

## ENZYME-BASED CO<sub>2</sub> CAPTURE FOR ALS

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## ABSTRACT

All living things are particularly sensitive to levels of carbon dioxide (CO<sub>2</sub>). Levels as low as 0.5% (1.7 times ambient) are detectable by humans and reported as stale air. High levels, beginning at 1.1%, adversely affect performance and ultimately impair consciousness in animals. High levels of CO<sub>2</sub> can adversely affect certain growth functions of plants such as seed set (===). In confined spaces with little spatial, physical or biological buffer capacity, e.g., in spacecraft, it is imperative to effect rigorous control of CO<sub>2</sub> to physiologically defined set points. For NASA applications such devices must not only be efficient but must exhibit high levels of reliability and robustness for safety conjoined with minimal mass and volume, use few if any consumables for economic reasons and low levels of astronaut intervention for efficiency. We have developed a novel enzyme-based contained liquid membrane (EBCLM) bioreactor for CO<sub>2</sub> capture applicable to these requirements. We report here on the design of the reactor and the application case studies. The results establish the feasibility of using this system to control CO<sub>2</sub> in crew and plant chambers.

The EBCLM can capture CO<sub>2</sub> from air at concentrations of less than 400 ppm to over 10,000 ppm, at or around ambient temperature and pressure. It exhibits selectivity of CO<sub>2</sub> versus N<sub>2</sub> of 1401:1 and CO<sub>2</sub> versus O<sub>2</sub> of 866:1 (???) . The CO<sub>2</sub> permeance is  $1.44 \times 10^{-7} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  (===  $\text{cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ ). Using the EBCLM with an inlet gas containing 1,000 ppm CO<sub>2</sub> yields a permeate containing more than 560,000 ppm CO<sub>2</sub> (dry). The EBCLM design is stable in the presence of either dry or humidified feed and sweep gases.

Keywords:

Carbon dioxide, Carbonic anhydrase, Bioreactor, Contained liquid membrane, Gas separation

## 1. Introduction

Human respiration releases a gas, CO<sub>2</sub>, which, as the concentration rises in the relatively small volume of a space ship, would result in performance impairment, unconsciousness and eventually death. A CO<sub>2</sub> control system is needed to capture this gas and avoid these undesirable consequences. However, capturing CO<sub>2</sub> from dilute streams (<1%), i.e., scavenging, is not easy. This device must be very sensitive. In addition, to be space certified, any device must be reliable and robust, low in mass, volume, and power, use little in the way of consumables, demand little human oversight and may not fail catastrophically. For low Earth orbit (LEO) missions these requirements are not as stringent as they will be for more distant missions (e.g., Mars) where self-sufficiency is paramount. In addition to performance and robustness the device must be small and light. NASA has developed an integrated measure of mass, power, consumables and maintenance time, known as equivalent system mass (Esm) to compare various devices contributing to an operational subsystem (Levri et al., ==, here the Air Recovery Subsystem (ARS)).

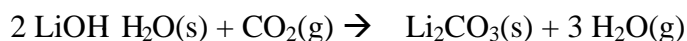
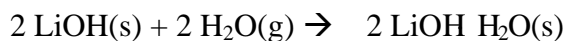
Previously we reported on progress towards developing a novel, highly efficient enzyme-based reactor that exhibits the requisite features (29-33). Those data showed that an enzyme-based facilitated transport CO<sub>2</sub> capture design could readily extract CO<sub>2</sub> from respiratory gas. The enzyme material could be immobilized to a variety of surfaces. We showed that enzyme mutants could be developed that retained full activity and that the enzyme could be stored in various ways for prolonged periods of time without untoward consequences. This last means that the structural elements of the reactor could be reactivated (regenerated) as needed for periods of

years using consumable materials provided in freeze dried packets where the total mass was minimal.

The design used in these early studies, a supported liquid membrane (SLM), suffered from evaporation induced breakthrough (26). We carried out a failure mode analysis (FMA) of this design to identify elements of weakness and strength and to devise strategies to increase the stability and robustness of this approach.

In this report we capitalize on these data and the FMA to introduce a new stable design that displays very high permeance ( $1.44 \times 10^{-7} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ ) while exhibiting selectivities vs. nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) that could allow this design to be used successfully for space missions.

At present, the principal  $\text{CO}_2$  capture technologies applied or pursued under Advanced Life Support (ALS) to manage respiratory  $\text{CO}_2$  are metal hydroxides (e.g., lithium hydroxide –  $\text{LiOH}$ ), metal oxides (e.g., silver oxide –  $\text{Ag}_2\text{O}$ ) (17), molecular sieves (e.g., CDRA – **Spell Out**), and solid and liquid amines (11). Lithium hydroxide scrubbers have been used extensively on nuclear submarines and past space missions including the Apollo program.  $\text{LiOH}$  spontaneously and exothermically reacts with  $\text{CO}_2$  to produce solid lithium carbonate ( $\text{Li}_2\text{CO}_3$ ).

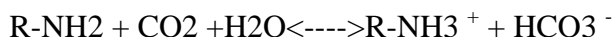


$$\Delta H^\circ = -25.2 \text{ kcal/mol}$$

However, the reaction chemistry is such that regenerating LiOH is difficult; this makes LiOH scrubbers non-reusable. The technique is less than ideal for a prolonged mission where scrubbers for hundreds of EVAs would have to be brought from Earth.

Metal oxides have also been used in past missions and are being used in the current spacesuit (EMU – extravehicular mobility unit). This system relies on the reaction chemistry of metal oxides to take carbon dioxide out of the system. While metal oxide canisters are reusable, the heavy metal substrates cause significant increases in system mass and volume. This problem is less significant when the system is deployed in micro-gravity, but it makes the system impractical for long duration EVAs (extravehicular activity) in environments where mass is a limiting factor (18).

The DARA (**Spell out**) system, a carbon dioxide removal technique that utilizes solid amines, is the better option. This system, co-developed by the European Space Agency and the German National Space Agency, uses a porous resin as a carrier for series of weak basic amine groups. The mechanism of reaction is:



The solid amine matrix (type DOR-SA-028), produced by Bayer A.G. is composed of a extremely porous polystyrene. While it is stable power requirements for management and maintenance of the system are too high to make the system practical for use on an EMU (11).

Our goal is to devise a CO<sub>2</sub> capture system with better performance but with lesser mass, volume and power demand. To do this we have devised a biomimetic approach capitalizing on nature's

ubiquitous CO<sub>2</sub> scavenger catalyst, carbonic anhydrase (CA – E.C. 4.2.1.1). It is the most efficient chemical “absorber” known. It affects capture of CO<sub>2</sub> by catalyzing two reversible reactions. The first generates a metal hydroxide --  $E^*Zn + HOH \rightleftharpoons E^*Zn-OH^- + H^+$  while the second uses the hydroxide to attack the carbonyl bond of CO<sub>2</sub> generating bicarbonate as the CO<sub>2</sub> equivalent --  $E^*Zn-OH^- + CO_2 \rightleftharpoons E^*Zn + HCO_3^-$ . When used in a membrane the CO<sub>2</sub> hydration reaction takes place at the CO<sub>2</sub>-rich gas side and the reverse reaction, the dehydration, occurs at the CO<sub>2</sub>-poor side of the membrane, i.e., the sweep gas side.

There are many CA isozymes as CA occurs in virtually all-living organisms ( $\rightleftharpoons$ ). The most efficient of the various CA isozymes is human erythrocyte CA (HCAII). It has a turnover number of  $1.6 \times 10^6$  molecules of CO<sub>2</sub> per molecule enzyme per second (36). This is far faster than chemical absorber molecules such as amines (2). Unlike the amines CA does not act as carrier (chaperone) creating a slowly diffusing molecule. Rather, it converts the CO<sub>2</sub> into bicarbonate, a compound that has exceedingly high solubility and relatively good diffusion characteristics. A CA-based CO<sub>2</sub> capture system qualifies as a hybrid absorber system – CA increases the solvation (solution) of CO<sub>2</sub> by its rapid conversion to bicarbonate while the solvent water acts a physical absorber of the produced bicarbonate.

The period of the 1960s and 1970s saw the first efforts at a biomimetic approach to CO<sub>2</sub> capture based on realization that the mammalian erythrocyte enzyme, CAII, was an unusually efficient and highly specific vehicle for CO<sub>2</sub> capture and “desorption” via the lung [Chang, Thomas, Enns., Otto & Quinn, Donaldson & Quinn, etc.] (12,14,26).

The early experiments started with diffusion mechanism studies. In 1971 Otto and Quinn (26) first used CA as an effective catalyst for hydration/dehydration reactions in a typical SLM system. They used a carbonate/bicarbonate solution as a core buffer to separate CO<sub>2</sub> from an air stream. They focused on the CA catalysis capacity and the effect of metal ions but did not directly evaluate the process by which CA separates CO<sub>2</sub>. Donaldson and Quinn (14) studied facilitated transport using both homogenous and heterogeneous CA membranes. They used the same diffusion cell design as that of Enns and of Otto and Quinn. In these studies they attempted to compensate for evaporation of solvent by using a humidified inlet gas. However, their project suffered because of the limited knowledge of enzyme chemistry available at that time and because of the limitations of SLM technology then in place.

These early studies were disappointing for two reasons. First, because of insufficient biochemical information then available, the buffer system chosen - commonly a self-generating carbonate/bicarbonate buffer - was insufficient to hold pH constant in the face of the acidification. Second, the SLM formed by soaking a filter in enzyme solution was very subject to evaporative losses, even in the face of feed gas humidification, resulting in non-constant thickness, gas breakthrough and changes in enzyme concentration. For both of these reasons early SLMs exhibited poor stability and selectivity.

The most successful strategy was the use of a reservoir to replace lost solvent (6Basu ???). This design received a variety of names the most recent of which is the contained liquid membrane (CLM). Early examples, using a carbonate / bicarbonate solution in water as the core separation material still suffered from low selectivity for its low efficient facilitator.

In these experiments we combined the best elements of CLM design with high catalytic efficiency of CA to demonstrate a CA-based membrane bioreactor. We started by evaluating the resistance of different parts in this membrane system. This allowed us to design it in such a way that it could work efficiently. The case application study was carried out here too. The data indicate successful development of a system capable of extracting CO<sub>2</sub> at partial pressure found in air and enriching it 600-fold (**560-fold ???**) to yield a permeate concentration of more than 56% CO<sub>2</sub> in a single pass.

## 2. Experimental

### 2.1 Materials

We used bovine carbonic anhydrase (BCAII - Sigma Chemical Co.) as the enzyme catalyst. 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 was used as the screen membrane (Celgard PP-2400). The PP-2400 is 25.4 μm thick, 35% porosity, with 41 nm x 120 nm pores and a tortuosity value of 5. The thickness of the liquid membrane was controlled by the use of 180μm thick polyester mesh spacers (Small Parts Inc., CMY-200). Air (Matheson) was ultra zero, argon (Matheson) was ultra high purity and CO<sub>2</sub> (Matheson) was high purity.

### 2.2 Bioreactor configuration and test stand setup

As shown in Fig 1, the membrane is constructed by sandwiching a CA containing phosphate buffered solution between two polypropylene membranes. These, in turn, are supported by two pieces of metal sheet. The effective area is 380.1mm<sup>2</sup>. The thickness of the aqueous phase was

varied from 80 $\mu\text{m}$  (**how does this fit with 180 $\mu\text{m}$  statement above ???**) to 630 $\mu\text{m}$ . The liquid membrane volume was maintained by means of a reservoir. The feed gas stream consisted of a mixture of  $\text{CO}_2$  in zero air delivered via an Environics mass flow controller (Environics, Series 2020 – NIST-traceable calibration). Argon was used as the sweep gas stream. It was delivered to the test cell after passing through a purification column (OMI-4, Supelco) to remove any residual  $\text{CO}_2$ . Delivery was regulated by the Environics mass flow controller. The feed and sweep gases could be humidified to the extent desired by means of polysulfone dehumidifiers operated in reverse.

$\text{CO}_2$ -free gas was used to initiate each test (Fig.2 **does not appear relevant**). After passing through the test cell, the out gas (retentate or reject) was delivered to a residual gas analyzing mass spectrometer (Questor IV, ABB Extrel) to measure concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The separation performance was calculated based on the flow rate and the composition of the feed and sweep gases. Separation performance measures used in this paper include selectivity ( $\alpha$ ) and permeance (Q), calculated as shown below:

$$Q = \frac{J}{\Delta P}$$

$$a = \frac{Q_i}{Q_j}$$

J is the gas flux through the membrane and  $\Delta P$  is the partial pressure difference across the membrane. The unit of Q is  $\text{mol m}^{-2} \text{Pa}^{-1} \text{s}^{-1}$ , i and j are permeance for species i and j, respectively.

### 3. Results and Discussion

Based on the design described above, we first examined the transport resistance for different layers. This was done by measuring diffusive flow across the membrane components using membrane inlet mass spectrometry (Tu, 19==). Then we evaluate the effect of the CO<sub>2</sub> concentration under laboratory conditions (pure gases) and compared this performance to that seen when using an ersatz cabin gas and a plant gas sample from the growth chamber. We also evaluated the use of partial vacuum on the sweep side. The object of these last studies was to evaluate the effect of VOCs and of vacuum on the separation performance of our membrane separation system.

#### 3.1. Mass Transfer Studies - Flux Resistance of Polymer Membranes vs. Liquid Membrane

As a flat sheet model the CLM consists of the metal screen, the polymer support, the screen and spacer together with liquid phase and then a second metal screen, the polymer support. The support is used to supply the mechanical strength to the system. It should contribute minimal transport resistance. The membrane that was used to contain the liquid phase should be microporous and gas permeable such that it will have minimal effect on the mass transport resistance. At the same time the membrane should be hydrophobic to prevent water intrusion into the pores and the pore size should be in a range that will not allow large water loss. The spacer was used to control this liquid thickness and the reservoir was used to maintain the liquid level in the core.

We measured the passive diffusion rate across each membrane component individually to determine their contribution to the total mass transfer resistance. Test configurations included

metal support, polypropylene membrane and polycarbonate membrane, spacer and the liquid film with and without CA. We delivered a test gas to the feed side of the test cell. The mass spectrometer probe, covered with a silicon membrane, was in the permeate chamber. We use diffusion resistance to describe the transport resistance. The diffusion resistance equals to the reciprocal of permeance that is similar to Ohm's law:

$$I = \frac{E}{R}$$

Where I is current, U is voltage and R is resistance. Similarly:

$$J = P * \Delta P = \frac{\Delta P}{1/Q}$$

Where J is flux,  $\Delta P$  is partial pressure difference across the membrane,  $1/Q$  is the reciprocal of permeance which was used as the parameter to evaluate the diffusion resistance.

Figure 3 illustrates the diffusion resistance for each of these components without the liquid phase. The data show that the resistance of all of those parts including metal support, polymer membrane and the combination of metal support and polymer membrane is at the same level: less than  $35 \text{ m}^2\text{-s-Pa/mol}$ . Among them, the resistance of metal support is far less than that of polymer membrane. In figure 4 #1 is the system with liquid phase that did not contain CA. When CA was added (#2 and #3) the diffusion resistance of the system decreases to less than one third of that without CA. It clearly showed that CA successfully decreases  $\text{CO}_2$  diffusion resistance of  $\text{CO}_2$ . Comparing figure 3 with figure 4, it is clear that  $\text{CO}_2$  diffusion resistance of the system with only buffer solution as liquid phase is 3000 times greater than that of the system without

liquid phase. The resistance of the system with CA and buffer is 800 times greater than that of the system without liquid phase. This result indicates that the main diffusion resistance of our current design is that of the liquid part even with CA in the buffer solution. Thus, the effective membrane area will depend on the area of the larger resistance parts and it is the area of liquid phase in our design as reported elsewhere (6). From the point of view of diffusion resistance, CA is the key material to decrease the resistance so as to realize the performance increase of this system. Because the diffusion resistance of polymer membrane is only one eighth of that of the total resistance, we have considerable freedom to choose among different polymer membranes to satisfy other requirements. In figure 4, comparing #2 with #3, shows that the diffusion resistance will further decrease if CO<sub>2</sub> in feed side directly contacts the CA buffer solution (#3). This indicates that the hydrophobic membrane produces another resistance once liquid phase was applied. It might be because of that the boundary layer was formed within the pores of the membrane when the CO<sub>2</sub> interfacial hydration rate is very fast as is the case in the presence of CA catalysis.

### 3.2 Feed CO<sub>2</sub> concentration

Feed stream CO<sub>2</sub> concentration depends on specific application requirements. In space station, the CO<sub>2</sub> concentration should be controlled lower than 0.10% (pCO<sub>2</sub> = 101.30 Pa), in the EMU application the CO<sub>2</sub> concentration is about 0.50% with a total pressure of 29.65Kpa (pCO<sub>2</sub> = 148.24 Pa). In this paper we investigated CO<sub>2</sub> concentrations over a range of 0.04% to 1.00% (pCO<sub>2</sub> = 40.52 to 1013.00 Pa). CA concentration is 166.67μM and the thickness of liquid phase is 330μm. This value was chosen from prior studies. It corresponds to the point of maximal selectivity index value – selectivity \* permeance. The buffer concentration is 20mM and pH is 7.85. Figure 5 shows the effect of CO<sub>2</sub> concentration on separation performance. With increase

of CO<sub>2</sub> concentration both selectivity and permeance decreased. The increase in selectivity reflects the significant CO<sub>2</sub> facilitation at low pCO<sub>2</sub>. This is due to the presence of a relatively large number of CA molecules and the lesser effect of CA facilitation as pCO<sub>2</sub> increases due to the large number of CO<sub>2</sub> molecules without access to CA. Figure 5 shows that the transition concentration is around 0.2%, pCO<sub>2</sub> = 202.6 Pa. When CO<sub>2</sub> concentration is greater than 0.2%, the separation performance decreases dramatically. From the point view of effect of partial pressure, it is very clear that this design could work efficiently to maintain CO<sub>2</sub> level in EMU or space station for CO<sub>2</sub>; the pCO<sub>2</sub> that must be managed is less than 202.6 Pa.

### 3.3 Effect of the ersatz cabin gas

One possible application of this system is to remove CO<sub>2</sub> from the space station life support system. Here the various pieces of equipment off gas a wide variety of volatile organics (VOCs) (24). One concern with enzymes is their susceptibility to VOCs. Thus it was necessary to evaluate the effect of concentrated organic compound on CA activity. Table 1 lists the VOC composition of an ersatz cabin gas; methanol and benzene are overloaded as a more strenuous test. The VOC mixture was carefully made and then balanced with the laboratory air modified to contain a CO<sub>2</sub> concentration of 0.2%. This ersatz gas was used as feed and argon as the sweep gas. The liquid membrane was made by dissolving 5mg/ml CA into 75mM phosphate buffer solution. The pH value of this buffer solution is 8.0 and the thickness of liquid phase is 330µm. The experiment was carried out at 30°C. Figure 6 shows the result after a 22 runtime. The result shows that CO<sub>2</sub> separation performance did not decrease during this period. This indicates that CA could maintain activity even under this extreme condition. At the start the performance is somewhat lower; the separation performance at 2 hours is very close to that at 22 hours. One

possible reason is that at the beginning, the buffer solution has the capacity to hold certain amount bicarbonate ions so that not all of CO<sub>2</sub> could permeate through the membrane to be captured in the sweep side. Contrarywise, the permeation rate of O<sub>2</sub> and N<sub>2</sub> will not change as time passes as the solubility of those two gases is so low and not facilitated. Once CO<sub>2</sub> hydration rate and bicarbonate ion dehydration rate reaches a balance, the separation performance will not change much as shown in Figure 6 where the separation performance was nearly the same at 2hours and 22hours. **Why use the start time data at all?**

### 3.4 Plant chamber gas

Long-term expedition into space requires that all of materials in the closed life support system must be recycled. One possible solution is to use a plant chamber to produce food from the waste produced in the life-supported system. CO<sub>2</sub> is important to plant metabolism; most plants favor 0.1%-0.15% CO<sub>2</sub>, For this reason it is very important to control the CO<sub>2</sub> level in the plant chamber to achieve the highest possible growth rate. CO<sub>2</sub> is produced by humans in the cabin and consumed in the plant chamber. It is important to control CO<sub>2</sub> level in both of those two chambers to optimize their performance. However, plants also emit VOCs during growth. It is important to see if these VOCs may have a deleterious effect on CA activity. Figure 7 illustrates the effect of VOCs from greenhouse gas on CA activity. Here the feed gas was directly obtained from the tomato plant zone of the greenhouse. CO<sub>2</sub> concentration in this gas is 0.04%. The other conditions are the same as shown above for cabin gas. The result shows that the separation performance increased after 30hr running. We observed a denser CA layer formed in the interface of the liquid membrane. This may be due to water evaporation from the liquid membrane. This concentrated CA will decrease O<sub>2</sub> and N<sub>2</sub> solubility and increase CO<sub>2</sub> hydration

rate and dehydration rate such that the both selectivity and permeance increase with time. More importantly, this result clearly shows that there is no negative effect of VOCs from plants on the separation performance of our system.

### 3.5 Sweep method effect

Generally speaking, in gas separation, it is necessary to remove the permeate at the sweep side to maintain an effective driving force across the membrane. One common way is to use an inert gas such as argon or helium. Recently, we reported a theoretical analysis on use of water vapor as sweep gas to produce high purity CO<sub>2</sub> (15). In that work we found that using different gases (argon, air) as sweep gas will result in similar separation profiles when aided by a vacuum of –85 kPa. In this paper, we evaluate the effect of different flow rates when some of the feed gas was also used as the sweep, i.e., in bypass mode, aided by a partial vacuum (–85 kPa).

Figure 8 illustrates the calculated driving force for different cases. With no gas flow on the permeate side – the permeate side is filled with argon or in the presence of a partial vacuum (–85 kPa), the driving force reaches 0 once equilibrium is achieved. In contrast, the driving force for pure argon or air at 4ccm or 10ccm under –85 kPa vacuum are almost the same. This value indicates that these three cases should work well. Fig.9 illustrates the effect of different flow rate under –85 kPa vacuum. The membrane was PP-2400. 5mg/ml CA was dissolved into 75mM phosphate buffer to form a liquid phase at pH of 8.0. The test was run at 30°C with the CO<sub>2</sub> in feed at 0.1%. Because of measurement limitations of the mass spectrometer given the very low permeate, we measured the CO<sub>2</sub> concentration on the retentate side to indicate separation performance (y-axis in figure 8). It shows that under –85 kPa vacuum, CO<sub>2</sub> concentration first

decreased and then went up. This indicates that at the beginning CO<sub>2</sub> was hydrated and dissolved in the buffer solution, once bicarbonate ions in solution reached the saturated state, no more CO<sub>2</sub> could be accepted in the buffer. Thus, CO<sub>2</sub> concentration in the retentate begins to increase. In this case, because the vacuum is not strong enough to move the CO<sub>2</sub> on the permeate side, the CO<sub>2</sub> accumulates on the permeate side and the driving force will decrease gradually. Once the driving force is small enough, no CO<sub>2</sub> could pass through the membrane resulting in no further separation. If we use an air sweep at a flow rate of 4 ccm CO<sub>2</sub> could be move efficiently and continuously reinitiating separation. As airflow rate increased, a higher driving force could be realized to achieve lower CO<sub>2</sub> on the retentate side. This result suggests that a moderate vacuum plus a bypass gas as a sweep is a good selection to produce high driving force. If water vapor is used as the sweep, by providing it on the permeate side, we could get the high purity CO<sub>2</sub> by our current design. We have shown previously (15) that when using a water vapor sweep, elevated temperature will reduce the magnitude of the vacuum needed to achieve the same CO<sub>2</sub> enrichment.

### 3.6 Relative Merit

To determine the significance of these data we compared the performance of these membranes with that of a polyethyleneimine/polyvinyl alcohol membrane and with two recent published reports by Sirkar and colleagues (9,10,19) using glycerol based CML. In figure 11 the data are plotted using a more traditional permeance vs. selectivity profile. Figure 10 illustrates the same data replotted to highlight performance comparison using separation index as a measure. It shows our recent result is preferred over the CO<sub>2</sub> partial pressure range required by NASA. In both cases it is clear that EBCLM bioreactor showed the highest permeance than other designs.

Further increases in selectivity for the CLM bioreactor will strengthen its lead as the best CO<sub>2</sub> capture system known.

#### 4. Conclusion

The CA membrane bioreactor presented here performs extremely well. In our current design, most of the diffusion resistance comes from the liquid phase. This design gives us wide freedom to choose different base membrane materials and conditions. The experiment on the effect of VOCs in both cabin and plant gas shows that there is no negative effect on CA activity during one day evaluation. The sweep method development shows that we can use several different means of achieving a high CO<sub>2</sub> product. Work is ongoing in our group towards improving the response properties of this design and to further understanding this reactor design.

#### 5. ACKNOWLEDGEMENTS

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Tables:

Table 1 VOCs in cabin gas

Table 2 VOCs in plant chamber gas

Figures:

Figure 1. Test cell configuration

Figure 2. Test stand

Figure 3. Nominal transport resistance of the system without liquid phase

Figure 4. Nominal transport resistance of the system without liquid phase

Figure 5. CO<sub>2</sub> concentration versus separation performance

Figure 6. Effect of cabin gas VOCs

Figure 7. Effect of plant chamber gas VOCs

Figure 8. Calculated driving force

Figure 9. Effect of flow rate on separation performance under –85 kPa

Figure 11. Permeance versus selectivity

Figure 10. CO<sub>2</sub> partial pressure versus separation index

**NB: File is too big. Simply copy illustrations or attach Excel file, do not link.**

Table 1.

COMPOUND	FORM	M.W.	FORMULA	SMAC mg/m <sup>3</sup>	ERSATZ mg/m <sup>3</sup>
Methane	G	16.04	CH <sub>4</sub>	3800	3800
Isoprene	L	68.11	C <sub>5</sub> H <sub>8</sub>	560	560
Methanol	L	32.04	CH <sub>3</sub> OH	9	21
Ethanol	L	46.07	C <sub>2</sub> H <sub>5</sub> OH	2000	2000
1-Butanol	L	84.2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	80	80
Acetone	L	58.08	CH <sub>3</sub> COCH <sub>3</sub>	50	50
Methyl Ethyl Ketone (MEK)	L	72.1	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	30	30
Ethyl Acetate	L	88.1	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	180	180
Benzene	L	78.11	C <sub>6</sub> H <sub>6</sub>	0.1	5.6
Toluene	L	92.13	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	60	60
Benzaldehyde	L	106.12	C <sub>6</sub> H <sub>5</sub> CHO	173	173
Carbon Monoxide	G	28.01	CO	10	10

Compound	Scan	Rate (mg/hr)
d-8 Toluene (i.s.=internal std.)	316	-
cyclohexanone	400	0.16
alpha-pinene	439	0.29
cymene isomer	458	1.54
myrcene	470	1.02
2-carene	478	17.55
sabinene	486	4.27
cymene isomer	494	27.68
ocimene	501	0.42
terpinene	508	0.63
branched alkane c6-c8	513	0.06
terpinolene	524	1.27
undecane	536	0.17
terpinene isomer	540	0.22
unk. terpene epoxide	546	0.03
unk. alkyl benzene	549	0.10
c-10 branched alkene	558	0.07
c-12 branched alkene	610	0.06
alkane c12-13	626	0.07
alkane c-12	633	0.06
delta-element	653	2.00
copaene	673	0.08
unk. sesquiterpene	677	0.13
caryophyllene	693	6.27
calarene	700	0.21
a-caryophyllene	707	1.21
b-cubebene	718	0.20
branched hydrocarbon (>c12)	742	0.05
branched hydrocarbon (>c12)	763	0.06
Total (excluding IS)		65.89

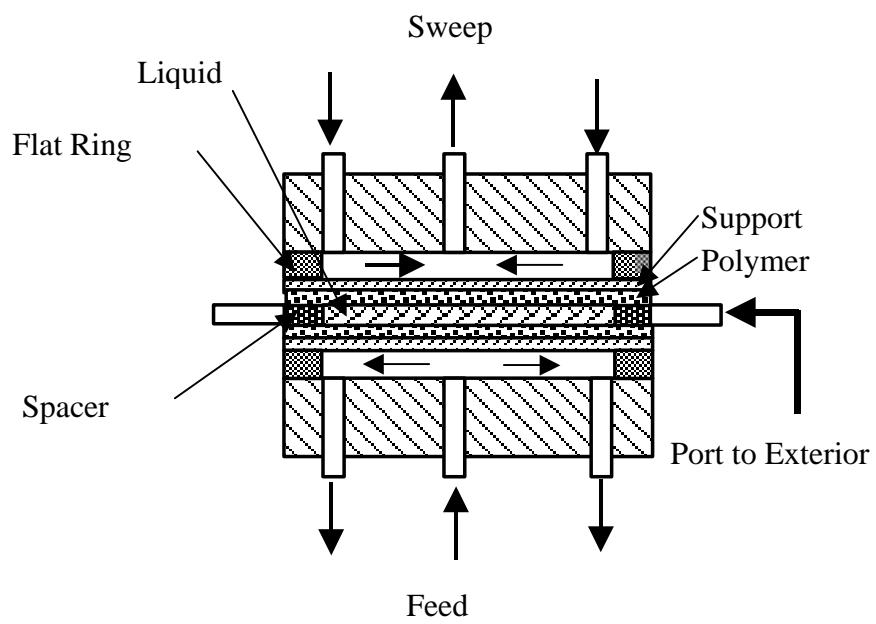
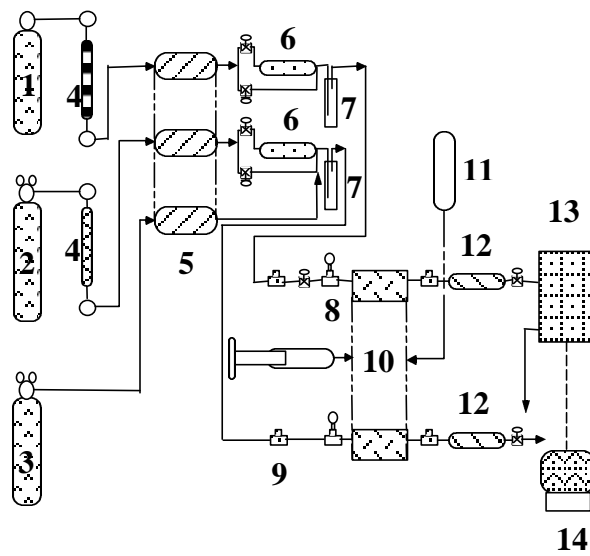


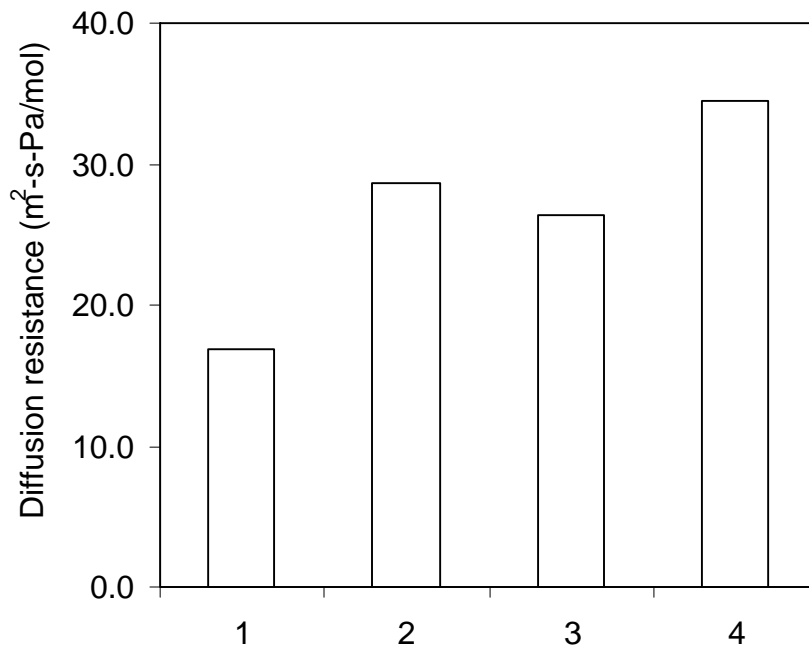
Fig. 1.



- |                                    |                                     |
|------------------------------------|-------------------------------------|
| 1- Ar                              | 8- Pressure gauge                   |
| 2- Air                             | 9- Temperature/humidity Sample port |
| 3- CO <sub>2</sub>                 | 10- Test cell                       |
| 4- CO <sub>2</sub> purified column | 11- Reservoir                       |
| 5- Mass flow controller system     | 12- Mass flow meter                 |
| 6- Humidifier                      | 13- Mass Spectrometer               |
| 7- Trap                            | 14- Computer                        |

Fig. 2.

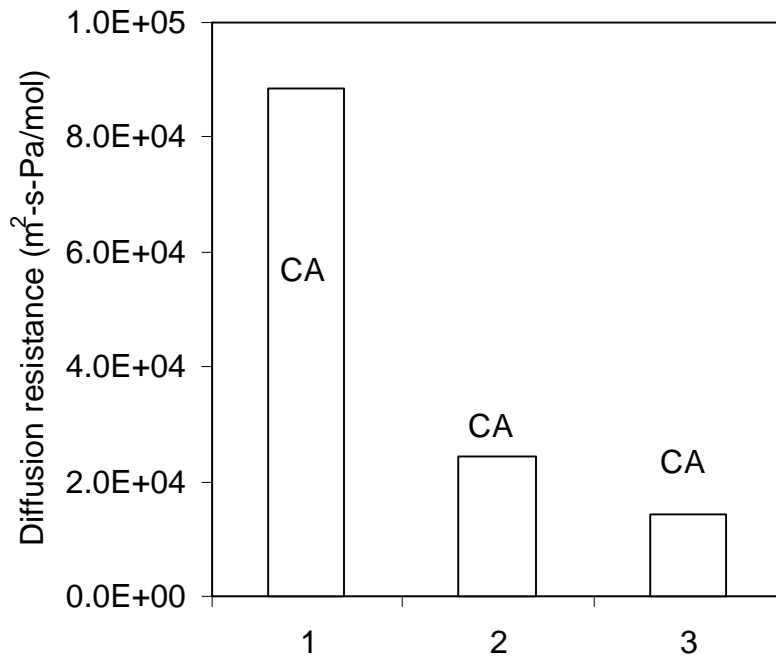
**Not called out in text**



1. Metal support
2. Polymer membrane - PC 0.2µm
3. Metal support + Polymer membrane
4. Metal support / Polymer membrane / Spacer 180 µm / Polymer membrane

Fig. 3.

**Shade columns; define PC**



- 1.Metal Support / PC 0.2 mm / Buffer-side Feed
- 2.Feed=>Metal support / PC 0.2 mm / Buffer + CA
- 3.Metal Support / PC 0.2 mm / Buffer + CA<=side Feed

Fig. 4.

**Shade columns; define PC; column 1 should not have CA; is the unit mm or mM?**

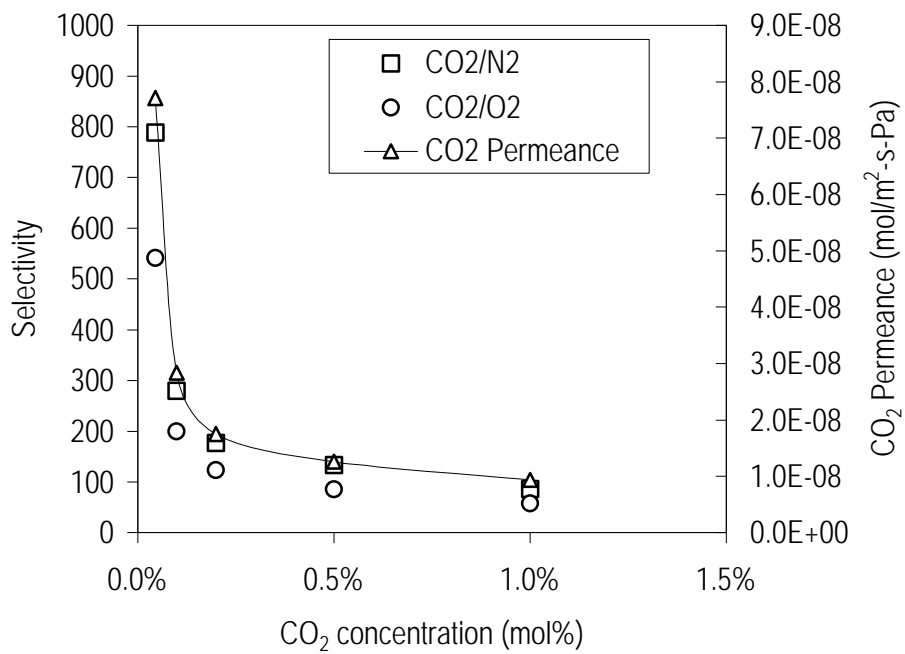


Fig. 5.

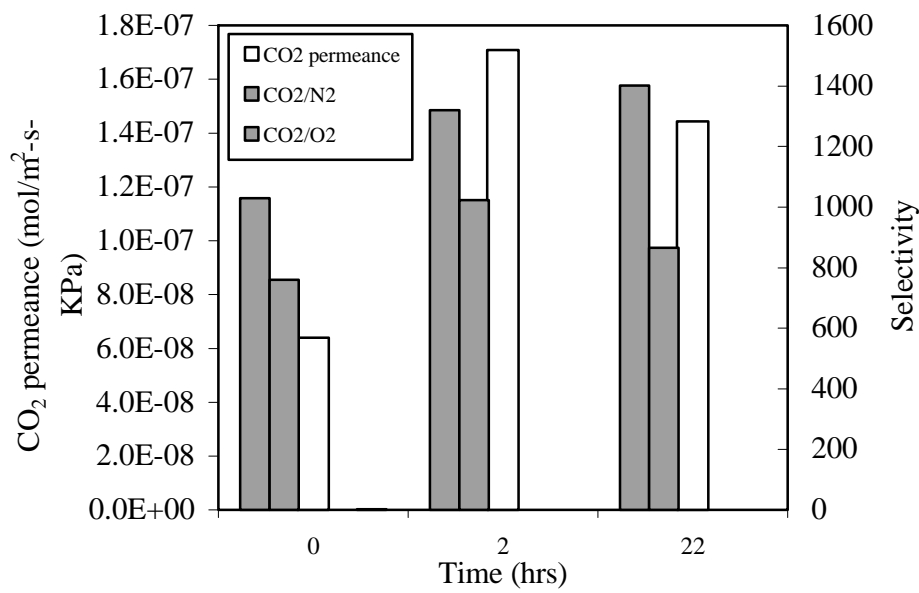


Fig. 6.

**Is time 0 needed?; Label in figure as ersatz cabin gas**

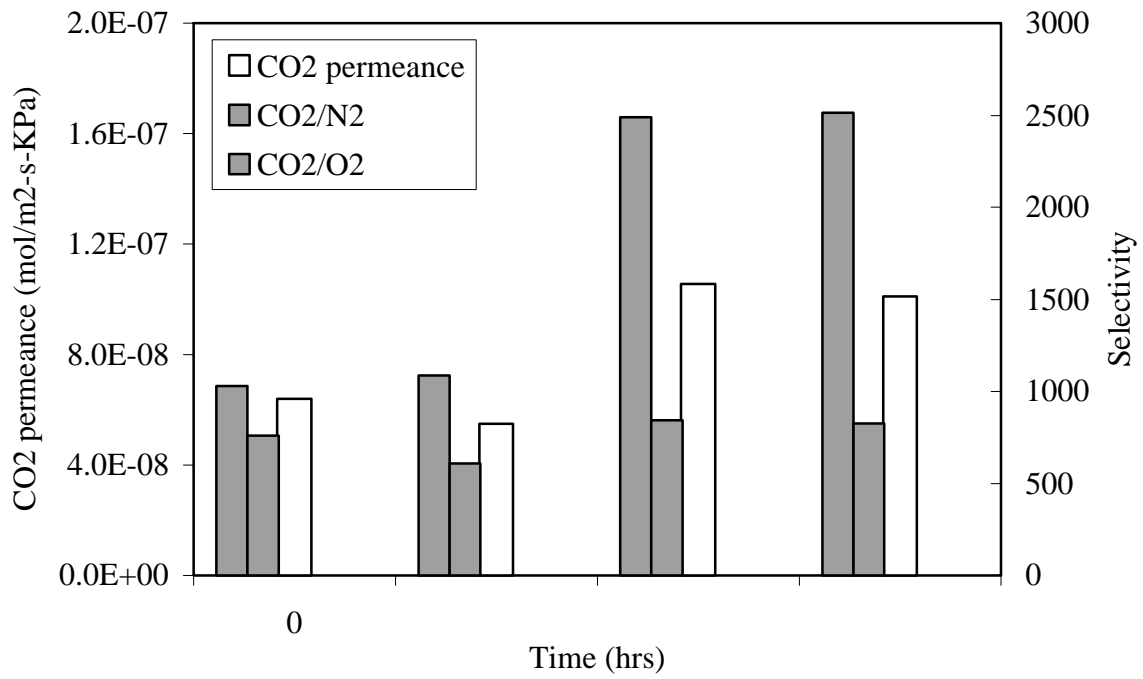


Fig. 7.

**Label in figure as Tomato Gas VOC; time marks are missing**



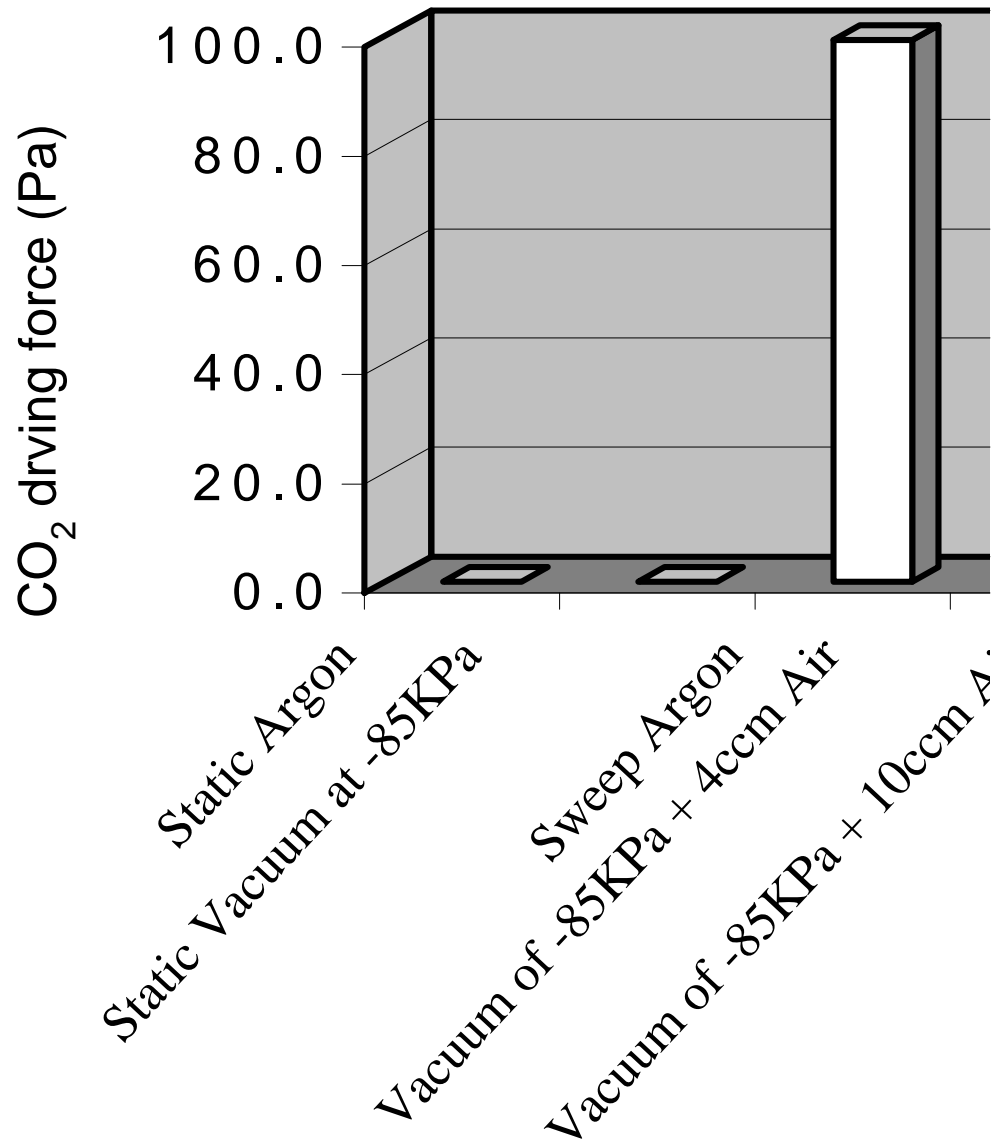


Fig. 8.

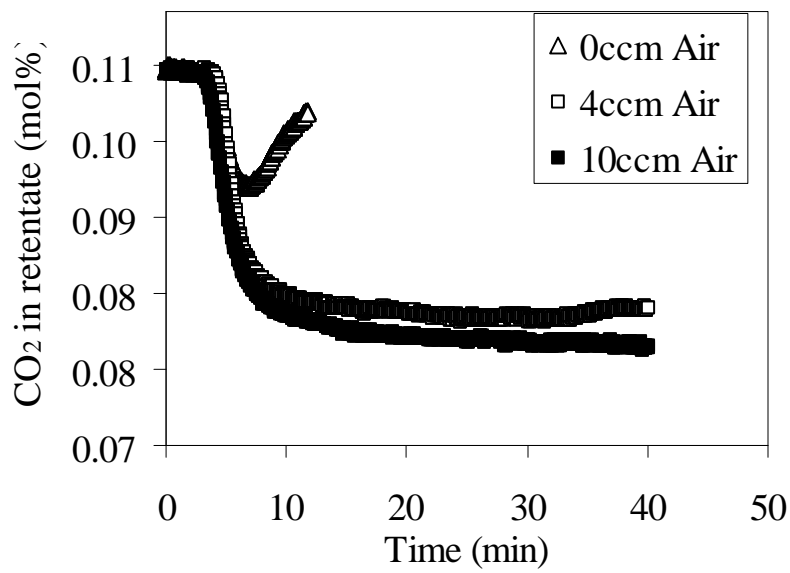


Fig. 9.

**Do the data for 0ccm air extend back to the baseline?**

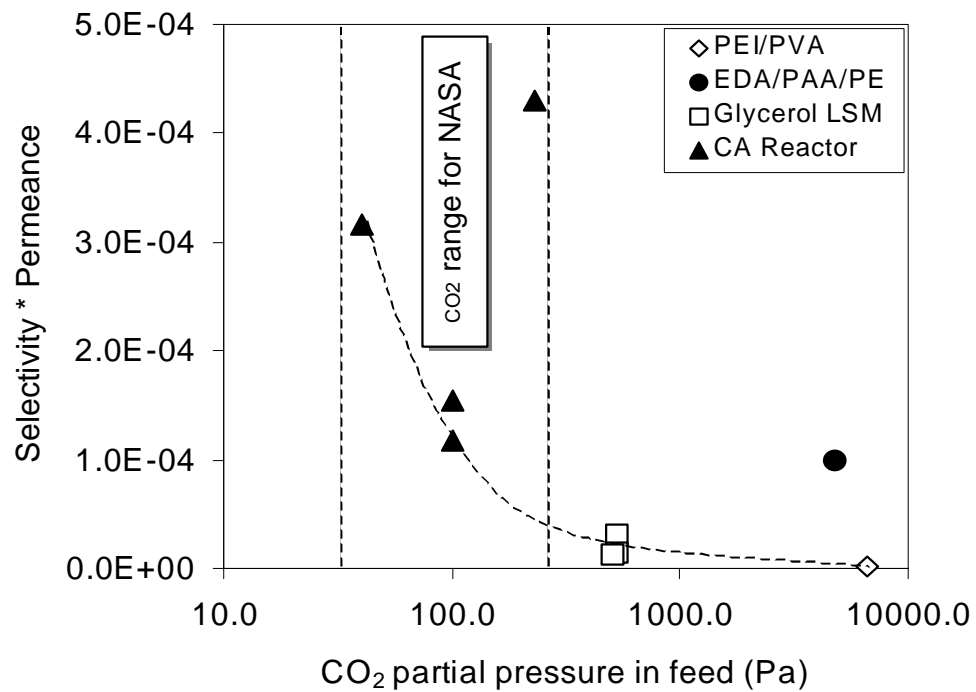


Fig. 11.

**NB: changed order; for triangles indicated different experiments or times**

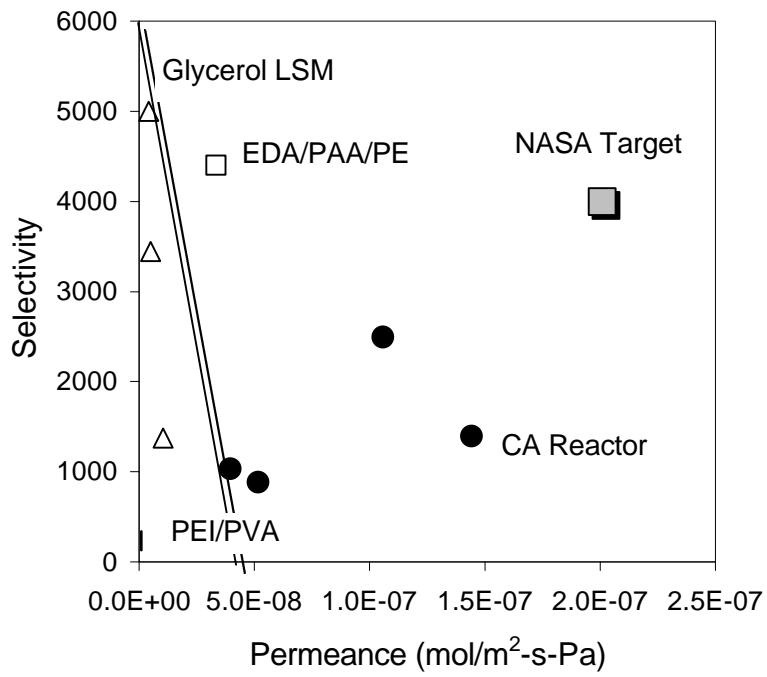


Fig. 10.

**NB: changed order; date or otherwise label triangles. Explain the downward (left) line. Add an upward right line for our data going towards NASA target.**