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CO_2 CAPTURE USING ENZYME BASED MEMBRANE REACTORS

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Introduction

Fossil fuels will remain the mainstay of energy production well into the 21st century. About 75% of the world's commercial energy comes from fossil fuels, and about 84% of the energy used in the United States is derived from fossil fuels [DOE, 1999]. The capture and sequestration of 80% or more of this CO_2 would significantly contribute to reduction in the quantity of CO_2 emitted. CO_2 is routinely separated and captured as a by-product from industrial processes. We have been seeking ways to maximize the operation of the enzyme carbonic anhydrase (CA – E.C.4.2.1.1) to extract CO_2 by virtue of its catalysis of CO_2 to bicarbonate and the converse. By arranging the enzyme such that it operates at two gas-liquid interfaces, the first the feed side exposed to gas rich in CO_2, the second the sweep side, exposed to gas lean in CO_2, the partial pressure difference causes the CO_2 to leave the rich stream and be delivered to the lean stream.

With regard to the chemical engineering we have examined a variety of designs utilizing microporous hydrophobic polymer membranes to separate the gas and liquid phases. This membrane-based gas permeation process for CO_2 removal, recovery, and concentration is superior to other membrane processes in the following ways:

1. The dramatic increase in permeance due to the use of the enzyme CA. CA catalyzes the hydration of CO_2 during its chemical absorption (conversion from CO_2 to bicarbonate) from the feed gas into the liquid membrane and then catalyzes the dehydration of bicarbonate during its stripping from the liquid membrane to the sweep gas [Ge et al, 2001, 2002; Trachtenberg et al, 2003]. The hydration and dehydration kinetics of CO_2 are the mass transport controlling steps in chemical absorption by aqueous solutions [Astarita, et al, 1989].
2. The numerous salt mixtures and buffer materials that can serve as the facilitating environment to support the absorption and desorption of CO_2. These low viscosity working fluids contrast with the more than 10X increase in viscosity evident with aqueous amine solutions of 20 to 40wt%. Our salt/buffer solutions can have a high ionic strength. This not only supports a high absorbing capacity for CO_2 but also promotes a salting-out effect that acts to decrease solubility of non-reactive gases, e.g., N_2 or O_2 and thereby increases selectivity.
3. A flowing (convective) liquid membrane will further increase the CO_2 permeation flux by reducing stagnant and boundary layer effects.

Design and Construction of Hollow Fiber, Enzyme-Based, Membrane Reactors

We generated two distinct hollow fiber (HF) reactor designs. Each of the designs used the hollow fiber material known as X30-240 manufactured by Celgard, Inc. (Membrana GmbH, Polypore, Inc.). The hollow fibers are made of a microporous polypropylene (PP) material with a bore diameter of 240µm and a shell diameter of 300µm. The porosity is 40% and the pores have an average diameter of 30nm.

The first design was a <u>spiral wound hollow fiber</u> array (SWHF). We made two examples of this design, each containing 180 feed and 180 sweep fibers with a length of 19cm yielding a contact area of 0.032m^2 (all values are rounded) for each the feed and the sweep, The difference between these examples was the thickness of the CLM, i.e., the spacing between fiber arrays. This was accomplished by varying the number of spacer layers that separate the hollow fiber mats. Thus the shell tube internal diameter in the reactor with only 1 spacer layer was 0.95cm (0.372" ID, 0.5" OD) while that with 2 spacer layers was 1.6cm (0.625" ID, 0.75" OD).

The design consists of four layers – feed gas HF, CLM separator, sweep gas HF, and CLM separator (Fig. 1). The layers are assembled flat and are then rolled around a central mandrill and inserted into a shell structure. The respective feed and sweep fibers are separated during assembly, as seen in Figure 1. At one end the fibers enter as the feed and sweep respectively. They exit in like manner at the opposite end as the retentate and permeate fibers. Access is provided to the body (shell side) at the entry and exit zones allowing circulation of the CLM fluid [Lin, 1996]. By use of convection the CLM fluid passes through a sample reservoir where its constituent make-up and enzyme activity can be monitored, supplemented or modified as required for optimal module performance.

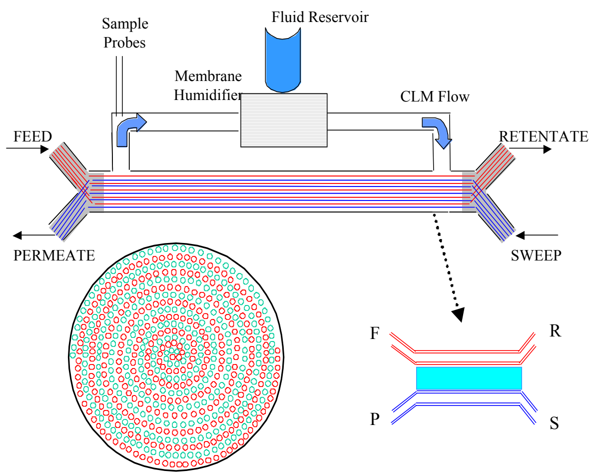

Figure 1. Schematic illustration of SWHF reactor design – axial and cross-sectional views with CLM circulation path.

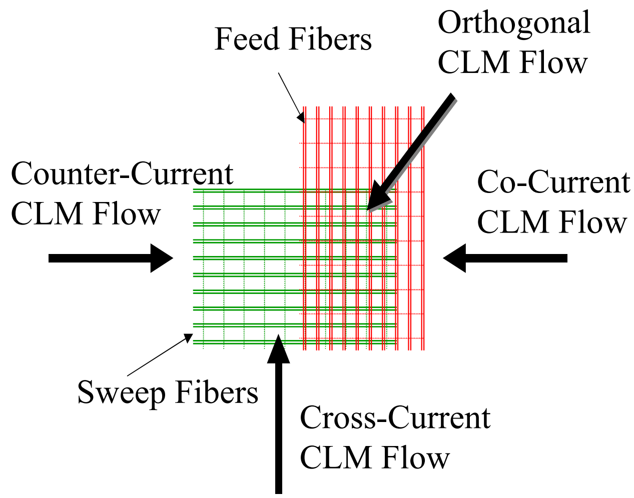

Figure 2. Schematic illustration of the orthogonal CAHF reactor

The second reactor design is known as the cuboidal array hollow fiber (CAHF). The CAHF is made by laying the hollow fiber mats one on top of another, separated by the requisite number of spacer layers. The fibers are oriented at right angles to one another (Fig. 2). In this design the housing allows the fibers to terminate directly at the edge of the reactor body. A cover containing a plenum can then be used to provide the feed gas or capture the retentate or to provide the sweep gas or capturing the permeate. The test cell membrane is 100mm on edge. The hollow fiber surface area, using 1 layer of feed and sweep fibers, each, has a surface area of $0.019m^2$ (value is rounded). The CLM thickness in this design was 700µm.

In both of these designs the liquid membrane is located on the shell side of the hollow fiber module. This allows the feed gas (CO_2 contaminated flue gas) to flow through the bore of one set of hollow fibers while vacuum or sweep gas is provided to the second set fibers to extract the permeate product. The CAHF was easier to construct, modify and administer than is the SWHF design. As will be described below the performance of the SWHF and CAHF did not differ significantly though the CLM pressure drop was lower for the CAHF.

CLM Thickness and Flow Rate

As stated before, we designed and constructed SWHF reactors with CLM thickness of 170µm and 310µm and CAHF reactors with CLM thickness of 200µm and 700µm. For this work we wished to examine the effect of convection in the separation process. There were two reasons for this concern. The first was that the low permeance seen during initial work using hollow fiber membrane arrays under diffusion conditions suggested that not all of the hollow fiber surface area was involved in the transport. Rather only that portion of the feed and sweep hollow fibers adjacent to one another seemed to be involved. The expected benefit of convection was that much more of the surface area could be utilized. The second was that bicarbonate diffuses more slowly than does N_2 or O_2. We hoped that convection would equalize the transport. At the same time we were concerned that the high convection rate might act similarly to a thin membrane and reduce selectivity.

In all of these tests we used a sample gas containing 5%-20% CO_2, with N_2 and O_2 proportionate to their concentrations in air. The relative humidity ranged from 0–100%. We installed a peristaltic pump to circulate the CLM. The CLM was caused to flow either longitudinally, i.e., parallel to the axis of the fibers in the SWHF reactor or transversely, i.e., cross-current, in the CAHF reactor. Figure 3 illustrates the effect of circulation rate on permeance and selectivity for a SWHF with CLM of 310µm thickness. Similar data are shown in Fig. 4 for the orthogonal fiber CAHF reactor with CLM of 700µm thickness.

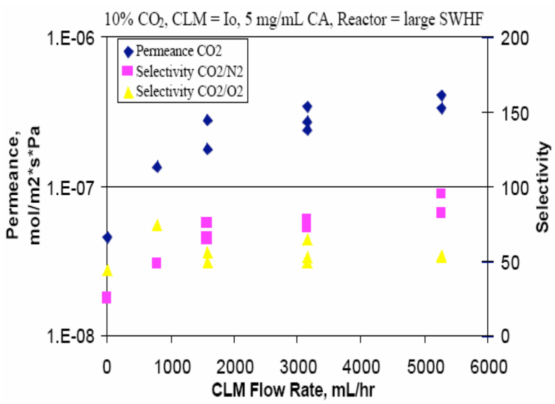

Figure 3. Permeance and selectivity vs. CLM flow rate for the 3/4" O.D. SWHF reactor.

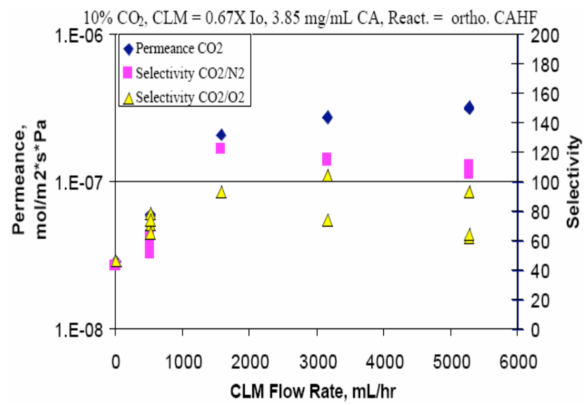

Figure 4. Permeance and selectivity vs. CLM flow rate for the orthogonal CAHF reactor.

The curves demonstrate that in both cases increasing convection rate improves both permeance and selectivity. Initially the permeance of N_2 or O_2 also rise in similar fashion with increase in convective rate but they do not have nearly as great permeance as does CO_2. For the flow rates we used the curves do not asymptote though they may well come to an asymptote at higher flow rates since the rate of increase continues to diminish. We were limited in upper flow rate by the peristaltic pumps used. At about 2,000ml/hr we achieved about 87% of the maximal benefit seen. At these flow rates the shell velocity for the SWHF was 2852.2cm/hr while that for the CAHF was only 19.2cm/hr. No data are shown for the small diameter SWHF reactor with a CLM of 170µm because, despite several manufactures, we could not get adequate CLM flow through this module. The backpressure was also very high and it was not always possible to eliminate channeling. Initial data on the parallel fiber CAHF with CLM of 200µm were similar to those for the 700µm CLM.

In conclusion, our data indicate that convection provides a substantial benefit over diffusion for both CO_2 permeance and selectivity independent of CLM thickness. They also indicate that the selectivity increases with convection rate, again independent of CLM thickness. This observation was unexpected. The data show that while the flow rates are the same for the two different designs the flow velocities are quite different.

CLM Composition / Reactive Transport Model

There are a very large number of physical and chemical parameters that can be altered in search of an optimization strategy. We elected to carry out computer modeling (StreamAnalyzer® software from OLI Systems, Inc. of Morris Plains, NJ) of a number of the contributing factors and to couple this with selective tests of the enzyme and of the reactors to validate the modeling. Using the software we have been able to construct a large number of salt and buffer mixtures targeted towards obtaining the best enzyme performance while reducing the permeance of interfering gases, e.g., N_2 or O_2.

Buffer Construction and Considerations

The pKa values for the phosphate buffer system are pK_{H2PO4-}=2.15, $pK_{HPO4=}$=7.2, pK_{PO4---}=12.35. Similarly, the pKa values for the $CsHCO_3$-glycine facilitator/buffer are pK_{COOH}=2.34, pK_{NH3+}=9.6. The pKa values for the CO_2/bicarbonate/carbonate system are pK_{HCO3-}=6.35, $pK_{CO3=}$=10.33. Thus, the phosphate buffer gives better buffering in the pH range preferred by CA, 6 to 8. However, at higher pH, preferred for absorption/hydration the two buffer systems are similar. At all times these buffers are in competition with the naturally forming CO_2/bicarbonate/carbonate buffer. As long as the exogenous buffer/natural buffer has a ratio of >1.5 then pH stability can be guaranteed. As the pCO_2 in the feed increases the ionic strength of the exogenous buffer needs to be increased to maintain a suitable working ratio. From these considerations, derived from our modeling we have come to understand that a phosphate buffer would work perfectly well for a feed CO_2 of at least 25%. The data also show that the $CsHCO_3$-glycine facilitator/buffer will work quite well. One major concern however, is the effect of this buffer on the activity of the enzyme. Bicarbonate is simultaneously an end product inhibitor for the hydration and a substrate for the dehydration. However, as the dehydration is 4.46-times slower than the hydration the effect of elevated bicarbonate is to decrease the hydration rate. This was clearly seen in the rate at which the system would come to equilibrium for a step change in feed gas CO_2. For the phosphate buffer equilibrium took about 90 minutes while a similar change, e.g., 10% to 20%, would requires more than twice as long for the $CsHCO_3$-glycine system. This indicated that the enzyme activity was reduced.

Using this model the most important characteristic of the buffer was its ability to maintain stable pH across the liquid membrane film. The carbonate-bicarbonate buffer does not provide as robust support either for continued physical absorption or for enzyme catalyzed absorption due to the difference in pKa values. In addition, in all cases, the pH is adversely affected at both the absorption and desorption interfaces by the localized reaction chemistry. One consequence is a reduction in the amount of CO_2 captured and transported.

The effect of buffer system on performance is shown in Figure 5 (phosphate buffer) and Figure 6 (bicarbonate/glycine buffer). The permeance is relatively similar though somewhat better for the phosphate system. In contrast selectivity is better for the bicarbonate/glycine system. These differences probably represent the bicarbonate inhibition of the enzyme hydration but improved salting out of the non-reactive gases due to the latter buffer.

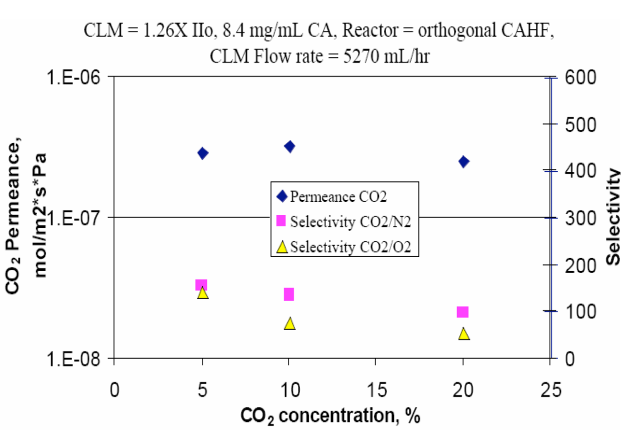

Figure 5: CO_2 permeance using a phosphate buffer system.

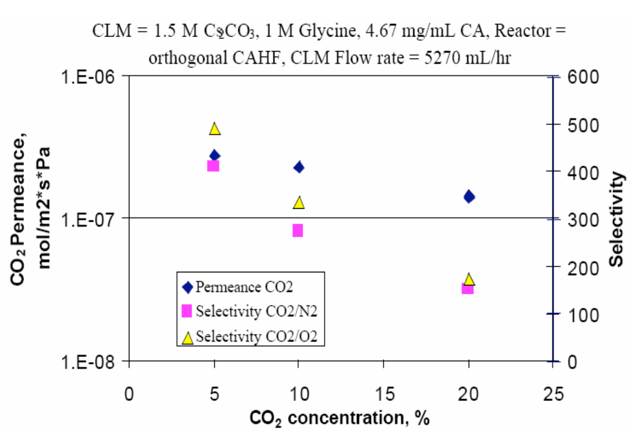

Figure 6: CO_2 permeance using a bicarbonate/glycine buffer system.

Summary/Conclusions

A variety of HF reactors containing an enzyme-based contained liquid membrane have been designed to extract CO_2 from mixed gas streams similar to those that would be encountered from flue gas stacks. They show a permeance of $3.8*10^{-7}$ moles CO_2/m^2*s*Pa with a feed gas of 10% CO_2. This value is equivalent to 2262 GPU. In contrast, polymer membranes typically yield GPU values of 100 or less. The selectivity vs. N_2 is as much as 110 and 100 vs. O_2 for 20% CO_2. At 10% CO_2 the selectivity for N_2 increases to 140. The CO_2 extraction fraction is on the order of 50%. The permeate stream achieves CO_2 concentrations of 95%, 96.5% and 97% for feed streams of 5%, 10% and 20%, respectively. In addition our modeling efforts show that we can effectively carry out experiments *in silico* that are confirmed *in vitro*. Our data, with CO_2 permeance one to three orders of magnitude greater than that reported by others shows the potential and promise of our approach. The ability to concentrate CO_2 so effectively from a dilute stream, and to achieve a value in excess of the 95% needed to justify compression, is a unique accomplishment for any membrane system. Economically it is also unique compared with other means of concentrating CO_2 from dilute streams.

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