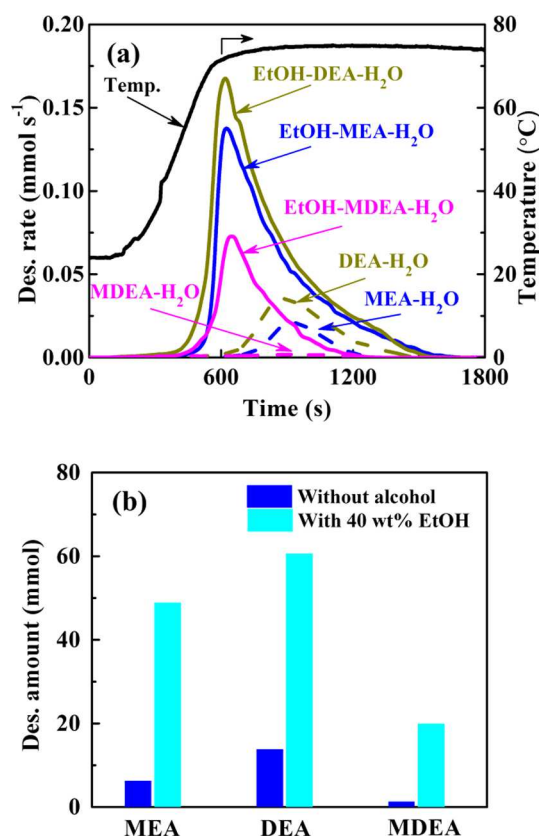


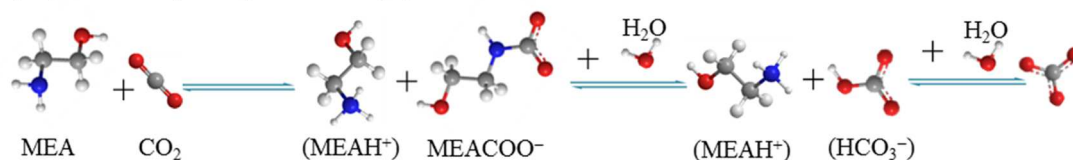
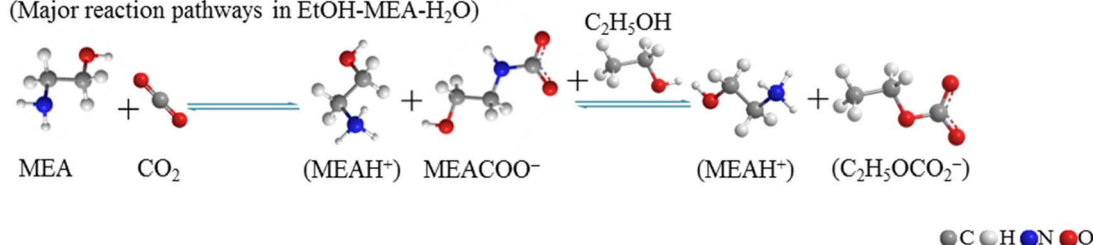
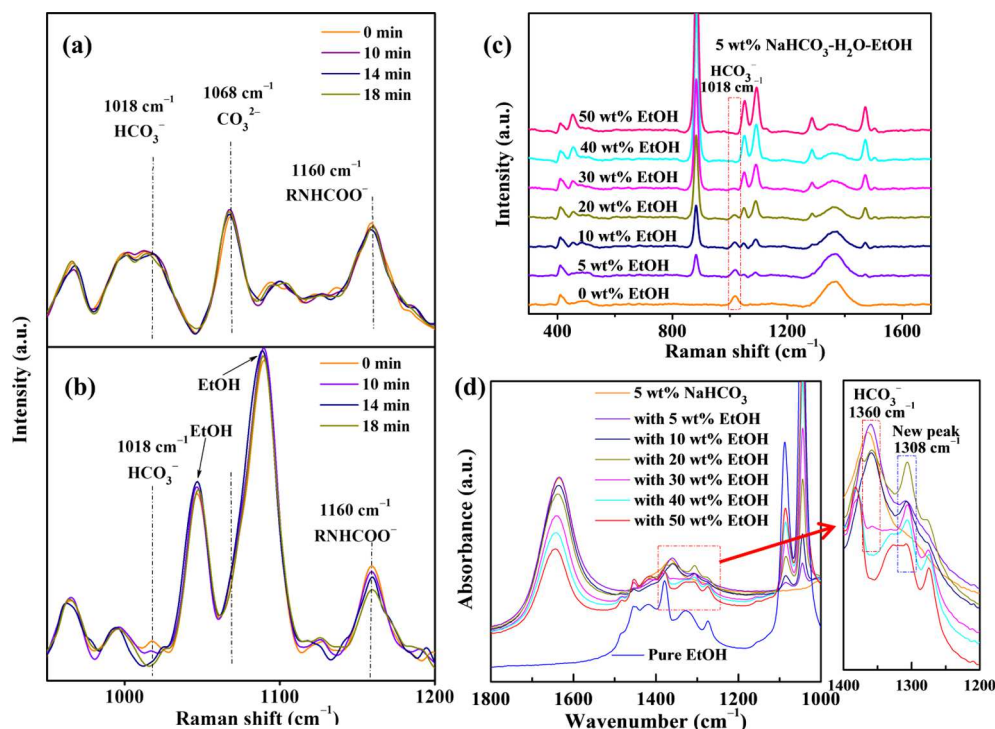
Fig. 3. Effect of 40 wt% EtOH on CO₂ desorption from different spent amines. (a) The rates of CO₂ desorption from spent amine-based sorbents without and with uses of EtOH. (b) The quantities of desorbed CO₂ from spent amine-based sorbents without and with uses of EtOH.

at 75 °C practical. Such a low desorption temperature requirement makes the utilization of the low-temperature waste heat of thermal power plants in sorbent regeneration feasible, an effective pathway for a significant reduction in the energy penalty resulting from CO₂ capture.

The variation of the quantities of CO₂ desorbed with time is given in Fig. 1c. The alcohols-MEA-water sorbents not only enhance the CO₂ desorption kinetics but also increase the total quantities of CO₂ desorbed. Only 6.27 mmol CO₂ is desorbed from the spent MH sorbent, however, the butanol-MEA-H₂O sorbent desorbs 11.4 mmol CO₂. The rapid kinetics of the isopropanol-MEA-H₂O sorbent result in 11.5 mmol of CO₂ desorption within 650 s and a high total CO₂ desorption amount of 41.6 mmol. Extraordinarily, 48.9 mmol CO₂ is desorbed from spent EMH sorbent, about 6.8 times higher than that of spent MH sorbent, 6.27 mmol. Percentage increase in CO₂ desorption quantity due to the presence of 40 wt% EtOH is shown in Fig. 1d. In comparison with the CO₂ desorption of MH sorbent, the cumulatively desorbed CO₂ quantity of the spent EMH is found to be 53 times higher than that of MH at 709 s.

3.2. Effect of ethanol concentration on CO₂ capture

EMH sorbents with different EtOH concentrations from 0 to 50 wt% were used to investigate the effect of EtOH concentration on CO₂ capture. The EtOH concentration did not significantly affect the CO₂ absorption of MEA based sorbents (Fig. S2 and Table S1). However, the EtOH concentration significantly affects the CO₂ desorption of MEA based sorbents. The desorption capacity of spent sorbents increased significantly from 0.0188 to 0.1468 mol CO₂ mol⁻¹ MEA with the increase of EtOH concentration from 0 to 40 wt% at 75 °C. Further increase of the EtOH concentration from 40 to 50 wt% barely increases

(Major reaction pathways in MEA-H₂O)(Major reaction pathways in EtOH-MEA-H₂O)Fig. 4. Major reaction pathways of CO₂ capture with MH and EMH sorbents.Fig. 5. Characterization with Raman and FT-IR spectroscopy. (a) Raman spectra of MEA-H₂O at different desorption times. (b) Raman spectra of EtOH-MEA-H₂O at different desorption times. (c) Raman spectra of the liquid of 5 wt%NaHCO₃-H₂O-EtOH mixtures with various EtOH amount. (d) FT-IR spectra of the liquid of 5 wt%NaHCO₃-H₂O-EtOH mixtures with various EtOH amount.

cyclic CO₂ sorption capacity.

To further illustrate the effect of EtOH concentration on the CO₂ desorption, the CO₂ desorption rates of the spent 20 wt% MEA sorbents with different EtOH concentrations are presented in Fig. 2a. It clearly shows that the maximum CO₂ desorption rate of the sorbents increases with EtOH concentration within 0–40 wt%. Moreover, the increase in EtOH concentration shortens the time needed for reaching the maximum desorption rates. The addition of 10 wt% EtOH increases the maximum desorption rate from 0.0213 to 0.0647 mmol/s and shortens the required time from 928 to 771 s. The spent sorbent with 40 wt% EtOH showed the highest rate of 0.137 mmol/s among all tested MEA sorbents. Fig. 2b further shows that the EMH sorbent improves desorption kinetics and amount in the 0–40 wt% range of EtOH. The addition of 10 wt% EtOH improves the quantity of the CO₂ desorption from 6.27 mmol to 17.9 mmol, an increase by 1.9 times. The EMH sorbent with 40 wt% EtOH only takes 702 s to desorb 6.27 mmol and desorbs

48.9 mmol of CO₂ at the end of desorption. The CO₂ desorption characteristics of the MEA sorbent change barely with the further increase in the EtOH concentration within 40–50 wt%. Clearly, the optimal EtOH concentration is 40 wt% and thus is used for further studies.

3.3. Effect of ethanol on different amine-based sorbents

To investigate whether the EtOH also works for other amines, 20 wt% diethanolamine (DEA) and 20 wt% methyl diethanolamine (MDEA) based sorbents were also tested. Although the addition of EtOH improves the CO₂ absorption of DEA and MDEA based sorbents within the first 2500 s (Fig. S3), these two sorbents show slightly reduced CO₂ loadings after 5400 s of absorption (Table 2). However, the addition of EtOH significantly improves the CO₂ desorption capacity of DEA and MDEA based sorbents. As shown in Table 2, the addition of 40 wt% EtOH significantly increases the CO₂ desorption capacity of 20 wt%

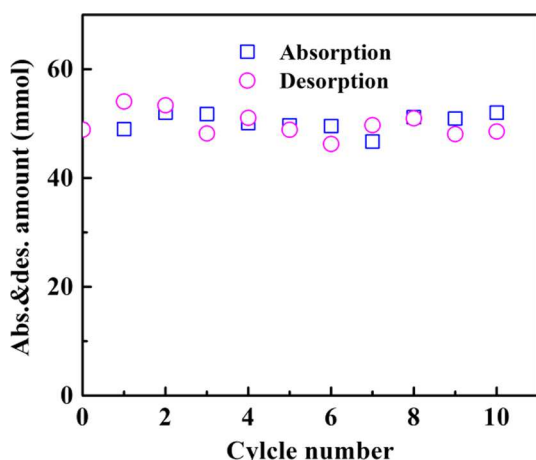


Fig. 6. Stability of EtOH-MEA-H₂O sorbent with 20 wt% MEA, 40 wt% EtOH, and 40 wt% H₂O.

DEA based sorbent from 0.0726 to 0.3184 mol CO₂ mol⁻¹ DEA, increased by 3.4 times. For 20 wt% MDEA based sorbent, the EtOH-MDEA-H₂O remarkably improves the desorption capacity from 0.0131 to 0.2061 mol CO₂ mol⁻¹ MDEA, increased by 14.8 times. The high desorption capacity at 75 °C makes practical implication of this technology feasible.

The rates of CO₂ desorption from the spent sorbents with and without alcohols are presented in Fig. 3a. Similar to that observed in MEA based sorbents, the addition of 40 wt% EtOH significantly increases the maximum CO₂ desorption rates of both DEA and MDEA based sorbents with lower temperatures and shorter time. As shown in Fig. 3a, desorption rate of the spent EtOH-DEA-H₂O sorbent reaches 0.168 mmol s⁻¹ at as early as 617 s, while the desorption rate of the spent DEA-H₂O sorbent is only 0.00229 mmol s⁻¹ at the same time point. Similarly, EtOH-MDEA-H₂O sorbent shows the maximum desorption rate of 0.0727 mmol s⁻¹ at 643 s, about 36 times increase compared with the maximum rate of 0.00190 mmol s⁻¹ achieved by MDEA-H₂O sorbent. The effect of EtOH on the quantity of desorbed CO₂ is showed in Fig. 3b. Only 13.8 mmol CO₂ is desorbed from the spent DEA-H₂O sorbent, while the EtOH-DEA-H₂O sorbent significantly improves CO₂ desorption amount to 60.6 mmol. The EtOH also increases the desorbed CO₂ of MDEA based sorbent from 1.26 to 19.9 mmol. These results clearly illustrate that the addition of EtOH can drastically enhance the CO₂ desorption of different amine-based sorbents, including primary amine, secondary amine, and tertiary amine, at low regeneration temperatures.

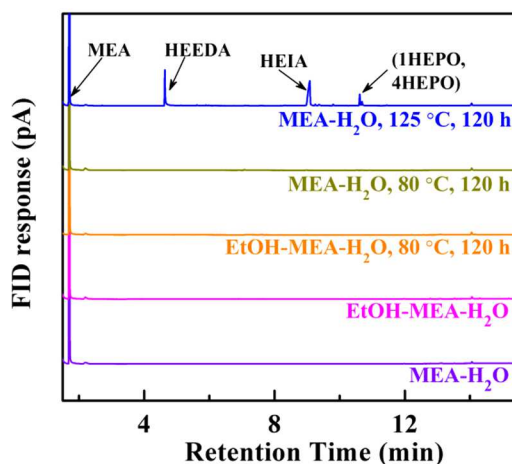


Fig. 7. GC chromatograms of the MEA solutions before and after degradation experiments.

Table 3
Summary of thermal degradation experiment results of MEA based solvents.

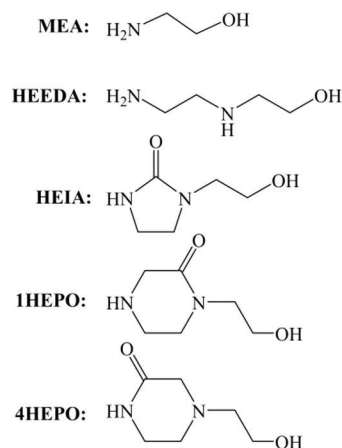
20 wt% MEA solvents	Temperature (°C)	Time (h)	Change of FID peak area of MEA (%)
MEA-H ₂ O	125	120	-26.2 ± 0.6
MEA-H ₂ O	80	120	0.8 ± 2
EtOH-MEA-H ₂ O	80	120	-0.6 ± 1

3.4. Mechanism

EtOH is a multifunctional additive in the novel CO₂ capture process. Firstly, EtOH can change the reaction pathway by forming C₂H₅OCO₂⁻ instead of HCO₃⁻ that is difficult to decompose (Fig. 4). As shown in Fig. 5a and b, unlike MH showing strong Raman peaks of both HCO₃⁻ and CO₃²⁻, the spent EMH sorbent only shows a tiny HCO₃⁻ peak. These results indicate that the reaction pathway in EMH is different from that in MH. Raman experiments with NaHCO₃ and EtOH mixtures show that the HCO₃⁻ peak decreases with the concentration of EtOH (Fig. 5c), a clear sign of confirming the interaction between HCO₃⁻ and EtOH. While the HCO₃⁻ peak also decreases with the concentration of EtOH in Fourier transform infrared (FT-IR) spectra (Fig. 5d) of NaHCO₃ and EtOH mixtures, a new peak at 1308 cm⁻¹ not associated with HCO₃⁻ and EtOH increases with increase in the EtOH concentration within 0 to 20 wt%. The new peak can be attributed to C₂H₅OCO₂⁻ resulting from the reaction between NaHCO₃ and EtOH [34,46]. Also, EtOH can reduce the dielectric constant of the solvent and thus is able to reduce the basic strength of the sorbent, which benefits the release of acidic CO₂ from spent EMH sorbent at a lower temperature [47]. The reduced basic strength may also lower the activation energy of CO₂ desorption. Moreover, the addition of EtOH can lower the CO₂ concentration in the vapor phase, which can shift the equilibrium to lower CO₂ concentrations in MEA solvents and facilitate the CO₂ desorption at lower temperatures [48].

3.5. Stability and thermal degradation

Amine thermal degradation is one of the problems caused by high-temperature regeneration, which leads to the loss of amines and also the increase in operation cost [49–51]. Moreover, the degraded amines may react with nitrogen oxides to form some carcinogenic nitrosamines in the atmosphere [14,15]. One of the advantages of the low regeneration temperature achieved in this work is that it can minimize the amine degradation and the environmental impacts caused by thermal degradation. The stability of EMH was elucidated by 10 cycle tests. As shown in Fig. 6, no obvious decrease in desorption



performance is observed within 10 cycle tests. The stable cyclic performance indicates that not only does MEA remain stable during the cyclic tests but also EtOH and MEA vapor are well condensed without significant loss. Gas chromatography (GC) analysis and infrared spectroscopy (IR, Fig. S7) analysis of the spent MEA solutions also confirm that MEA and EtOH remain stable during the cyclic tests. Thermal degradation experiments of the spent MEA solution with CO₂ loading of 0.4 mol CO₂ per mole of MEA were conducted at 80 °C and 125 °C for 120 h to further confirm the advantage of low-temperature regeneration in this work. As shown in Fig. 7, the results from GC for both MH and EMH solutions do not show detectable degradation products after the experiment at 80 °C for 120 h. However, major degradation products such as *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA), *N*-(2-hydroxyethyl)-imidazolidin-2-one (HEIA), 1-(2-hydroxyethyl)-piperazin-2-one (1HEPO), and 4-(2-hydroxyethyl)-piperazin-2-one (4HEPO) are detected for MH treated at 125 °C for 120 h. The peak area of MEA decreases by $26.2 \pm 0.6\%$ after MH is treated at 125 °C for 120 h (Table 3). While EMH treated at 80 °C for 120 h only shows a negligible decrease of $0.6 \pm 1\%$. In sum, the low-temperature CO₂ desorption can effectively reduce the amine solvent degradation rate and avoid environmental impacts caused by degradation byproducts, leading to operation costs saving and environmental protection in the real application.

4. Conclusions

EtOH has demonstrated its great potential in significantly improving CO₂ desorption performance of primary, secondary, and tertiary amines based sorbents at much low temperatures, which makes the utilization of waste heat or low-value heat in power plants as the energy source for sorbent regeneration possible. Three possible promoting mechanisms are proposed and discussed in this work. Raman and Fourier transform infrared characterizations demonstrated that the addition of ethanol changes the reaction pathway of CO₂ capture. The resultant low-temperature CO₂ desorption can effectively prevent amines from degradation, which is desired for reducing operation cost and alleviating the negative environmental impacts of amine and its decomposition byproducts. The research could inspire people's interests in developing low temperature but fast CO₂ capture pathways.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apenergy.2019.113696>.

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