SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Daniel O'Connor
FACULTY ADVISOR:	Casey O'Brien
PROJECT PERIOD:	May 22 – July 28
PROJECT TITLE:	Tuning CO2 Conversion of Amine-based Polymer Catalyst Through Structural Modification Via Quaternization
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**( ) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear ( ) Smart Storage and Distribution ( ) Transformation Solar (x) 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
Study how chain length affects P4VP performance as catalyst	Determined a positive trend between chain length and catalytic activity	95%
Study how differing alkyl halides affect P4VP performance as catalyst	Determined iodine had preformed better in wet conditions compared to Bromine	80%
Study how crosslinking P4VP affects its performance as a catalyst	Determined crosslinking successfully improved stability	75%

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
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	Data collected expected to be used in future paper.
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	Summer Undergraduate Research Symposium Poster Presentation, July 27, University of Notre Dame

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?

My research experience allowed me to continue my data collection for the research I had been doing throughout the previous year. My grad advisor was a huge help and was always available to answer questions. This experience also helped me discern what I would like to do after graduating.

FINAL WRITTEN REPORT

As global temperatures continue to rise, reducing the Carbon Dioxide concentration in the atmosphere becomes an increasingly prominent global concern, with current sorbent-based methods for removing CO_2 from the atmosphere being inefficient and energy intensive. Developing a catalytic membrane that can integrate CO_2 capture and conversion into a single unit process has the potential to offer a more energy efficient and cost-effective alternative for reducing the CO_2 concentration in our atmosphere. Through previous work, poly(4-vinylpyridine) (P4VP) based membranes have shown to be permeable and selective for CO_2 separation from mixed gases and are catalytically active for cyclic carbonate synthesis at mild temperatures. The primary objective for my research was to study how various structural modifications achieved with differing alkyl halides impact the catalytic activity and stability of P4VP for the reaction of cyclic carbonate synthesis from CO_2 and Epichlorohydrin. P4VP samples with varying chain lengths and halide groups, shown in figure 5, were tested within batch reactions for their catalytic activity in dry and wet conditions. A concern stemming from these experiments was the instability of longer chained quaternization samples, which out preformed shorter chained samples with respect to cyclic carbonate production at the cost of being more soluble. To tackle this challenge various crosslinked quaternization samples with varying chain length and halide group were created and tested in dry and wet conditions. Figure 8 and 9 display the results.

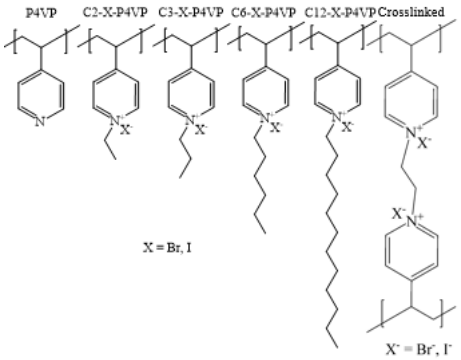

Figure 5. Sample P4VP structures tested in this study

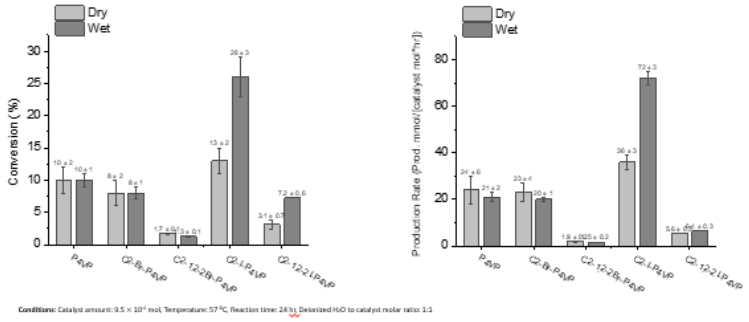

Figure 8. Conversion and production rate comparing alkyl halides and crosslinking

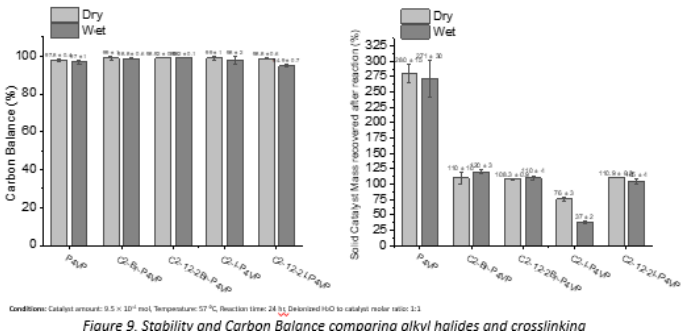

Figure 9. Stability and Carbon Balance comparing alkyl halides and crosslinking

From these results we see Iodine showed higher performance than Bromine; Bromine's performance was further hindered in wet conditions while Iodine demonstrated improved performance. Bromine's higher electronegativity and nucleophilicity led to interference in interactions with water leading to this reduced performance. By examining the crosslinked data, we found crosslinking samples decreased performance greatly due to these samples having their active sites connected and therefore less available for reactions. From figure 9 we see quaternized samples generally showed higher Carbon Balance due to not quaternizing with the reactants since it is already quaternized. This is also why the recovered catalyst for unquaternized P4VP is nearly three times the original amount. While Bromine and Iodine samples exhibited differing results, in general crosslinking increased stability at the cost of performance for both.

From my research we were able to conclude that less electronegative counter ions such as iodine are preferable for quaternizing the catalyst as it performed better in wet conditions. This is preferable because the air is humid and therefore our CO_2 capturing membrane would ideally perform well in the presence of water. We also determined crosslinking effectively improves stability (at the cost of conversion efficiency) thus crosslinking with longer chained alkyl dihalides is favorable due to increasing performance while retaining stability, presenting viable options for membrane preparation due to bulkier alkyl groups showing higher CO_2 conversion because they increase halogen counter ion availability for reaction by interfering with the intermolecular bond with the pyridine group cation and halogen counter ion.