



## Investigation of Biocatalytic Absorption and Ultrasound-Assisted Desorption Performance of CO<sub>2</sub> Capture

### CO<sub>2</sub> Yakalamasının Biyokatalitik Absorpsiyon ve Ultrasonik-Destekli Desorpsiyon Performansının İncelenmesi

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#### ABSTRACT

The CO<sub>2</sub> absorption-desorption performance of non-aqueous solutions comprising a sterically hindered amine system (2-amino-2-ethyl-1,3-propanediol (AEPD): 1-hexanol) was investigated in a gas-liquid stirred cell reactor under sequential absorption-desorption cycles. The absorption capacity and initial absorption rate were calculated for different concentrations of AEPD: 1-hexanol at 303 K and 2 bar absolute pressure. Increasing the amount of AEPD increased the CO<sub>2</sub> absorption capacity. The biocatalytic effect of a constant amount of carbonic anhydrase (CA) on the CO<sub>2</sub> absorption performance was also investigated, and the CA enzyme was found to increase the total amount of absorbed CO<sub>2</sub>. The CO<sub>2</sub> loading of AEPD: 1-hexanol and CA activated AEPD: 1-hexanol were 0.88 and 0.97 mol CO<sub>2</sub>/mol AEPD, respectively. CO<sub>2</sub> desorption experiments were performed in different sequences of the same experimental set-up at 363 K and 1.1 bar absolute N<sub>2</sub> pressure. The effect of ultrasonic irradiation on the desorption performance of 0.1 g/L CA catalyzed AEPD: 1-hexanol system was also investigated. It was observed that ultrasonic assistance shortened the desorption time and enhanced the desorption rate. Furthermore, the effectiveness of regeneration, the reusability, and performance loss of AEPD: 1-hexanol, in the presence and absence of CA, were analyzed by Fourier transform infrared spectrometry.

#### Key Words

CO<sub>2</sub> capture, carbonic anhydrase, FTIR, sterically hindered amine.

#### ÖZ

Sterik engelli amin sisteminin susuz çözeltisinin (2-amino-2-etil-1,3-propandiol (AEPD): 1-hekzanol) ardışık CO<sub>2</sub> absorpsiyon-desorpsiyon performansı gaz-sıvı karıştırmalı hücre reaktöründe incelenmiştir. Farklı AEPD: 1-hekzanol konsantrasyonları için absorpsiyon kapasitesi ve başlangıç absorpsiyon hızı 303 K ve 2 bar mutlak basınçta hesaplanmıştır. AEPD miktarının artırılması CO<sub>2</sub> absorpsiyon kapasitesini arttırmıştır. Sabit miktarda karbonik anhidrazın (CA) CO<sub>2</sub> absorpsiyon performansı üzerindeki biyokatalitik etkisi de araştırılmış, ve CA enziminin toplam absorplanan CO<sub>2</sub> miktarını arttırdığı bulunmuştur. AEPD: 1-hekzanol ve CA ile aktiveleştirilen AEPD: 1-hekzanolün CO<sub>2</sub> yüklemesi sırasıyla 0.88 ve 0.97 mol CO<sub>2</sub>/mol AEPD bulunmuştur. CO<sub>2</sub> desorpsiyon deneyleri, 363 K ve 1.1 bar mutlak N<sub>2</sub> basıncında aynı deney düzeneğinin farklı diziliminde gerçekleştirilmiştir. Ultrasonik ışınlamanın 0.1 g/L CA katalizli AEPD: 1-hekzanol sisteminin desorpsiyon performansı üzerindeki etkisi de araştırılmıştır. Ultrasonik desteğin desorpsiyon süresini kısalttığı ve desorpsiyon hızını arttırdığı gözlenmiştir. Ayrıca, AEPD:1-Hekzanol sisteminin, CA yokluğunda ve varlığındaki, rejenerasyonun etkinliği, yeniden kullanılabilirliği ve performans kaybı Fourier dönüşümü kızılötesi spektrometresi ile analiz edilmiştir.

#### Anahtar Kelimeler

CO<sub>2</sub> yakalama, karbonik anhidraz, FTIR, sterik engelli amin.

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## INTRODUCTION

The emission of carbon dioxide (CO<sub>2</sub>), one of the primary greenhouse gases (GHGs) responsible for global warming, is increasing. CO<sub>2</sub> absorbs less heat per molecule than do other greenhouse gases such as methane (CH<sub>4</sub>) or nitrous oxide (N<sub>2</sub>O). However, CO<sub>2</sub> is more abundant and stays much longer in the atmosphere [1]. Atmospheric CO<sub>2</sub> concentrations have reached an alarming level of around 410 ppm in 2019, according to the International Energy Agency report [2]. Anthropogenic CO<sub>2</sub> emissions mainly result from the transportation and burning of fossil fuels for energy [3], while electricity generation and the power sector are responsible for the lion's share of non-anthropogenic CO<sub>2</sub> emissions [4]. Therefore, reduction of CO<sub>2</sub> emissions is an important topic on the global agenda to fight climate change.

The absorption–desorption process using aqueous amine solvents has been demonstrated as widely-used methodology for post-combustion CO<sub>2</sub> capture (PCC) [5]. Aqueous 30 wt% monoethanolamine (MEA) is considered a benchmark solution for CO<sub>2</sub> separation from bulk CO<sub>2</sub> gas streams. Even though aqueous amine-based absorbents have good CO<sub>2</sub> absorption characteristics, a large amount of energy is required during regeneration. The regeneration heat for aqueous 30 wt% MEA is around 4 GJ/ton CO<sub>2</sub> [6, 7]. Solvent regeneration is energetically demanding, representing about 70% to 80% of the total energy consumption [8]. The high specific heat of water increases the sensible heat, and the low boiling point of water results in vaporization during the regeneration process, leading to solvent loss [9]. This high energy demand is the driving force behind the development of new solvents with lower regeneration energy consumption. In recent years, there have been several proposals for using water-lean or non-aqueous amine solutions due to their energy-saving potential, but there is still a significant gap from the desired level [7, 10-16]. The widely known organic solvent, 1-hexanol, has a high boiling point but lower heat capacity and vaporization enthalpy than those of water. In the present study, 1-hexanol is proposed as a non-aqueous medium for cyclic CO<sub>2</sub> absorption and desorption.

MEA, a widely known primary amine, shows higher reactivity with CO<sub>2</sub>, has low viscosity, and is inexpensive and easily available; however, its corrosive and volatile nature, as well as low CO<sub>2</sub> loading (mol CO<sub>2</sub>/mol MEA=

0.5), have necessitated the search for more efficient absorbents [17]. Primary and secondary amines commonly react with CO<sub>2</sub> to form stable carbamate anions, while tertiary amines form bicarbonate ions [18]. Tertiary amines are known to have higher CO<sub>2</sub> loading capacity (mol CO<sub>2</sub>/mol amine ≈1.0) but lower thermal stability and low kinetics. In this context, sterically hindered amines (SHAs) have been suggested as a viable alternative to primary, secondary, and tertiary amines as efficient absorbents for carbon capture. SHAs have a functional group located close to the amino group. The resulting steric hindrance produces weaker C-N bonds upon reaction with CO<sub>2</sub>, because of which lower energy is required for solvent regeneration [19]. SHAs have been strongly recommended as potential absorbents due to their high theoretical loading capacity of up to 1.0 mol CO<sub>2</sub>/mol amine [20]. Although SHAs show lower reaction kinetics than do primary and secondary amines, they show faster reaction kinetics than do tertiary amines [21]. 2-Amino-2-methyl-1-propanol (AMP), which is the sterically hindered form of MEA, has been intensively studied [14, 22-26]. The findings led to the introduction of cost-effective and easily regenerable nonaqueous CO<sub>2</sub> absorbents, based on the sterically hindered primary amine, 2-amino-2-ethyl-1,3-propanediol (AEPD), i.e. AEPD: 1-hexanol solution. AEPD is a potentially useful sterically hindered amine that forms an unstable carbamate upon reaction with CO<sub>2</sub>.

Piperazine (PZ) and its derivatives are commonly used promoters to enhance the CO<sub>2</sub> kinetics and absorption capacity [27-30]. This study proposes the use of biocatalysts to promote the CO<sub>2</sub> absorption–desorption process. The ubiquitous occurrence of carbonic anhydrase (CA) enzyme in nature and its kinetic potential make it a good biocatalyst for the reversible reactions between CO<sub>2</sub> and amines. CA from bovine erythrocytes is a widely reported biocatalyst for the CO<sub>2</sub> hydration process. Although there have been many studies on the biocatalytic effect of CA on CO<sub>2</sub> absorption kinetics, the effect of CO<sub>2</sub> loading in gas-liquid reactors has not been examined yet [31-36].

A novel solvent regeneration technique, called the ultrasound-assisted method, was also used to enhance the desorption performance and further reduce the energy consumption. Bubbles produced during the ultrasonic irradiation generated shockwaves, which increased the interfacial area between the gas and the liquid, resulting in enhanced mass transfer [37-40]. This triggered

the degassing action, leading to more efficient removal of  $\text{CO}_2$  from the loaded solution. The superior performance of this ultrasound-assisted technique makes it a potentially attractive alternative to the traditional desorption process. The knowledge obtained contributed to the literature, as well as formed the basis for the development of a new generation of more efficient  $\text{CO}_2$  capture technologies [39]. This new understanding will help the industry achieve significant savings in terms of both capital and operating costs of  $\text{CO}_2$  capture and separation processes, which can significantly reduce the greenhouse gas effects and benefit the environment.

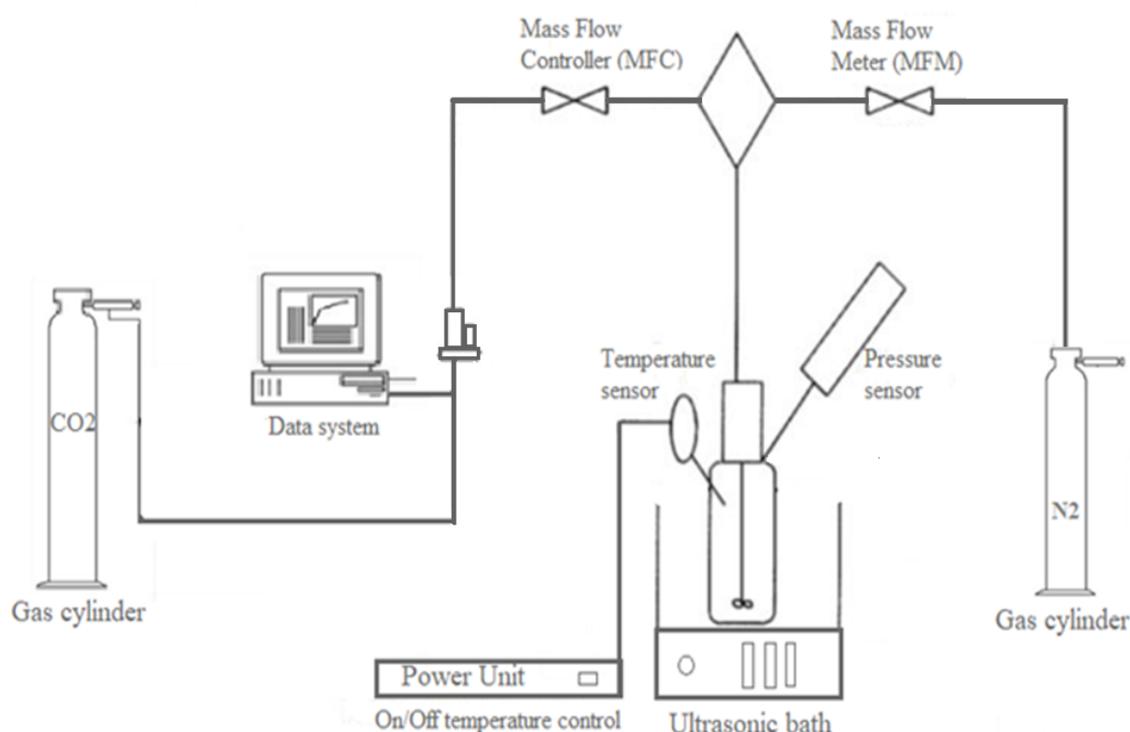
## MATERIALS and METHODS

### Gas-liquid stirred cell contact reactor

Gas absorption and desorption experiments were performed in a gas-liquid stirred cell reactor (model RD-CSTR 200, Sinerji, Turkey). The experimental set-up consisted of a stainless-steel reactor with a heating jacket, a PID-controlled power control unit, and a data acquisition system (Figure 1). The other important compo-

nents of the reactor system are a mass flow controller (MFC) and a mass flow meter (MFM). The stainless-steel reactor has a driver motor capable of a stirring rate of 50-500 rpm, along with digital temperature and pressure sensors connected to a data acquisition system. The system can operate under a wide range of temperature and pressure conditions, 293-373 K and 0-10 bar, respectively.

In this study, the  $\text{CO}_2$  absorption performance of AEPD: 1-hexanol, in the presence and absence of CA, was investigated with the help of high-precision flowmeters connected to the stirred reactor. The effect of amine concentrations, and the presence of CA enzyme on  $\text{CO}_2$  absorption capacity were discussed. During an experimental run, the inlet and outlet flow rates of  $\text{CO}_2$  were measured by the MFM and MFC and recorded at 10 s intervals until the MFM values approached the set MFC values. The difference between the inlet and outlet gas streams corresponded to the amount of  $\text{CO}_2$  absorbed. The total amount of  $\text{CO}_2$  captured by the solvent was calculated by the numerical integration method. This cal-



**Figure 1.** Systematic view of experimental set-up of gas- liquid contact reactor

culated cumulative volumetric amount was converted to absorbed CO<sub>2</sub> in moles by applying the necessary unit changes. The initial absorption rates (mol/s) were calculated from the slopes of the initial and the linear region of the CO<sub>2</sub> loading plot, as shown in Figure 2. Then, this loading rate was divided by the cross-sectional area of the reactor to obtain the general expression for the initial absorption rate (mol/m<sup>2</sup>.s). The convenience of the initial absorption rates for a fast reaction was investigated according to the first-order reaction rate equation proposed by Danckwerts [41]. This equation provides solubility, diffusivity and reaction rate in the combined form,  $A/(D_A k_0)^{0.5}$ . To satisfy pseudo first-order conditions, a gas-liquid contact reactor must operate at high concentration ranges of reactants. Opportunely, this concentration range matches to industrial conditions well. It should be noted that, the reaction of CO<sub>2</sub> is actually reversible. However, as in our case, if we take into account only the initial gas absorption (i.e. fresh solvent), the back pressure of dissolved CO<sub>2</sub> will be negligible and Equation 1 will be applicable.

$$\bar{R} = A^* \sqrt{D_A k_0} \quad (1)$$

Where,  $\bar{R}$  is the measured CO<sub>2</sub> absorption rate (mol/m<sup>2</sup>s),  $A^*$  is solubility of dissolved CO<sub>2</sub> at the gas-liquid interface (mol/m<sup>3</sup>),  $D_A$  is the molecular diffusivity of dissolved CO<sub>2</sub> (m<sup>2</sup>/s) and  $k_0$  is the pseudo-first order reaction rate constant (s<sup>-1</sup>).

In the absorption experiments, the stirred reactor tank pressure was maintained at 2 bar absolute CO<sub>2</sub> pressure, the temperature was maintained at 303 K, and the MFC was set to 10 sccm. Since the absorption process occurs at constant pressure, there was a continuous CO<sub>2</sub> input into the system, equivalent to the amount of CO<sub>2</sub> absorbed by the reactive solution. The change in the flow rates measured by the MFM and MFC during a typical experimental run, and the CO<sub>2</sub> loading as a function of time are plotted as shown in Figure 2.

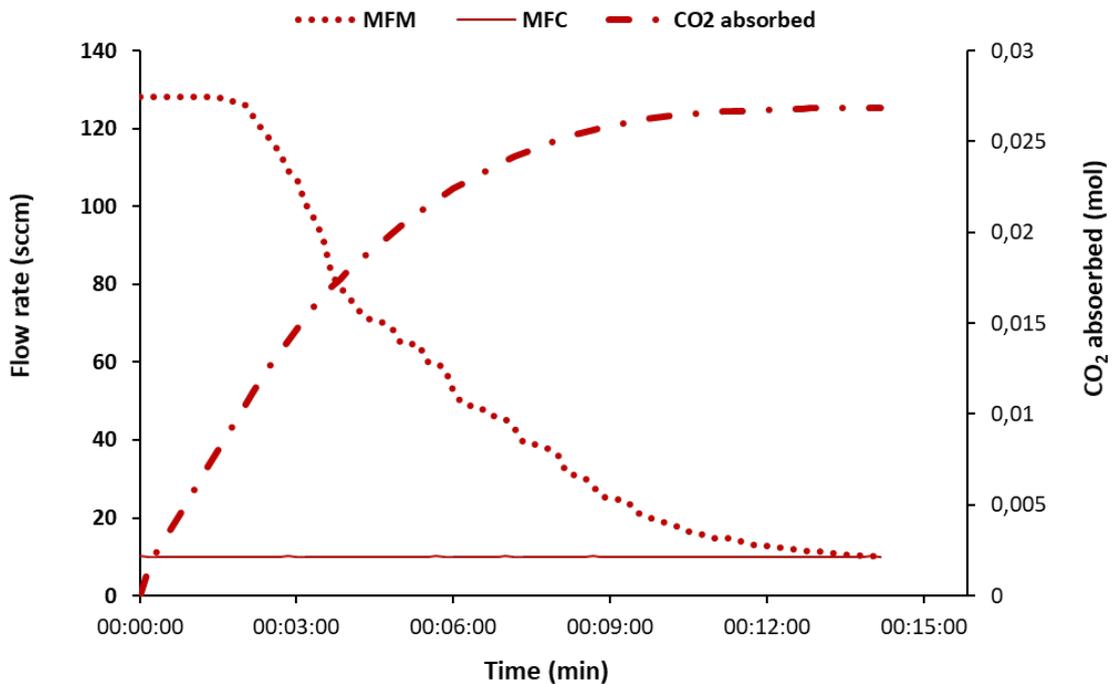


Figure 2. Typical absorption graph of 1.0 M AEED: 1-hexanol at 303 K and 2 bar.

It was noticed that the absorption rate of the fresh AEPD:1-hexanol solution decreases over time as the solution is saturated with CO<sub>2</sub>. The area between the MFC and MFM curves gives the amount of CO<sub>2</sub> absorbed throughout an experimental run. Toward the end of the experiment, the flow value observed in the MFM approached the value of the previously determined MFC and reached equilibrium. Equalization of the MFM and MFC values meant that the solution would not be able to capture any more CO<sub>2</sub>.

In addition, different sequences of the same experimental set-up were used to test the reusability of the solutions and to examine the desorption performance. In the desorption experiments, CO<sub>2</sub> was removed from the loaded solution by simple heating and sweeping with an inert gas such as nitrogen (N<sub>2</sub>). CO<sub>2</sub> desorption experiments on AEPD:1-hexanol systems, for different concentrations, were performed at 363 K and 1.1 bar absolute N<sub>2</sub> pressure. Ultrasound-assisted desorption experiments were performed in a Bandelin, DL 514 BH model ultrasonic bath with a constant wave frequency of 37 kHz, at 333 K and 1.1 bar absolute N<sub>2</sub> pressure.

In order to investigate the reversibility and performance losses of the SHA solutions, the consecutive absorption-desorption experiments were repeated for 3 cycles. In addition, Fourier infrared transform (FTIR) spectroscopy analyses were performed to demonstrate the regeneration effectiveness and the cyclic perfor-

mance of CO<sub>2</sub>-rich and CO<sub>2</sub>-lean SHA solutions in the presence and absence of CA. An FTIR analyzer (Thermo Scientific- NICOLET 6700) was used for detecting the functional groups and characterizing the chemical bonds. Further details of the gas-liquid contact reactor and experimental procedure can be found in the literature [12, 42, 43].

## RESULTS and DISCUSSION

### Absorption-desorption performance

Gas absorption experiments on the 30 mL AEPD: 1-hexanol system in the presence and absence of CA were performed at 303 K and 2 bar CO<sub>2</sub> absolute pressure in a gas-liquid contact reactor. The AEPD: 1-hexanol system was exposed to at least 3 capture and release cycles in order to investigate its reusability and cyclic capacity. Each experimental set was repeated 3 times and the average of 3 replicate experiments were represented. The absorption capacity and initial absorption rate of the consecutive absorption-desorption experiments for the 0.5 M AEPD: 1-hexanol system are summarized in Table 1. The highest CO<sub>2</sub> loading capacity was reached in the first absorption cycle whereupon a slight decrease was observed in subsequent cycles (Table 1). The absorption capacity loss of the AEPD: 1-hexanol system after the third regeneration cycle was found to be 25%. This can be referred to the incomplete removal of CO<sub>2</sub> during desorption cycle, which was carried out at 363 K and 1.1 bar absolute pressure.

**Table 1.** Cyclic absorption capacities and initial absorption rate of 0.5 M AEPD: 1-hexanol.

0.5 M AEPD: 1-hexanol: CA	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0126	1.84
2 <sup>nd</sup> Absorption	0.0104	1.29
3 <sup>rd</sup> Absorption	0.0091	1.14

**Table 2.** Cyclic absorption capacities and initial absorption rate of 0.75 M AEPD: 1-hexanol.

0.75 M AEPD: 1-hexanol	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0197	1.59
2 <sup>nd</sup> Absorption	0.0178	1.47
3 <sup>rd</sup> Absorption	0.0149	1.31

**Table 3.** Cyclic absorption capacities and initial absorption rate of 1.0 M AEPD: 1-hexanol.

1.0 M AEPD: 1-hexanol	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0267	2.27
2 <sup>nd</sup> Absorption	0.0241	1.98
3 <sup>rd</sup> Absorption	0.0206	1.63

Furthermore, a reduction in the initial absorption rate was observed with a decrease in the absorption capacity. The absorption capacity and initial absorption rate of 0.75 M AEPD: 1-hexanol and 1.0 M AEPD: 1-hexanol systems are reported in Tables 2 and 3, respectively.

As expected, the absorption capacity increased with increasing concentrations of the SHA, as shown in Tables 2 and 3. However, no such analogy was observed for the initial absorption rates.

CO<sub>2</sub> absorption experiments of the CA-activated AEPD: 1-hexanol system were performed at 303 K and 2 bar absolute pressure. The absorption capacity and initial absorption rate for different concentrations of the CA-catalyzed AEPD: 1-hexanol system are presented in Tables 4-6. The amount of CA enzyme added to various

concentrations of the AEPD: 1-hexanol system was set at 0.1 g/L. Desorption experiments were performed at 333 K to avoid the denaturation of the CA enzyme. As is evident from Tables 4-6, the highest CO<sub>2</sub> loading capacity was observed in the first absorption, after which a slight decrease was observed in the subsequent absorption cycles. The absorption capacity loss of the CA-activated AEPD: 1-hexanol systems after the third regeneration cycle was found to be 15%.

Both the CO<sub>2</sub> absorption capacity and the initial absorption rate of the CA-catalyzed AEPD: 1-hexanol system were higher than those of the uncatalyzed system. In order to calculate the actual stoichiometry of the reaction between CO<sub>2</sub> and the AEPD: 1-hexanol systems, the first CO<sub>2</sub> absorption capacity was plotted against the corresponding amount of AEPD (Figure 3).

**Table 4.** Cyclic absorption capacities and initial absorption rate of 0.5 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA.

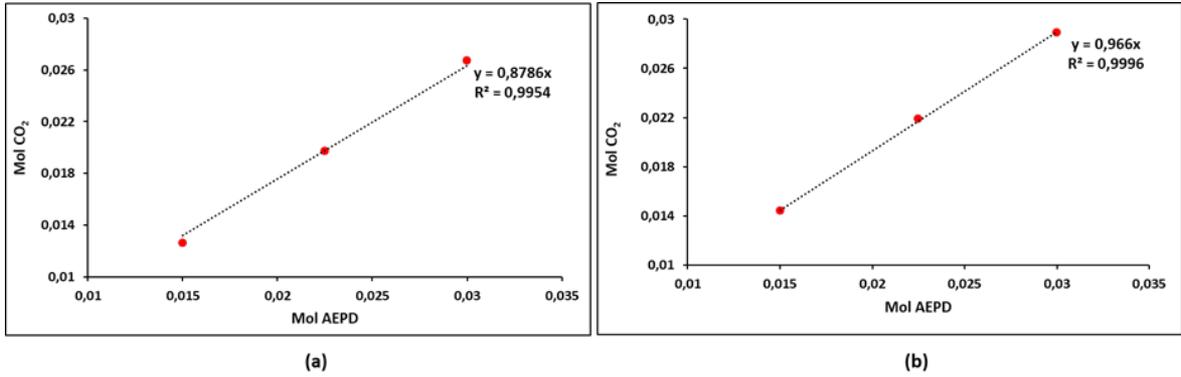
0.5 M AEPD: 1-hexanol: CA	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0144	2.36
2 <sup>nd</sup> Absorption	0.0132	2.21
3 <sup>rd</sup> Absorption	0.0121	1.85

**Table 5.** Cyclic absorption capacities and initial absorption rate of 0.75 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA.

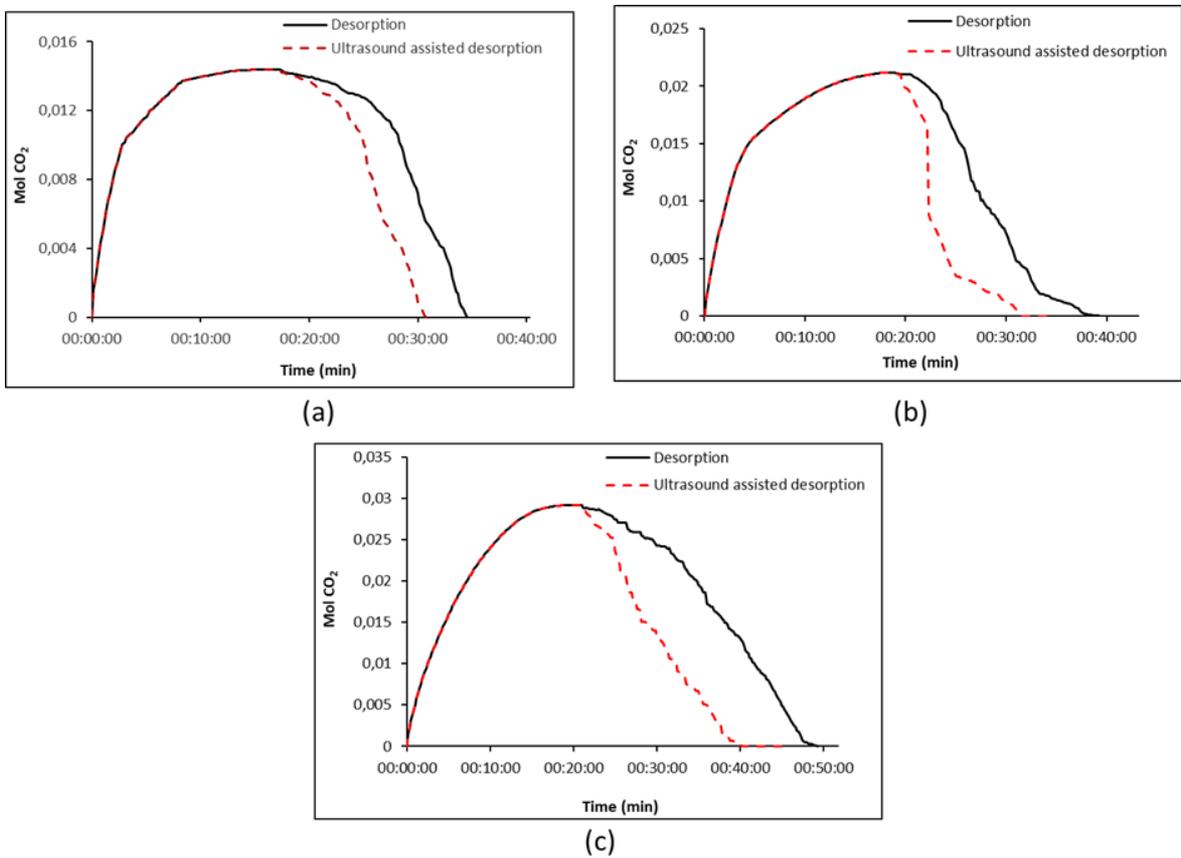
0.75 M AEPD: 1-hexanol: CA	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0219	2.41
2 <sup>nd</sup> Absorption	0.0208	2.25
3 <sup>rd</sup> Absorption	0.0189	2.18

**Table 6.** Cyclic absorption capacities and initial absorption rate of 1.0 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA.

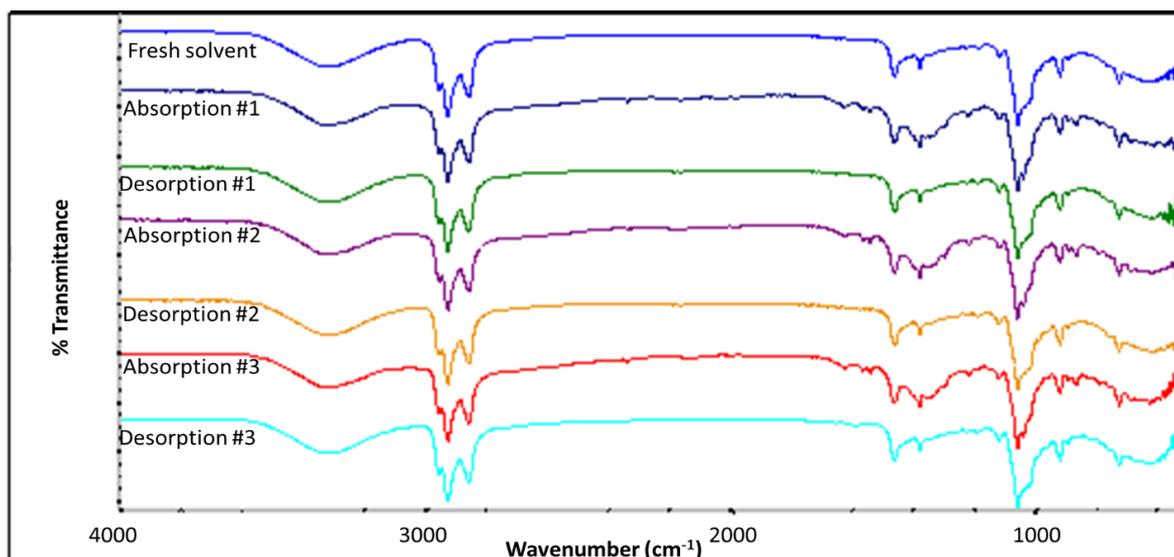
1.0 M AEPD: 1-hexanol: CA	Absorption capacity (mol)	Initial absorption rate (kmol/m <sup>2</sup> .s) x (10 <sup>5</sup> )
1 <sup>st</sup> Absorption	0.0289	2.54
2 <sup>nd</sup> Absorption	0.0263	2.37
3 <sup>rd</sup> Absorption	0.0247	2.21



**Figure 3.** CO<sub>2</sub> loading graphs of (a) AEPD: 1-hexanol system (b) AEPD: 1-hexanol system catalysed by 0.1 g/L CA at 303 K.



**Figure 4.** Ultrasound-assisted desorption performances for (a) 0.5 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA (b) 0.75 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA (c) 1.0 M AEPD: 1-hexanol system catalysed by 0.1 g/L CA.



**Figure 5.** FTIR spectrum of AEPD: 1-hexanol system for 3 absorption-desorption cycles.

AEPD: 1-hexanol is capable of capturing 0.88 moles of  $\text{CO}_2$  per mole of AEPD and AEPD: 1-hexanol system catalyzed by 0.1 g/L CA is capable of capturing 0.97 moles of  $\text{CO}_2$  per mole of AEPD (Figure 3). The  $\text{CO}_2$  absorption capacities for the AEPD: 1-hexanol systems are much higher than the theoretical value of 0.5 mol  $\text{CO}_2$ /mol MEA. [44]. As per the literature, the  $\text{CO}_2$  loading of tertiary amines is close to 0.9 mol  $\text{CO}_2$ /mol amine, except for MDEA [44]. The  $\text{CO}_2$  loading in aqueous MDEA allowed for the capture of 0.63 mol  $\text{CO}_2$ /mol MDEA, as reported by Jaafari et al., and 0.52 mol  $\text{CO}_2$ /mol MDEA, as reported by Hadri et al. [6, 29]. The  $\text{CO}_2$  absorption capacity of AMP in ethane-1,2-diol was reported to be 0.71 by Im et al. [45]. These results indicate that the loading capacity of a non-aqueous solution of a sterically hindered primary amine (AEPD: 1-hexanol) was superior to that of the benchmark  $\text{CO}_2$  capturing agents. This in turn implies that if AEPD: 1-hexanol systems are employed, either in the presence or absence of CA, the solvent circulation rate of an absorber-desorber system will be accordingly decreased.

#### Ultrasound-assisted desorption studies

Ultrasound-assisted desorption studies were performed in a gas-liquid stirred cell contact reactor under 37 kHz ultrasonic irradiation.  $\text{CO}_2$  absorption was carried out at 303 K and 2 bar absolute pressure, desorption at 333 K and 1.1 bar absolute pressure, and ultrasound-assisted desorption at 333 K and 1.1 bar absolute pressure. The experiments on the AEPD: 1-hexanol systems were

performed in the presence of 0.1 g/L CA. The experimental results for the absorption and desorption performed under the abovementioned conditions showed that the  $\text{CO}_2$  loading and absorption time increase with an increase in the AEPD concentration for each solvent system (Figure 4).

From the above results, it can be concluded that ultrasound-assisted desorption of the 0.1 g/L CA-catalyzed AEPD: 1-hexanol system is beneficial in terms of enhancement of both the  $\text{CO}_2$  desorption rate and the  $\text{CO}_2$  desorption capacity. It was observed that ultrasound irradiation significantly shortened the  $\text{CO}_2$  desorption time for biocatalytic  $\text{CO}_2$  capture by AEPD: 1-hexanol. Ultrasonic irradiation in the desorption process intensified bubble formation and decreased the gas-liquid mass transfer resistance, especially at the initial stage.

#### FTIR analyses

FTIR analyses were performed to study the regenerability and absorption-desorption performance losses of non-SHA solutions. A fresh AEPD:1-hexanol solvent,  $\text{CO}_2$ -rich solvent after absorption at 303 K and 2 bar pressure, and a  $\text{CO}_2$ -lean solvent after desorption by heat treatment at 363 K under  $\text{N}_2$  bubbling were examined for 3 absorption-desorption cycles. The FTIR spectra of the AEPD: 1-hexanol system are presented in Figure 5.

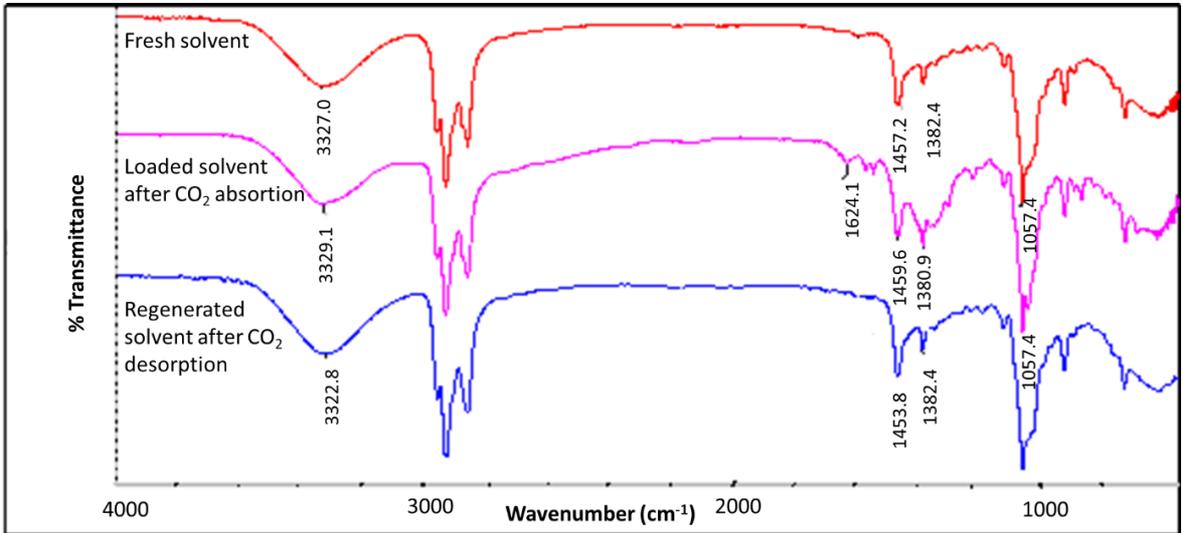


Figure 6. FTIR spectrum of AEPD: 1-hexanol system for the first absorption-desorption cycle.

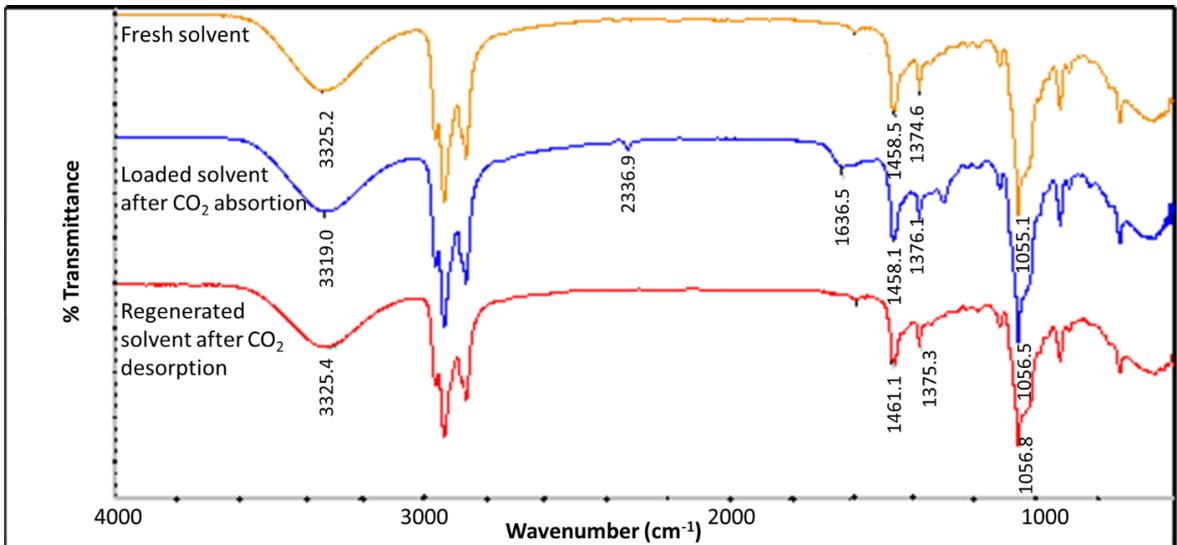


Figure 7. FTIR spectrum of AEPD: 1-hexanol system catalysed by 0.1 g/L CA.

In order to better understand the absorption-desorption performance of the AEPD:1-hexanol system, the FTIR spectrum of the fresh solvent, CO<sub>2</sub>-loaded solvent after the first absorption, and CO<sub>2</sub>-lean solvent after the first desorption were recorded (Figure 6). Fingerprint peaks for the -OH group were observed in the 3300-3400 cm<sup>-1</sup> region, while AEPD showed a characteristic peak at ~1050 cm<sup>-1</sup>. Peaks for the C=O bond in the CO<sub>2</sub>-loaded solvent were observed between 1600 and 1650 cm<sup>-1</sup>. After desorption, the fingerprint peaks for the C=O bond almost disappeared, and the spectrum of the lean solvent became similar to that of the fresh solvent.

The same procedure was repeated to observe the biocatalytic CO<sub>2</sub> absorption-desorption performance of the AEPD: 1-hexanol solution in the presence of 0.1 g/L CA. The FTIR spectra of the fresh solvent, loaded solvent after the first absorption at 303 K and 2 bar, and the lean solvent after the first desorption by heat treatment at 333 K under N<sub>2</sub> bubbling are presented in Figure 7. The characteristic fingerprint peak of the CA enzyme was observed at ~2330 cm<sup>-1</sup>. The results of the FTIR spectral analyses showed that the CA-activated non-SHA solution can be regenerated at 333 K, which is far below the boiling point of 1-hexanol and other components of the solution, thus providing a significant advantage in preventing solvent loss by evaporation. This behavior could result in significant energy saving for post-combustion CO<sub>2</sub> removal systems, where the traditional solvents require high energy in the form of latent heat.

Finally, ultrasound-assisted desorption was performed at 333 K under N<sub>2</sub> bubbling to study the effect of ultrasound irradiation on the CO<sub>2</sub> desorption performance. The FTIR spectra of the fresh AEPD: 1-hexanol system catalyzed by 0.1 g/L CA, CO<sub>2</sub>-loaded solvent after absorption, and CO<sub>2</sub>-lean solvent after ultrasound-assisted desorption are shown in Figure 8.

After regeneration of the solution through ultrasound-assisted CO<sub>2</sub> desorption, the loaded spectrum was converted to the lean solvent spectrum, which is almost identical to the spectrum of the fresh solvent.

### Conclusion

In the present study, the cyclic absorption and desorption performance of different concentrations of an AEPD:1-hexanol system was studied in a stirred cell gas-liquid reactor. The biocatalytic effect of CA on the absorption capacity was also investigated. With the addition of 0.1 g/L CA, the loading of 0.88 mole CO<sub>2</sub>/mol AEPD was enhanced to 0.97 mol CO<sub>2</sub>/mol AEPD, which is much higher than the theoretical value of 0.5 mol CO<sub>2</sub>/mol MEA for MEA. The obtained results clearly show that the absorption capacity of the AEPD: 1-hexanol system can be enhanced by the addition of small amounts of CA. Thus, CO<sub>2</sub> capture using the proposed solvent system could be achieved with a lesser amount of reactant than that required for traditional amine systems. The AEPD: 1-hexanol system was recycled.

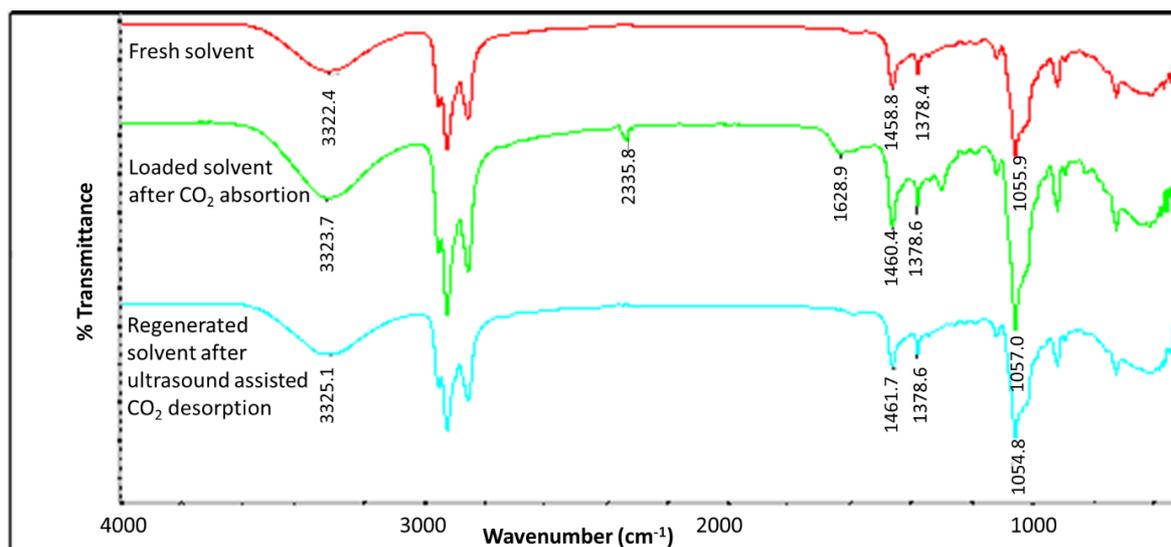


Figure 8. FTIR spectrum of AEPD: 1-hexanol system catalysed by 0.1 g/L CA (in the presence of ultrasound-assisted desorption).

cluded at least 3 times by desorption at 363 K and 1.1 bar absolute  $N_2$  pressure. The CA-catalyzed AEPD: 1-hexanol system was also recycled at least 3 times at 333 K, without any considerable loss of capture capacity. These results indicate that this non-aqueous SHA system can be regenerated by simple heating, without boiling or any phase change. Thus, a conventional heavy-duty reboiler may not be required for regeneration. Further, the use of ultrasound-assisted desorption led to a significant increase in the desorption capacity and desorption rate, implying that this technique can minimize the energy consumption for regeneration. Finally, FTIR analyses confirmed the regeneration of the proposed solvent system at much lower temperatures than the boiling points of AEPD or 1-hexanol. To sum up, the AEPD: 1-hexanol solvent system, both in the presence and absence of CA, has potential application as a commercial solvent due to its high  $CO_2$  loading, low volatility, and less energy demand for regeneration by virtue of its non-aqueous nature.

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