CO_2 Capture by Means of an Enzyme-Based Reactor

R.M. COWAN,[a] J.-J. GE,[a] Y.-J. QIN,[b] M.L. McGREGOR,[c] AND M.C. TRACHTENBERG[a,b]

[a]*Sapient's Institute, New Brunswick, New Jersey, USA*

[b]*Carbozyme, Inc., Bordentown, New Jersey, USA*

[c]*McGregor & Associates, Spring, Texas, USA*

ABSTRACT: We report a means for efficient and selective extraction of carbon dioxide (CO_2) at low to medium concentration from mixed gas streams. CO_2 capture was accomplished by use of a novel enzyme-based, facilitated transport contained liquid membrane (EBCLM) reactor. The parametric studies we report explore both structural and operational parameters of this design. The structural parameters include carbonic anhydrase (CA) concentration, buffer concentration and pH, and liquid membrane thickness. The operational parameters are temperature, humidity of the inlet gas stream, and CO_2 concentration in the feed stream. The data show that this system effectively captures CO_2 over the range 400 ppm to at least 100,000 ppm, at or around ambient temperature and pressure. In a single pass across this homogeneous catalyst design, given a feed of 0.1% CO_2, the selectivity of CO_2 versus N_2 is 1,090 : 1 and CO_2 versus O_2 is 790 : 1. CO_2 permeance is 4.71×10^{-8} mol m^{-2} Pa^{-1} sec^{-1}. The CLM design results in a system that is very stable even in the presence of dry feed and sweep gases.

KEYWORDS: carbon dioxide; carbonic anhydrase; CO_2 separation; contained liquid membrane; gas separation

INTRODUCTION

CO_2 separation technologies are becoming ever more important in fields such as life support for space exploration, agricultural greenhouses, reduction of atmospheric greenhouse gas levels, and enrichment (sweetening) of natural gas. Many different technologies have been developed to separate CO_2 from gas mixtures.[1–6]

At low to moderate pCO_2, chemical and physical absorption in liquid media and physical adsorption to solids are the most effective approaches.[6,7] Chemical absorption relies on a reactive absorbent, that is, a promoter, facilitator, or catalyst that reacts with the CO_2, preferably at the gas–liquid interface. This reaction increases either or both the rate and magnitude of CO_2 solubility or the subsequent evolution of the gas from the liquid. Beginning with the Girdler patent of 1931, there has been extensive study of bulk fluid, homogeneous reactant, alkanolamine-based chemical

Address for correspondence: M.C. Trachtenberg, Sapient's Institute, Cook College, Rutgers University, 20 Ag Extension Way, New Brunswick, NJ 08901-8500, USA. Voice: 732-932-8875; fax: 732-932-7931.
miket@aesop.rutgers.edu

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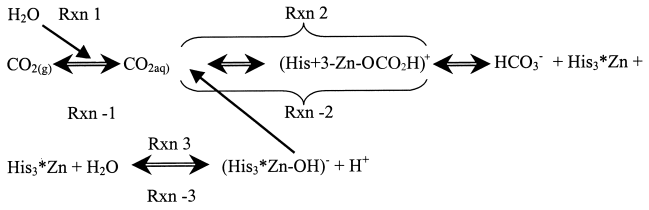
absorption, and facilitated transport.[6] However, cost, maintenance, safety, and environmental issues that surround the use of amines in bulk fluid systems present significant impediments to their application outside of industrial acid gas scrubbing. Therefore, there still exists a substantial need for the development of alternative approaches.

There are two approaches to take in addressing the limitations of the bulk fluid alkanolamine based CO_2 separation systems. One is to change the chemistry of the system by using alternative promoters, facilitators, and/or catalysts. Ideally the alternative chemistry will yield a system that is more efficient, cheaper, faster, safer, and more environmentally friendly. None of the alternative chemistries identified previously (alkali carbonates,[8] glycinates,[9] arsenites,[8] novel amines,[10,11] or crown ethers[12]) can meet the desired requirements. However, the biological catalyst (enzyme) carbonic anhydrase (CA–EC 4.2.1.1)[13–19] shows great promise. CA is the most efficient catalyst for CO_2 hydration and dehydration (absorption and desorption),[13–15] particularly for application at low pCO_2 and near ambient temperature. The second approach is to move from a bulk fluid design to a membrane design. The benefits are higher efficiency, lower energy costs, and greater separation per unit volume of reactor. Liquid membrane designs are attractive in comparison with nonporous polymer membranes of equal thickness because they decrease transport resistance so that high permeance is achieved together with high selectivity. Use of this concept for CO_2 separation was first explored in the 1960s.[8,18] We demonstrate in this work that the design parameters of a liquid membrane can be carefully tailored to the desired product and operating conditions. This is a distinct benefit over other membranes.

The mammalian isozyme, human CA type 2 (HCAII), found in erythrocytes has a maximum turnover number of 1.6×10^6 mol $[CO_2]$/mol [CA] sec.[19] The maximum turnover number for the bovine analog (BCAII) is about 33% lower. The catalytic site is a zinc atom covalently bound to three histidine molecules.[20] CA catalyzes the reversible hydration of CO_2 by a two-step process.[21] In the first step CA hydrolyzes water to capture a hydroxyl releasing a proton (Rxn 3). In the second the hydroxyl attacks the carbonyl bond of CO_2 to yield bicarbonate and the unreacted enzyme (Rxn 2). This is the hydration step and it occurs at the CO_2-rich side. At the CO_2-lean side the reverse reactions (Rxn 2, Rxn 3, Rxn 1, respectively) occur, liberating CO_2, which can then evolve into the permeate stream. As shown later in FIGURE 3B, CA changes the rate at which the hydration and dehydration reactions occur at a given pH. This allows for increased transport of CO_2 as the dissolved ionic species, HCO_3^- and CO_3^{2-}, and therefore increased separation performance through increases in both CO_2 permeance and selectivity of CO_2 versus other gases.

From the viewpoint of solution and diffusion mechanisms, the enzyme functions as a facilitator. More correctly, it is a catalyst and, unlike amines and other chemical combining reactants, does not itself participate in the transport process as a chaperone. Only small ionized species, principally bicarbonate and carbonate, diffuse across the membrane.



The earliest studies related to CA-based membrane systems typically used supported liquid membrane (SLM) designs, with CA dissolved in an aqueous buffer solution. The solution was trapped in the pores of a filter membrane or in a proteic matrix.[8,14,18,22] These studies successfully demonstrated the ability of these designs to selectively extract CO_2 from mixed gas streams. The majority of these early studies used a feed CO_2 concentration of about 5% at 1 atm. However, feed CO_2 concentrations as high as 100% have also been studied.[23] The most common approach taken in the early work was to not add any external buffer, but instead to allow pH to be controlled by the carbonic acid–bicarbonate–carbonate solution that formed spontaneously;[13–15] others used dilute phosphate buffers.[8,17,18,22] The one notable exception to the use of dilute buffer solutions was the work done by Ward.[8] He used CA in a high concentration (2 M) $KHCO_3$ solution to facilitate CO_2 uptake. However, Ward did not attempt to optimize the high strength bicarbonate–CA system and it is likely his results were far from optimal. The use of bicarbonate–carbonate buffers has been shown to decrease the rate at which CA catalyzes CO_2 hydration[14,18,24,25] with the 50% inhibitory concentration for bicarbonate generally reported to be near 60 mM.[13–15]

Alper and Deckwer studied the effect of buffer systems on the kinetics of absorption of CO_2 from air into a well-mixed solution, that is, hydration rate.[26] Using a feed CO_2 concentration of 100% at 1 atm they found little difference between the performance of a 0.5 M carbonate buffer at pH 9.6 and that of 0.5 M phosphate buffer at pH 11.1. They also studied interactions between the buffer strength and CA concentration, finding that there needs to be a balance between these (i.e., higher enzyme concentrations require higher buffer concentrations) or the adsorption rate can become limited through depletion of OH^- (i.e., decreased local pH) at the gas liquid interface. This is important because, as is shown later in FIGURE 2A, the rate of CA catalysis of CO_2 hydration falls off quickly as pH decreases below pH 7.5 to 7.0.[17,27] A similar concern with respect to pH, buffer strength, and CA concentration occurs at the permeate side of the membrane where the dehydration reaction occurs. In this case the rate of the CA catalyzed reaction decreases rapidly as pH is increased above 6.5 to 7.0.[17,27]

In contrast to a 5% feed CO_2, the concentration of CO_2 in air is about 0.035% and in closed life support systems, for example, a space station, the uppermost value is limited to no more than 0.5% at 1 atm. Plants grown in greenhouses prefer CO_2 levels of 0.05–0.15% at 1 atm. Operation at higher levels of CO_2 (e.g., greater than 5%) may be useful for some applications (e.g., removal of CO_2 from stack gas) and it is convenient for an initial feasibility study (so as to simplify the analytical requirements). If the ultimate use of the technology involves the separation of CO_2 from air and/or respiratory gases, it is important to perform experiments within the relevant CO_2 concentration range and with the relevant gas mixture.

Using a CA catalyzed SLM, Trachtenberg and his colleagues showed that CO_2 concentrations as low as 0.1% and as high as 10% could be extracted from air at 1 atm.[24] Later studies by Trachtenberg[28] showed that CO_2 could be extracted from air having CO_2 concentrations as low as 0.04%. However, despite rigorous control of the feed and the sweep side humidity it was impossible to maintain SLM designs operative for periods in excess of one day. This is as expected since a known disadvantage of SLM designs is their instability due to evaporative water loss.[29] Typically solvent loss leads to catalyst loss or inactivation. This was not the case here because of the large size of CA (30 kD) and the fact that it can be repeatedly dried and rehydrated without loss of activity.[24] Furthermore, in contrast to the limited lifetime of the SLM, we have successfully operated the flat sheet EBCLM for eight days without failure and a more recent hollow fiber EBCLM for 40 days.[30] Finally, crosslinked CA has been shown to remain active for as long as three months while in use within a contained gel membrane.[22]

Many strategies have been investigated for improving the stability of supported liquid membranes, however, the most reliable approach that can be used to ensure stability is a contained liquid membrane, CLM, instead of an SLM. CLMs are made by sandwiching the liquid between two polymer membranes and stabilizing against failure due to solvent loss through use of a reservoir of liquid membrane solvent to continuously resupply the core liquid.[31–34] (For a thorough review of methods for stabilizing SLMs see Kemperman *et al.*, 1996,[35] subsequent work by Kemperman and colleagues,[36–38] and the work of others of others.[39])

In this paper, we report on an examination of the influences that both structural and operational parameters of a CA based contained liquid membrane exert on separation performance (CO_2 permeance and selectivity of CO_2 versus N_2 and O_2). The structural parameters studied include: carbonic anhydrase (CA) concentration, buffer concentration and pH, and liquid membrane thickness. The operational parameters studied are temperature, humidity of inlet gas stream, and CO_2 concentration in feed stream. The results of these studies provide a first level optimization of CA-based contained liquid membrane (CLM) system and prove its utility as a means for separating CO_2 from low concentration CO_2 sources, such as air and respiratory gas.

EXPERIMENTAL

Materials

The enzyme catalyst used was bovine carbonic anhydrase type 2 (activity 3,240 W-A units, BCAII, Sigma Chemical Co.). The buffer was compounded from monobasic anhydrous potassium phosphate (99.0% purity, Sigma) and dibasic anhydrous sodium phosphate (99.5% purity, Fisher Scientific). Microporous polypropylene (Celgard PP-2400) was used to contain the liquid membrane. PP-2400 is 25.4 μm thick, with 41 nm × 120 nm pores, 30% porosity, and has a tortuosity factor of 5.[29] The thickness of the liquid membrane was controlled by the use of woven polyester mesh spacers (Small Parts Inc., CMY-200) constructed as an annulus around the active liquid membrane area. Air (Matheson) was ultra zero, argon (Matheson) was ultra high purity, and CO_2 (Matheson) was high purity.

Reactor Configuration and Test Stand Setup

The liquid membrane (22 mm diameter, effective area 380 mm^2) was constructed by sandwiching a CA containing phosphate buffered solution between two polypropylene membranes (see FIGURE 1 A). The thickness of the aqueous phase was varied from 70 µm to 670 µm by the use of annular spacers. The liquid membrane fluid volume was maintained by hydrostatic fluid addition from a reservoir. This slight positive pressure within the liquid phase also served to ensure a constant liquid

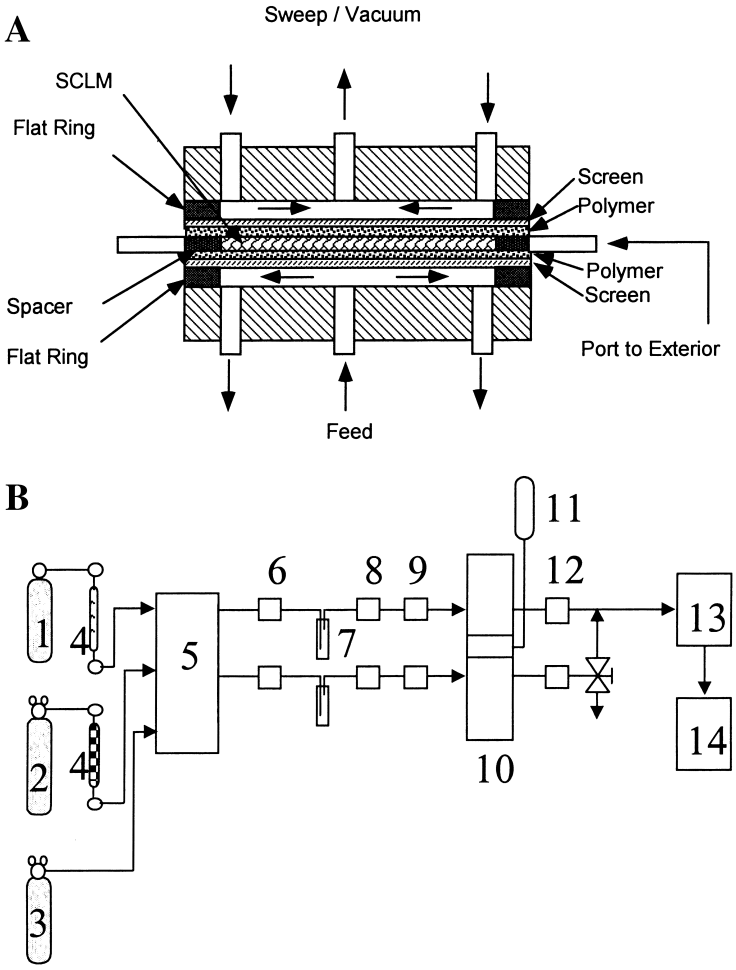


FIGURE 1. Schematic illustration of **(A)** test cell and **(B)** test stand. KEY: 1, argon; 2, air; 3, CO_2; 4, CO_2 purified column; 5, mass flow controller system; 6, humidifier; 7, trap; 8, pressure gauge; 9, temperature/humidity probe; 10, test cell; 11, reservoir; 12, mass flow meter; 13, mass spectrometer; and 14, computer.

membrane thickness and prevent separation between the polymer membrane and the metal support. The test stand setup is schematically illustrated in FIGURE 1B. The feed gas stream consisted of a mixture of CO_2 in air. Argon, treated to remove any residual CO_2 (OMI-4, Supelco), was used as the sweep gas stream. Delivery of all gases was regulated by an Environics mass flow controller (Series 2020, NIST-traceable calibration). The feed and sweep gases could be humidified to the extent desired by means of polysulfone humidifiers operated in reverse. A humidity monitor (Vasalia) was present in the sweep gas between the reactor and the mass spectrometer. After passing through the test cell the permeate (sweep) was delivered to a residual gas analyzing mass spectrometer (Questor IV, ABB Extrel) where concentrations of N_2, O_2, argon, CO_2, and H_2O were measured and recorded to electronic data files.

Separation performance was calculated based on the flow rate and the composition of the feed and sweep gases. The separation performance measures we used were permeance (Q) and selectivity (α). $Q_i = J_i/\Delta P_i$, J is the gas flux through the membrane, ΔP is the partial pressure difference across the membrane,

, and .

Q is expressed in units of $\mathrm{mol\,m^{-2}\,Pa^{-1}\,sec^{-1}}$ and α is a dimensionless ratio. All permeance and selectivity values given are plotted as means with error bars (plus and minus one standard deviation of the mean) to represent the measurement error.

Unless otherwise noted, the feed gas contained 0.1% CO_2 in air; argon was used as the sweep gas and evaluations were carried out at 30°C. CO_2-free gas was used to initiate each test. CA was dissolved in phosphate buffer as a homogeneous catalyst.

RESULTS

CA Concentration

Factors inherent to the enzyme include the isozyme, the spatial distribution in the liquid (homogeneous versus heterogeneous) and the concentration. Spatial distribution of CA is important because the catalytic reaction is limited to the gas–liquid interface. With a homogeneously distributed enzyme catalysis, capacity at the interface is linearly related to the CA concentration. Historically, CA concentrations used in homogenous mode were less than 4 mg/mL (133.33 μM),[14,18,24,25] although one example of a concentration in excess of 30 mg/mL is known.[23] We tested four enzyme concentrations—1, 2, 3, and 5 mg/mL (33, 67, 100, and 166 μM).

The effect of CA concentration on selectivity and CO_2 permeance is shown in FIGURE 2A. Both the selectivity of CO_2 versus N_2 or O_2 and CO_2 permeance increase as the CA concentration increases from 33 μM (1 mg/mL) to 100 μM (3 mg/mL). There is a le mg/mL).

As shown in FIGURE 3B, we evaluated separation performance at five pH values: 6.80, 7.04, 7.5, 8.0, and 8.5. The data shown in FIGURE 3B clearly illustrate the optimum performance for the conditions studied (20mM phosphate buffer, 0.1% CO_2 in 1atm air) to occur at pH8. The reasons for this are given in the discussion.

Thickness of the Liquid Phase

Most membrane separation methods force a tradeoff between permeance and selectivity on the basis of membrane thickness. Whereas selectivity increases with membrane thickness, thus providing greater separation, permeance decreases due to the increase in diffusion path length. The advantage in selectivity occurs because

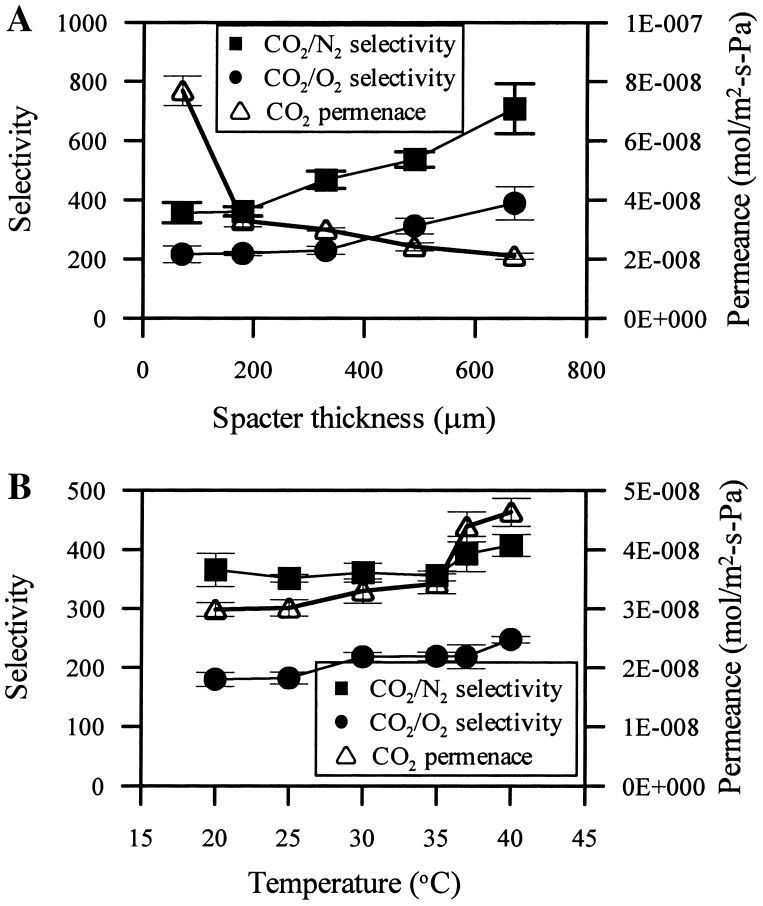


FIGURE 4. Effect of **(A)** liquid membrane thickness and **(B)** temperature on separation performance. Test conditions: **(A)** buffer, 20mM buffer; pH = 8.0; thickness, variable; CO_2, 0.1% in air; CA, 33.3mM (1mg/mL); T = 30°C. **(B)** buffer, 20mM phosphate; pH = 8.0; thickness, 180μm; CO_2, 0.1% in air; CA, 33.3mM (1mg/mL); T, variable.

the rate of decrease in CO_2 permeance is lower than the rate in decrease of O_2 and N_2 permeance. Prior work tended to use liquid impregnated filters (SLM) with the membrane thickness (typically 60μm to 160μm) given by the swollen thickness of the filter.[16,24]

Unlike the SLM, in which maximum thickness is limited by physical parameters, such a capillary force, the CLM design allows us to freely vary thickness without such limitations. We examined liquid membranes of five different thicknesses—70, 180, 330, 490, and 670μm. FIGURE 4A illustrates the separation performance versus liquid phase thickness. As expected, we observed that selectivity increased with increasing thickness, whereas CO_2 permeance decreases. The permeance values of CO_2, O_2, and N_2 were all very high when the liquid membrane thickness was only 60μm (low selectivities show that O_2 and N_2 permeances were also high). Second, for a liquid membrane of 180μm thickness and above the rate at which CO_2 permeance decreases with increasing thickness is relatively constant (first order). Third, the selectivity of CO_2 versus O_2 and CO_2 versus N_2 increase relatively linearly with thickness. FIGURE 4A illustrates the sharp decrease in permeance as thickness increased from 75μm to 200μm. This decrease in permeance continued, although more slowly, as the liquid membrane thickness was increased to 670μm. In contrast to the varying rate of change seen for CO_2 permeance, the rate of change in selectivity was relatively constant. It was seen to be almost linear over the entire range of thickness studied. The slope of the selectivity versus thickness curve for CO_2:N_2 is far steeper than that for CO_2:O_2.

Temperature

Temperature is very important to this system as it impacts both CA activity and the solubility and diffusivity of all the dissolved species (O_2, N_2, CO_2, and the CO_2 equivalents HCO_3^- and CO_3^{2-}). BCAII starts to denature at about 40°C.[40] To detail the effect of temperature on membrane transport performance we examined the following temperatures: 20, 25, 30, 37, and 40°C. FIGURE 4B illustrates the effect of temperature on separation performance.

The data show a positive relationship between both selectivity and permeance with temperature. Up to 35°C selectivity and permeance changed modestly. However, further increases in temperature to 37°C and 40°C showed substantial increases in CO_2 permeance, but only moderate increases in selectivities. These results suggest that substantial increases in performance are possible with only moderate increases in temperature.

Humidity

Unlike an SLM, which is subject to catastrophic failure from liquid loss due to evaporation, when a CLM design is used there is little risk of failure. Furthermore, provided effective management of the liquid membrane chemistry (i.e., buffer and CA concentration) is provided, the CLM based system should show little or no sensitivity to humidity in the feed or sweep gases. In the experiments conducted here we tested four humidity values: 4, 27, 53, and 74%.

FIGURE 5A shows that the EBCLM performed largely independent of changes in humidity in the inlet stream over the test range of humidity, although there was a

slight selectivity increase as humidity increased. As expected, the system proved to provide stable operation even with very low humidity feed gas (operation for up to 24 hours). This has been further supported in more recent studies (data not shown), where dry feed gas (0% humidity) was used for a period of eight days without loss of system performance.

CO_2 Concentration

The design requirements for this reactor are directly influenced by the feed stream CO_2 concentration (pCO_2). In a space station (e.g., International Space Station Freedom) or a transport vehicle (e.g., Space Shuttle) the CO_2 concentration should be

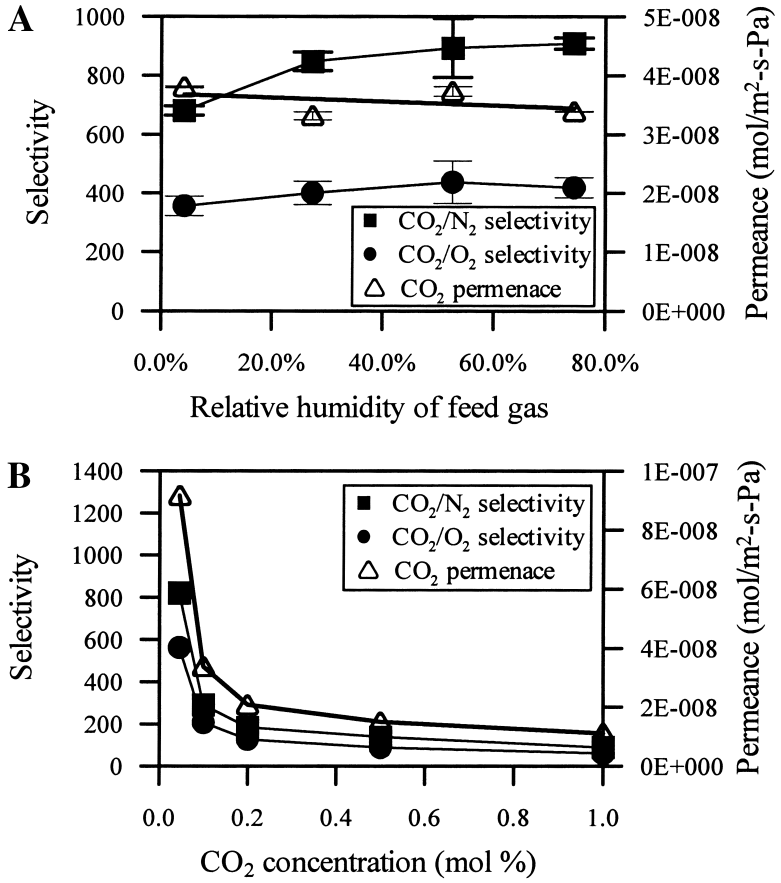


FIGURE 5. **(A)** Effect of feed stream humidity on separation performance, and **(B)** separation performance as a function of CO_2 concentration in the feed stream. Test conditions: **(A)** buffer, 50 mM phosphate; pH = 8.0; thickness, 330 µm; CO_2, 0.1% in air; CA, 33.3 µM (1 mg/mL); T = 30°C. **(B)** buffer, 20 mM phosphate; pH = 7.85; thickness, 330 µm; CO_2, variable; CA, 166.67 µM (5 mg/mL); T = 30°C.

controlled to values lower than 0.1% (pCO_2 = 101.30 Pa). In contrast, in an extravehicular mobility unit (EMU–spacesuit) the CO_2 concentration should be no more than 0.5% at a total pressure of 29.65 kPa (pCO_2 = 148.24 Pa). In these experiments we investigated CO_2 concentrations over a range from 0.04% to 1.00% (pCO_2 = 40.52 to 1,013.00 Pa) in air at 1 atm.

FIGURE 5B illustrates permeance and selectivity as a function of the CO_2 concentration in the feed. There is a rapid drop in both CO_2 permeance and selectivity as CO_2 concentration is increased from 0.04 to 0.1%. This rate of decline decreases markedly as CO_2 concentration is increased further, with only slight decreases in permeance and selectivity occurring as the CO_2 concentration is increased from 0.2 to 1.0%.

DISCUSSION

We previously performed a detailed analysis of the various parameters that can influence EBCLM performance.[28] This analysis revealed a high level of interdependence among the various parameters. The optimum value of a given parameter depends not only on the separation requirements (i.e., feed stream CO_2 concentration), but also on the value of other adjustable parameters. For example, the optimum buffer pH depends not only on the feed stream CO_2 concentration, but also on the buffer strength and perhaps even the CA concentration (and *vice versa*). Therefore, to obtain a true global optimum for even a single separation condition it is necessary to perform studies that are more extensive than those reported here. In this work we report initial efforts toward this end by separately varying several structural and operational characteristics of this complex system, such that a first level optimization might be achieved. Future work will involve more extensive studies needed to more closely approach a global optimum. In general, for a given pCO_2, selectivity is the goal most easily controlled accepting whatever tradeoff in permeance is needed.

CA Concentration

Transport of CO_2 in this facilitated reactor design includes two scenarios. One is the uncatalyzed diffusion of CO_2 directly across the membrane. The other is that CO_2 is catalytically hydrated to bicarbonate ions on contact with the CA and then the bicarbonate ions diffuse through the membrane to the permeate surface. At the permeate side, the bicarbonate ions are dehydrated and CO_2 released from the membrane. Because solubility of CO_2 in water (0.053 wt%, 0.012 M, at 25°C) is much less than that of bicarbonate (with Na^+ as a counter ion, bicarbonate solubility is 9.32 wt%, 2.1 M, at 25°C; i.e., 175 times greater),[15] the transport capacity for CO_2 is much greater in HCO_3^- form than for $CO_{2(aq)}$ even though the diffusivity for $CO_{2(aq)}$ is greater than that for HCO_3^-. Furthermore, although the hydration and dissociation of CO_2 to form bicarbonate (and the reverse dehydration) does occur naturally without catalysis by CA, the catalyzed rates (depending on pH) can easily be hundreds to thousands of times higher. Thus, the results suggest that for the conditions used (pH, CO_2 in feed, etc.) when the CA concentration was low there was less CA present than that required to carry out conversion of all the CO_2 at a maximum rate (i.e., the available CA was likely saturated). Therefore, increasing the amount of CA

available increased CO_2 permeance. Increasing selectivities were observed because neither O_2 nor N_2 react with CA. Therefore, the permeance of each of these gases is not directly effected by the presence of more CA and continues to diffuse across as dissolved gases (N_2 solubility is 0.0134 STP mL/mL H_2O and is 0.0261 STP mL/mL H_2O for O_2 at 30°C). The leveling off of the increase in selectivity provides the most obvious evidence of the decreasing benefit of adding more CA. Note that when feed streams with higher CO_2 concentrations are used there will be a need for greater rates of hydration and dehydration of CO_2 and, therefore, higher CA concentrations are likely to be needed to achieve maximum selectivity and CO_2 permeance. This is also true if changes in other parameters increase the required hydration and dehydration rates.

Buffer Concentration and pH

A robust buffer is needed to moderate the pH changes that can accompany the reactions catalyzed by CA. As stated above (see RESULTS) the reactions that occur at the feed side produce hydrogen ions forcing the local environment toward decreased pH values. This decreases the activity of the CA for catalyzing CO_2 hydration. The opposite trend occurs at the sweep side of the liquid membrane, where consumption of hydrogen ions tends to force the pH to increase. This also decreases the activity of CA for catalysis of the dehydration reaction.

From the data presented in FIGURE 3A it appears the optimum pH should be close to 6.4 because that is the pH where the maximum rate of hydration and dehydration occur if we require them to be equal and to be carried out at the same pH. This is what would be expected for a perfect buffer. However, with the use of weaker buffers we know the feed side pH will be lower than the bulk pH (pH will tend toward the pH of the phosphate buffer in equilibrium with the feed stream CO_2 concentration). We also know that the sweep side pH should tend toward the value in equilibrium with the sweep stream CO_2 concentration (for the phosphate buffer this is the make-up concentration—i.e., that reported in FIG. 3B). Therefore, it appears, at the pH optimum of 8 that we observed (for this 0.1% CO_2 feed, 20 mM phosphate buffer, 33 μM CA, 180 μm-thick liquid membrane), this occurred as a result of substantial acidification of the system. Looking at FIGURE 3A, assuming: (1) the rate of hydration equals the rate of dehydration; (2) the uncatalyzed reactions were insignificant; and (3) the sweep side local pH was 8.0, it appears the feed side pH was close to 5.4 thus indicating the buffer strength was too low. This is in good agreement with the results presented in FIGURE 2B that indicated improved performance at increased buffer strengths. However, the true optimum can only be found through a combined search of the pH and the buffer concentration (and this optimum is a function of pCO_2). From our analysis it seems clear that, in the presence of a stronger buffer, the optimum pH will be lower and will approach pH 6.4 forcing this curve to shift to the left for the same CO_2 load.

CLM Thickness

Because CO_2 permeance decreases and selectivity increases with increased liquid membrane thickness there will exist some optimum thickness at which the best overall separation performance is achieved. However, this optimum point is not only a

function of the feed composition and the need for removal of CO_2 from the feed, but also the requirements of the desired composition of the permeate (sweep). As is well known,[41] if the membrane is particularly thin, permeance increases dramatically. This is the case at 60μm; at the same time, the selectivity is low because of the relatively high N_2 and O_2 permeances due to bulk movement of these gases across this thin water film. To effect adequate selectivity it is necessary to have sufficient thickness to serve as a barrier resistance to the flux of unwanted species, thereby emphasizing the benefits of the chemical facilitation.

Temperature

Enzyme activity is typically a linear function of temperature with a Q_{10} of about 2. For CA, the upper temperature bound, using ordinary mammalian isozymes, is about 40°C. At the same time, water is evaporating from the membrane cooling the reactor and the higher the operating temperature the greater the evaporative cooling. We can calculate a first approximation to the surface temperature. A third contributor is that the water vapor flow may disturb any boundary gas layers. Thus, while both selectivity and permeance increase with temperature at present, due to the actions of at least three processes, the non-linear response cannot be adequately explained.

In future studies we have the option of using other isozymes, including those known to operate at higher temperature, even to 70°C.[42] By means of such isozymes it may be possible to attain greater selectivity and permeance by operating at a higher temperature.

Humidity

The stability of the CLM bioreactor design is particularly important since changes in solvent level and loss of solvent have, historically, been a principal reason underlying the failure of SLM type liquid membranes. Early efforts to reduce evaporation of water from the core solution of SLMs relied on increasing the humidity of the inlet gas stream. This approach was not satisfactory.[33] The current design, modeled after that of Sirkar and colleagues,[32,33] exhibits the level of stability needed for long-term use under field conditions.

CO_2 Concentration

The ability of an enzyme-based CLM (EBCLM), using a biological catalyst, to capture CO_2 is principally a function of the CO_2 concentration, CA concentration, buffer concentration, membrane area, and the feed and sweep gas flow rates. Proper management of these parameters can achieve as high a permeance as is required. The data in FIGURE 5B reflect the performance of this particular reactor, given the operating conditions we selected. As demonstrated in the RESULTS section the ability of this liquid membrane to maintain the desired pH at the feed and permeate sides is crucial to successful operation.

CONCLUSIONS

The CA membrane bioreactor presented here performed extremely well. The best operating conditions demonstrated here for the 0.1% feed, phosphate buffered design were pH 8.0, buffer strength 50 mM, membrane thickness of 330 μm, and temperature 30°C. When these conditions were applied together we found separation performance corresponding to a CO_2 permeance of 4.71×10^{-8} mol m^{-2} Pa^{-1} sec^{-1} (1.41×10^{-4} cm^3 cm^{-2} cmHg^{-1} sec^{-1}), and selectivities of CO_2 versus N_2 and O_2 of 1,090 : 1 and 790 : 1, respectively.

The data show that the preferred concentrations of CA and of buffer are a function of the feed CO_2 concentration. Preferred membrane thickness is determined principally by the desired selectivity and secondarily by desired permeance. The preferred temperature is a function of CA activity and of water evaporation and cooling. The optimal buffer pH is a function of the CO_2 concentration and of the buffer strength. Work is ongoing in our group toward improving the response properties of this design and to further understand this reactor design.

ACKNOWLEDGMENTS

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