Development of Permselective Composite Membranes for CO_2 Separation

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Introduction

- Global industrialization has led to an increase in CO_2 emissions.
- Current industrialized separation methods rely heavily on energy intensive technologies (i.e., current CO_2 separation technologies).
- Membranes provide a positive barrier for CO_2 gas separations; this unique separation mechanism avoids energy cost associated with phase change, unlike the traditional amine absorption process.

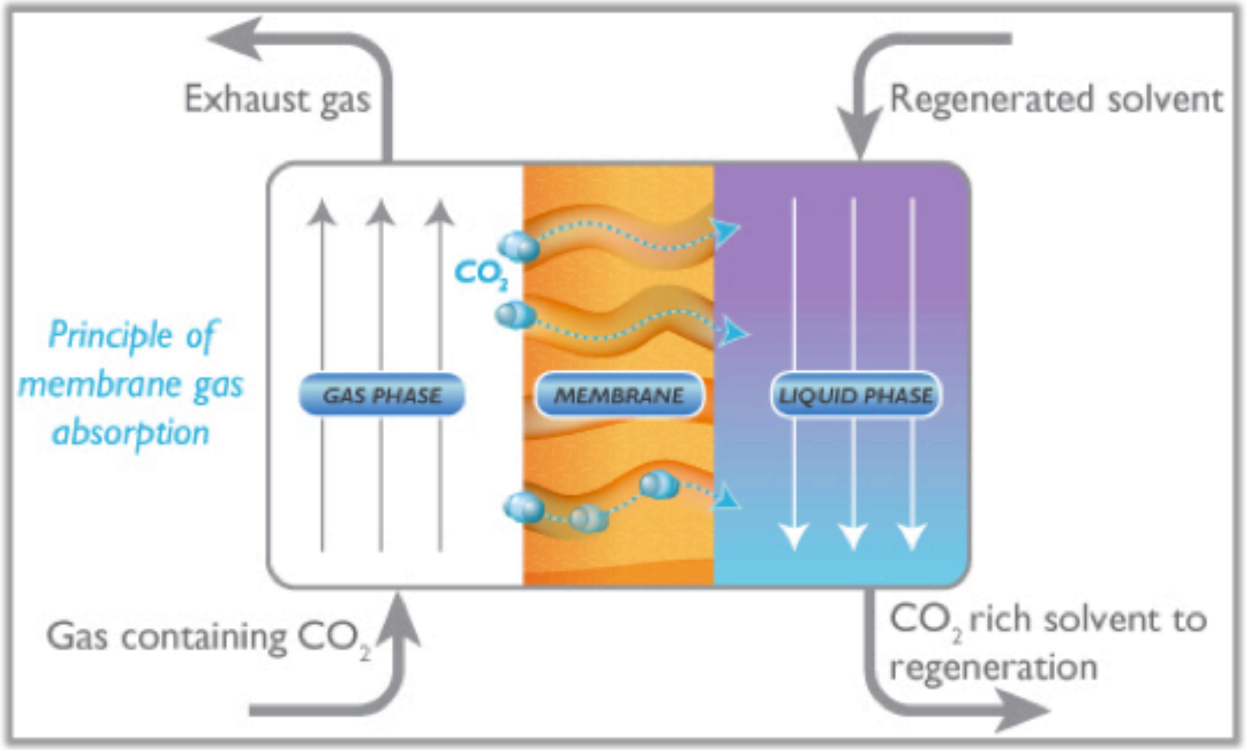


FIGURE 1: Gas Absorption via Membranes (Reproduced from: "CO2 Capture/Separation Technologies." *CO2CRC* http://www.co2crc.com.au/aboutccs/cap_membranes.html)

Objectives

- To develop fabrication methods that yield composite membranes with consistent CO_2 separation performance
- To measure the CO_2 permeance and ideal CO_2/N_2 selectivities as a function of pressure for three systems: (1) uncoated polyacrylonitrile (PAN) and polyethersulfone (PES) membranes, (2) support membranes coated by a fluorinated polymer gutter layer, and (3) support membranes coated consecutively by the gutter layer and a CO_2 selective layer of perfluorocyclobutyl (PFCB) polymer (Detailed in Figure 2)

Experimental Methods

- ❖ Bare membranes were washed in a MeOH bath and then dried.
- ❖ Membranes were then dip-coated into a fluorinated polymer acting as the gutter layer and vacuum dried.
- ❖ Plasma treatment followed proceeded by a water soak period before coating the membrane in the CO_2 selective PFCB layer.
- ❖ A permeance testing apparatus (Figure 3) was then utilized to determine the permeance by inducing various pressures across the membrane and recording the flux.

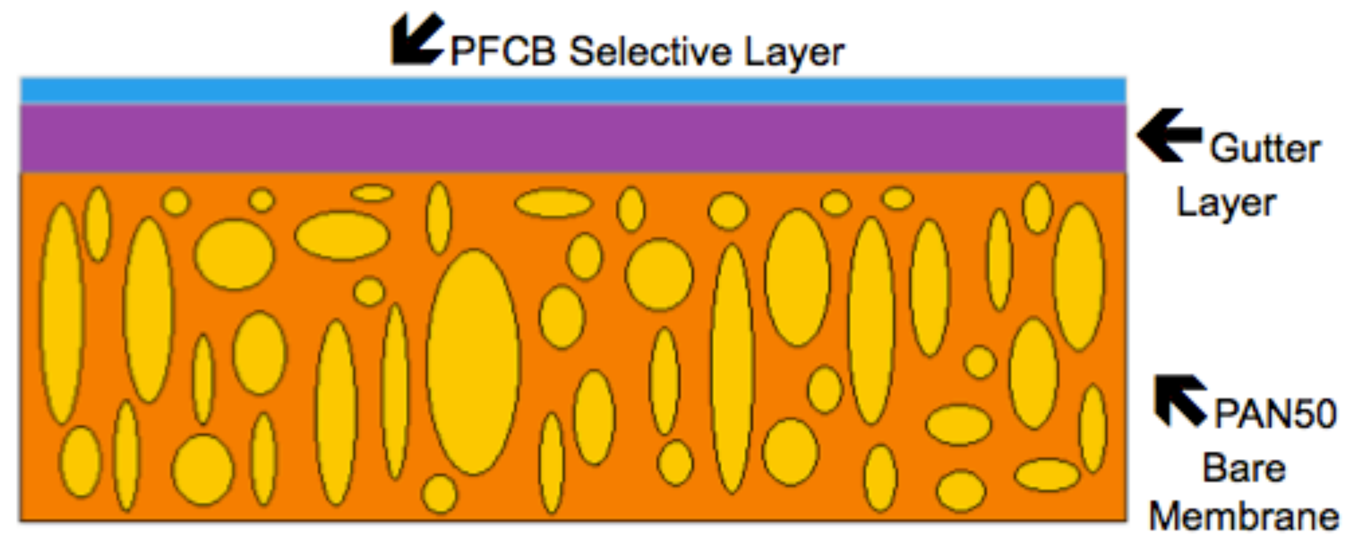


FIGURE 2: Composite Membrane

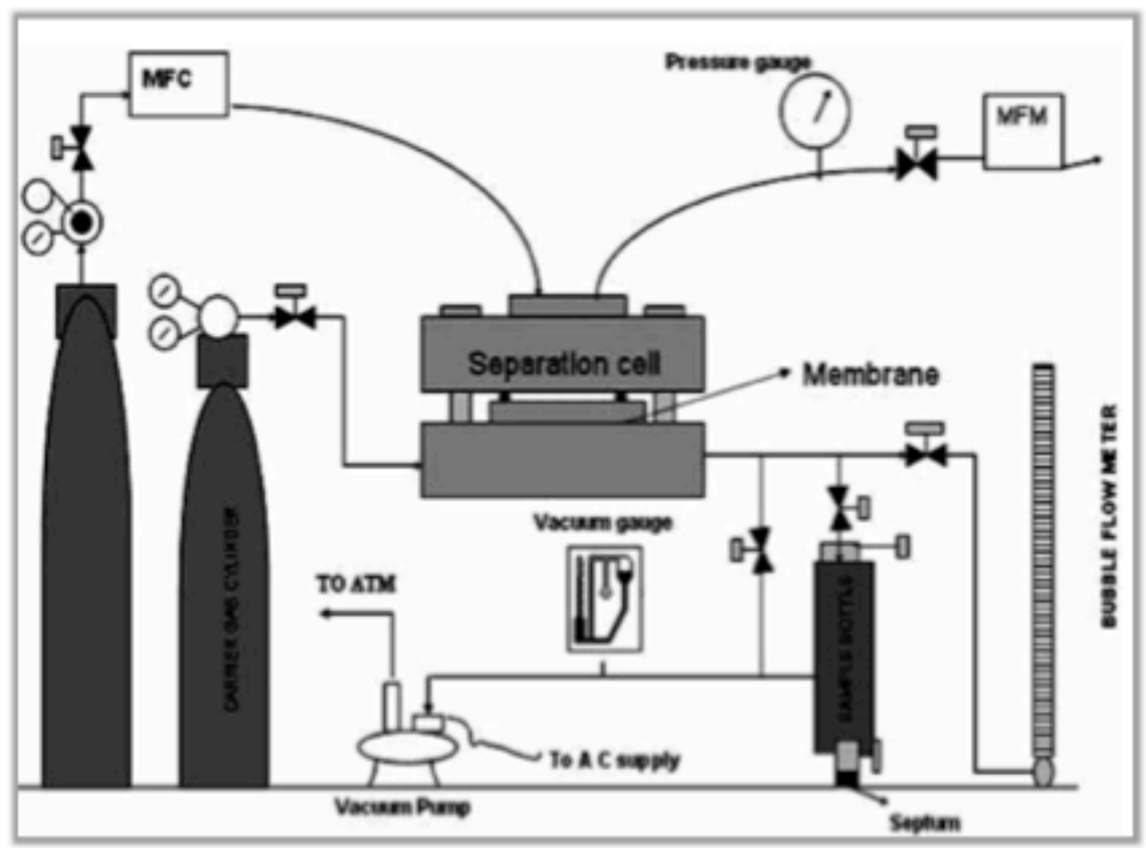
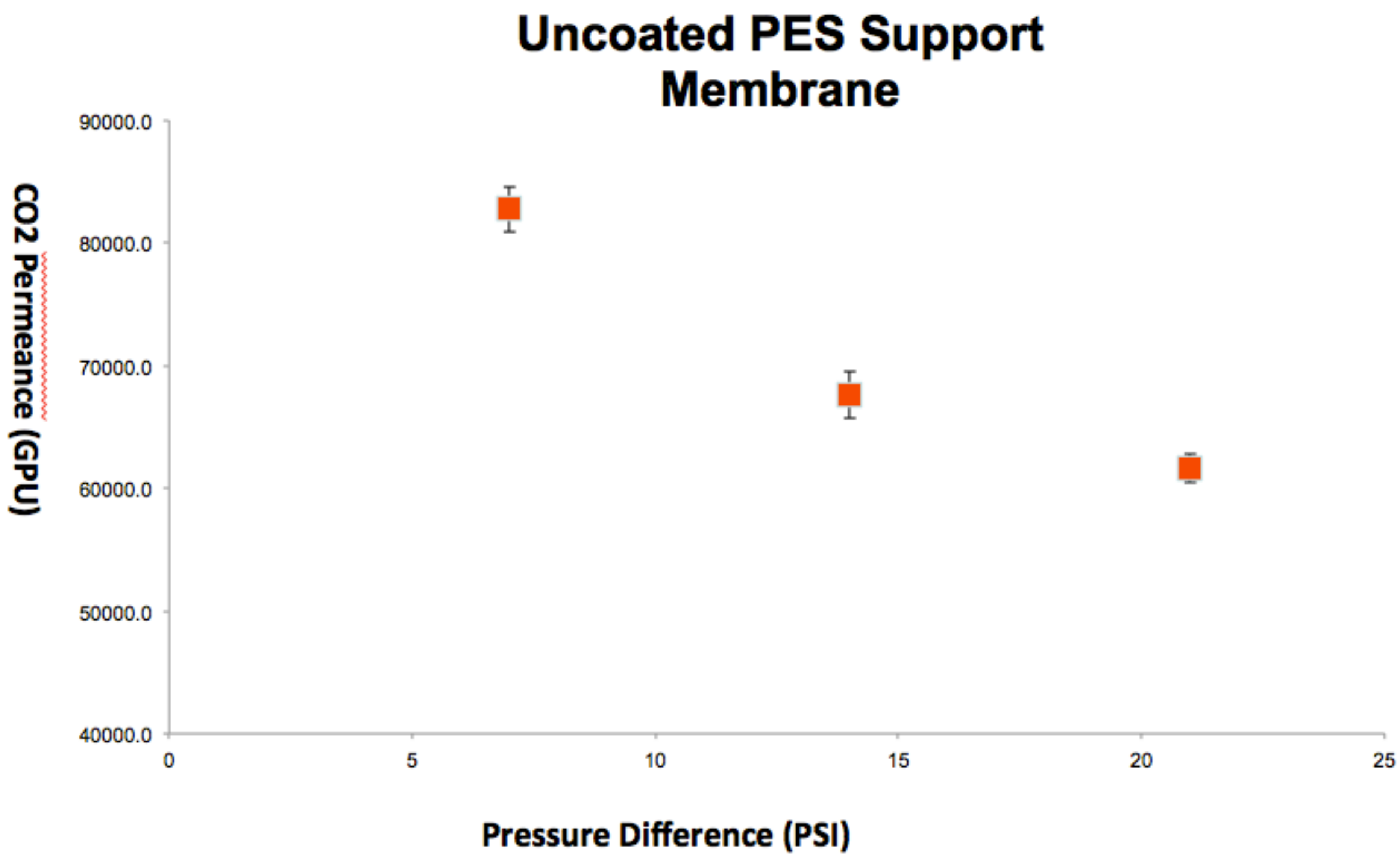


FIGURE 3: Experimental Setup for Gas Separation Testing (Reproduced from: Sridhar, S. et al. *Separation and Purification Reviews* 36.2 (2007): 113-174)

Results and Discussion



Selectivity

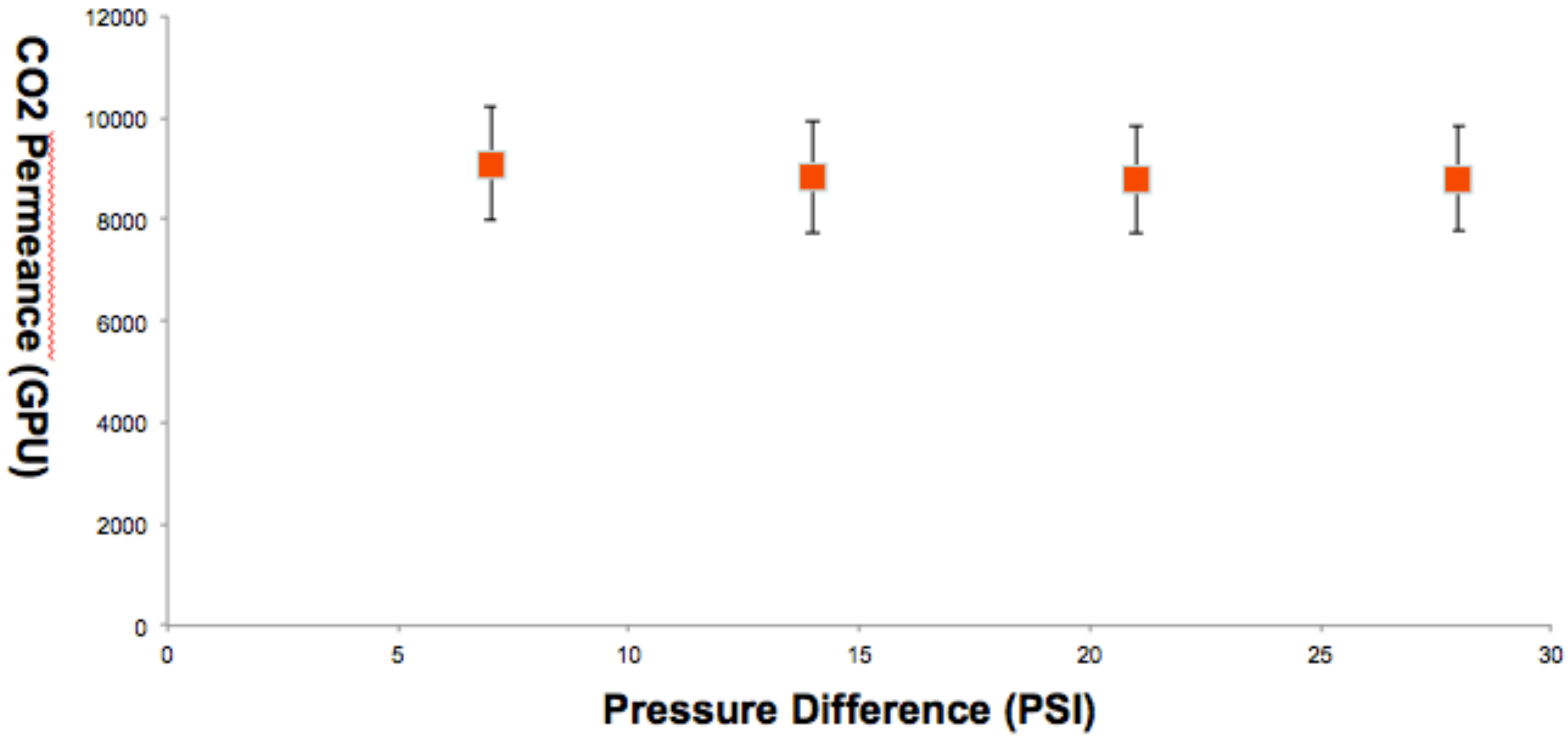
ΔP (PSI)	CO2/N2
7	0.848±0.005
14	0.817±0.005
21	0.790±0.14

Pore Size

ΔP (PSI)	(nm)
7	50.9±4.2
14	39.8±3.1
21	26.3±17.6

- Selectivity and pore size is agreeable with the Knudsen Diffusion mechanism

Coated and Untreated PES20 membrane



Overall Selectivity

ΔP (PSI)	CO2/N2
7	4.95±0.23
14	5.20±0.01
21	5.01±0.02
28	4.96±0.01

Intrinsic selectivity of the gutter layer

ΔP (PSI)	CO2/N2
7	5.49±0.21
14	5.59±0.31
21	5.55±0.36
28	5.32±0.28

- The composite membrane made before plasma treatment is reasonably consistent
- Intrinsic selectivity estimated through the resistance equation is different from the overall performance of the composite

Resistance Equation

$$\frac{1}{Perm_T} = \frac{1}{Perm_{GL}} + \frac{1}{Perm_{BM}}$$

Surface Modification Performance Data

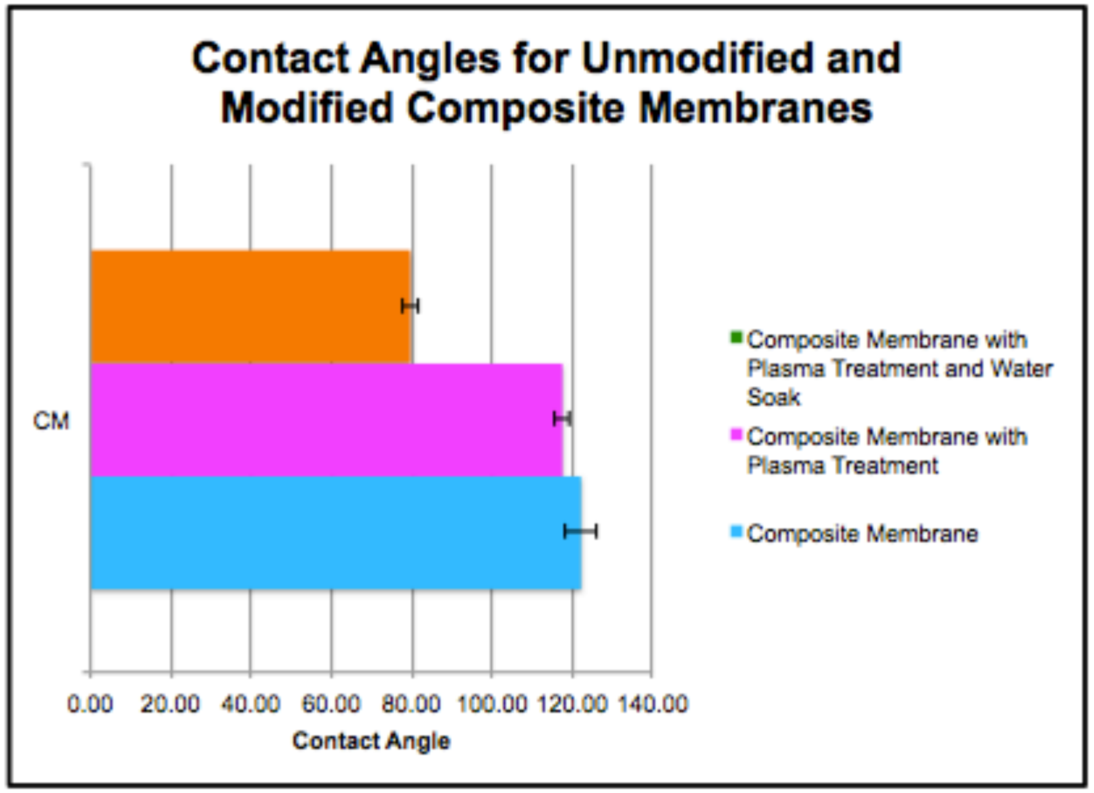


FIGURE 6: Contact Angle Measurements for Modified and Unmodified Composite Membranes

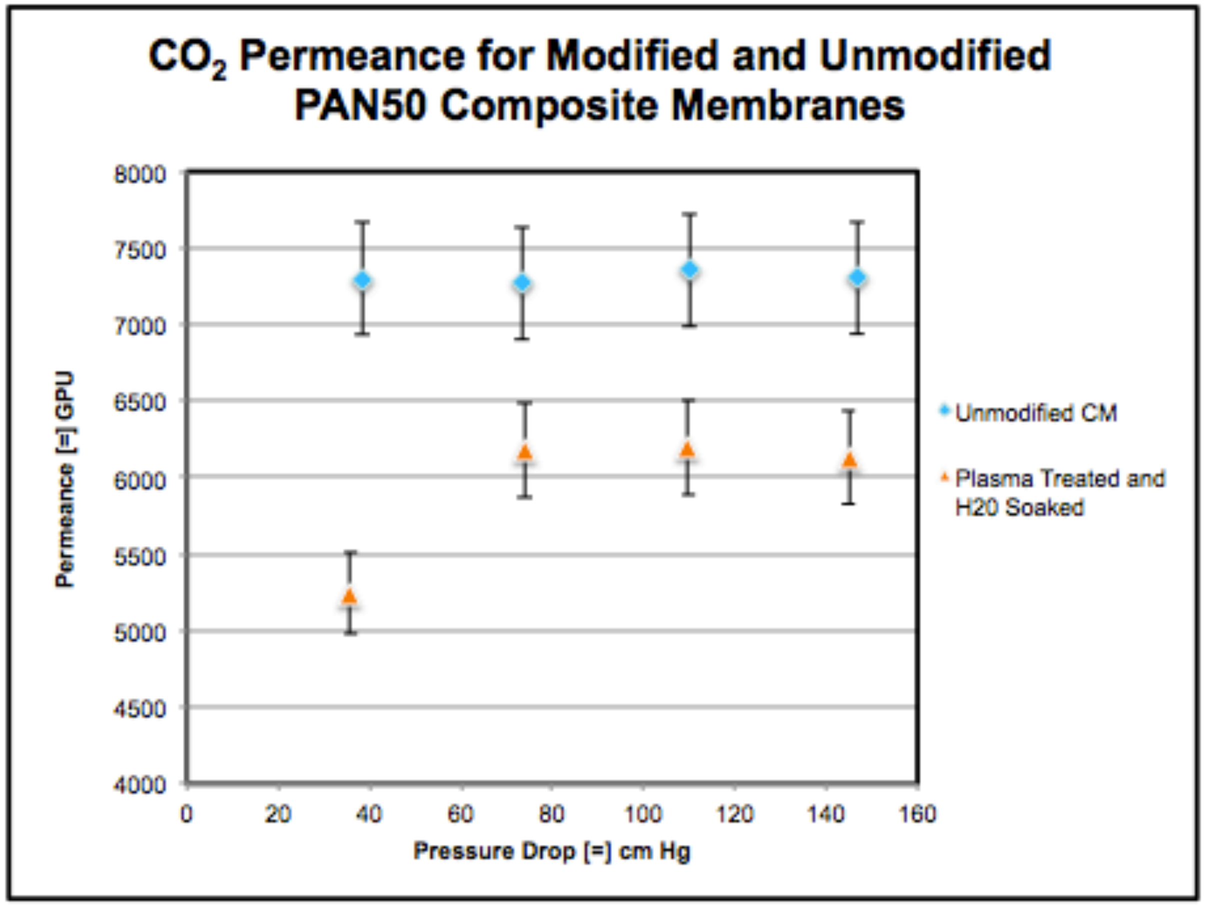


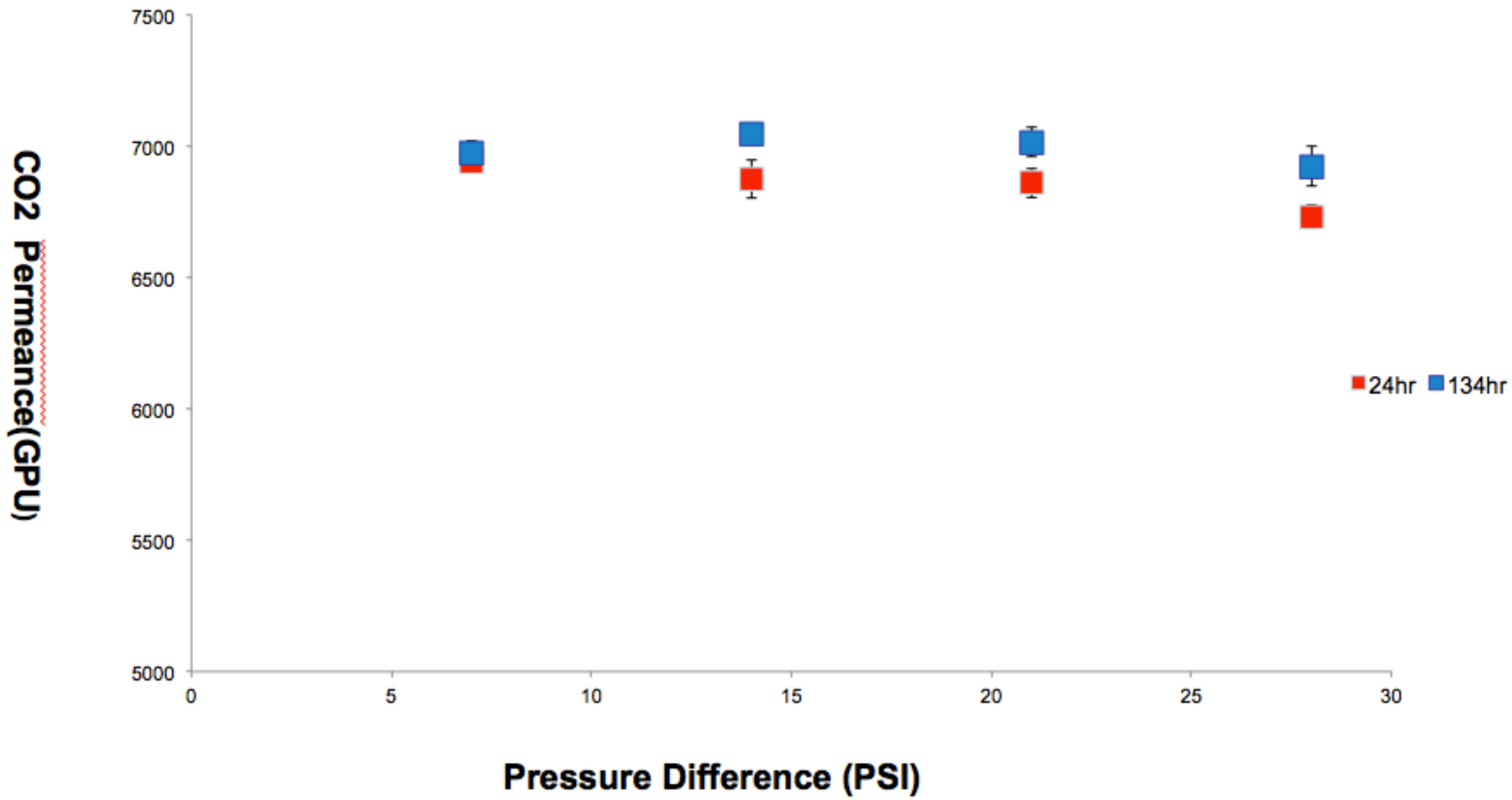
FIGURE 7: Modified and Unmodified CO_2 Permeance for Composite Membrane

- Membrane modification (e.g., Argon plasma treatment and water soak) increased the surface energy of the membrane while etching minimal amounts of gutter layer from the surface.
- Modification decreased permeance and CO_2/N_2 selectivity.

TABLE 2: Modified and Unmodified Composite Membrane Selectivities

ΔP	Unmodified CO_2/N_2	Modified CO_2/N_2
7	5.28 ± 0.039	4.70 ± 0.036
14	5.05 ± 0.053	4.81 ± 0.035
21	5.03 ± 0.028	4.75 ± 0.025
28	4.93 ± 0.072	4.71 ± 0.03

Aging Effects of Treated and Washed Composite Membrane



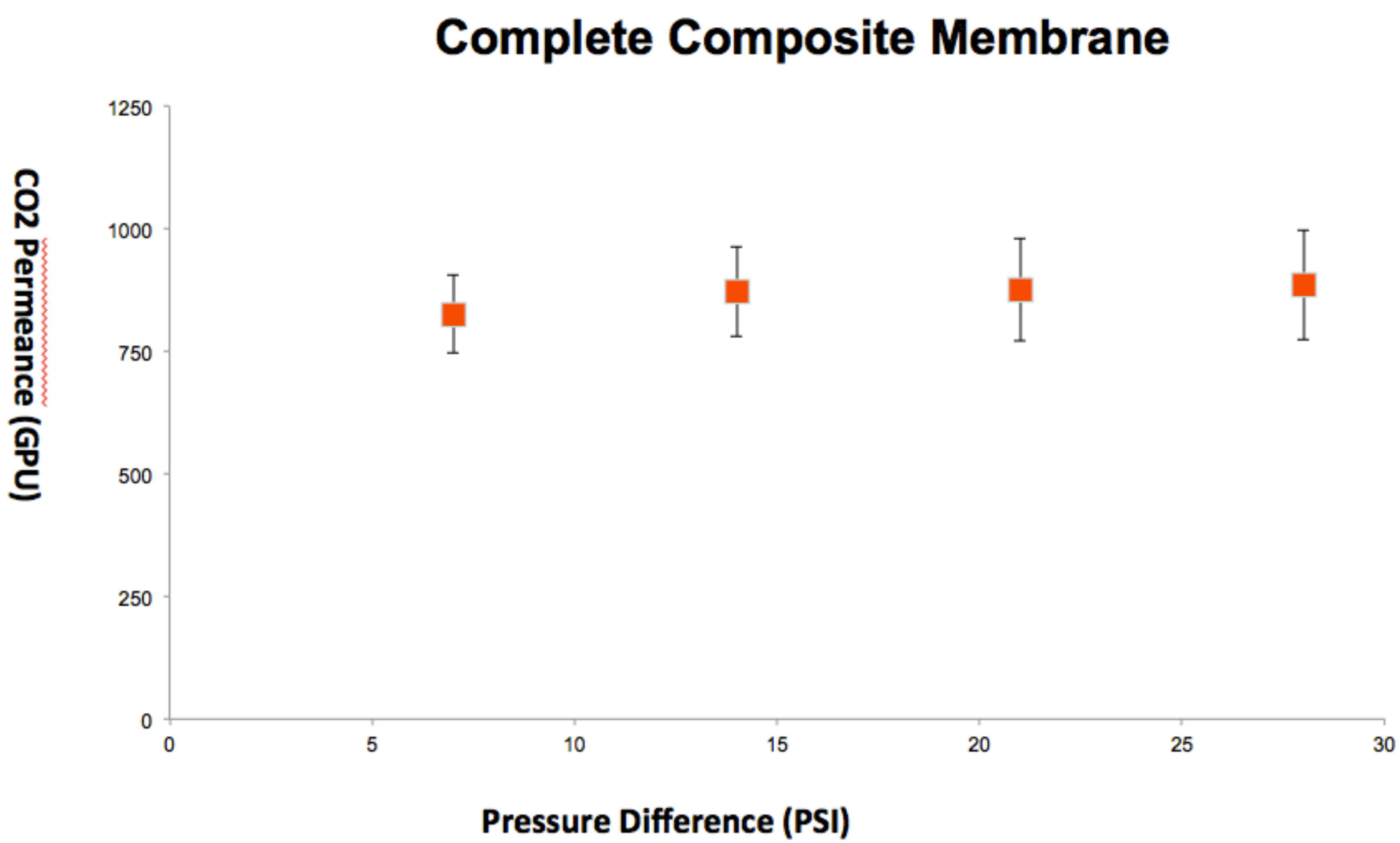
Overall Selectivity 24hr

ΔP (PSI)	CO2/N2
7	5.17±0.05
14	4.98±0.04
21	4.90±0.11
28	4.66±0.03

Overall Selectivity 134hr

ΔP (PSI)	CO2/N2
7	5.20±0.01
14	5.01±0.02
21	4.96±0.01
28	4.71±0.04

- After 110 hours of physical aging, the permeance of the membrane increased slightly while the selectivity remained the same
- The cause is likely evaporating water



Overall Selectivity

ΔP (PSI)	CO_2/N_2
7	7.68±0.04
14	8.11±0.41
21	7.94±0.31
28	8.13±0.63

- Low selectivity suggests defects on the surface of the thin film

Conclusions

- The composite membrane fabrication process proved to be highly sensitive to each procedural step, mandating consistency in the methodology for constructing these membranes.
- Intrinsic permselectivity values for the gutter layer and PFCB layer can be modeled by resistance in series.
- Permeance values, relatively high compared to current literature reports, decreased with the addition of each polymer layer; however, selectivity was greatly increased.

Future Work

- A study of plasticization effects on the CO_2 selective PFCB layer can potentially elucidate the impacts of plasticization.
- Industrial applicability of this composite membrane technology can be determined by carrying out permeance testing utilizing a mixed gas composition (Figure 8).

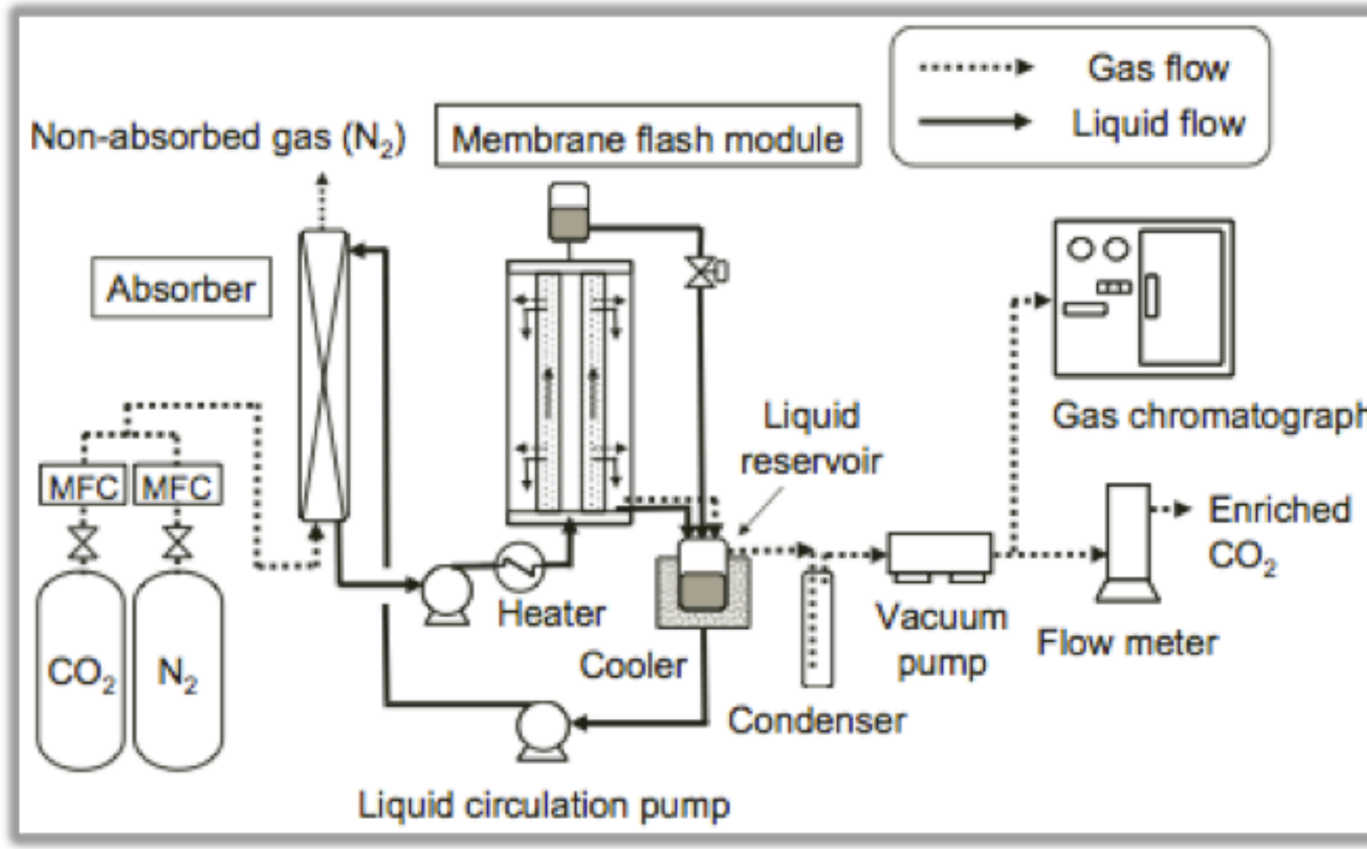


FIGURE 8: Experimental Setup for Mixed Gas Separations (Reproduced from: Okabe, K. et al. *Energy Procedia* 1.1 (2009): 1281-1288)