



## Aqueous hydrazine as a promising candidate for capturing carbon dioxide



Kyu Hyung Lee<sup>a</sup>, Byeongno Lee<sup>a</sup>, Ju Hee Lee<sup>a</sup>, Jong Kyun You<sup>b</sup>, Ki Tae Park<sup>b</sup>, Il Hyun Baek<sup>b</sup>, Nam Hwi Hur<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Sogang University, Seoul 121-742, Republic of Korea

<sup>b</sup> Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 305-343, Republic of Korea

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### ABSTRACT

Hydrazine, which is the simplest diamine, was investigated for its viability as a sorbent for carbon dioxide (CO<sub>2</sub>) capture from flue gas using lab scale experiments. It has a high CO<sub>2</sub> absorption capacity due to its low molecular weight. The overall mass transfer coefficient of aqueous hydrazine (32 wt%) is about 2.9 times higher than that of the benchmark monoethanolamine (MEA, 30 wt%), indicating that the absorption rate of CO<sub>2</sub> in aqueous hydrazine is remarkably fast. Furthermore, the cyclic capacity of aqueous hydrazine is comparable to that of MEA. Aqueous hydrazine has demonstrated the ability to capture and release CO<sub>2</sub> for three cycles without changing its absorption capacity. In addition, aqueous hydrazine does not show any indication of thermal degradation up to 90 °C. These advantages could lead to a substantial reduction of the cost of electricity, making aqueous hydrazine a promising new sorbent for post-combustion CO<sub>2</sub> capture applications.

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### 1. Introduction

The capture and storage of carbon dioxide (CO<sub>2</sub>) from flue gas has attracted tremendous interest that is due mainly to serious concern on global warming caused mostly by CO<sub>2</sub> (Raupach et al., 2007; Bhowm and Freeman, 2011; Haszeldine, 2009; Orr, 2009; Markewitz et al., 2012; Boot-Handford et al., 2014; D'Alessandro et al., 2010). Numerous sorbents have been developed for post-combustion CO<sub>2</sub> capture, which include alkanolamines (Rochelle, 2009; Rodriguez et al., 2011; Bishnoi and Rochelle, 2002; Rainbolt et al., 2011; Faramarzi et al., 2009), diamines (Zhou et al., 2010; Speyer et al., 2010), chilled ammonia (Peltier, 2008; Darde et al., 2010), CO<sub>2</sub>-binding organic liquids (Heldebrant et al., 2011; Zhang et al., 2013; Mathias et al., 2013), non-amine based solvents (Li et al., 2005; Chang et al., 2013), ionic liquids (Bates et al., 2002; Bara et al., 2009; Shannon et al., 2013), and phase-changing sorbents (Perry et al., 2010, 2012). Monoethanolamine (MEA) has been the most extensively studied solvent for CO<sub>2</sub> capture applications (Rochelle, 2009; Liu et al., 1999; Freguia and Rochelle, 2003; Fan et al., 2009; Conway et al., 2011; Han et al., 2011; Zhu et al., 2012; Supap et al., 2001). Compared with other alkanolamines, it has several advantages such as its fast absorption rate, high absorbing capacity, and

low molecular weight (M.W.). However, MEA has some drawbacks for use at industrial-scale. It requires a large amount of energy in the regeneration process and undergoes thermal and oxidative degradations in the continuous absorption process.

To reduce the cost of electricity in the MEA-based process, blended solvents consisting of MEA and other amines have been developed. Piperazine (PZ) is a secondary diamine with a six-membered ring that has two nitrogen atoms at opposite positions, which is employed with the MEA solvent as a rate promoter (Speyer et al., 2010; Dugas and Rochelle, 2011; Dang and Rochelle, 2003). The MEA sorbent formulated with PZ increases the CO<sub>2</sub> absorption rate by 50–100% compared with that of MEA alone. Bishnoi and Rochelle (2002) investigated the use of PZ alone as a sorbent for CO<sub>2</sub> capture. They reported that the CO<sub>2</sub> absorption rate of PZ was enhanced to more than twice that of MEA. The working capacity of PZ is also about double that of MEA. Aqueous ethylenediamine (EDA), which is a primary diamine, has been studied for the purpose of CO<sub>2</sub> removal (Zhou et al., 2010). By comparison with MEA, the working capacity of EDA is larger but its CO<sub>2</sub> absorption rate is slower. Despite these extensive efforts, novel solvents that can satisfy several technological requirements of the CO<sub>2</sub> capture process such as high absorption capacity, fast absorption rate, low regeneration heat, and high stability remain a significant challenge.

Hydrazine (NH<sub>2</sub>NH<sub>2</sub>) is a potentially carcinogenic liquid, and the physical properties of hydrazine are close to those of water. Hydrazine forms an azeotrope with water at 69 wt% of hydrazine,

\* Corresponding author. Tel.: +82 2 705 8440; fax: +82 2 701 0967.  
E-mail address: [nhhur@sogang.ac.kr](mailto:nhhur@sogang.ac.kr) (N.H. Hur).

which makes aqueous hydrazine non-volatile and relatively safe (Schmidt, 2001). Especially at low hydrazine contents water prevails the vapor phase, which drastically reduces the toxicity of hydrazine. Niemeier and Kjell (2013) reported that dilution plays an important role in increasing the intrinsic safety of aqueous hydrazine. Aqueous hydrazine, instead of hydrazine, is thus used as a blowing agent (Berins, 2002) and a precursor to make various high-value chemicals widely (Loiseau et al., 2011; Silva et al., 2008).

Hydrazine is the simplest diamine and a weak base ( $pK_a \sim 8.10$ ). Similar to PZ and EDA, it has two amine groups, which enable it to capture  $CO_2$  efficiently. Recently, we found that hydrazine readily reacts with  $CO_2$ , yielding a simple 1:1 adduct of hydrazine and  $CO_2$  (Lee et al., 2011). And this led us to consider hydrazine as a potential  $CO_2$  sorbent. The  $CO_2$  absorption capacity of hydrazine is expected to be higher than that of MEA. Typically, two equivalents of MEA react with  $CO_2$  to form a carbamate with a 2:1 molar ratio while hydrazine captures  $CO_2$  to form a 1:1 adduct. Moreover, the M.W. of hydrazine (32.04 g/mol) is just over half that of MEA (61.08 g/mol), implying that hydrazine has a higher  $CO_2$  capacity per gram (31.25 mmol/g) than that of MEA. These characteristics motivated us to investigate the  $CO_2$  absorption capability of aqueous hydrazine. To our knowledge, this is the first study to report on the use of aqueous hydrazine for the capture of  $CO_2$ . To address the potential use of aqueous hydrazine as a  $CO_2$  scavenger, its performance was investigated in terms of its absorption capacity, cyclic capacity, overall mass transfer coefficient, viscosity, and thermal stability. The results are compared to those of a benchmark 30 wt% MEA solution.

## 2. Materials and methods

### 2.1. Materials

All chemical reagents such as hydrazine hydrate, mono ethanol amine (MEA), and methyl diethanol amine (MDEA) with purities in excess of 99% were purchased from Sigma–Aldrich, and they were all used as received without further purification. Hydrazine hydrate, MEA, and MDEA were diluted with de-ionized water to make corresponding sorbents with a range of concentrations.  $CO_2$  and  $N_2$  gases with purities in excess of 99.99% were purchased from Donga Specialty Gas. The partial  $CO_2$  pressure was balanced with  $N_2$ . *Precaution:* The aqueous hydrazine solution could be harmful for health due to its sublimation character. At ambient temperatures, the vapor pressure of hydrazine in 24 wt% aqueous solution is about 5000 ppm. Accordingly, the equipment of effective ventilation is highly recommended for handling the hydrazine solution to avoid vapor inhalation. See the MSDS and the related reports for details (Niemeier and Kjell, 2013; Young, 2009).

### 2.2. $CO_2$ absorption tests

All preliminary experiments were performed in a Büchi 25 mL pressure vessel. The absorption capacities of hydrazine and MEA were studied at 25 °C and in a range of  $CO_2$  partial pressure from 1 to 3 bar. The amount of  $CO_2$  uptake was measured by the change in weight of a sorbent after absorption of  $CO_2$ . In a typical measurement, the 32 wt% hydrazine solution was loaded into a Büchi 25 mL pressure vessel, subjected to 1 bar of  $CO_2$ , and monitored for any weight changes. The weight gained by the hydrazine solution within the cell was measured as a function of time by a mass balance. The corresponding weight change was then used to calculate the absorption amount (mole or gram of  $CO_2$ ). Other absorption measurements as a function of concentration were also performed in the pressure vessel under the similar conditions. For comparison,

the  $CO_2$  uptake of aqueous MEA was also performed with the same methodology.

### 2.3. Thermal stability

Thermal degradation experiments were performed at 90 °C in air using a 25 mL pressure vessel. First, aqueous hydrazine (32 wt%) was loaded into the vessel and exposed to  $CO_2$  at 40 °C and 1 bar. After complete sorption of  $CO_2$ , the vessel was then heated at 90 °C in air to detach  $CO_2$  from sorbent. The absorption and desorption cycles of  $CO_2$  were repeated three times (Fig. S1). The weight change was measured as a function of time by a mass balance. For comparison, the absorption and desorption cycles of  $CO_2$  of MEA (50 wt%) was also performed by the same methodology.

### 2.4. Cyclic capacity

The schematic diagram of the apparatus used in this work is shown in Fig. S2; it is a semi-batch absorption system designed to measure the  $CO_2$  absorption capacity of a solution. The apparatus consists of four main parts: a gas blender for supplying the gas mixture, a continuous stirred tank reactor, a water bath for maintaining the reactor at constant temperature, and an on-line gas chromatography instrument (GC, Agilent 6890N) to monitor the amount of  $CO_2$ . To simulate representative flue gas conditions, the capacity was measured at 1 bar with a partial  $CO_2$  pressure of 0.15 bar. Absorption and desorption experiments were done at 40 °C and 90 °C, respectively. The sorbent was fed into the system and the gas mixture was supplied continuously to the bottom of the reactor through a sparger to form fine bubbles at a flow rate of 1 L/min. The internal volume of the stainless steel reactor is 2 L. The temperature and pressure inside the reactor were measured by using a K-type thermocouple and a pressure transmitter (PSCH0030K, Sensys), respectively. For all experiments, the volumes of sorbents were maintained at 1 L, and the solutions were all stirred at 500 rpm. The concentrations of  $CO_2$  dissolved in the sorbent and those of  $CO_2$  discharged after reaction with the sorbents were measured by a GC. The  $CO_2$  loading for the sorbent was determined when the loading value of the  $CO_2$  achieved a near-constant value.

### 2.5. Overall mass transfer coefficient

The overall mass transfer coefficient of  $CO_2$  in the sorbent was measured by the wetted-wall column (WWC) method at 40 °C. The WWC was built according to the designs of known columns reported in the literature (Cullinane and Rochelle, 2006). The experimental apparatus is schematically shown in Fig. S3. The WWC consists of a stainless steel tube that is 90 mm in height and 12.6 mm in diameter, and this tube is enclosed by a cylindrical thick-walled glass shell. The whole chamber is also surrounded by a second thick-walled glass shell. The sorbent was pumped up through the column at a constant flow rate of 150 mL/min, which was maintained by constant liquid-flow pump. The feed gas was supplied from the bottom of the chamber at a flow rate of 5 L/min, and this gas contacted counter-currently with the liquid sorbent. Both the gas and liquid phases were preheated to a temperature of 40 °C, which was maintained by the temperature-controlled bath. The concentration of  $CO_2$  in the feed gas was in the range of 3–9% (v/v), and this was varied by mass flow controller (Brooks, 5850E). The gas concentrations were continuously analyzed using ND-IR (non-dispersion infrared spectroscopy, FE). Measurement of the respective  $CO_2$  contents in the inlet and outlet gas streams provided the  $CO_2$  partial pressure and  $CO_2$  flux between gas and liquid. The overall mass transfer coefficient ( $K_G$ ) was calculated by the following procedure.

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