

## Selection of new absorbents for carbon dioxide capture

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### Abstract

This work focuses on selecting new absorbents for CO<sub>2</sub> capture. Absorption of CO<sub>2</sub> was studied at 40 °C using both single and mixed amine-based absorbents. The experimental results show that most absorbents tested have a poorer performance than MEA, but that aqueous AEEA might be a possible contender. In addition to the absorption measurements, the VLE of CO<sub>2</sub> in the selected absorbent, the aqueous 2.9 M AEEA, were studied at 40 and 120 °C. The equilibrium partial pressures of CO<sub>2</sub> in the aqueous 2.9 M AEEA at the temperature of removal (40 °C) and that of regeneration (120 °C) are lower than for aqueous 5.0 M MEA, but the maximum net cyclic capacity is somewhat higher.

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### 1. Introduction

Removal of acidic gases, e.g., carbon dioxide (CO<sub>2</sub>), is an important industrial operation. Carbon dioxide is produced in large quantities by many important industries such as fossil fuel fired power plants, steel production, chemical and petrochemical manufacturing, cement production and natural gas purification. The reasons for CO<sub>2</sub> removal are traditionally technical and economical concerns. Carbon dioxide present in natural gas will reduce the heating value of the gas, and as an acidic component, it has the potential to cause corrosion in pipes and process equipment and also to cause catalyst poisoning in ammonia synthesis [1]. Natural gas pipe lines usually permit from 1% to 2% CO<sub>2</sub> and sometimes as high as 5% [2]. In the past decades, CO<sub>2</sub> removal from flue gas streams started as a potentially economic source of CO<sub>2</sub>, mainly for enhanced

oil recovery (EOR) operations. Moreover, CO<sub>2</sub> was also produced for other industrial applications such as carbonation of brine, welding as an inert gas, food and beverage carbonation, dry ice, urea production and soda ash industry [3,4]. However, environmental concerns, such as global climate change, are now focused as one of the most important and challenging environmental issues facing the world community and have motivated intensive research on CO<sub>2</sub> capture and sequestration. Carbon dioxide, as one of the greenhouse gases (GHG), is currently responsible for over 60% of the enhanced greenhouse effect, methane (CH<sub>4</sub>) contributes 20% and the remaining 20% is caused by nitrous oxide (N<sub>2</sub>O), a number of industrial gases and ozone. Scientific evidence now strongly suggests that increased levels of GHG may lead to higher temperature and cause climate change on a global scale. Various climate models estimate that the global average temperature may rise by about 1.4–5.8 °C by the year 2100 [5].

A wide range of technologies currently exists for separation and capture of CO<sub>2</sub> from gas streams as given in Ref. [3]. Such systems have been used in the chemical industry and in the production of technical gases for industrial and laboratory use [6]. Absorption with amine-based

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absorbents is the most common technology for CO<sub>2</sub> removal today. It is a process with considerable inherent problems, particularly when used on large gas flows, e.g., exhaust resulting from fossil fuel fired power stations. The processes are bulky, leading to large investment costs and high energy consumption, and the absorbents in use today are not stable and form degradation products that need to be handled.

A chemical that is to be used as a new commercial absorbent for removal of CO<sub>2</sub> will require both a high net cyclic capacity and high reaction/absorption rate for CO<sub>2</sub>, as well as high chemical stability, low vapor pressure and low corrosiveness. Aqueous solutions of alkanolamines are the most commonly used chemical absorbents for the removal of acidic gases (CO<sub>2</sub> and H<sub>2</sub>S) from natural, refinery and synthesis gas streams. Among them, aqueous monoethanolamine (MEA) as a primary amine has been used extensively for this purpose, especially for removal of CO<sub>2</sub>. It has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and, thus, high absorbing capacity on a mass basis and reasonable thermal stability and thermal degradation rate. The disadvantages of MEA include high enthalpy of reaction with CO<sub>2</sub>, leading to higher disorder energy consumption, the formation of a stable carbamate and also the formation of degradation products with COS or oxygen bearing gases, inability to remove mercaptans, vaporization losses because of high vapor pressure and more corrosive than many other alkanolamines and, thus, needs corrosion inhibitors when used in higher concentration [7–10]. Because of its wide use and advantages compared to other alkanolamines, MEA is set as a base case in this work. The parameters evaluated here are the absorption rate and the cyclic capacity.

This work focuses on selecting new absorbents for CO<sub>2</sub> capture using a screening method giving the absorption rate as function of loading, a molar ratio between CO<sub>2</sub> absorbed and the absorbent used. The vapor–liquid equilibria (VLE) of CO<sub>2</sub> in a selected absorbent at temperature of removal (40 °C) and that of regeneration (120 °C) were also studied. The objective of the work described here is to select new and more acceptable absorbents or absorbent mixtures whose absorption rate and net cyclic capacity are higher than the existing ones, thereby reducing the energy consumption of the removal process.

## 2. Materials and methods

### 2.1. Materials

The CO<sub>2</sub> (min. 99.99 mol.%) and N<sub>2</sub> (min. 99.6 and 99.999 mol.%) gases used were obtained from AGA Gas GmbH. The alkanolamines were obtained from Acros Organics and used without further purification. Those selected were monoethanolamine (MEA) – [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OH], 2-(butylamino)ethanol (BEA) – [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>OH], *N*-methyldiethanolamine (MDEA) – [CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>],

2-(methylamino)ethanol (MMEA) – [CH<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>OH], 2-(ethylamino)ethanol (EMEA) – [CH<sub>3</sub>CH<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>OH], 2-(2-aminoethyl-amino)ethanol (AEEA) – [H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>OH], and their reported purities were not less than 99%, 98%, 98.5%, 99%, 98% and 97%, respectively. Other absorbent chemicals tested were piperazine (PZ) – [–NH(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>–] (Acros Organics, min. 99 mass%) and potassium salt of taurine (PT), which was prepared by neutralizing taurine [2-aminoethanesulfonic acid – H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>–SO<sub>3</sub>H] (Acros Organics, 99 mass%) with an equi-molar amount of potassium hydroxide (KOH) (Merck, p.a.).

### 2.2. Screening apparatus

The absorbent selection experiments were performed in a screening apparatus as shown in Fig. 1. The apparatus, designed to operate at atmospheric pressure and temperatures up to 80 °C, consists of six 1 L glass absorbers, six K type thermocouples, a HETO circulating heater (Type 02 T 623), a Hartmann & Braun Uras 3G IR CO<sub>2</sub> analyzer and a BRONKHORST HI-TEC N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>S mass flow controller (Type E-7100). The data acquisition system uses LabVIEW. Before starting the experiment, a CO<sub>2</sub>–N<sub>2</sub> gas mixture containing 10 vol.% CO<sub>2</sub> with flow rate of 5 NL min<sup>–1</sup> was circulated through a by pass valve to calibrate the analyzer. As the process started, the by pass valve closed automatically. The gas mixture was passed through a water saturator and then to the absorber containing 750 mL of absorbent, being either a single or mixed absorbent. The gas phase leaving the absorber was cooled, and the CO<sub>2</sub> content directly determined by IR analysis. The temperature of the water bath was maintained at 40 ± 0.1 °C. The gas CO<sub>2</sub> content, the temperatures and the gas flow rates were collected by the LabVIEW data acquisition system. The process automatically terminated when the concentration of CO<sub>2</sub> in the outlet reached 9.5 vol.% (9.5 kPa CO<sub>2</sub> partial pressure). After terminating the experiment, a liquid sample was then analyzed by the barium chloride method. The amount of HCl not used to dissolve BaCO<sub>3</sub> was titrated with 0.1 M (mol L<sup>–1</sup>) NaOH using an automatic titrator (Metrohm 702 SM Titrino) with end point pH 5.2.

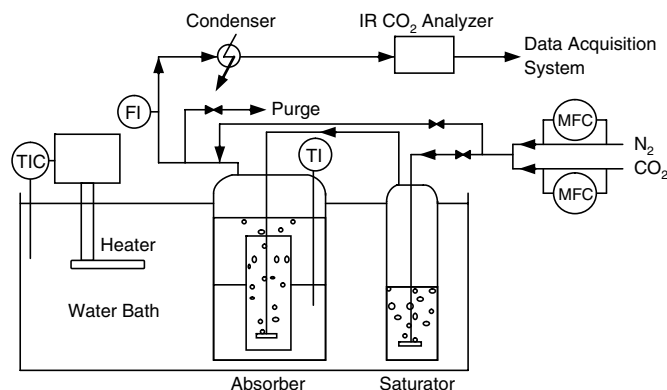


Fig. 1. Screening apparatus for CO<sub>2</sub> capture.

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