SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Zoe Barnette
FACULTY ADVISOR:	Dr. Casey O'Brien
PROJECT PERIOD:	Summer 2021
PROJECT TITLE:	Polyvinylamine-based Facilitated Transport Membranes for CO_2 Capture
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**(X) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution ( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Determine how PVAm affects membrane performance	Adding PVAm to solution led to better CO_2 permeance and selectivity. It also increased membrane stability when test for long times and at high temperatures.	70%
Determine which quaternized PVP performs best	A C2-PVP membrane performs best with the highest permeance and selectivity.	90%
Determine how the pH of the solution affects the membrane	PVAm has a pH of 10/11, so a higher PVP pH allows for best mixing and ultimately better performance. A pH of 8/9 had the highest permeance, but a pH of 10/11 was more stable.	50%
Determine the optimal solution conditions to achieve the best performance	So far, a 16% C2-PVP + 0.6% PVAm solution at a pH of 8/9 has performed the best but was not very stable.	40%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	(Sponsor, Project Title, PIs, Submission Date, Proposal Amount)
EXTERNAL AWARDS RECEIVED	(Sponsor, Project Title, PIs, Award Date, Award Amount)
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	(Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	(Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s)
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	(Event, Presentation Title, Presentation Date, Location)
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	(Purpose, Title, Date Received)
INTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
EXTERNAL COLLABORATIONS FOSTERED	(Name, Organization, Purpose of Affiliation, and Frequency of Interactions)
WEBSITE(S) FEATURING RESEARCH PROJECT	(URL)
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models,	(Please describe each item in detail)

curricula, instruments, education programs, outreach for ND Energy and other groups)	

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

I really appreciated my time in the O'Brien lab because there was something new to do or make each day. I had worked in a biochem lab before, but I performed the same task over and over again which I did not find interesting. I really enjoyed the exploration process that I was a part of because I could see the progress we were making in terms of finding the perfect solution — it was almost like a puzzle.

I am also very interested in the renewable energy field within chemical engineering, so this was a great chance to get involved in some of the developing work in this field. As I continue my career path, whether in industry or research, this experience will be a great reference for the potential technology that could help our environment.

Everyone in the lab was very welcoming and full of great advice about graduate school. They were always willing to answer any questions I had about the lab work as well as help me through some of the more difficult lab techniques. Overall, I found this research experience very engaging and informative. More time is needed to find the optimal solution, but unfortunately I am only working in this lab for the summer. I look forward to seeing the lab's future findings!

FINAL WRITTEN REPORT

Current industrial scale CO_2 capture and CO_2 conversion technologies rely on inefficient steps, such as energy-intensive regeneration and limited mass transfer due to dilute atmospheric CO_2 concentrations. The development of a catalytic polymeric membrane technology could improve upon current practices by acting as both the capture and conversion medium of CO_2 , eliminating the regeneration step and producing value-added chemicals. Figure 1 is a schematic of the catalytic membrane system, showing both the CO_2 capture and conversion steps.

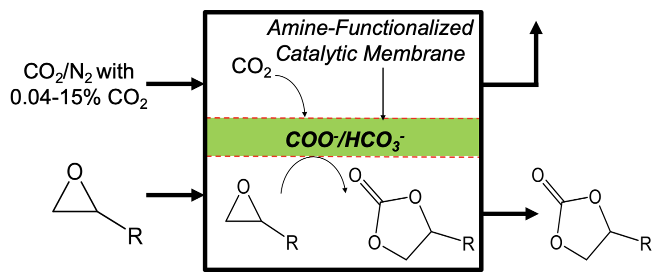

Figure 1. Schematic Representation of the Amine-Functionalized Catalytic Membrane System

As Figure 1 shows, the membrane (green) captures CO_2 from the air, transports it through, and then reacts the CO_2 with a epoxide ring to form a cyclic carbonate. These cyclic carbonates are very favorable to produce because (1) no CO_2 bonds are broken and (2) they can continue into valuable chemicals for cosmetics, paint, and even food. This catalytic membrane process would not only eliminate some of the CO_2 from the air but also produce molecules with a lot of diverse potential.

The main objective of this summer's research project was to determine what variations of quaternized poly(4-vinylpyridine) membrane allow for the best v permeance as well as the best CO_2 over N_2 selectivity. It is difficult to achieve both a high permeance and a high selectivity. Increasing permeance means allowing more CO_2 through which generally increases the amount of N_2, ultimately lowering the selectivity. However, by altering the PVP structure, the pH, the addition of polyvinylamine (PVAm), and the concentrations, the best solution could be tested using gas chromatography.

All of the membranes tested had a quaternized poly(4-vinylpyridine) base — a particularly promising polymeric membranes due to their high CO_2 permeance and high selectivity, derived from their unique facilitated CO_2 transport mechanism and their high catalytic activity for cyclic carbonate synthesis. The structure was altered by adding a carbon chain to the nitrogen atom in the PVP. Carbon chain lengths ranged from C1 to C12. The recent data shows that a bromoethane quaternized PVP-based polymer (C2-PVP) performs the best overall to achieve a high CO_2 permeance and a decent CO_2 to N_2 selectivity ratio when tested at room temperature. Graphs **A**, **B**, and **C** in Figure 2 compare the permeance and selectivity of C1, C2, and C3, respectively.

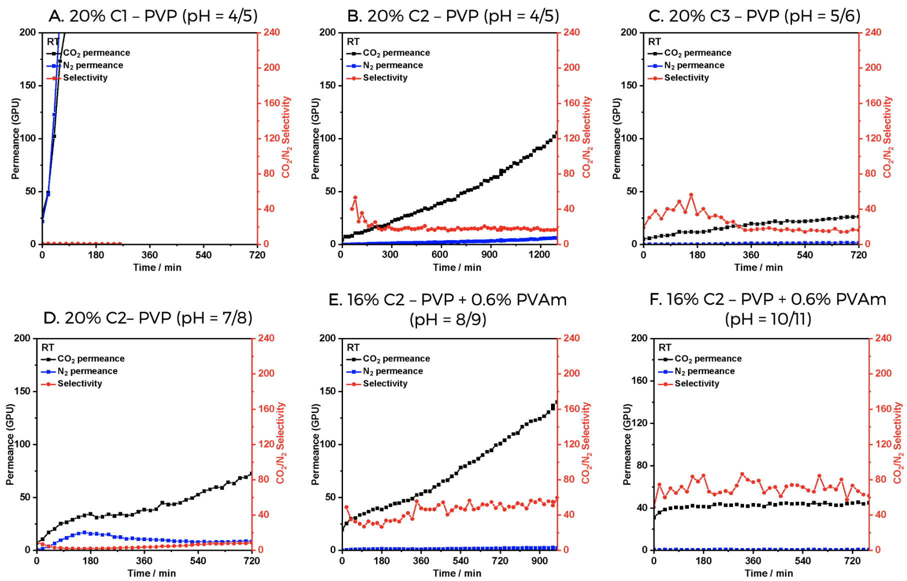

Figure 2. Time vs. CO_2 Permeance (black), N_2 Permeance (blue), and CO_2/N_2 Selectivity (red) for Different PVP Membranes

Graph **B** shows the greatest CO_2 permeance of the top row and a decent selectivity. Graph **A** for C1-PVP has no selectivity and graph **C** for C3-PVP has a very low permeance. Graphs **E** and **F** demonstrate the membrane performance when PVAm is added. PVAm is a fixed-carrier polymer known to stabilize membranes. In this case, it also increases CO_2 permeance and selectivity. The pH levels of the PVP solution were altered as well. Without the PVAm, a pH of 4/5 (Graph **B**) performed better than a higher pH of 7/8 (Graph **D**). However, pH levels were also altered before adding PVAm which has a natural pH of 10/11. In this case the higher pH PVP solutions performed better, most likely due to better mixing. Graphs **E** and **F** are at two different pH levels and pose an interesting result. Both have fairly similar selectivity values, but graph **E** has a higher CO_2 permeance. Graph **F**, on the other hand, is much more stable, but at a lower permeance. Both stability and a high CO_2 permeance are preferred so it is difficult to choose just one as the best. The concentrations of PVP and PVAm were also varied to improve solution mixing as well as to adjust for any imbalance between permeance and selectivity due to polymer-type or pH changes. A concentration of 20% PVP to water showed the best results and are used in Figure 2.

So far, the best mixed solution so far is 20% C2-PVP with a pH 8/9 mixed with 3 % PVAm to form the solution in Graph **E**. Further experimentation is needed to find the optimal solution to produce both high permeance and selectivity as well as ensure stability. Doing so would aid future work on CO_2 conversion via epoxides into cyclic carbonates to eventually produce those valuable chemicals.