

CO₂ Capture: Enzyme vs. Amine

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Abstract

Chemical absorption of CO₂ operates via one of two processes - formation of carbonate/bicarbonate mixtures or formation of carbamates, some of which then convert into bicarbonate. Desorption is generally linked to regeneration of the initial reactant allowing repeat of the cycle. The result is a duty cycle limited chemical shuttle. Due to the high absorptive binding energy desorption requires an equal, and costly, energy investment. An alternate strategy is to employ a reversible or catalyzed reversible reaction. With a high turnover rate catalyst bicarbonate production occurs very rapidly. Desorption of CO₂ from the liquid is rate-limiting.

We compared the efficacy of CO₂ capture using diethanolamine (DEA) and bicarbonate/carbonic anhydrase (CA) under identical conditions and in the same hollow fiber permeator operating across a thin liquid film (a contained liquid membrane - CLM). CO₂ ranged from 1% to 20%, DEA concentration was 20% or 30%(wt) and CA 3.0g/l + 1.0M bicarbonate. At 10% CO₂, 20% DEA performs only 1/3 as well as CA/bicarbonate. At 15% CO₂ feed concentration, permeance with the CA/bicarbonate system is more than twice that of 20% DEA, and 52% greater than 30% DEA. In addition, the selectivity is always better for the CA/bicarbonate solution. Examination of a variety of literature reports using supported liquid membranes or immobilized liquid membranes showed that CA mixtures always performed well; permeance and selectivity trade-offs were as expected.

The bicarbonate/CA liquid membrane, strongly out performed DEA while operating in a no-flow hollow fiber, contained liquid membrane permeator with separation governed by CO₂ partial pressure differences and requiring no additional energy.

1. Introduction

Carbon dioxide (CO₂), a major greenhouse gases, is the major contributor to global warming (Marland et al., 2003). About 24 gigatonnes (Gt) of CO₂ are released into atmosphere each year due to human activities (1Gt = 1*10⁹ metric tonnes) (Marland et al., 2003), capture and sequestration is thus critical for environmental preservation. Existing technologies using absorption, adsorption and reactive absorption can capture the CO₂ but they cannot do so economically. This is largely due to the need for thermally driven desorption. As long as hydrocarbons remain the principal source of power more efficient technologies will be needed to provide economical, post-combustion capture. The large installed base of coal, oil and natural gas burning power plants as well as abundant supplies of coal mean that post-combustion methods will remain important for a long time and thus economical post-combustion clean-up technologies are essential.

As the fuel gas or other CO₂ containing gas streams generated from the power plants or other sources are at low pressure and high temperature, chemical absorption instead of physical absorption have been using for CO₂ capture. Three major types of chemical absorption media have been used - alkali hydroxides, alkali carbonates, and various amines (including amino acids and ammonia) (Feron et al., 2002; Astarita, 1983; Ciferno et al., 2005). Alkali hydroxides and alkali carbonates operate by increasing available OH⁻ species resulting in the formation of carbonate/bicarbonate mixtures. The pyramidal nitrogen in amines, especially alkanolamines, reacts directly with the carbonyl bond to form carbamates. Other chemicals, like water, can also be used as absorption media, as CO₂ can react with water to form bicarbonate. However, the reaction must be enhanced by the use of a catalyst that fosters the conversion of CO₂ to bicarbonate to make it practical. Carbonic anhydrase (CA – E.C. 4.2.1.1) is known to be the fastest catalyst for the reaction.

Normally, AN Absorber/Stripper design is used to allow CO₂ in the untreated gas to react with the above chemical absorption media in the Absorber and then regenerate these media in the Stripper. Relatively pure CO₂ comes out of the Stripper and can be pressurized for sequestration or use. This design uses discrete units, and incurs two costs – fluid pumping and a thermal swing, the last to promote desorption.

As membranes, liquid or polymer, were shown to be a promising technology to capture CO₂ in a cost-effective way, many efforts considered the use of a single component device, a facilitated transport membrane. This was done to simplify the design and to avoid the two major costs associated with the two-component design. The designs explored took the physical form of supported liquid membranes (SLM), also called immobilized liquid membranes (ILM). Later these evolved into contained liquid membranes (CLM). The advantage of the CLM is that evaporative loss and subsequent deactivation of the chemical facilitator, common to the SLM, is avoided and regeneration or replacement of the CLM is easily accomplished. In the CLM design absorption occurs at the feed gas face and desorption at the sweep face of the facilitated transport liquid membrane. Flux is driven by a partial pressure difference.

Three chemistries have been examined in SLM or CLM mode by previous investigators – carbonate/bicarbonate designs alone or with a facilitator, CA or arsenious acid, and diethanolamine. Arsenious acid is one example of a lone electron pair promoter (Astarita et al., 1983). Ward and Robb (1967) measured the permeance of CO₂ and O₂ in porous cellulose acetate films impregnated with saturated (6.4M) cesium bicarbonate solutions. For a 5.0% CO₂ feed gas at 1.0 atm and sweep side CO₂ partial pressure of 0.005 – 0.026 atm, the CO₂ permeance averaged 3.13×10^{-9} mol/m² s Pa, and the CO₂/O₂ selectivity was 1,500. With 2M potassium bicarbonate and 2g/L (67.8μM) of CA, the CO₂ permeance increased by approximately six-fold, to about 1.8×10^{-8} mol/m² s Pa. The CO₂/O₂ selectivity was not given. With a saturated cesium bicarbonate solution containing 0.5M sodium arsenite, the permeance increased about three-fold, to about 1.0×10^{-8} mol/m² s Pa, while selectivity rose to 4,100.

Suchdeo and Schultz (1974) immobilized a solution of 1.0M sodium bicarbonate and 0.5 g/L (16.9μM) CA in a highly porous membrane. The best CO₂ permeance they obtained was about 1.8×10^{-8} mol/m² s Pa with a CO₂/O₂ separation factor of about 250. Guha et al. (1990) used an SLM of aqueous diethanolamine (DEA) for the separation of CO₂ and N₂. Using a 20% (wt) DEA solution, 5.0% CO₂ feed gas at 3.7atm total pressure and pure helium as sweep gas, the CO₂ permeance was 1.27×10^{-8} mol/m² s Pa with a CO₂/N₂ selectivity of 276. The same group also used DEA and K₂CO₃ in the HFCLM for the separation of biogas (1989).

All these previous efforts used SLM or ILM designs. Our work addresses the development of contained liquid membrane (CLM) designs where the CLM is held between two layers of microporous polymer. The CLM can be constructed as flat sheet, spiral wound or hollow fiber design. These facilitated transport membranes support absorption and desorption in a single device driven only by partial pressure differences. In our hollow fiber design the device consists of multiple sets of hollow fiber feed fibers and hollow fiber sweep fibers arranged orthogonally while the carrier fluid, the CLM, moves in a mutually orthogonal direction.

Data from the foregoing experiments is very difficult to compare due to physical, chemical and operational differences. To overcome these limitations, in this paper, we compare the facilitative effects of bicarbonate/CA and DEA in our HFCLM device. Facilitation is expressed in terms of permeance and selectivity and was compared using both experimental data and numerical simulation. The model used for the latter includes the known chemical reaction mechanism, as well as various factors affecting the transport such as temperature and ionic strength. Such simulations can be used to optimize the transport process, and provides the basis for the comparison of different facilitators.

2. Theory

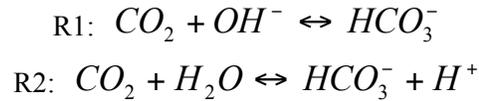
At the absorption (or feed) side, the chemical reaction rapidly converts CO₂ into other species in the liquid membrane. These species diffuse through the liquid film under their concentration gradients. At the desorption (or sweep) side, they are converted back to CO₂, which is carried away by the sweep (gas, liquid or vacuum). Thus, in addition to transport of the dissolved CO₂ across the liquid

membrane, there is an additional mechanism of CO₂ transport that greatly improves the total CO₂ mass transfer.

Each facilitator has its own reaction mechanism. Carbonate and amine react directly with dissolved CO₂, while CA and arsenite act as catalysts for the CO₂-H₂O reaction.

Amines

Two reactions occur when CO₂ is absorbed by aqueous alkaline solutions:



Reaction R1 is very fast, compared to Reaction R2. For any solution at pH > 10, reaction R1 will be more than 30 times as fast as reaction R2 (Danckwerts, 1970).

The reaction of a secondary amine (R₁R₂NH) with dissolved CO₂ is generally described by a zwitterionic mechanism yielding a two-step sequence (Versteeg et al., 1996). The first step is the formation of an intermediate zwitterion:



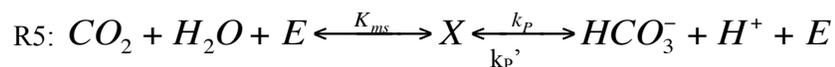
The zwitterion is deprotonated by the base present in the solution, forming a carbamate ion and a protonated base



The reason for selecting a secondary amine as a facilitator is the relatively greater ease of chemical reversibility between the secondary amine and CO₂. Primary amines react with CO₂ much more rapidly, but the binding constant is higher and desorption is difficult and energy consuming. The tertiary amine/CO₂ reaction is too slow.

Enzyme Facilitation

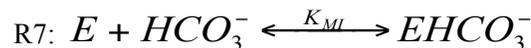
Suchdeo and Schultz (1974) gave the mechanism of CA-catalyzed CO₂ hydration and dehydration simply as:



where E is the enzyme species (E⁻, EH), X the enzyme-substrate complex (ECO₂⁻, EHCO₂). CA utilizes a ping-pong mechanism to create OH⁻ by decomposing H₂O, thus generating a proton (Silverman, 1983). For this reaction to occur, the following reaction also must be involved:



The reverse reaction is



The turnover of CA is greater than 1*10⁶ s⁻¹ making it the fastest known catalyst for the CO₂ hydration reaction (Kalifah, 1971). Thus, the overall reaction rate (CO₂ hydration rate) could greatly exceed that of other facilitators. However, the actual reaction rate is also proportional to the CA concentration in the liquid membrane. In this work the CA concentration used was ~100μM (3g/L) though it is possible to increase the CA concentration to as much as 1mM (30g/L) in bulk solution. The CO₂ hydration and dehydration reactions are also highly pH dependent. As CO₂ reacts with H₂O,

the liquid membrane is acidified and chemical equilibrium is easily reached. One way to overcome this problem is to use a buffer or to add an alkaline bicarbonate/or carbonate to the solution. A liquid membrane containing CA and an alkaline carbonate is an effective way of using CA for purposes of CO₂ separation (Ge et al., 2002).

3. Experimental

Microporous polypropylene hollow fiber membrane mat, Celgard[®] X30-240, obtained from Membrana-Charlotte (Charlotte, NC), was assembled into a multi-layer facilitated transport membrane core. The outer diameter of the fiber is 300 μ m, the inner diameter 240 μ m, nominal porosity is 40% and effective pore size is 0.04 μ m. The feed fiber mat and sweep fiber mat are arranged perpendicularly (X-Y direction) in alternate layers as the HFCLM (hollow fiber contained liquid membrane) core. The total feed membrane area is about 0.1885m². The liquid membrane flows in the Z-direction. The thickness of the liquid membrane is controlled by the yarn diameter used to weave the hollow fiber mat. This is taken as the minimum achievable CLM thickness. Should a thicker liquid membrane be needed, additional spacing materials (such as cheesecloth) can be sandwiched between the hollow fiber mats.

Air containing a specific percentage of CO₂ was fed to the feed fibers via a computerized mass flow controller (EnviroNics, Series 2020). Ultrahigh purity argon was used as the sweep. The pressures of feed and sweep streams are slightly above the atmospheric pressure. Both feed and sweep gas streams were humidified by Nafion Humidifiers. The HFCLM facilitated transport membrane device was placed in a liquid bath to control the operating temperature at constant 25°C. The composition of every gas stream was analyzed by a residual gas analyzing mass spectrometer (Extrel).

Various CLM liquid mixtures were prepared by the specific chemicals and concentrations.

4. Results

Figures 1A and 1B illustrate the transmembrane CO₂ and ion concentration profiles generated by numeric simulation for facilitated transport of CO₂ achieved by DEA (1A) and a CA-bicarbonate/carbonate solution (1B). The data are expressed as dimensionless concentration across a liquid membrane of dimensionless thickness.

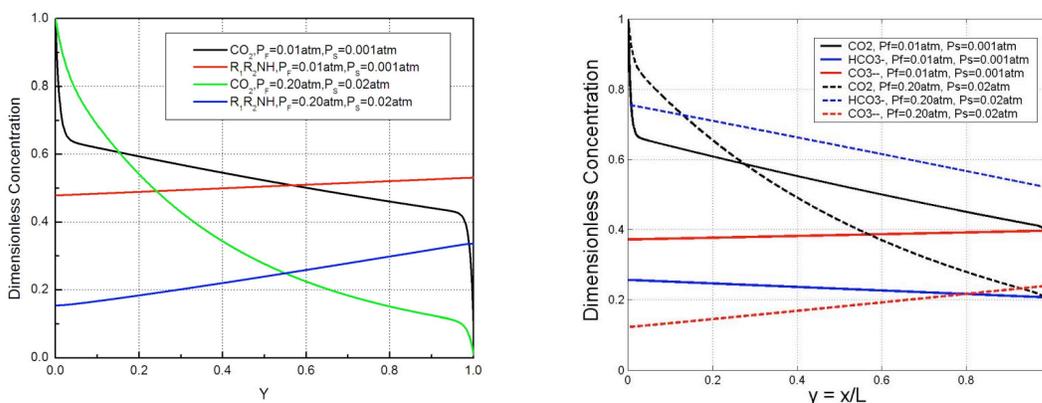


Fig. 1. Simulated transport of CO₂ across a liquid membrane of normalized thickness. (A) DEA (left); (B) CA + NaHCO₃ (right).

The experimental parameters used for this simulation are: L(CLM thickness) = 200 μ m, CO₂%_(f) = 1.0%, CO₂%_(s) = 0.1%; or CO₂%_(f) = 20.0%, CO₂%_(s) = 2.0%, P_f (Feed-side total pressure) = P_s (Sweep-side total pressure) = 101.3 kPa, T (temperature) = 298.15 K. In Fig. (1A) [DEA] = 20%(wt). In Fig. (1B) [CA] = ~100 μ M, [NaHCO₃] = 1.0M. At both concentrations the total pressure of the feed and sweep were fixed as was the ratio of feed/sweep CO₂ concentration.

At a feed of 1.0% CO₂ the CO₂ concentration distributions across the liquid membrane appear similar for both chemistries with a sharp slope near the gas-liquid interface, just as expected. Overall, the slope is slightly greater for CA than for DEA. This indicates a stronger, more rapid interfacial reaction with CA. However, the small difference will be observed again in Figure 2 as the permeance curves approach one another at low pCO₂. In contrast, at the higher feed CO₂ concentration, 20%, the interfacial effects in Figs. 1A and 1B, are more dramatic for CA. This is especially clear at the sweep side. The predicted facilitation in the CA case is validated in Figure 2 as at 20% CO₂ the CA and DEA curves diverge.

Figure 2 illustrates a numeric simulation of permeance across the facilitated transport membranes. It illustrates the dependence of CO₂ permeance on the CO₂ driving force for DEA (at 20%wt and 30%wt), CA and non-catalyzed bicarbonate films. All parameters are the same as in Figure 1. Figure 2 shows that at maximum CA turnover, the CA-containing facilitated transport membrane is predicted to yield higher permeance than is the case with either 20% or 30% DEA, save at 1% CO₂ and 30% DEA. The magnitude of the facilitatory effect of CA on a carbonate/bicarbonate system is clear when comparing the permeance of 1.0M NaHCO₃ with and without CA. The benefit is more than 10-fold at high pCO₂ and about 50-fold at low pCO₂. At 15.0% CO₂ feed concentration, the permeance with the CA-containing liquid membrane is predicted to be more than twice that of 20% DEA, and 52% greater than is the case with 30% DEA.

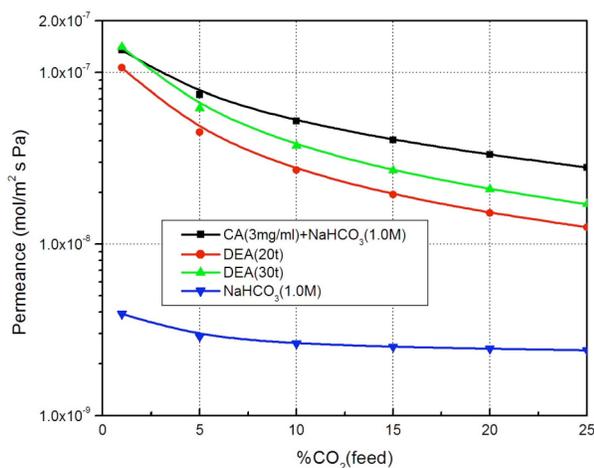


Fig.2. Simulation data illustrating the CO₂ permeance as a function of feed CO₂ concentration for each of four cases - ~100μM CA + 1M NaHCO₃, 20% or 30% DEA, and 1M NaHCO₃ alone.

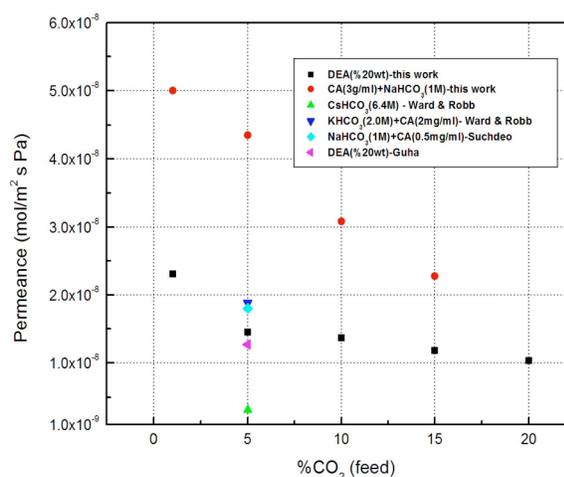


Fig.3. Experimental data to illustrate CO₂ permeance as a function of feed pCO₂. The graph compares data from these experiments (~100 μM CA + 1M NaHCO₃; 20% and 30% DEA) with those from Ward and Robb (1967), Suchdeo and Schultz (1974) and Ghua et al. (1990).

In Figures 3 and 4 we illustrate experimental results from this work, obtained with CLMs containing CA/bicarbonate, DEA or As/bicarbonate, with data from the literature, using the same and related chemistry, in SLM or alternate hollow fiber configurations. In our experiments the CA/bicarbonate CLM performed better than did the DEA at all values up to 20% CO₂ with the difference being greatest at low pCO₂. Both CA/bicarbonate and DEA exhibited greater permeance than did the As/bicarbonate CLM at all pCO₂ values tested.

Many of the literature data points were obtained with a feed gas containing 5.0% CO₂. These include the CA/bicarbonate SLM data from Ward and Robb (1967), as well as the As/bicarbonate and bicarbonate data from Ward and Robb, and the DEA hollow fiber data from Guha et al (1990). All of these chemistries performed considerably less well than did either our CA/bicarbonate HFCLM or our

DEA HFCLM. The Ward and Robb data, using 6.4N CsHCO_3 alone, yielded the poorest performance. Addition of 0.5M arsenite improved performance somewhat. The beneficial effect of arsenite is obvious when these data are compared with our membrane containing 1/10 the arsenite and half the bicarbonate used by Ward and Robb yet showing similar permeance. The Ward and Robb data clearly illustrate the preferential benefit of CA. Replacement of arsenite with CA (necessitating reduction in bicarbonate to minimize CA inhibition), resulted in further permeance increase. The beneficial effect of CA is reinforced in Suchdeo and Schultz (1974) who got similar performance. In fact, their results are superior those obtained with 20% DEA using any hollow fiber design. DEA, used in the HFCLM design, yielded better performance than did DEA in a non-structured hollow fiber array. However, as noted above, the CA HFCLM design was clearly superior at all CO_2 concentrations up to 20% to any other chemistry or any other liquid membrane geometry. For example, at 10% CO_2 feed, the measured CO_2 permeance effected by 20%wt DEA is only 33.5% of that achieved using CA/bicarbonate.

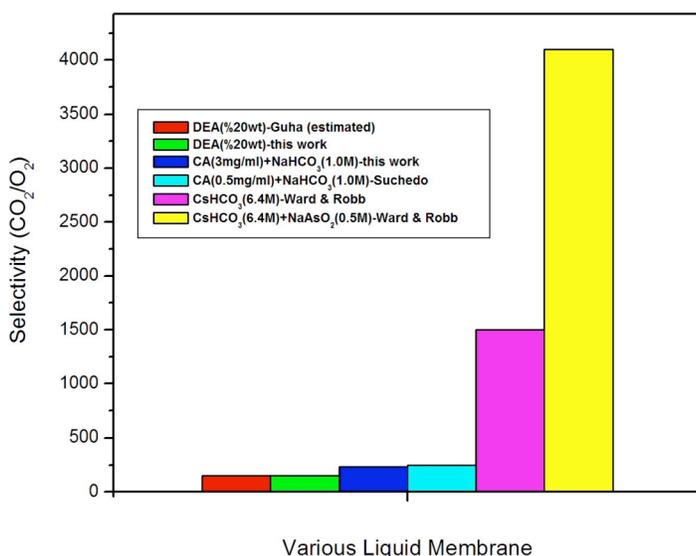


Fig. 4. A comparison of selectivity values for CO_2/O_2 at a feed of 5.0% CO_2 for each of the facilitators illustrated in Fig. 3.

and Stripper configuration, a more comprehensive comparison is needed for the selection of right technology to capture CO_2 economically.

Further, each of these facilitators has distinct limitations. Amines, for example, are corrosive and corrosiveness increases with temperature and concentration. Performance decreasing corrosion inhibitors are needed to allow long-term operation. Similarly, amines are oxygen sensitive, particularly with elevated temperature and require routine replenishment. Conversely, the long-term stability of CA may also be a concern. Good short-term stability has been demonstrated, i.e., up to 40d or discontinuous use and more than 50 days of continuous use. In addition, literature reports, using immobilized enzyme, indicate lifetimes of 3-6 months (David et al., 1974; Crumblis et al., 1988).

These data were obtained using a variety of design configurations and experimental conditions (e.g., CO_2 partial pressure difference, liquid membrane thickness and chemical composition). Since CO_2 permeance is highly dependent on these parameters direct comparison is difficult. Non-the-less, the data provide some understanding of the effectiveness of each facilitator in promoting CO_2 transport across a thin liquid membrane.

Figure 4 illustrates the CO_2/O_2 selectivities obtained experimentally for a CO_2 feed concentration of 5.0%. The data show that the CO_2/O_2 selectivity is much higher for liquid membranes containing high salt concentrations. This is due to the well-known “salting out” effect. However, the permeance drops significantly when the salt concentration in the liquid membrane becomes too high (Fig. 3). Thus, there is a trade-off between permeance and selectivity, and an optimized salt concentration can be found through simulation or experiments.

5. Discussion

The comparisons presented are based only upon CO_2 permeance and CO_2/O_2 selectivity for the configuration of SLM/ILM and HFCLM. As amine has been used primarily with Absorber

6. Conclusions

We compared facilitated CO₂ transport across a liquid membrane containing three different facilitators: the biocatalyst CA, the secondary amine DEA and various alkaline carbonates. The performance of each facilitator was illustrated in terms of the CO₂ permeance and CO₂/O₂ selectivity. Liquid membranes made of CA and alkaline carbonate gave higher permeance than that made of DEA or alkaline alone. CA was consistently the superior facilitator.

For future developments additional factors have to be included for a comprehensive comparison. The optimum choice of liquid membrane composition will be determined not only on the basis of chemical performance, but must also include economic considerations and ease of operation. We expect to test a larger-scale industrial application of CA for CO₂ separation in the near future.

Acknowledgements

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