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Ultrasound-assisted Desorption of CO_2 from Carbon Dioxide Binding Organic Liquids

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Abstract

CO_2 absorption/desorption performance of 2-tert-Butyl-1,1,3,3-tetramethylguanidine (BTMG) and 1-Hexanol blend, which is a novel carbon dioxide binding organic liquid (CO_2BOL) system, was studied in order to investigate the behavior of ultrasound-assisted desorption. Pure CO_2 was first absorbed into a 10 wt percent BTMG solution in a semi-batch stirred reactor at 303 K and at 2 atm until equilibrium was reached, followed by ultrasound-assisted desorption at 353 K under nitrogen atmosphere. Experiments were repeated in the absence of ultrasound, keeping everything else the same. The CO_2 loading of BTMG:1-Hexanol solvent system was found to be a very favourable ratio of 1.05 mol CO_2/mol BTMG. When compared with conventional desorption, ultrasound-assisted desorption resulted in enhanced desorption rate so that the solvent regeneration time was significantly shortened. Enhancement of desorption rate was most significant/vigorous at the initial stages of desorption process. Further, regeneration of this CO_2BOL was possible at 353 K without any phase change. Experimental results clearly show that the ultrasound-assisted desorption is an effective process intensification tool leading to significantly minimised energy consumption for regeneration. To ensure effectiveness of regeneration, reversibility of the solvent system was also investigated by using Fourier transform infrared spectrometry.

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1. Introduction

The increasing concentration of atmospheric CO_2 is now a problem of global concern. Although the consequences of atmospheric CO_2 are still evolving, there is compelling evidence that the global environmental system is undergoing profound changes, such as warming. These global problems, directly resulting from the elevated atmospheric CO_2, will ultimately affect everyone. Therefore there is an urgent need for efficient carbon dioxide capture from point sources such as thermal power plants, as well as specific process plants. To that effect, it is universally accepted that the chemical absorption is the most appropriate technology. Here, an optimized solvent must possess appropriate dual function, that is, it must increase CO_2 loading while also enhancing the absorption rate. Recently, a novel organic solvent system termed carbon dioxide binding organic liquids (CO_2BOL) has been proposed for CO_2 capture [1]. CO_2BOL is based on a liquid mixture of a linear alcohol and an amidine or guanidine base that chemically binds CO_2 to form an amidinium or guanidinium alkyl carbonate salt. The reaction of CO_2BOL and carbon dioxide can be reversed without the need to boil the solvent system, thus eliminating the need for latent heat of evaporation. Although there is a considerable amount of published work for absorption kinetics of some of the CO_2BOL [1, 3], there is hardly any work for CO_2 desorption from them. Indeed, desorption studies from any amine-based solvent are limited even though the energy requirement –therefore the feasibility- of absorption/desorption process heavily depends on the stripping efficiency.

This paper suggests a promising method (that is, ultrasound-assisted desorption) which is superior to conventional stripping process since it could significantly reduce the regeneration temperature –hence, solvent degradation [4-7] (According to Davis and Rochelle, a reduction in desorption temperature by 17 °C reduces degradation of the MEA solution 4 times [8]). In addition, it reduces energy consumption, increases desorption capacity and often shortens the duration of desorption. A new process, which does not require vaporization enthalpy for the solvent regeneration (hence reboiler) and does not contain conventional desorption column (desorberless), will be developed when the ultrasonic desorption performed as an example of process intensification.

The aim of this work is twofold. First, it considers absorption/desorption behaviour of one of the promising CO_2BOLs, namely 2-tert-Butil-1,1,3,3-tetrametilguanidin (BTMG)/ 1-Hekzanol. BTMG, which is a guanidine, was chosen since it reacts with CO_2 at a rate comparable to commercially exploited amines such as alkanolamine solutions [3]. Second, effect of ultrasound irradiation is investigated since it is envisaged that regeneration at a temperature range much below the boiling point of solvent may not be as vigorous as the conventional reboiler. It is a well-known fact that ultrasound leads to cavitation and nucleation in the liquid and thus the formation of bubbles [2]. Once formed, it could be relatively easy for bubbles to grow as more gas diffuses to the bubbles and becomes part of the bubble. In this way ultrasound irradiation makes it easy for gas to escape in the form of bubbles. The enhanced desorption at lower temperatures -which will lead to a reduction of the CO_2 capture cost- is the main incentive behind ultrasound application.

2. Experimental

2.1. Reagents

BTMG: 2-tert-Butyl-1,1,3,3-tetramethylguanidine with ≥97.0 purity (CAS no. 29166-72-1) was supplied by Sigma-Aldrich (St. Louis, MO, USA). 1-Hexanol (reagent-grade, CAS no. 111-27-3) with 98% purity were purchased by

Sigma-Aldrich. CO_2 with a purity of 99.99% was obtained from Linde (Munich, Germany). Reagent grade chemicals were used without further purification.

2.2. Experimental Method

Both absorption and desorption experiments were carried out in a semi batch stirred reactor. Fig. 1 shows the experimental set-up schematically. For all experiments stirrer speed was kept constant at 500 rpm. 30 ml solvent consisting of 10 wt. percent BTMG in 1-hexanol were placed in the stirred reactor and pure carbon dioxide was fed from a cylinder while keeping the outlet flow rate constant at 10 $sccm^3$/min by a mass flow controller. The flow rate of carbon dioxide was measured and recorded as function of time. Temperature was kept at 303 K while the pressure was 1 barg. Absorption experiment was continued until the inlet flow rate dropped to 10 $sccm^3$/min which meant that the solvent was completely loaded. Then the temperature was raised to 353 K and at the same time CO_2 supply was closed and N_2 supply was opened at a constant flowrate of 50 $sccm^3$/min. At the same time the flow rate of gas was started to record as function of time. Initially, the flow rate of leaving gas was high since it contained not only the nitrogen fed to the reactor but also the desorbed CO_2. Eventually, the flow rate of outgoing gas started to drop and became equal to the incoming nitrogen flow rate which meant that desorption process finished.

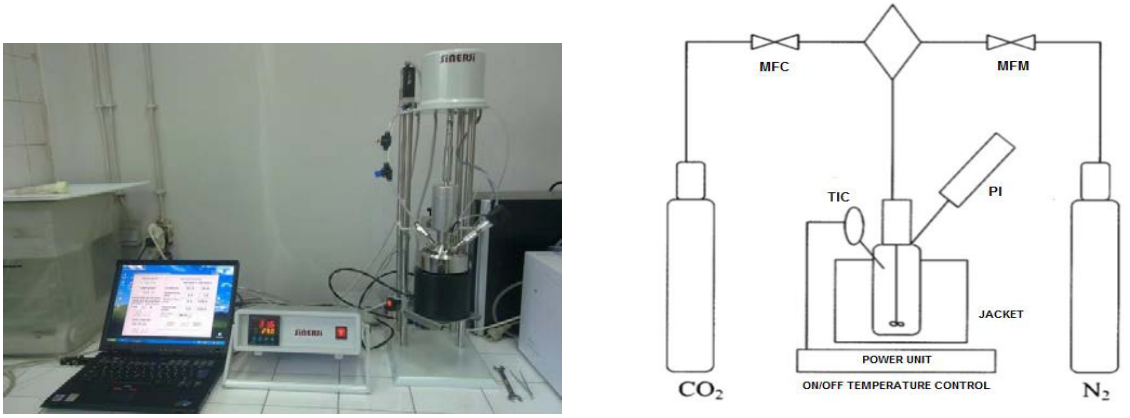

Fig. 1. Schematic diagram of experimental gas-liquid reactor set-up (excluding ultrasound irradiation equipment).

Ultrasound-assisted desorption performance studies of the BTMG:1-Hexanol system were carried out in Bandelin, DL 514 BH Model Ultrasonic Cleaner with constant wave frequency 35 kHz. Since the frequency of ultrasonic wave was found to have minor influence on desorption, a constant frequency was applied in this study [4].

3. Results and discussion

The absorption-desorption performances of CO_2BOL system, consisting of 10 wt. percent BTMG in 1-Hexanol, were carried out to investigate the effect of ultrasound on desorption experimentally. A duplicate experiment was carried out in a similar fashion. Here, the absorption experiments was identical and the only difference was that during desorption 37 kHz ultrasound irradiation at 353 K was applied. Fig. 2 shows all three experiments; namely, (1) CO_2 absorption at 303 K and 1barg, (2) desorption at 353 K and 1 bar and (3) ultrasound assisted desorption at 353 K and 1bar Nitrogen. It was found that the ultrasound-assistance increases the CO_2 desorption rate, desorption capacity

significantly and decreased desorption time. Desorption was vigorous at initial stages and this behavior can be attributed to intense bubble formation.

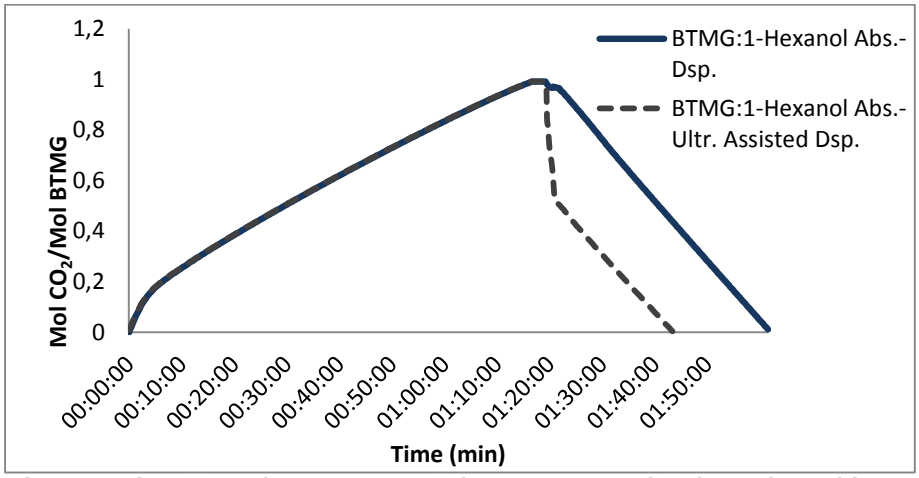

Fig. 2. Typical experimental run: (1) CO_2 absorption at 303 K, (2) desorption at 353 K and (3) ultrasound assisted desorption at 353 K

The consecutive absorption/desorption experiments were repeated for 5 times and the cyclic performance of the CO_2BOL system was investigated. The results are summarized in Table 1.

Table 1. Cyclic performance of the 10 % BTMG: 1-Hexanol system

		Normal Desorption		Ultrasound- Assisted Desorption	
10 % BTMG: 1-Hexanol	**Mol CO_2 Absorbed**	**Mol CO_2 Desorbed**	**Time (min)**	**Mol CO_2 Desorbed**	**Time (min)**
Absorption #1	0.0149	0.0145	42	0.0149	24
Absorption #2	0.0123	0.0118	39	0.0121	22
Absorption #3	0.0118	0.0110	34	0.0115	20
Absorption #4	0.0101	0.0096	24	0.0099	16
Absorption #5	0.0089	0.0078	11	0.0089	7

Reversibility and performance losses of CO_2BOL were further analyzed by Fourier transform infrared spectrometry (FTIR) in the range of 400-4000 cm^{-1}. FTIR analysis of fresh, CO_2 rich and CO_2 lean CO_2BOL solutions were conducted. It was found that the FTIR spectra of the lean solvent did not become virtually identical to the spectra of the fresh solvent after desorption. This behavior confirmed that complete reversibility of the reaction between CO_2 and this CO_2BOL did not take place at 353 K. However, if we consider much higher boiling point of solvent, there is ample room for carrying desorption experiments at temperatures slightly higher than 353 K.

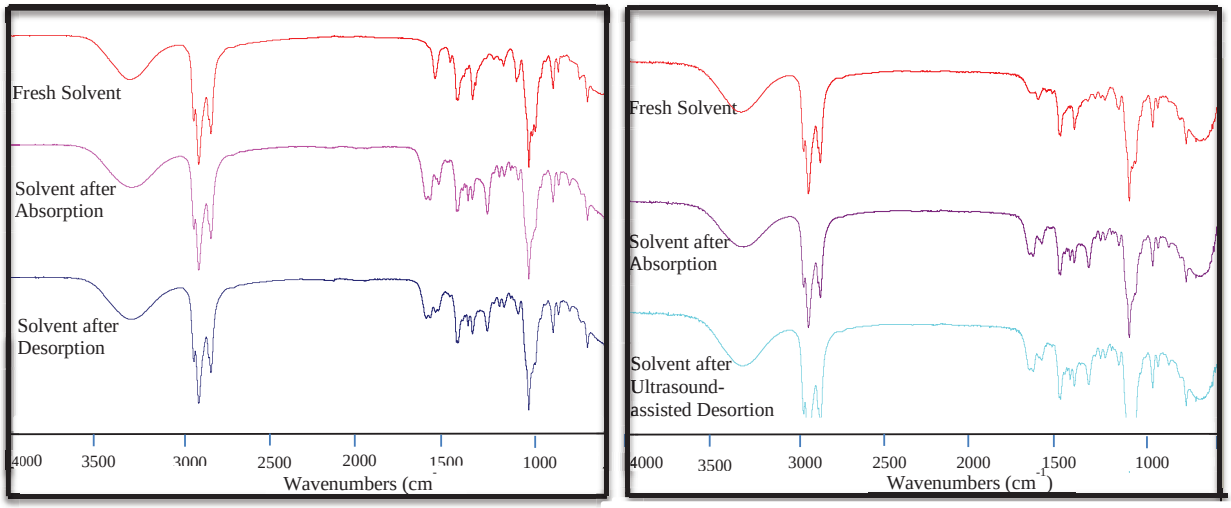

Fig. 3. FTIR output of the BTMG:1-Hexanol system

4. Conclusion

In a nutshell, the results of this work indicate that BTMG /1-hexanol solvent system has potentials of being a commercial solvent. That is, it has high loading ratio than common aqueous alkanolamine solution while its reaction rate is not inferior to them [3]. As shown by this work, the solvent can be regenerated without boiling it. Further, desorption capacity and duration can be enhanced significantly by applying ultrasound irradiation. The work is currently continuing to determine the optimum desorption temperature and irradiation frequency and other relevant parameters in order to establish the significance of ultrasound intensified desorption.

Nomenclature

Abs./Dsp. : Absorption /Desorption

BTMG : 2-tert-Butil-1,1,3,3-tetrametilguanidin

CO_2BOL : Carbon dioxide binding organic liquid

FTIR : Fourier transform infrared spectrometry

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