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Enzyme carbonic anhydrase accelerated CO₂ absorption in membrane contactor

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Abstract

Membrane contactors offer a promising alternative to conventional CO₂ absorption processes using columns. In a membrane contactor the advantages of absorption technology and membrane technology are combined as direct contact of the solution and gas feed stream is avoided by membrane barrier. In this study, the possibility of employing the enzyme carbonic anhydrase (CA) for the acceleration of CO₂ reaction in MDEA and MEA solution in combination with the use of a membrane contactor was investigated in a lab scale module. The membranes employed in this study were microporous and specifically chosen to have both hydrophobic (bulk) and hydrophilic (surface) properties in order to avoid wetting of solution and reduce fouling by the enzymes simultaneously. By adding the enzyme carbonic anhydrase (CA), a significant improvement of CO₂ absorption rate was observed in MDEA solution while a negative effect was observed in MEA solution. Meanwhile the porous hydrophobic membranes were coated with a highly selective poly(ionic liquids) layer increasing the affinity of CO₂ towards the interfacial area and hence also the driving force. The concept may initially appear counter intuitive, as the dense membrane layer introduces an added resistance, however the active membrane material gave promising results and was observed to accelerate CO₂ transport in MDEA solution. The combination of both enzyme and PILs resulted in synergies, which significantly improved CO₂ absorption in MDEA solution.

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1. Introduction

Membrane contactors offer a promising alternative to conventional CO₂ absorption processes using columns [1]. The principle of this technology is that the CO₂ absorption occurs when the gas stream contacts with the liquid phase flowing on the opposite side of the membrane. While passed through the membrane contactor, CO₂ will be absorbed by the solution and will be removed from the interfacial area. The CO₂ will be subsequently desorbed at an external desorption unit to regenerate the solution. The solution may be the same as used for absorption in column, however, the hydrophobic membrane defines the interfacial area between gas and liquid phase very precisely [2]. This makes the prediction of mass transfer more reliable than in conventional columns. In a membrane contactor the advantages of absorption technology and membrane technology are combined [3], as direct contact by mixing of the solution and gas feed stream is avoided. The major benefit of membrane contactors is the provision of large surface (interfacial) areas per volume as accompanied by the prevention of dispersion of the two phases as well as solution losses. Operation problems that are observed in absorption columns such as foaming, channeling and entrainment are minimized by means of the well-defined contacting area in the membrane contactor. The possibility of independent control of gas and liquid phases may in addition give very convenient operation flexibility. As is the case with a membrane system, the membrane contactor process can be easily up- and down-scaled by changing the number of modules.

In contrast to membrane technology where nonporous membranes are used (subsequently the permeance and selectivity are limited with trade-off), the membrane contactor uses microporous membranes which can considerably enhance the gas permeance without selectivity consideration since the solution can take CO₂ exclusively (selectivity is ideally infinite). However, if the membrane pores are filled with the liquid (wetted), the mass transfer resistance of the CO₂ through the membrane becomes significant, resulting in economically unviable operation. This wetting tendency is a result of combined properties of membrane (hydrophobicity)-absorbent liquid (surface tension).

CO₂ capture in absorption towers with monoethanolamine (MEA) solution, has to date been the most investigated technology. Although MEA has a fast CO₂ absorption rate, its use results in issues including corrosion of equipment, high regeneration energy and degradation which results in environmental problems from release of degradation byproducts. MDEA (N-methyldiethanolamine) is a good alternative as it has a lower energy requirement for solution regeneration at the desorption stage, is less corrosive and has greater chemical stability. The slower reaction rate (absorption of CO₂) is the major drawback of such solution. Since enzyme carbonic anhydrase (CA) is reported to catalyze CO₂ fixation in nature by hydrating CO₂ to bicarbonate [4], it is expected that use of the efficient biocatalyst can enhance the CO₂ absorption rate.

In this study, the possibility of employing the enzyme carbonic anhydrase (CA) for the acceleration of CO₂ reaction in MDEA in combination with the use of a membrane contactor was investigated in a lab scale module. The membranes employed in this study were microporous and specifically chosen to have both hydrophobic (bulk) and hydrophilic (surface) properties in order to avoid wetting of solution and reduce fouling by the enzymes simultaneously. Fig. 1 illustrates the concept of this study: the solution system may be activated with enzymes which catalyse the CO₂ absorption/desorption reactions. Additionally a porous hydrophobic membrane may be coated with a highly selective poly(ionic liquids) layer increasing the affinity of CO₂ towards the interfacial area and hence also the driving force. The concept may initially appear counter intuitive, as the dense membrane layer introduces an added resistance, however the active membrane material gave promising results and was observed to accelerate CO₂ transport. The selective membrane materials was based on a blend of Poly(ionic liquid)s and Zinc salt tailored for CO₂ transport.

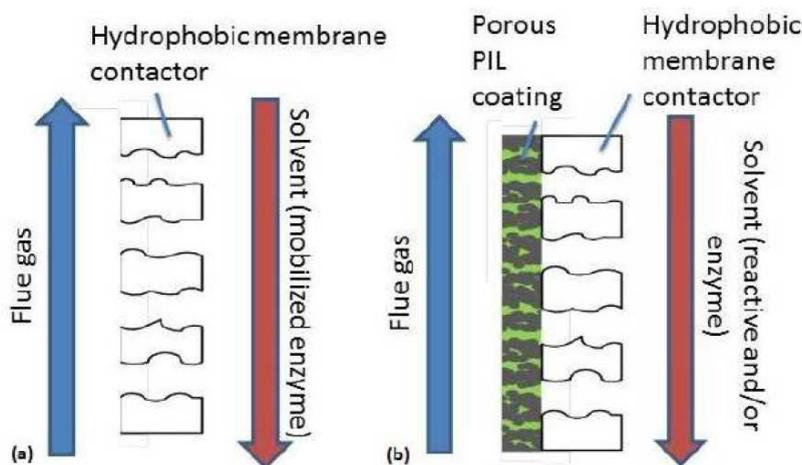


Fig. 1. Membrane contactor concepts in this study: (a) adding an enzyme (Carbonic Anhydrase) for acceleration of CO₂ reaction in solution and (b) adding CO₂ selective PILs layer for facilitating CO₂ transport on hydrophobic membrane.

Nomenclature

CA	Carbonic Anhydrase
PILs	Poly(Ionic Liquids)
MEA	Monoethanolamine
MDEA	N-methyldiethanolamine
TFC membrane	Thin Film Composite Membrane
PVDF	Polyvinylidene difluoride
MWCO	Molecular weight cut-off

2. Experimental method

2.1. Materials and membrane preparation

To maximize the merits of the membrane contactor, the following aspects were considered to choose support membrane material: operational stability (critical entry pressure/breakthrough pressure), chemical & thermal stability against amine solution, mass transfer rate/resistance, commercial availability and cost & environmental issues. The addition of enzyme into amine-water solution will make a change in surface tension (preferably higher surface tension). Coating support membrane with PILs was a challenging task because support membrane needed preferably to be hydrophobic to prevent wetting while PILs could be either hydrophilic or hydrophobic. Hydrophilic surface was preferred to reduce fouling by proteins (enzymes) as well. Considering all these aspects, it could be a best combination if chemically stable membranes had both characters, e.g. one surface side is hydrophilic while the other surface side or inner volume of the membrane is hydrophobic. Such membranes are commercially available from some membrane suppliers. Among the membranes based on fluoro-polymers, ETNA01PP support manufactured by Alfa Laval AS was employed as support for further coating of PILs. The ETNA01PP support is composite ultrafiltration membrane which consists of a porous polypropylene (PP) base and a dense polyvinylidene fluoride (PVDF) layer on one side. The PVDF layer is surface treated for a higher hydrophilicity and is proven to have superior fouling properties compared to conventional [5].

The important factor for the choice of suitable PILs was the permeability of CO₂, which should be as high as possible combined with good coating property on support. The PILs among various kinds of PILs used for this study

2.2. Experimental method

The absorption tests were performed using the laboratory scale membrane contactor set-up available at SINTEF (Norway). A schematic diagram is presented in Fig. 4.

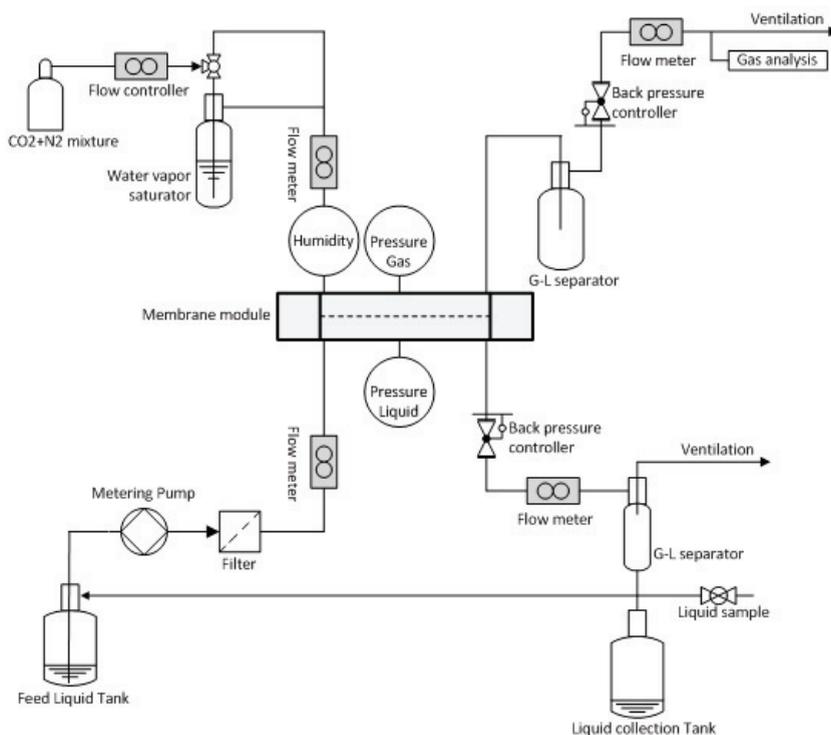


Fig. 4. Schematic diagram of the membrane contactor experimental set-up.

The major components constituting the liquid line include: liquid feed tank, liquid pump, mass flow meters and a liquid collection tank. The pressure is regulated by a back pressure controller. The solution after the membrane contactor module passed through a cooling bath and gas-liquid separator before being recycled into the feed. Since the solution was recycled, the CO_2 loading constantly rose during the experiments. The baseline temperature of all the experiments was set to 35°C . The solutions used for this study were 30wt% MEA and 30wt% MDEA for comparison where a small amount of the enzyme was added. The enzyme was added on basis of weight fraction (1wt%) without any additives supplied by Novozymes AS (Denmark). MDEA was chosen over the more commonly used monoethanolamine (MEA) because of the superior enhancement possibilities.

The deployed premixed feed gas consisted of 15vol.% CO_2 and 85 vol.% N_2 , which sufficiently represented flue gases from coal-fired power plants. The feed gas pressure was varied from slightly higher than atmospheric to ca. 2bar.

The experiment was started if both gas and liquid flows were established without any leakage through the membrane. The critical entry pressures on either side were considered to prevent solution intrusion into gas side and/or gas bubbling into solution side. During the experiments, liquid samples were taken in regular intervals. The samples were titrated to analyze the CO_2 concentration (CO_2 loading) of the solution.

3. Results and discussion

3.1. Enzyme effect on CO₂ absorption in MEA solution

The CO₂ absorption rate was not enhanced for 30wt.% MEA when carbonic anhydrase enzyme was added under the investigated operating conditions as shown in Fig. 5. The carbonic anhydrase (CA) promotes bicarbonate formation towards equilibrium. It may be explained that the carbonic anhydrase does not accelerate the specific reaction between MEA with CO₂. It was also supposed that the carbonic anhydrase varies its shape and spatial orientation under the given environment to hinder the transport of CO₂. Kunze et al. [6] explained the no-effect of enzyme specifically on MEA solution as follows: since MEA is already a comparably fast solution and the reaction rate is mainly influenced by the concentration of the components and the temperature. The faster the chemical reaction itself, the less acceleration can be obtained by the addition of carbonic anhydrase.

3.2. Combined effect of enzyme and PILs on CO₂ absorption rate

CO₂ absorption rates were measured for comparison under different cases: MDEA solution only, carbonic anhydrase added to MDEA solution and both carbonic anhydrase and PILs applied for MDEA solution. The addition of enzyme enhanced the CO₂ absorption rate in MDEA solution by about 1.7times. With the addition of enzyme to the MDEA solution together with the coating of PILs (F9:1(M10)) on ETNA01PP showed considerable enhancement. The catalytic effect (CE) in Table 1 is a measure to show chemical capability of adding carbonic anhydrase and PILs to the individual solution system to increase absorption rate. The combination of enzyme and PILs resulted in a synergetic effect in absorption rate by about twice that of the pure solution system without enzyme or active PILs layer on the membrane surface.

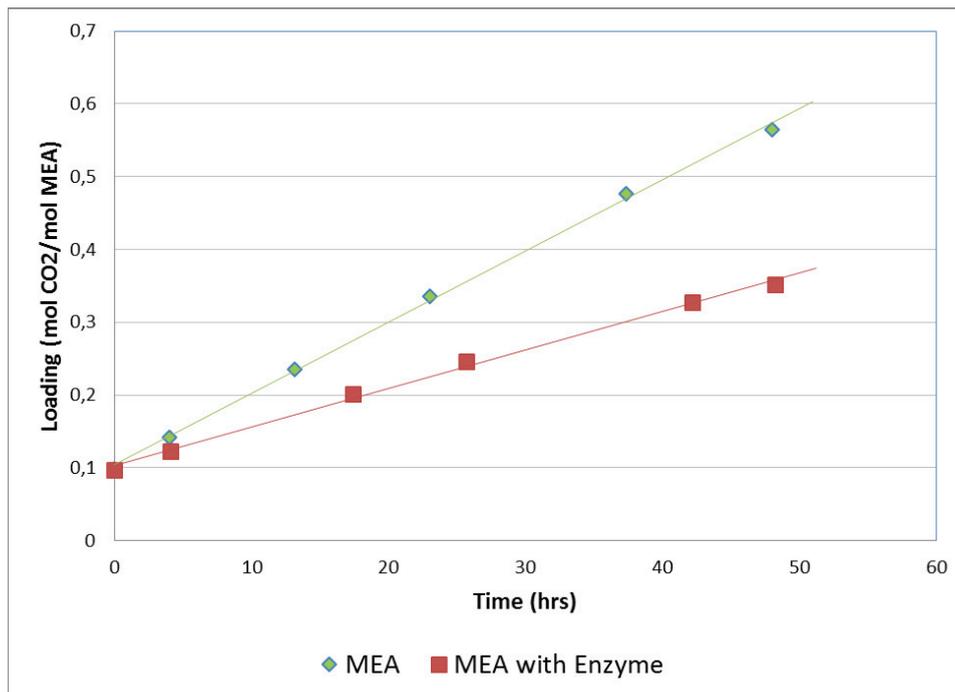


Fig. 5. Negative effect of enzyme on CO₂ absorption when added to MEA solution (35°C, feed gas 15vol.% CO₂ and 85vol.% N₂ at 2.1bara, 1wt.% carbonic anhydrase, MEA 30wt% in water at 1.1bara, ETNA01PP).

Table 1. Catalytic effect obtained from addition of CA and application of selective PILs layer to solution solutions. MEA and MDEA at 35°C is set as the baseline, respectively. (35°C, feed gas 15vol.% CO₂ and 85vol.% N₂ at 1.3bara, 1wt% carbonic anhydrase, MDEA or MEA 30wt% in water at 1.1bara, PILs (F9:1(M10)) coated on ETNA01PP).

Solution system	CO ₂ flux (mol/m ² /h)	Catalytic effect (CE)
		CE= $\frac{\text{CO}_2 \text{ absorption rate with CA (and PILs)}}{\text{CO}_2 \text{ absorption rate without CA (baseline)}}$
30% MDEA (baseline)	0.113	1
30% MDEA with CA	0.190	1.67
30% MDEA with CA and PILs	0.246	2.17

3.3. Effect of support materials

ETNA01PP and ETNA10PP are ultrafiltration membranes made of same materials and they differ only in molecular weight cut-off (MWCO), which is 1000 Dalton and 10000 Dalton, respectively. The effect of using a more open pore structure for enhanced mass transfer was investigated for the hybrid system. It was expected that more open structured ETNA10PP with higher MWCO to show higher CO₂ flow rate than ETNA01PP. However, under the given same condition, both coated with F9:1 PILs, ETANA01PP showed higher flow rate as shown in Fig. 5. A possible explanation is that enzymes are more easily filling the larger pathways (pores) which would physically block and reduce the mass transport of CO₂ though the enzymes are facilitating the reaction of CO₂ with amine aqueous solutions.

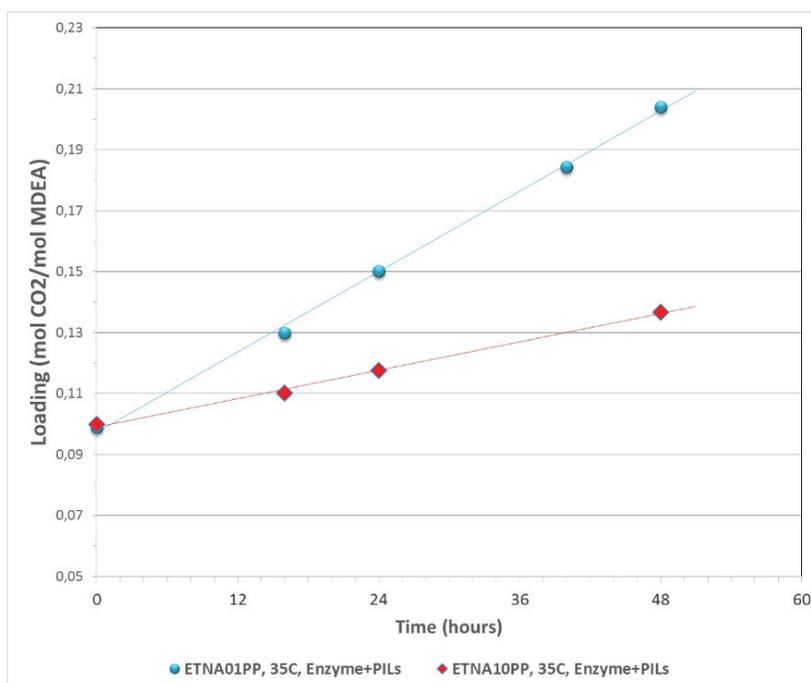


Fig. 5. Effect of different support materials on CO₂ absorption (35°C, feed gas 15vol.% CO₂ and 85vol.% N₂ at 1.3bara, 1wt% carbonic anhydrase, MDEA 30wt% in water at 1.1bara, PILs (F9:1(M10)) coated on ETNA01PP and ETNA10PP).

4. Conclusion

Using the developed membrane contactor test rig at SINTEF, the effect of enzyme and PILs on the CO₂ absorption in MDEA and MEA solution was investigated. Commercial membrane supports with dual character of hydrophilicity and hydrophobicity were employed to accommodate enzyme together with PILs in the amine based solution.

With a proper selection of PILs it has been proven a significant improvement due to the presence of enzyme in the MDEA solution and synergetic improvement by additional application of PILs on the membrane surface. The improved result by enzyme only in MDEA solution confirms that carbonic anhydrase concerns bicarbonate forming mechanism. The most promising results for the hybrid system were obtained with use of a specific PIL blend (F9:1(M10), Solvionic) combined with carbonic anhydrase (Novozymes AS) in 30wt% MDEA at low feed gas pressure (1.3 bara) and a feed gas of 15% CO₂ in N₂. The combined effect of the applied PIL layer and added enzymes enhanced the absorption rate by a factor of >2 in aqueous MDEA solution (30wt%) compared with the MDEA .

The use of MDEA solution with a lower heat of reaction could provide the benefits for the CO₂. This study demonstrated the potential to overcome the drawback of the slow reaction of MDEA with CO₂ by introducing kinetic promoter, e.g. carbonic anhydrase enzymes [7] and PILs.

Acknowledgements

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