PROJECT REPORTS

RESEARCH PROJECT REPORTS

THRUST 4:

PROCESS SYNTHESIS & DESIGN, LIFE CYCLE ANALYSIS AND ENVIRONMENTAL IMPACT

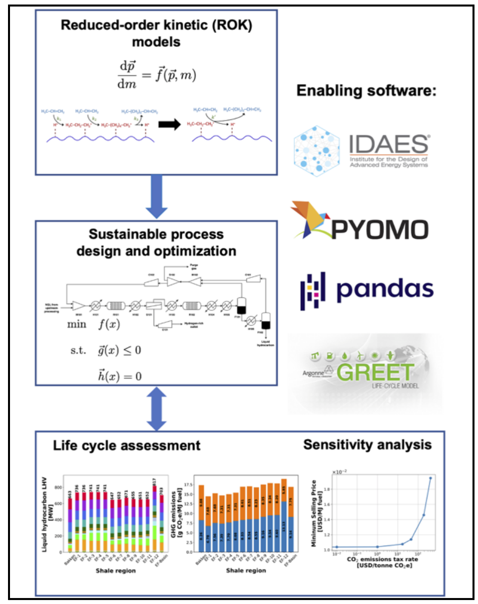
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T4P8 Multiscale Modeling for Reactor Design and Optimization* ***Project Lead:*** *Alexander Dowling (UND)*

F: Alexander Dowling (UND)
GS: Kanishka Ghosh (UND), Damian Agi (UND – new)

Project Goals

- Overall: develop mathematical modeling and computational approaches to integrate Thrust 2 data (microkinetic (MK) simulations, laboratory observations, chemical intuition) into oligomerization reactor design.
- Embed reduced order kinetic (ROK) models built/validated with Thrust 2 data into AspenPlus simulations (in collaboration with Purdue team for other Thrust 4 projects).
- Perform detailed reactor design optimization; via sensitivity analysis, set performance goals and identify opportunities for oligomerization catalysis improvements.



Barriers

- Thrust 2 microkinetic models include O(4000) rate laws and O(900) species. It is computationally intractable to include these models directly in process simulations (especially with recycle streams).
- Existing microkinetic model reduction strategies have only been applied to systems with a single product of interest. In contrast, for oligomerization, it is critical to predict the product distribution.

Methodologies

- Perform nonlinear regression and model selection to build reduced-order kinetic models.
- Numerical solve nonlinear dynamic optimization problems to compute optimal reactor design.
- Perform life cycle analysis.

Research Achievements

- Published paper on reduced order modeling and dynamic optimization strategy. https://doi.org/10.3389/fceng.2022.898685
- Incorporated ROK model into full process optimization with life-cycle analysis (LCA). Demonstrated modeling and optimization reduces GHG emissions up to 30% compared to literature. This highlights the importance of more accurate oligormization models. Manuscript is under review/revisions with *ACS Sustainable Chemistry & Engineering.*
- K. Ghosh successfully defended PhD and joined Eli Lilly as a research scientist. D. Agi joined CISTAR to continue this project.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:**

This project provides a critical link between Thrust 2, Thrust 4, and Thrust 7, Ultimately, the oligomerization reactor is one of the (if not the) most important unit operations for a CISTAR process to deliver specific products.

- **Abstract:**

In this project, we explore reduced-order kinetic (ROK) models to incorporate molecular-level detail in reactor design and ultimately provide bottom-up and top-down systems analysis for novel CISTAR processes. We first seek to determine if existing oligomerization reduced-order kinetic models from literature adequately emulate microkinetic model predictions in an effort to reduce the size and complexity of the kinetic differential equation model to be used for detailed reactor design. We use weighted least-squares approach to reparametrize the reduced-order model using a library of 73 microkinetic model simulations (from Thrust 2) over a range of temperatures, pressures, and flow conditions. The fitted reduced-order kinetic (ROK) models are simulated over process-relevant operating conditions to determine thermodynamic and kinetic extrapolability and differentiate between candidate models with comparable in-sample fit quality. Next, an iterative model identifiability analysis is performed to reduce parameter "sloppiness" and improve parameter estimate confidence. Finally, we use nonlinear optimization to compute the optimal reactor temperature profiles, catalyst loading, and feed compositions to maximize the production of high-value olefins to be used as gasoline and diesel additives. Orthogonal collocation on finite elements is applied to discretize the differential algebraic equation model into sparse algebraic constraints that are efficiently solved with Ipopt in the Pyomo modeling environment.

Reactor optimization results indicate significant differences in predicted conversion and product distributions stemming from model-form uncertainty associated with reduced-order kinetic model choice and fit quality. Quantification of this uncertainty and its propagation to the process level will facilitate more confident predictions and robust process design. Recent results from this past year successfully integrate the ROK models into a large process optimization with rigorous heat integration and life cycle analysis.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

This past year successfully integrate the ROK models into a large process optimization with rigorous heat integration and life cycle analysis. Here is the abstract for a manuscript summarizing these key finding under revision for *ACS Suistainable Chemistry & Engineering*.

Shale gas is revolutionizing U.S. and global energy and chemical commodities and can serve as a bridge fuel to a sustainable decarbonized economy. This work develops an equation-oriented (EO) multiscale modeling framework in open-source IDAES that tractably incorporates microkinetic detail in process design using reduced-order kinetic (ROK) models along with simultaneous heat integration and life cycle analysis. Using multiscale and multiobjective optimization, we simultaneously minimize the minimum selling price of liquid hydrocarbons (e.g., liquid fuels/additives from shale gas) and process emissions (via a CO_2 tax). Optimization reduces GHG emissions per MJ fuel produced by over 35\% compared to literature and achieves a carbon efficiency of 87%. The optimizer changes the recycling rate, temperatures, and pressures to mitigate the effect of ROK model-form uncertainty on product portfolio predictions. Moreover, we show the optimal process design is insensitive to changing the CO_2 tax rate. Finally, EO enables a fast sensitivity analysis of shale gas composition variability across 12 regions of the Eagle Ford basin. These results highlight the benefits of the open-source EO approach: fast, scalable, customized, and reproducible systems analysis and optimization for sustainable energy technologies beyond shale utilization.

- **Interdependence:**

This project is at the interface of Thrusts 2 and 4/7. As such, Prof. Dowling and graduate student Ghosh (now Agi) regularly participate in recurring meetings for both Thrusts and help facilitate broader communication.

- **Testbed Impact and Value:**

This project, which develops oligomerization reactor modeling and optimization capabilities, is relevant to both Testbeds 1 and 2.

<u>Section 3: Specific Plans for Next 12 Months</u>

Challenges and Current Status:

Our work to date has demonstrated the overall approach is valid to model oligomerization on Bronsted acid zeolites. Moreover, we have show how to use these models for process optimization with life cycle analysis.

- **Specific Plans - (i) Improve and validate ROK models and extend to other catalysts:**

By design, the library of ROK models can be adopted to emulate oligomerization and cracking reactions irrespective of the feed olefin. Similar to our current approach, we will use ethylene oligomerization microkinetic model simulations to recalibrate the ROK models and analyze them for thermodynamic and kinetic extrapolability. Currently, we have access to a set of simulations at low conversion from Thrust 2 for ethylene oligomerization using Nickel-acid zeolites which will be used to validate the ROK models. Access to testbed experimental data will help improve the fidelity of the models further. During the next year, we will continue to work with Thrust 2 and deepen collaborations with the Testbeds to obtain these data. As the microkinetic model for ethylene oligomerization evolves, we need to be mindful of the modeling assumptions for each iteration of the model and maintain separate instances of the ROK models. As a contingency, if the ROK modeling approach proves not transferable to ethylene oligomerization, we will pivot to machine learning based surrogate models (e.g., Gaussian process regression) to predict the product distribution.

- **Specific Plans - (ii) Evaluate possibility to consider membrane reactors**

D. Agi and Prof. Dowling bring extensively expertise in modeling membrane reactors from a previous research project. During this next year, we plan to explore how our modeling expertise complements ongoing experimental efforts in CISTAR. Our goal is to assess if there is a low-effort/high-value opportunity to leverage our existing generalized modeling methods.

<u>Section 4: Papers and IP</u>

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Agi, D., Jones, K.J, Watson, M.J., Lynch, H.G., Dougher, M., Chen, X., Carlozo, M.N., Dowling, A.W., "Computational toolkits for model-based design and optimization," *Current Opinion in Chemical Engineering*, revisions submitted.
2. Ghosh, K., Salas, S.D., Garciadiego, A., Dunn, J.S., Dowling, A.W., "Multiscale Equation-Oriented Optimization Decreases the Carbon Intensity of Shale Gas to Liquid Fuel Processes," *ACS Suistainable Chemistry & Engineering*, under revision.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T4P10 Decarbonization of Alkane Dehydrogenation Reactors Through Renewable Electric Heating*
Project Lead: *Cornelius Masuku (PU)*

F: Rakesh Agrawal (PU), David Bernal (PU), Fabio Ribeiro (PU), Jeff Siirola (PU)		
GS: Yufei Zhao (PU)		
PD: Chengtian Cui (PU)	**UG:** John R. Ueding (PU)	**S:** Yury Zvinevich (PU)

Project Goals

- To produce a number of Electrified Reactor Designs for the most Energy Intensive Endothermic Reactions in the Chemical Industry, such as Ethane Dehydrogenation, and Steam-Methane Reforming among others.

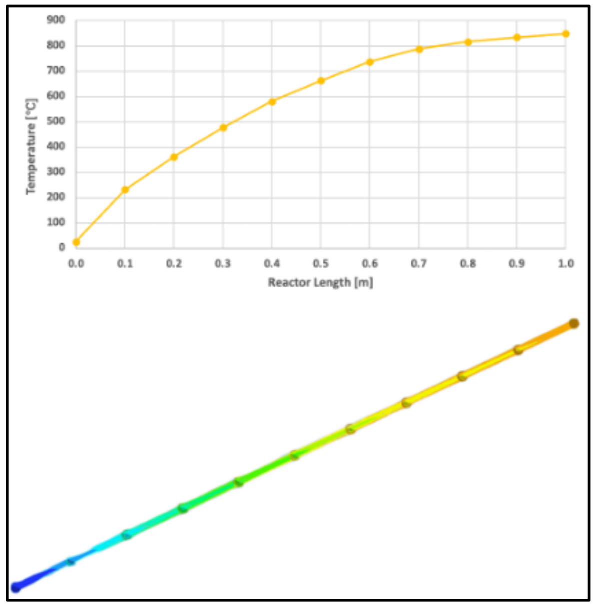


Figure 1: Computational Fluid Dynamics Model Results

Barriers

- The main barrier is the construction of the new types of reactors. Some of the concepts to be applied have been known for a while but have never been applied to chemical reactors. This opens up opportunities for the integration of cross-disciplinary concepts for the advancement of the Chemical Industry.

Methodologies

- Aim to start with a Resistive heated Ethane Cracking Reactor;
- Then follow up with an Inductive Heated Ethane Cracking Reactor;
- Use the information from those initial designs to inform a new Electrified design for Steam-Methane Reformer (SMR).

Research Achievements

- Relevant literature has been reviewed.
- Preliminary calculations have been made on ANSYS packages:
  - A simplified reactor design with inductive coils has been simulated on ANSYS Maxwell 3D to calculate the electrical properties required to generate the energy required for the reactor.
  - Information from the Maxwell 3D model was sent to ANSYS Steady-State Thermal to get the full temperature profile of the reactor structure.
- This information will be sent to ANSYS Fluent to incorporate the fluid flow and the temperature profile of the fluid.
- We have also developed a dynamic heterogeneous SMR reactor model in Aspen Custom Modeler to simulate the dynamic response of the reactor.

Section 2: Project Summary Brief

The initial focus of the project is on the design of an inductively heated Steam-Methane reforming reactor as an example of the widely applied endothermic process in the chemical industry. The initial simplified design with homogeneous kinetics has been implemented in ANSYS packages. The next step is to implement a 2-D heterogeneous model. Few design parameters will be considered such as heating rate, different current flows to different parts of the reactor, the dynamic response of the reactor to changes in the heat profile, among others. The most promising design will be demonstrated at a laboratory scale.

- **The Project's Role in Support of the Strategic Plan:**Curbing carbon dioxide emissions while maintaining quality of life is a global challenge for manufacturing processes that requires process innovation. The need to decarbonize chemical manufacturing creates an opportunity to not only create processes that produce no emissions but are much more efficient, cost effective and process intensified. Performing chemical synthesis with renewable electricity can reduce carbon emissions by replacing energy from the burning of carbon-based fuels with energy supplied by ‘green’ electrons. This goal can be achieved in some cases by simply replacing heat supplied by combustion with electrical heating from renewable sources.
- **Abstract:**In this project, we plan to build a lab-scale reactor to try out various electrically heated alkane dehydrogenation reactions starting with ethane dehydrogenation (cracking) which would later be expanded to propane and other short-chain alkanes. The electrical heating mechanism would range from conductive or resistance heating, to induction heating, among others.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
    - Our collaborator, Edwin Rodriquez, has an electrified reactor design that we have contacted companies to manufacture for us. This should be installed in the lab to start getting experimental results as soon as it is constructed.
    - We have completed an inductively heated reactor design with simplified kinetics and we are working on implementing the detailed kinetics which has not been done in literature for this system before.
    - We have also developed a dynamic heterogeneous SMR reactor model in Aspen Custom Modeler to simulate the dynamic response of the reactor to ascertain its suitability to operate with time-varying availability of renewable electricity.
- **Interdependence:** Working closely with the Ethane Dehydrogenation reactor design team (T4-P9).

- **Technical Targets:** The main target is the laboratory scale implementation of electrified reactors.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** We are currently implementing the reactor model on Aspen Custom Modeler. The next step is to implement the kinetics on ANSYS Chemkin-Pro. This requires the gas-phase kinetics file, surface kinetics file, and a thermodynamic file with the process input parameters and conditions. The Chemkin-Pro will be integrated into the ANSYS Fluent to get the composition profiles within the entire reactor. This will result in a full 3D model of the reactor. The challenge is to get all those ANSYS packages communicating with each other.
- **Path to Targets Summary:** We have one graduate student and one postdoctoral researcher working on this and we plan to recruit another graduate student to help achieve the targets.
- **Specific Plans Organized by Challenge:** We also plan to work with Prof. Agrawal's student working on the resistive heated reactor to implement his design at Zucrow Lab.

THRUST 7:
SYSTEMS-LEVEL DECARBONIZATION & ANALYSIS FOR FUELS & CHEMICALS

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T7P2 CISTAR Fuel in an Evolving Energy Landscape* ***Project Lead:*** *Jennifer Dunn (NU)*

F: Jennifer Dunn (NU), David Allen (UTA)	
PD: Santiago Salas (until 4/30/23); Qining Wang (starting 7/1/2023)	**RET:** Whitney Regan

Project Goals

- Identify scenarios in which carbon neutral deployment of the U.S. unique shale gas resource catalyze the scale-up of low-carbon energy sources such as hydrogen, biofuels, and electrification.

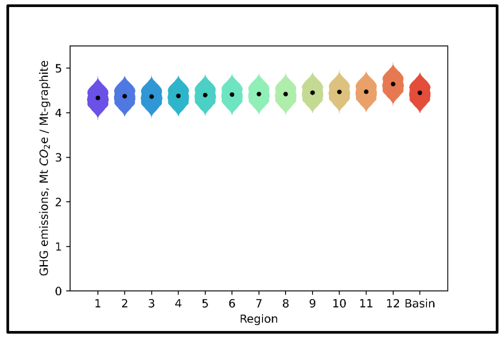


Figure 1: We have analyzed the life-cycle greenhouse gas (GHG) emissions of graphite produced from methane pyrolysis, one pathway that harnesses the nation's natural gas resources and generates products that aren't combusted and bridge to a clean energy future (graphite for batteries, hydrogen). Across the 12 regions of the Eagle Ford, graphite can be produced with this technology with about half of the GHG emissions of conventionally-produced synthetic graphite.

Barriers

- Data regarding energy and water consumption, direct greenhouse gas emissions from technologies in scenarios may not be available or may not be available for scaled-up versions of these technologies.

Methodologies

- Life cycle assessment

Research Achievements

- Manuscript describing LCA of graphite from methane pyrolysis finalized, to be submitted to Environmental Science and Technology
- Analysis of energy and GHG implications of blending hydrogen (initially produced from natural gas) into natural gas for use in industrial boilers commenced.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** With commitments in place to reduce GHG emissions from the natural gas supply chain and, nationally, to reduce fossil fuel resource use by 50% prior to 2030, the best use of this resources is under discussion. This project supports CISTAR's unique role in the national discussion concerning how we use this resource to bridge towards next-generation, low greenhouse gas intensity energy concurrent with disrupters, including electrification and international conflicts.
- **Abstract:** Within this project, we identify scenarios in which carbon neutral deployment of the U.S. unique shale gas resource catalyzes the scale-up of low-carbon energy sources such as hydrogen, biofuels, and electrification. We have investigated enhanced oil recovery as one potential scenario, integrating with biofuels production as another, and producing graphite for energy storage as a third. We are now considering natural gas as a hydrogen feedstock as electrolytic hydrogen production scales. We are exploring consequential life cycle assessment (CLCA) models to capture changes that occur to natural gas systems as the U.S. energy landscape undergoes the disruption of grid and fuel decarbonization along with potential changes in the chemicals and plastics sectors such as increased plastics recycling.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:** We have completed our analysis of methane pyrolysis to produce hydrogen and graphite and are nearing submission of a manuscript.

  Our analysis adopts the system boundary in Figure 1 below.

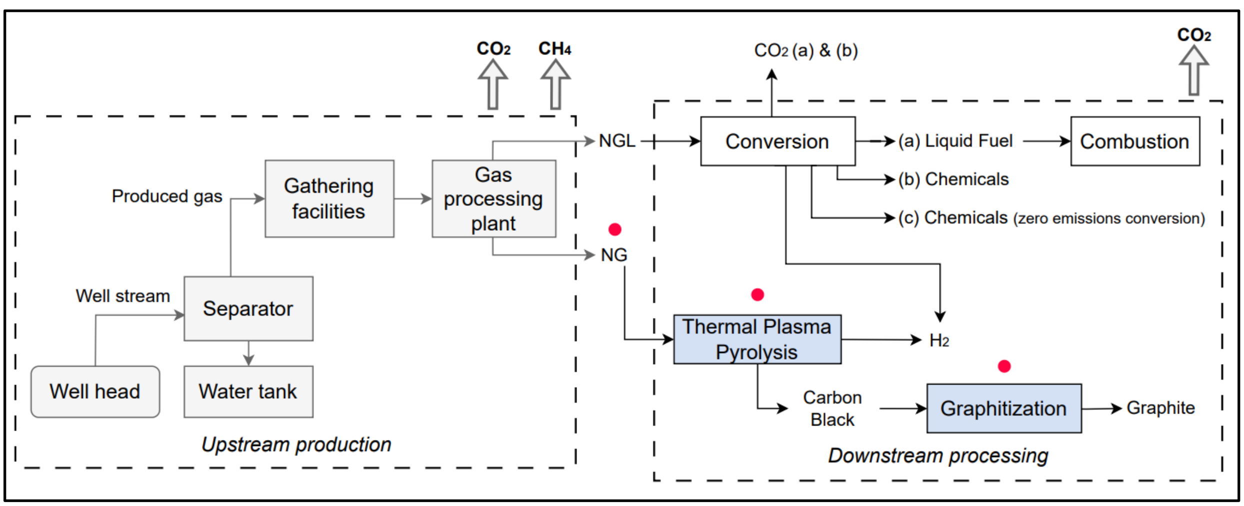


Figure 1. System boundary for evaluating GHG emissions associated with synthetic graphite and H_2 production by thermal plasma pyrolysis of NG. The NGL stream is converted into H_2 and (a) Liquid fuels, (b) Chemicals, and (c) Chemicals that assume net-zero technology (i.e., electrified reactors that use renewable electricity). The red dots denote process variables that include process uncertainty.

In addition to the results displayed in the quad chart for production of graphite, we also generated results for the generation of hydrogen from methane pyrolysis adopting a market value co-product handling method as displayed in Figure 2. Hydrogen produced by methane pyrolysis is in the range of blue hydrogen production (e.g., steam methane reforming with carbon capture and sequestration).

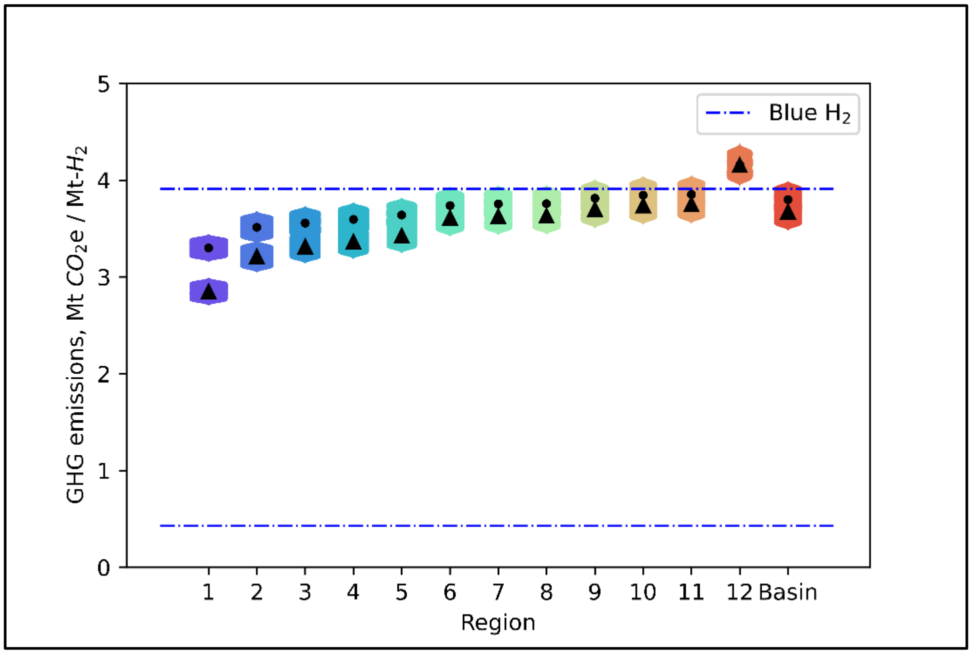


Figure 2. GHG emissions Mt-CO_2e per Mt-H_2. Violin diagrams illustrate the dispersion of results. Circles represent average values for Scenario a and Scenario b (Fig 1), and triangles represent average values of Scenario c. In these results, electricity is provided by the Texas grid. The range of "blue" H_2 GHG emissions is 0.43 to 3.9 Mt-CO_2/Mt-H_2.

We have established scenarios for blending hydrogen from multiple sources (steam methane reforming, autothermal reforming with and without carbon capture and sequestration, electrolysis) with natural gas for use in boilers. The analysis uses a county-level inventory of boilers our group has developed and published.

- **Interdependence:** This project is interdependent with T4-T7P4 which provides insights into emissions from natural gas systems. It also interacts with Thrust 4, leveraging gprocess modeling results and insights.
- **Testbed Impact and Value:** This project may integrate data and results from testbed projects.
- **Technical Targets:** This project is not guided by technical targets but may be used to inform them.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** A post-doc completed his term at Northwestern in April and we had a three month gap until a new post-doctoral researcher joined our team.
- **Path to Targets Summary:** We will have our methane pyrolysis paper submitted within the next several weeks. We expect to complete our analysis of the effects of hydrogen blending with natural gas for combustion in boilers this project year (year 7).
- **Specific Plans Organized by Challenge:** We continue to work towards an improved understanding of CLCA modeling of hydrogen systems.

Section 4: Papers and IP

1. Salas, S. D., Dunn, J. B. Methane to Graphite: Decarbonizing Natural Gas Systems while Fulfilling U.S. Critical Mineral Targets. *In preparation for submission to Environmental Science and Technology.*

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T7-T4P3 Decarbonization and Systems Analysis of Chemical Manufacturing Networks* ***Project Lead:*** *Mark A. Stadtherr (UTA)*

F: David T. Allen (UTA), Thomas F. Edgar (UTA)

GS: Ioannis Giannikopoulos (UTA), Alkiviadis Skouteris (UTA)

Project Goals

- Perform economic and environmental assessment of CISTAR technology within the hydrocarbon industry ecosystem and its potential impact on industry structure. Questions of interest include:
- At what manufacturing cost would CISTAR processes (olefins, aromatics) be adopted by the petrochemicals industry?
- What are the optimal trade-offs between economic and carbon emission goals in the hydrocarbons industry and what is the role of CISTAR technology in this regard?
- What is the impact on the petrochemicals industry of a future low-carbon transportation sector? How might this influence the CISTAR product slate?
- How might CISTAR technology facilitate the usage of variable renewable energy sources (wind, solar) by the industry?

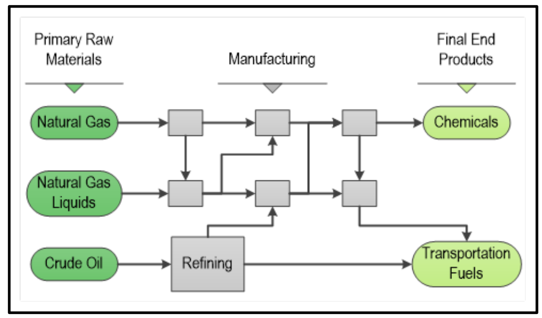


Figure: The hydrocarbon industry ecosystem

Barriers

- Complexity of interactions and interdependencies within the industry creates a barrier to analysis
- Changes in boundary conditions (feedstock supplies, product demands) and introduction of new technologies can have impacts affecting the entire industry

Methodologies

- Develop optimization-based, input-output network models of the hydrocarbons industry
  - Superstructure model of all commercially viable technology
  - Distributed, geospatial model of commercially installed technology
- Develop cost propagation procedure to enable solution of nonlinear optimization problem using successive linear programming
- Use multi-objective optimization approach to consider economic vs. emissions tradeoffs
- Expand scope of modeling to include interfaces with coupled infrastructures (e.g., electricity grid; variable renewable energy resources)

Research Achievements

- Continued development and refinement of network models of the U.S. chemical manufacturing and refining industries.
- Completed multi-objective (profit, carbon emissions) optimization study on connecting a variable renewable energy source (wind farm and battery energy storage system) to a small-scale chemical processing network (shale gas processing plant supplying natural gas liquids for conversion to chemicals). Paper submitted for publication.
- Completed study showing how to formulate the nonlinear network optimization problem as a mixed-integer nonlinear programming problem for technology assessment studies, with comparisons to a successive linear programming approach. Paper submitted for publication.
- Completed multi-objective (profit, carbon emissions) optimization study showing impact of different levels of decarbonization on the hydrocarbon industry structure. Paper in preparation.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** Technology developed by CISTAR will be part of a larger manufacturing system that converts primary raw materials, such as natural gas, natural gas liquids (NGLs) and petroleum into a large number of final end products (chemicals and fuels). Economic and environmental assessment of CISTAR technology should be done in the context of this larger manufacturing network. Technology information from other thrusts can be used in connection with the models and methods of analysis developed in this project in order to study the viability of the technology within the larger industry, as well as its impact as the industry moves toward a lower-carbon future based on renewable energy and recycled resources. This will provide feedback to the other thrusts in terms of targets for product slate, process stoichiometry, production costs and decarbonization potential.

- **Abstract:** CISTAR technology aims to convert natural gas liquids (NGLs) to hydrocarbons suitable as transportation fuels or as petrochemical feedstocks. To assess the economic and environmental impact of this technology in the fuels and petrochemicals industry, we develop and use network models of the industry. For example, one model used is a nonlinear, optimization-based model that represents the U.S. refining and chemical manufacturing industries as a superstructure of over 800 different processes. We have used this model, and a related model that also includes geospatial information, to investigate production cost targets for potential CISTAR technologies (*Industrial & Engineering Chemistry Research*, 2021, 60, 12377-12389; *Industrial & Engineering Chemistry Research,* 2021, 60, 14801-14814). Our industry model has also been used to probe the impact on the petrochemicals industry of an electrified transportation sector, including evaluation of potential for application of CISTAR technology in this context (*Industrial & Engineering Chemistry Research,* 2022, **61**, 12169-12179). We have now completed a multi-objective (profit, carbon emissions) optimization study on connecting a variable renewable energy source (wind farm and battery energy storage system) to a small-scale chemical processing network consisting of a shale gas processing plant supplying natural gas liquids for conversion to olefins and derivatives (paper submitted for publication). We have also completed a study showing how to formulate the nonlinear network optimization problem as a mixed-integer nonlinear programming (MINLP) problem for CISTAR technology assessment studies, with comparisons to a successive linear programming approach (paper submitted for publication). Finally, we have completed a multi-objective (profit, carbon emissions) optimization study showing the impact of different levels of decarbonization on the hydrocarbon industry structure (paper in preparation).

- **Significant Results for the Period 10/1/2022 to 9/30/2023:** In ongoing work, we have continued to develop, refine, and use an optimization-based network model that represents the U.S. refining and chemical manufacturing industries as a superstructure of over 800 different processes. This model includes nonlinear cost propagation features that may occur when the network is perturbed by the addition of a new technology, thus complicating technology assessment studies using the model.. To deal with this issue, we have developed a successive linear programming (SLP) approach, and also have shown how to formulate the problem as a mixed-integer nonlinear programming (MINLP) problem. We have evaluated the performance of the different approaches based on quality of results and computational efficiency. For comparisons, we initially used small prototype networks that feature structural properties of the industrial network, followed by application to full-scale, industry-wide problems. Results point to scalability issues with the MINLP approach, which can be overcome using the SLP formulation (Paper 1 in Section 4).

In an application of our network superstructure modeling approach (Paper 2 in Section 4), we conducted a multi-objective (profit, carbon emissions) optimization study on connecting a variable renewable energy source (wind farm and battery energy storage system) to a small-scale chemical processing network, namely a shale gas processing plant supplying natural gas liquids for conversion to chemicals, as shown in Figure 1.

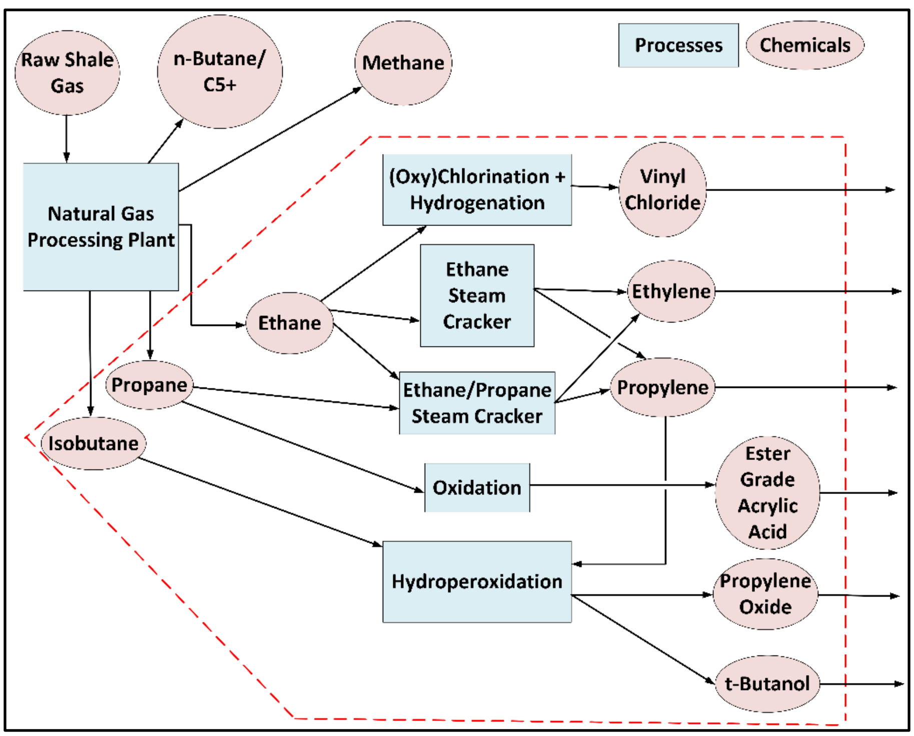


Figure 1. Process network superstructure. Dashed lines show boundaries of system studied. Energy sources and flows are not shown.

In this network, methane, butane and C5+ products from the gas processing plant are sold to the market, with ethane, propane and isobutane transferred to the chemical production system at a fixed, discounted internal price. The chemical production system can use these materials as feedstocks to produce chemicals, or can sell them to market. All the materials produced by the process network are either sold to market for a fixed price or used to produce other materials that are themselves sold. For all processes, electrical energy requirements can be met by connection to the electrical grid and thermal energy requirements can be met by using the locally available natural gas. However, there is an option to construct a wind farm to provide electrical power to the chemical processes, replacing or supplementing power from the grid. Furthermore, there is an option to fully electrify the chemical processes by using electrically-generated heat to supply the necessary thermal energy, thereby replacing fossil fuels usage.

In one study with this system, a multi-objective optimization study was conducted, using the ∑-constraint method, to study the adoptability and potential impact of the wind farm, in three different cases. The results are shown as a Pareto front (set of best compromise solutions) in Figure 2.

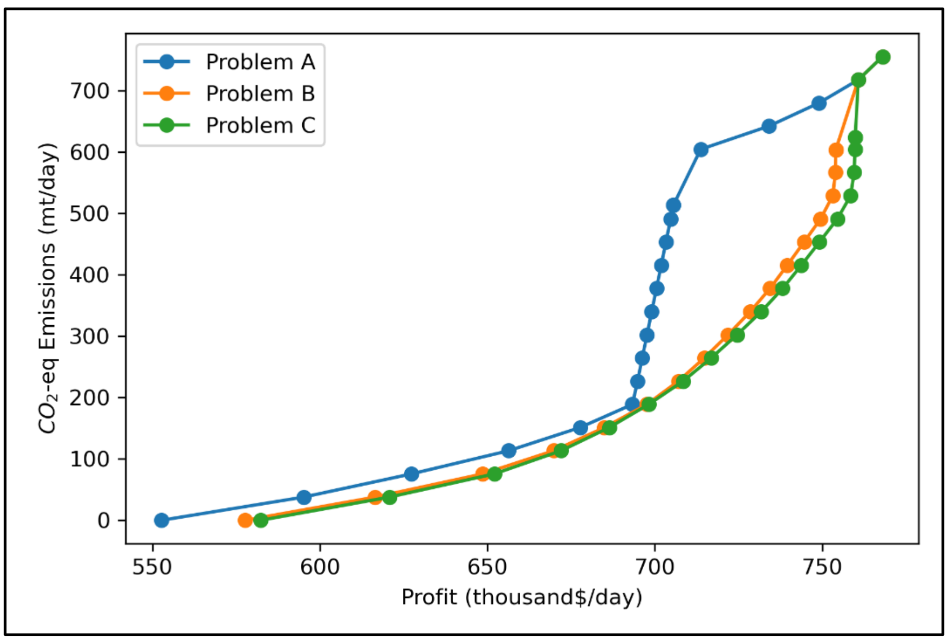


Figure 2. Pareto fronts for three cases: Problem A is the case of no connection to the electricity grid. In Problems B and C there is connection to the grid, with sales allowed at 90% (Problem B) or 100% (Problem C) of market price.

At the top point in the upper right (shared by all three Pareto fronts), there is no wind farm in the optimal solution. Now moving to the left (∑-constraints forcing lower carbon emission limits), there are sharp downturns in the Pareto fronts, which correspond to the decision in the optimal solution to build a wind farm. The wind farm first appears in the optimal industry when sales to the electrical grid are allowed, with only small differences due to the selling price (Problem B vs C), but as the emissions limit becomes stricter then also appears in the case of no sale to the grid (Problem A). The sharp downturns in the Pareto front when the wind farm is adopted indicate that significant reductions in emissions are possible with relatively small reductions in profit. A complete analysis of all the results (not shown) indicates that the adoption of the wind farm without connection to the electric grid is not as impactful (in terms of potential for decarbonization) as are the cases in which there is a connection and sales are made. The ability to sell the wind farm energy to the electrical grid motives, at looser emission limits, the adoption of the wind farm and the use of renewable energy by the process network. This indicates that connection to the electric grid is the optimal way to take full advantage of available renewable electricity sources. Various other studies with this model system were done, including a study of the impact of the optional battery energy storage system.

In another completed project (Paper 3 in Section 4), we applied multi-objective optimization analysis to our full-scale, industry-wide superstructure model. For this study, we determined the optimal industry structure for several different energy mix scenarios and decarbonization percentages, and made comparisons to study the short- and long-term impacts of decarbonization. An important takeaway from this analysis is that as relatively inexpensive renewable energy is increasingly available, there may be a switch to somewhat more energy intensive processes, if they are more efficient in some other regard (e.g., feedstock usage).

- **Interdependence:**

  The stoichiometry for CISTAR technology inserted into our network models are guided by interactions with the Thrust 4 group at Purdue and their Aspen Plus simulation work. The modeling work in this project helps provides targets for work in other Thrusts, e.g., the catalysis work in Thrusts 1 (dehydrogenation) and 2 (oligomerization).

- **Testbed Impact and Value:**

  This project is connected to all testbeds by helping to assess the potential CISTAR product slate using economic and environmental measures, and by helping to identify chemical targets for CISTAR technology.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:**

  The two graduate students who worked on this project have now completed and defended their Ph.D. theses. Dr. Alkiviadis Skouteris is now employed by Aspen Technology, Inc. Dr. Ioannis Giannikopoulos is now employed by ISO New England, Inc. (the electricity grid operator for the New England states). The remaining challenge is to publish the results of the work that has come out of this project.

- **Path to Targets Summary:**

  There are two papers (Papers 1 and 2 in Section 4) that have been submitted for publication. Work will be likely needed to revise these after feedback from reviewers. One paper (Paper 3 in Section 4) is in the final preparation stages, and some additional work is needed to put it into final form for journal submission. There is potential for some other topics covered in the Ph.D. theses to be published.

- **Specific Plans Organized by Challenge:**

  Editing, revision and other work related to publications will be done by project faculty, with assistance from the now departed PhD recipients as their time allows.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

  1. Alkiviadis Skouteris, Ioannis Giannikopoulos, Thomas F. Edgar, David T. Allen, Michael Baldea, and Mark A. Stadtherr, "Implementation of Nonlinear Variable-Cost Network Optimization Models for Technology Assessment in the Petrochemicals Industry," *Computers & Chemical Engineering*, submitted (2023).

  2. Ioannis Giannikopoulos, Alkiviadis Skouteris, David T. Allen, Michael Baldea, and Mark A. Stadtherr, "Integration of Renewable Energy Sources in Chemical Process Networks: Impact on Profit and CO_2 Emissions," Industrial & Engineering Chemistry Research, submitted (2023).

  3. Alkiviadis Skouteris, Ioannis Giannikopoulos, Thomas F. Edgar, Michael Baldea, David T. Allen, and Mark A. Stadtherr, "Multi-Objective Optimization of Production Cost and Carbon Emissions in the U.S. Petrochemicals Industry: Impacts of Decarbonization," in preparation (2023).

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T7-T4P4 Characterizing Light Alkane Resources and Life Cycle Assessments of CISTAR Processes*
Project Lead: *David Allen (UTA)*

F: David Allen, (UTA) Jennifer Dunn (NU)
PD: Qining Chen (UTA), Santiago Salas (NU, until 4/30/23), Qining Wang (since 7/1/23)

Project Goals

- Assess the spatial distribution of light alkane resources and their environmental effects.
- Assess the life cycle greenhouse gas, energy, and water footprints for the fuels and chemicals produced by CISTAR processes.

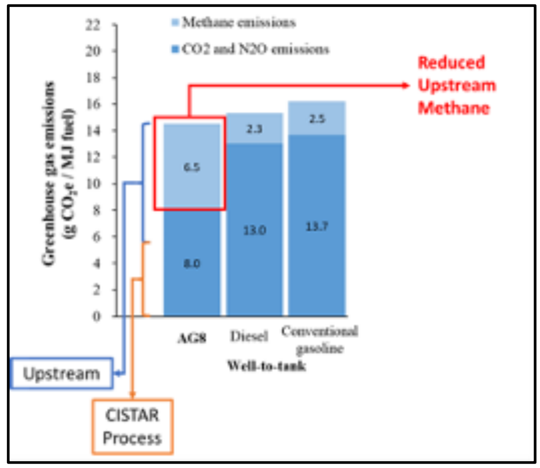


Figure: LCA results for CISTAR process AG8 shows lower-than-baseline emissions

Barriers

- Data limitations can pose barriers. To fill gaps in data, we develop models or estimates based on engineering assumptions.

Methodologies

- This project has been building base case data sets, using multiple years of production data in Texas as case studies, to map the availability, on a well by well basis, of NGL feedstocks. These detailed spatial mappings are being used to determine the detailed compositions of potential CISTAR feedstocks, to determine how those compositions and flow rates change over time, and to assess the different scales at which CISTAR processes might operate.

Research Achievements

- We have continued to update life cycle assessments for CISTAR fuels and chemicals
- We have published an analysis to highlight the benefits of quickly deploying rapidly-scalable methane emission reduction technology in the natural gas sector.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** A central concept of CISTAR is that distributed manufacturing of transportation fuels using natural gas liquids has potential economic advantages over centralized, large-scale production. The economic benefits and costs associated with this distributed manufacturing will depend on the characteristics of produced NGLs, the proximity of the production region to existing transport infrastructures, the available capacity in existing transport infrastructure, the location of demand, regulatory barriers, and other factors. Accordingly, this project has been essential in to assess the spatial distribution of light alkane resources. Furthermore, as CISTAR seeks responsible use of light hydrocarbons, the life cycle assessments this project develops are core to realizing that vision.

- **Abstract:** Within this project, we develop life cycle environmental effects of CISTAR fuels and a calculation platform that will allow the assessments to be continually updated as CISTAR processes evolve. This project has been building base case data sets, using multiple years of production data in Texas as case studies, to map the availability, on a well by well basis, of NGL feedstocks. These detailed spatial mappings are being used to determine the detailed compositions of potential CISTAR feedstocks, to determine how those compositions and flow rates change over time, and to assess the different scales at which CISTAR processes might operate. The project is considering how hydrogen from the CISTAR process may fit into national hydrogen production incentives in the Inflation Reduction Act.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

  We completed our analysis of scenarios that prioritize either methane emission reductions in the natural gas supply chain or the equivalent amount of carbon dioxide emissions reductions using carbon capture and sequestration. We considered scenarios with either 30% (Figure 1) or 80% reductions of natural gas supply chain emissions. Deploying off-the-shelf, relatively inexpensive methane emission reduction technology (Figure 2) brings relief from climate change’s effects sooner.

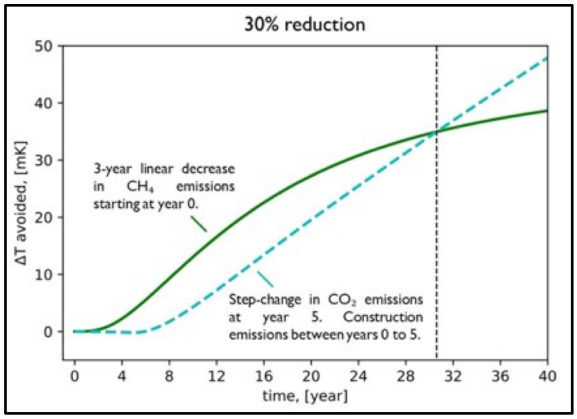


Figure 1. The resulting avoided surface temperature rise (mK) from reducing an equivalent amount of carbon dioxide (with carbon capture and sequestration at power plants) and methane (through cutting emissions in the natural gas supply chain).

It is important to note that reducing methane emissions in the natural gas supply chain can be very effective. In fact, 45% of well-to-gate emissions of CISTAR fuels could be reduced by mitigating upstream methane at negative or limited net cost (see quad chart figure). More than 50% of methane emissions can be reduced with economically beneficial measure considering mitigation costs and gas savings.

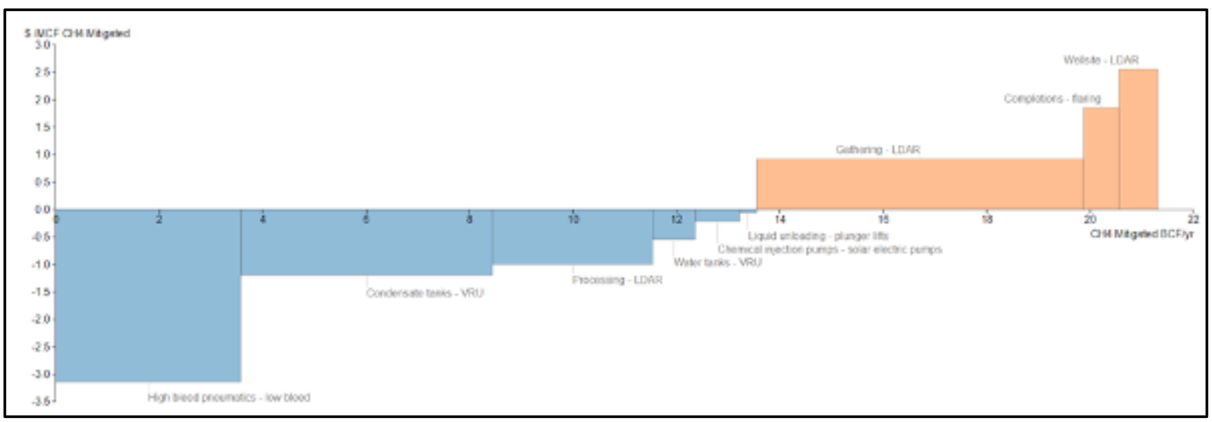


Figure 2. Marginal abatement cost curve for methane reductions in the Eagle Ford Shale by Source (VRU: Vapor recovery units, LDAR: Leak detection and repair).

- **Interdependence:** This project is interdependent with T7P2 which identify scenarios in which carbon neutral deployment of the U.S. unique shale gas resource catalyze the scale-up of low-carbon energy sources such as hydrogen, biofuels, and electrification. It also interacts with Thrust 4, leveraging process modeling results and insights.
- **Testbed Impact and Value:** This project may integrate data and results from testbed projects.

- **Technical Targets:** This project is not guided by technical targets but may be used to inform them.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** We are currently working towards an evaluation of how CISTAR processes, including those at refineries that might use CISTAR products, fit into national efforts to incentivize hydrogen production from multiple sources below a set greenhouse gas threshold.
- **Path to Targets Summary:** We intend to develop an analysis of challenges in calculating life-cycle greenhouse gas emissions from these pathways that are not explicitly included in legislation and policy but that could offer an opportunity to use the nation's natural gas and natural gas liquids towards a bridge to a clean energy future.
- **Specific Plans Organized by Challenge:** Data on hydrogen produced as a by-product at refineries and other industrial sites may be challenging to obtain, but we will leverage CISTAR's network analysis as needed (T7-P3) to fill gaps.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. J. B. Dunn, S. D. Salas, Q. Chen, D. T. Allen. Prioritize rapidly scalable methane reduction efforts to mitigate climate change. *Clean Technology and Environmental Policy*. **2023**. doi: 10.1007/s10098-023-02521-3.

THRUST 1:
DEHYDROGENATION

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T1P3 Regenerable, Thermally Stable Alkane Dehydrogenation Catalysts* ***Project Lead:*** *Abhaya Datye (UNM)*

F: Christina Li (PU), Jeffrey Miller (PU), Jeffrey Greeley (PU)	
GS: Ryan Alcala (UNM), Shan Jiang (PU), David Dean (PU), Yinan Xu (PU), Vamakshi Yadav (PU), Isabel Ibarra (UNM), Joanna Rosenberger (PU), Yu-Hsiang Cheng (PU)	
PD: Andrew DeLaRiva	**UG:** Isha Chauhan (PU), Aiden Littleton (UNM), Nkemdilim Azuka (PU)

Project Goals

- Development of stable and regenerable Pt-based intermetallic catalysts for dehydrogenation reactions.
- Develop strategies to mitigate catalyst deactivation, study the mechanism of coking over Pt and Pt alloys.
- Develop catalysts that can be regenerated without activity loss, using air, CO_2, or H_2O and to extend cycle times to minimize switching times for regeneration.
- To establish how the rate of coke formation, structure of coke products, and distribution of coke on the catalyst surface is impacted by Pt morphology and Pt alloy composition.

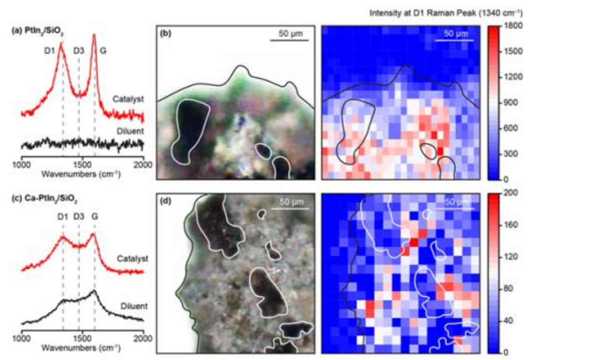


Figure 1: (a, c) Average Raman spectra on the catalyst and diluent fractions of undoped $PtIn_2/SiO_2$ and doped Ca-$PtIn_2/SiO_2$. (b, d) Optical image and corresponding Raman intensity map for the catalyst fractions of the undoped and doped samples.

Barriers

- Mechanisms (molecular-level understanding) of coke formation and migration to the support not well understood.
- There is no established method for measuring the rate of coke formation, coke products are often ill-defined and difficult to characterize.
- Understanding of how coke nucleates and grows on different Pt alloy compositions and morphologies is limited. Existing computational studies have focused on carbon growth on Ni and Fe, which can lead to carbon nanotube formation, but no analysis of alloys relevant to alkane dehydrogenation exists.

Methodologies

- Choice of support and particle size to minimize coke formation and achieve regeneration.
- Density functional calculations of graphene defect structures as models of amorphous coke

Characterization of coke via NMR, mass-spectrometry, and Raman.

Research Achievements

- Across all catalysts, the coking rate is dynamic in the first 10 minutes, rising initially and then declining rapidly to a steady state value. The TOF for coke formation does not depend strongly on nanoparticle size in the size regime studied herein (2-10 nm).
- Coke nucleation on smooth platinum terraces proceeds by a process of successive addition of carbon atoms to existing 5- and 6-membered carbon rings. The added carbon initially forms open structures, but addition of further carbon atoms closes these rings, and the process continues. Ring-like structures are also favored for nucleation and growth from platinum step edges.
- Demonstrated that co-feeding CO_2 improves catalyst lifetime. Initial results suggest that CO_2 can be used to regenerate a ceria supported Pt alloy catalyst.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** Alkane dehydrogenation is the first step in functionalizing natural gas liquids to convert them into liquid fuels and chemicals. To make the process suitable for distributed manufacturing, it is necessary to achieve enhanced selectivity, longer catalyst lifetime and facile catalyst regeneration. The initial focus of T1 was on the discovery and understanding of Pt-based intermetallic catalysts. This was coupled with theory and computational modeling to understand factors that control selectivity, with the aim of improving performance. Current work is focused on understanding deactivation mechanisms, the nature of coke formation and the role of the support, with the goal of developing thermally stable and regenerable catalysts for dehydrogenation. The alkane dehydrogenation catalysts developed in this project are coupled with olefin conversion catalysts, so that a liquid product can be produced (jointly with T3P5). This will help avoid separation steps which are commonly the most expensive part of the technology of producing olefins such as ethylene or propylene. Development of coke tolerant catalysts is also essential for achieving higher conversion (exceeding equilibrium) using high temperature membrane reactors to remove H_2 (jointly with T6P2).

- **Abstract:** We demonstrated in our previous work that the choice of optimal particle size allows complete regenerability on silica supports during oxidative regeneration at 420 °C without causing sintering or phase segregation of the Pt alloy nanoparticles. Since we do not see any significant catalyst sintering. carbon deposition as coke remains the primary pathway for catalyst deactivation. During the past year, we have focused on understanding coke deposition on the catalysts and alternate means of coke removal, such as in-situ feeding of CO_2. We synthesized our catalysts on a silica support because we found improved selectivity on this support, compared to the industrially used alumina supports. We demonstrated in our work over the past year, the ability to spatially resolve coke on the macro and micro scale using Raman spectroscopy and energy filtered transmission electron microscopy (EFTEM) (Figure 1 and Figure 2). Coupling EFTEM and EELS spectroscopy, both the spatial distribution and chemical composition can now be determined, on the nanoscale, adding another set of tools for supporting CISTAR goals. *In situ* temperature programmed oxidation has shown that the coke distribution in H_2 depleted environments, seen in the membrane reactor joint project with T6, is primarily located on the catalyst in contrast to how coke gets distributed under "normal" PDH conditions. This suggests that alternate strategies for managing catalyst deactivation will be needed to achieve the goals of membrane reactor technology to achieve conversions exceeding thermodynamic equilibrium by removal of H_2.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

- We have initiated studies of PDH catalysts post reaction to analyze the location of carbon deposition at the nanoscale. Initial results are shown in Figure 2 below, where the TEM image of the catalyst is on the right and the carbon EFTEM (Energy Filtered TEM) map is on the left. As demonstrated by us previously using TPO, the carbon is located primarily on the support. In future work, we will correlate the location of the carbon and the extent of catalyst deactivation.

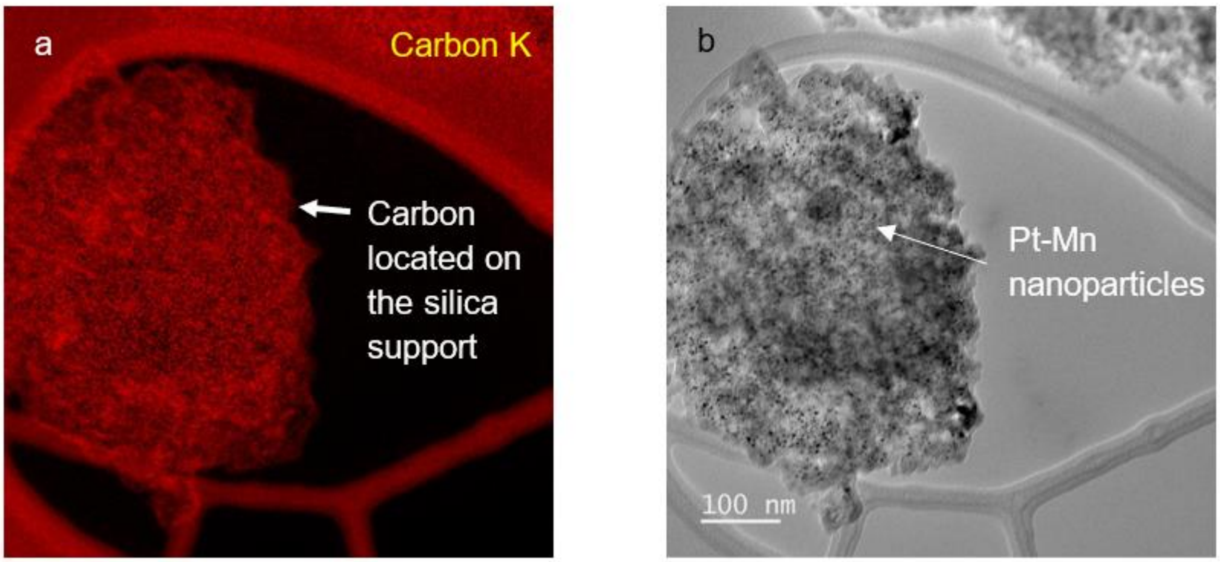


Figure 2: a) EFTEM carbon K edge map showing the presence of deposited carbon located on the silica support. The carbon support film also shows up as red in this image. b) TEM image of Pt-Mn/SiO_2 showing nanoparticles (small black dots) on the silica support.

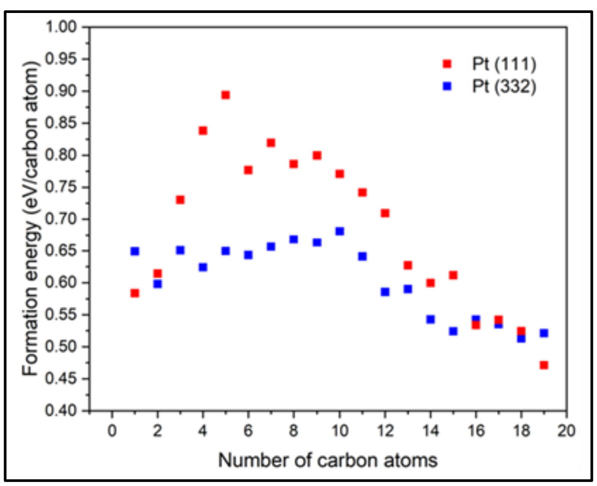


Figure 4. Formation energy of carbon structures as a function of the carbon coverage on platinum surfaces. The energetics of carbon growth on platinum steps (blue squares) are more favorable than on platinum terraces (red squares).

- We have found that coke nucleation on smooth platinum terraces proceeds by a process of successive addition of carbon atoms to existing 5- and 6-membered carbon rings. The added carbon initially forms open structures, but addition of further carbon atoms closes these rings, and the process continues. Ring-like structures are also favored for nucleation and growth from platinum step edges. Carbon growth on platinum steps involves significantly more energetically favorable structures than the corresponding growth on smooth terraces.

- In work done jointly with T6P3, we simulated the conditions that would be expected when propane dehydrogenation is carried out in a membrane reactor with H2 removal (15% conversion and 90% removal of H_2). Figure 2 shows how the Pt-Mn/SiO2 performs under these conditions. While we can achieve higher conversion (Fig. 2a) than equilibrium (~10% at this temperature), there is significant coke deposition and the distribution of the coke is different from that seen under normal PDH conditions (most of the coke is on the support, as seen in Figure 2). Here, the TPO (Figure 3b) shows more coke on the metal surface and less on the support.

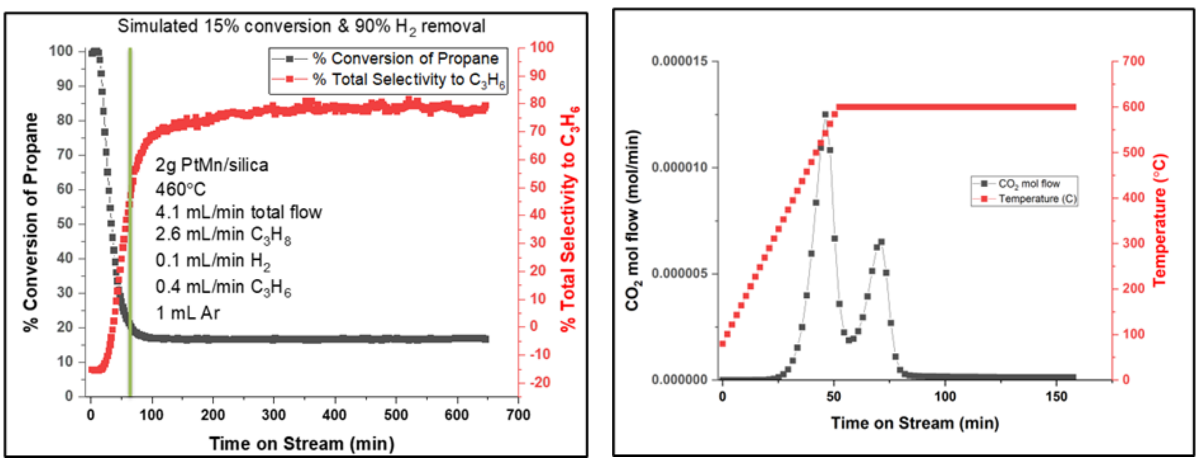


Figure 3: a) Conversion of propane in a H_2-depleted environment. The vertical green line shows the time taken for the reactants to go through the reactor and reach the GC. The black line shows the additional conversion that can be achieved over the 15% that we started with. But the low selectivity shows there is significant coke deposition. b) in situ TPO profile (black) of a PtMn/silica catalyst after 12 hr in H_2-depleted conditions at 460°C. The first peak arises from the metallic sites and the second one from the support. This distribution is different from that seen on the same catalyst in the normal PDH effluent (ie H2/C3H6 = 1).

- To investigate the role of catalyst support on coke deposition and loss of selectivity, we studied coke deposition by flowing propylene over various supports. The results of carbon deposition on silica and alumina supports are shown in Figure 4 confirming that silica is the better support for PDH catalysts since it does not lead to significant coke deposits.

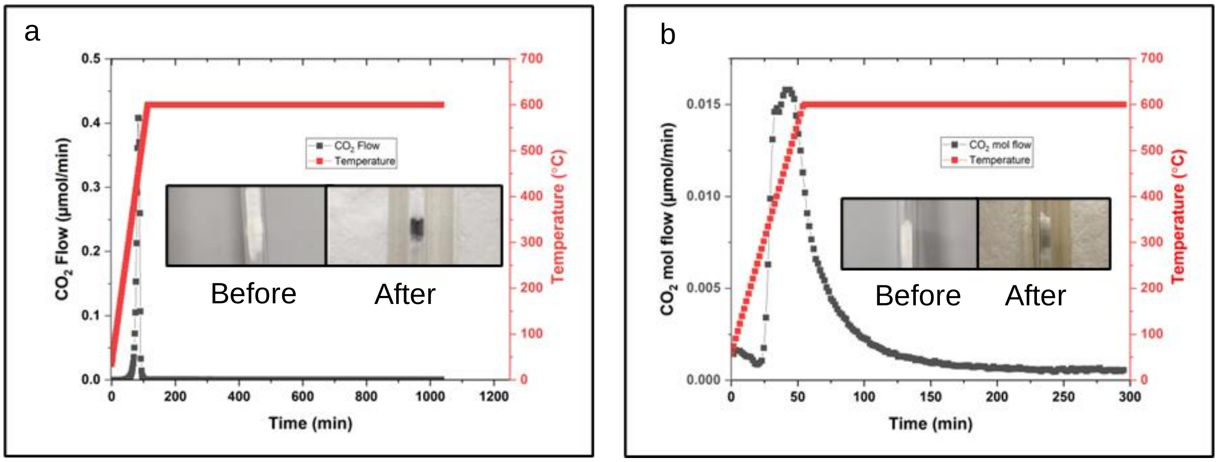


Figure 4. a) TPO of amorphous silica (Davisil 643) and (b) alpha alumina (obtained from Ceramtek) after 18.5 h on stream in 10% propylene balanced with inert. The insets show images of the sample before and after propylene exposure silica. Silica shows very little propensity for coking.

- We have explored the use of CO_2 as a soft oxidant, since it is very effective at gasifying coke on ceria supported catalysts. Figure 5 shows the typical deactivation behavior for PtMn/SiO_2 PDH catalysts. The catalyst at the end of run was treated in flowing CO2 and the CO production was monitored. As shown in Figure 5b, the deposited carbon was gasified to produce CO. The catalyst activity did not recover, so further optimization is needed. We found that the activity could be restored on ceria supports, which will be the focus of future work.

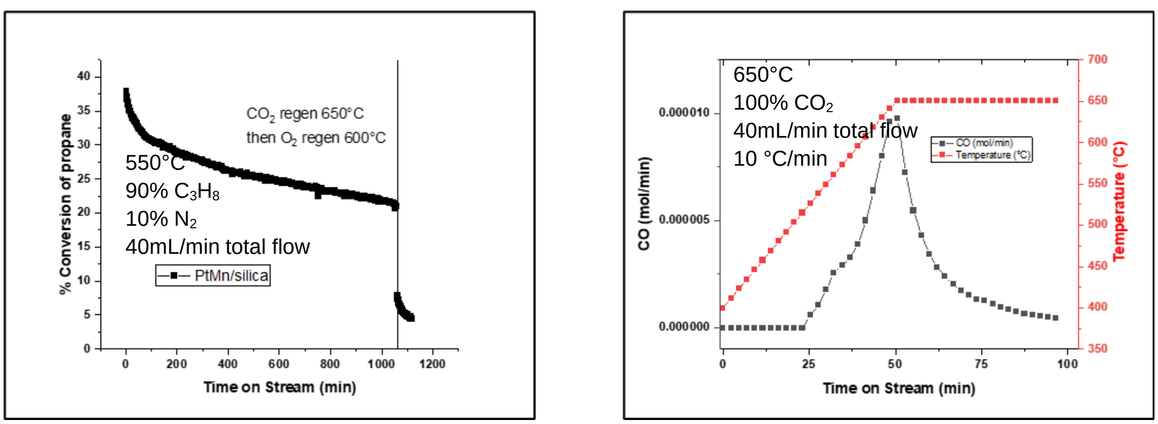


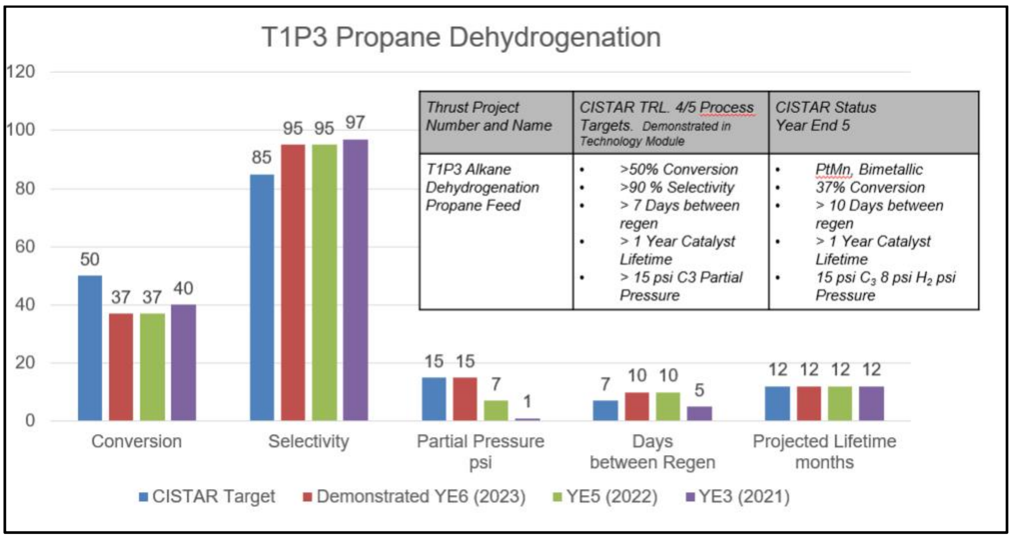
Figure 5. a) Conversion of propane during PDH on Pt-Mn/SiO2 catalysts. The deactivated catalyst was treated in CO_2 to determine if the coke could be removed by flowing CO_2. The results show that the onset of coke removal is at around 500 C, suggesting that co-fed CO_2 may also be effective at removing coke from the surface of the catalyst.

- **Interdependence:**
  - This project involves a multi-disciplinary, multi-university PI team with faculty from multiple thrusts participating. The results reported here include the research done by Li (T1, PU), Datye (T1, and T6, UNM), Greeley (T1 and T3, PU) and

Miller (T1 and T3, PU) who collaborate closely in this project to elucidate the best strategies for inhibiting catalyst deactivation and improving catalyst regeneration during high-temperature alkane dehydrogenation. Discussions on techno economic analysis of potential process options with Sawyer, Calverley, and Cook help define the targets and goals for this project.

  - The catalysts developed in T1P3 are being evaluated in T3P5 for dehydroaromatization. The improved lifetimes for dehydrogenation are critical to achieve longer term reactivity during aromatization.
  - In T6P2, these catalysts are being tested in high temperature membranes to investigate how removal of H_2 through the membrane can lead to conversions that exceed equilibrium, which will allow operation at lower temperatures and/or higher pressures.

- **Testbed Impact and Value:** Since the first step in the CISTAR process involves alkane dehydrogenation, which operates at high temperatures due to thermodynamic limitations, catalyst stability and optimal regeneration are issues relevant to Testbeds 2 and 3.
- **Technical Targets:**



Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:**
  - Coke deposition occurs on the metal surface and the support. The roles of each of these coke deposits on reactivity is not fully understood.
  - Under H_2-depleted conditions, coke deposition is very significant leading to deactivation.

- **Path to Targets Summary:**
  - Experiments to ascertain catalyst lifetime at 15 psi of alkane are underway in the Technology Module using both benchmark catalysts (PtSn) as well as the best CISTAR catalyst to date ($PtMn/SiO_2$). We will incorporate alkali doping into these materials for optimal integration with Tech Module testing.
- **Specific Plans Organized by Challenge:**
  - We plan to extend our coking methodology to more relevant feedstocks including ethylene and ethane and determine how each intermediate contributes to coke formation and catalyst deactivation using our size-controlled series of supported monometallic Pt nanoparticles. We then intend to study how the rate of coking is impacted by the formation of Pt-Sn, Pt-In, and Pt-Mn alloys.
  - We intend to complete our study of the effect of carbon coverage on nucleation and growth of coke on smooth and stepped platinum surfaces. To assess the kinetics of these processes, we will additionally calculate the diffusion barriers for carbon to cross platinum surface features and bind to the growing coke structures. We will also begin corresponding studies of carbon growth on Pt alloys and on silica-supported platinum nanoparticles.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Alcala, R., Dean, D.P., Chavan, I., Chang, C.-W., Burnside, B., Pham, H.N., Peterson, E., Miller, J.T., and Datye, A.K., Strategies for regeneration of Pt-alloy catalysts supported on silica for propane dehydrogenation. Applied Catalysis A: General, 2023. 658: p. 119157.
2. Porter, S., Ghosh, A., Liu, C.H., Kunwar, D., Thompson, C., Alcala, R., Dean, D.P., Miller, J.T., DeLaRiva, A., Pham, H., Peterson, E., Brearley, A., Watt, J., Kyriakidou, E.A., and Datye, A.K., *Biphasic Janus Particles Explain Self-Healing in Pt–Pd Diesel Oxidation Catalysts.* ACS Catalysis, 2023. **13**(8): p. 5456-5471.
3. Porter, S. and Datye, A.K., *Imaging of single atom catalysts*, in *Heterogeneous Inorganic Catalysts*, R.A. van Santen and E. Hensen, Editors. 2023, Elsevier: Oxford. p. 222-243.
4. Datye, A. and DeLaRiva, A., *Scanning Electron Microscopy (SEM)*, in *Springer Handbook of Advanced Catalyst Characterization*. 2023, Springer International Publishing Cham. p. 359-380.
5. Breckner, C.J., Pham, H.N., Dempsey, M.G., Perez-Ahuatl, M.A., Kohl, A.C., Lytle, C.N., Datye, A.K., and Miller, J.T., *The Role of Lewis Acid Sites in γ-Al2O3 Oligomerization.* ChemPhysChem, 2023: p. e202300244.
6. Zhang, W., Zhang, X., Wang, J., Ghosh, A., Zhu, J., LiBretto, N.J., Zhang, G., Datye, A.K., Liu, W., and Miller, J.T., *Bismuth-Modulated Surface Structural Evolution of*

Pd3Bi Intermetallic Alloy Catalysts for Selective Propane Dehydrogenation and Acetylene Semihydrogenation. ACS Catalysis, 2022. **12**(17): p. 10531-10545.

7. Yadav, V.; Rosenberger, J.; Bolton, B.; Zhu, K.; Escorcia, N.; Urbina, A.; Gounder, R.; Li, C. W. *Calcium Additives Enhance Coke Migration and Catalyst Stability for Pt-Based Catalysts in Ethane Dehydrogenation*. 2023, Submitted.
8. Talpade, A., Canning, G., Zhuchen, J., Arvay, J. Miller, J. T., Datye, A.K. and Ribeiro, F. H., *Catalytic reactivity of Pt sites for non-oxidative coupling of methane (NOCM)*, 2023, submitted.

- **Disclosures, Patents Filed for the Period 10/1/2022 to 9/30/2023:**

1. Riley, C.R., de la Riva, A., Chou, S.S., and Datye, A., *Efficient low-temperature, catalyst-free dehydrogenation of alkanes*. US Patent 11,708,312. Issued July 25, 2023.
2. De La Riva, A., Datye, A. K., Riley, C. R., *Single atom metal doped ceria for CO oxidation and HC hydrogenation/oxidation*, US patent 11,745,169 issued September 5, 2023

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T1P5 Non-Thermal Plasma-Assisted Alkane Dehydrogenation* ***Project Lead:*** *Jason Hicks (UND)*

F: Jason Hicks (UND), William Schneider (UND)
GS: Denver Haycock (UND), Russell Clarke (UND)
YS: Emma Loftus (UND), Mario Ruiz (UND)

Project Goals

- Develop non-thermal CISTAR process for the production of value-added products from light alkanes
- Identify drivers to performance (e.g., catalyst loading, specific energy input, plasma power, bulk temperature, gas composition) and develop relationships between catalyst structure and performance with plasma conditions, describing how the conditions affect rates, selectivities and deactivation.
- Identify appropriate catalysts to facilitate the reaction, focusing on CISTAR catalysts and/or synthesis of new materials for the desired conditions.
- Develop microkinetic models, informed by DFT calculations, that can describe experimental data and allow predicting performance under non-thermal stimulation to guide catalyst and process optimization and design.

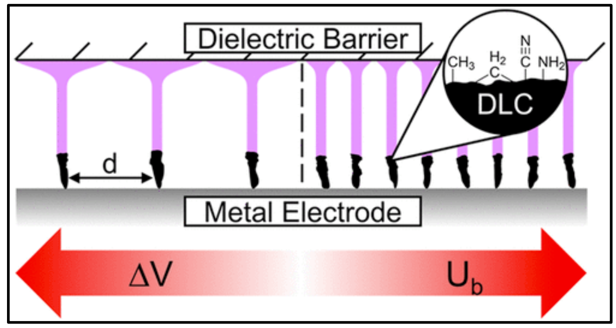


Figure: Dielectric barrier discharge (DBD) plasma produces valuable gas and liquid products from stimulation of light alkane feeds, although carbon formation is also observed. By controlling plasma conditions and reactor configurations, carbon growth can be reduced and inhibited.

Barriers

- The relative contributions of thermal reactions, plasma reaction, and plasma-assisted catalysis reactions are not fully understood
- Poor understanding of the role of the plasma (e.g., hot spots, plasma-phase reactions, packed-bed effects, plasma-catalyst interactions) in facilitating hydrocarbon activation and conversion and the impact of plasma stimulation on the structure and properties of the catalyst.
- Lack of knowledge on the appropriate catalyst under plasma stimulation.

Methodologies

- Plasma only experiments, plasma-catalysis experiments, monitoring time on stream, catalyst stability, and performance evaluation are assessed at different plasma input conditions.
- Catalysts are characterized before and after reaction, and carbon deposition is characterized to compare to thermal experiments.
- Combine experimental data, DFT and/or AIMD calculations, and kinetic modeling to elucidate underlying reaction mechanisms and rates.

Research Achievements

- Non-oxidative ethane reactions using NTP at 15 W and 400°C provided C4+ and ethylene carbon-selectivities of 32.9% and 24.8% respectively at an ethane conversion of 31.4%.
- Established control over plasma-only selectivity by varying input power. Specifically, we observed an increase in the ratio of gas-phase C4+ products compared to C1 formation (C4+/CH4) from 1.3 to 2.0 by increasing power from 5 W to 15 W.
- Established control over plasma-only selectivity through temperature control. Specifically, we observed an increase in the C2H4/CH4 ratio from 0.8 to 2.7 with increasing bulk gas temperature between 5°C and 400°C
- Determined conditions to inhibit coking in the reactor.
- Developed preliminary plasma-kinetic model to predict primary speciation of C_2H_6 exposed to an atmospheric pressure plasma

Section 2: Project Summary Brief

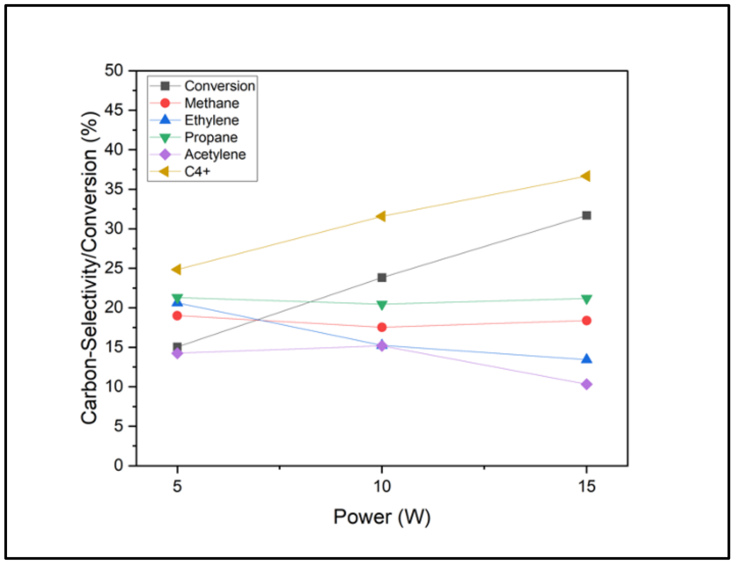
- **The Project's Role in Support of the Strategic Plan:** Within a typical shale gas stream, ethane is the most abundant C2+ hydrocarbon and is the primary target reactant for Thrust 1 efforts. The non-oxidative dehydrogenation of C2+ alkanes is endothermic and is thermodynamically favored at elevated temperatures and low pressures. For ethane in particular, thermodynamic limits on conversion are significant to quite elevated temperatures, where contributions of homogeneous reactions begin to dominate. Alternative approaches that drive the reaction at lower input temperatures could provide better control, lower energy demands, and would enhance the CISTAR portfolio and enable scientific advancement. Non-thermal plasma (NTP) approaches will significantly advance alkane activation and coupling processes of interest to CISTAR as follows: (1) lower temperatures than the thermal process, (2) high energy electrons for in situ generation of reactive species (electrons, radicals and excited species) to facilitate initial ethane activation, (3) synergy between catalyst and plasma species to facilitate selective transformation to olefins, and (4) because the NTP is non-equilibrium, conversions that exceed thermodynamic equilibrium limits. T1P5 connects directly to ongoing activities within Thrust 1 (T1P1/T1P3: thermal catalysis and T1P4: thermal cracking) by targeting low bulk temperature reactions stimulated by NTP.

- **Abstract:** Non-thermal plasmas (NTPs) are partially ionized gases characterized by a non-equilibrium in temperature between high energy electrons (>10,000 K) and low energy ions and neutrals (~ambient temperature). The energetic electrons are the primary driver for promoting gas-phase and/or surface reactions through collisions with neutral gas-phase molecules to form electronically, vibrationally, and rotationally excited species as well as radicals that react with increased activity over ground-state species and surfaces. When coupled with a catalyst, the synergy between the plasma and catalyst can activate and convert hydrocarbons at relatively low temperature using electrical energy input. This project addresses two primary questions: 1). How does the non-thermal plasma influence gas phase products and facilitate dehydrogenation pathways for increased olefin or higher molecular weight product selectivity? 2). When coupled with a catalyst, how does the NTP facilitate catalytic ethane dehydrogenation and how can the combination of NTP and catalysts be developed to improve the product slate?

  In Y6, we used nonthermal plasma activation of light alkanes as an encouraging decarbonization strategy to produce chemicals or fuels from abundant and/or flared carbon sources. Often many products are observed from plasma stimulation of light alkanes, and many experiments were performed to identify gas phase, liquid phase, and solid phase products and improve selectivity. Plasmas are intrinsically non-equilibrium, and predictions of plasma products are thus more complicated than traditional chemical kinetic models. We began with a model based on the concept of maximum entropy generation to predict long-time speciation of ethane exposed to a plasma. To predict finite time

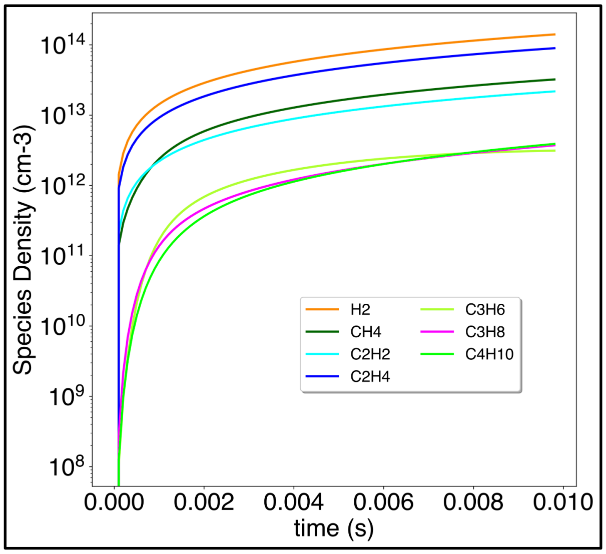
speciation, we turned to literature-reported cross-sections for ethane reactions in a plasma. We developed a microkinetic model that incorporated plasma-driven and thermal chemistries, and solved for given plasma conditions using the ZDPlaskin software. These results provide a platform upon which to understand how variations in plasma stimulation (composition, plasma power, temperature, intermittency) might be used to drive selectivity towards desired products.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
  - Preliminary results were collected for non-oxidative dehydrogenation and coupling of ethane by NTP-activation at various plasma powers at 5°C. It was found that the ethane conversion increased with increasing power, resulting in more coupling events and fewer dehydrogenation products. More C-C coupling resulted in higher concentrations of hydrogen in the products, which facilitated the hydrogenation of olefins back to alkanes. The larger molecular weight hydrocarbons condense on the walls of the reactor as liquids rather than coke. Thus, liquid products are favored at higher conversions and olefins are favored at lower conversions due to the presence of hydrogen.

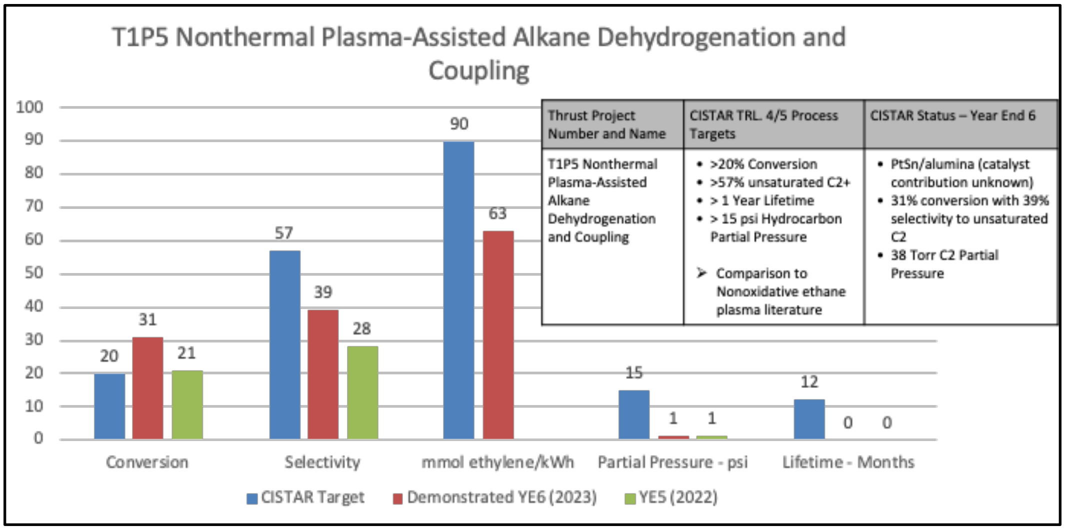


  - Higher bulk gas temperature improved ethylene carbon-selectivity from 14.3% at 5°C to 24.8% at 400°C. However, the stability decreased with increasing temperature due to the buildup of coke on the electrode. Thus, technology to prevent coking at higher temperatures will be important if ethylene is the desired product.
  - Unique patterns of carbon formation were observed on the inner electrode of the plasma reactor, and it was found that these patterns could be controlled by changing the applied voltage or the composition of the feed. Efforts to prevent this carbon from forming in the reactor through modification of the plasma proved.
  - We obtained preliminary 0D kinetic modeling results for ethane speciation as a function of external conditions, taking advantage of the algorithms implemented in ZDPlasKin. Selection of species and reactions are informed by literature. Thermal processes are described by Arrhenius-like expressions and electron-driven

processes by combining solutions to the Boltzmann Transport equation with tabulated cross-section data. We modeled ethane at 1 bar in a homogeneous, low-power-density plasma and solved for the low-carbon-number species evolution following plasma ignition. Time evolution of stable products are shown in the figure. The system reached a steady state by approximately 100 milliseconds. At these given conditions, ethane conversion is small (on the order of 0.1%) and selectivity strongly favors ethylene and hydrogen. These low conversions stand in contrast to our steady-state models based on "minimum entropy production" assumptions, for reasons to be determined.



- **Interdependence:** T1P5 officially started in Y6. The project is collaborative between the Hicks and Schneider groups at UND, and students on this project collaborate through Thrust 1 meetings and UND plasma meetings. Further, collaborations Thrust 2 have begun (identifying catalysts that facilitate gasoline production) and Thrust 1 (in situ and ex situ characterization of catalysts exposed to non-thermal plasma).
- **Testbed Impact and Value:** This project uses nontraditional chemistries. At this stage, the exact Testbed is unknown, but based on the initial results and possibilities, T1P5 could span Testbed 1, 2, and 3.
- **Technical Targets:** T1P5 is in the early stages of research and development (TRL 1). The technical targets are based on results from literature (Cameli et al., "Non-Oxidative Ethane Dehydrogenation in a Packed-Bed DBD Plasma Reactor", *Plasma Chemistry and Plasma Processing*, 2023, https://doi.org/10.1007/s11090-023-10343-w).



Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** The use of plasma stimulation to facilitate light alkane dehydrogenation and subsequent coupling is novel, with few literature examples highlighting non-oxidative ethane or propane dehydrogenation pathways. Pursuing this route will provide CISTAR a suite of technologies that are thermally- or electrically-driven which could operate in series or in parallel to generate desired products. Plasmas have been applied to C-H activation for catalytic processes including methane coupling, methane reforming and volatile organic compound (VOC) destruction. Several plausible hypotheses have been suggested in the literature to account for the enhanced C−H activation using plasma−catalyst combinations including (1) gas-phase electron impact-regulated hydrocarbon dissociation caused by the plasma, (2) the generation of increased-temperature catalytic sites by the plasma, (3) packed-bed effects due to enhanced electric fields from the use of porous dielectric materials, and (4) the direct interaction between active metal surfaces and species in the plasma. This project will focus on plasma-assisted conversion of light alkanes to olefins or other longer chain products. Models are essential to guide research, and we are building necessary capabilities.
- **Path to Targets Summary:** The project will capitalize on the current lab-scale systems available at UND to Thrust 1 researchers. Multiple reactors are available that can operate with plasma stimulation. As the project matures, consideration will be given to larger scale plasma systems and if these should be constructed or obtained through external collaborations. Simulations/modeling efforts will be developed by Thrust 1 researchers at UND.

- **Specific Plans Organized by Challenge:**
    - Perform a process variable screening study by measuring ethane conversion and product selectivity at different plasma powers, flow rates, gas compositions, and bulk gas temperature without a catalyst (plasma phase reactions). Correlate observations against reduced kinetic models of plasma chemistry based on available literature kinetics, exploring over a superset of the parameter space. Identify limits of plasma-only ethane conversion.
    - Determine plasma-catalyst synergy by performing similar process variable screening studies noted above in the presence of different catalysts. Perform detailed characterization of catalysts before and after plasma exposure through ongoing collaborations within Thrust 1. Couple predicted plasma-phase models with surface microkinetic mechanisms to predict/correlate observed and modeled synergies.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Clarke, R. J.; Hicks, J. C., "Self-Organization and Nitrogen Incorporation in Diamond-Like Carbon Microstructures Synthesized by Nonthermal Plasma.", *The Journal of Physical Chemistry C*, 127 (31), 15239-15245 (2023).
2. Poirier, D.; Hale, D.; Bourbon, P.; Hicks, J.C., "Toward Sustainable Production of N-Containing Products via Non-Thermal Plasma-Enhanced Conversion of Natural Gas Resources", submitted (under review).
3. Rivera-Castro, G.J., Scotto d'Apollonia, A.; Cho, Y.; Hicks, J.C., "Plasma-Catalyst Synergy in the One-Pot Non-Thermal Plasma-Assisted Synthesis of Aromatics from Methane", submitted (under review).

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T1P6 Decarbonizing Ethylene Production with Low-Temperature Electrolysis* ***Project Lead:*** *Brian Tackett*

F: Brian Tackett (PU)
GS: Po-Chun (Casper) Huang (PU)

Project Goals

- Develop electrocatalytic CISTAR process for the production of ethylene from light alkanes
- Identify appropriate electrochemical configuration (medium temperature solid-oxide electrolysis, ambient temperature non-aqueous liquid electrolysis) to enable energy efficient and selective electrocatalytic dehydrogenation reactions
- Quantify fundamental kinetic parameters for adsorption and reaction (adsorbate coverage, adsorbate identity, and binding strengths) as functions of potential and electrolyte identity.
- Identify appropriate catalysts to facilitate the reaction, by leveraging CISTAR catalysts and/or synthesis of new materials for the desired conditions.
- Develop activity and selectivity trends based on microkinetic modeling and quantified parameters to enable rational catalyst and system design.

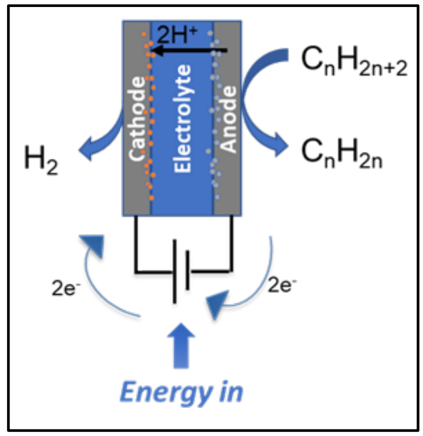


Figure: Electrochemical alkane dehydrogenation inherently separates the olefin product from the hydrogen product on spatially separate electrodes. This avoids equilibrium limitations of thermal dehydrogenations, which could substantially reduce the capital and operating expenses involved with downstream separations.

Barriers

- The extent to which electrolyte controls the reactivity and selectivity (due to conductivity in the solid oxide case, and due to solvation effects in the non-aqueous liquid case) is not well understood
- Protocols for systematic catalyst study in solid oxide electrolyte systems are not well defined and could be significantly impacted by synthesis procedures.
- Lack of knowledge on the appropriate catalyst under solid oxide electrolysis conditions and under non-aqueous liquid electrolysis conditions.

Methodologies

- Electrochemical mass spectrometry will be used to quantify sub-monolayer coverages and adsorption behavior under varying potential and electrolyte conditions for the non-aqueous liquid case.
- Relevant electrocatalysts for the solid-oxide electrolyte will be extensively characterized to understand structure-function-conductivity behavior

Research Achievements

- This project was newly started this summer, with a new 1st year PhD student. We have taken preliminary measurements of alkane reactivity on Pt in non-aqueous electrolyte and are assembling appropriate equipment to synthesize relevant solid-oxide electrolyte materials and catalysts.

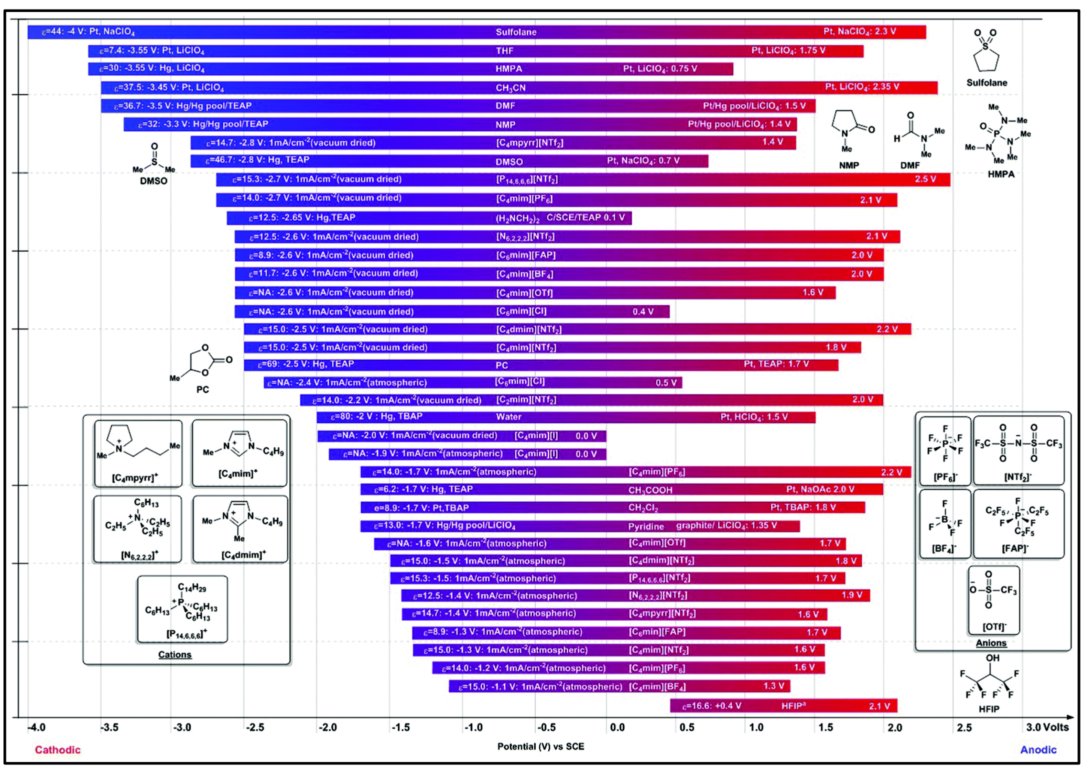
Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** Thrust 1 efforts primarily target dehydrogenation of ethane, which is abundant in North American Shale gas. Typical steam cracking of ethane to ethylene takes place at large centralized reactors that involve significant capital expense and energy input. In particular, the equilibrium limitations of ethane steam cracking, even at high temperatures, require substantial downstream separations to remove hydrogen and separate paraffin from olefin. Alternative approaches to drive the reaction non-thermally would add to the CISTAR portfolio, adding flexible technologies that could be used to meet site-specific demands. Low temperature electrocatalytic approaches will significantly advance alkane activation and dehydrogenation processes of interest to CISTAR by: (1) conducting dehydrogenation at lower temperatures than the thermal process, potentially even at ambient temperature; (2) reducing the capital expense of downstream separations units by inherently avoiding equilibrium limitations associated with the thermal process; (3) reducing the CO2 emissions associated with ethylene production by driving the reaction with (potentially renewable) electrons and by reducing the total energy required for separations, and; (4) enabling smaller distributed alkane processing as a result of smaller electrochemical reactors that do not require high temperature or extensive separations units. The project is also directly connected with other Thrust 1 projects, especially T1P1, T1P3, and T1P5 which involve catalytic dehydrogenation reactions which share fundamental principles with the electrocatalytic reactions targeted here. There is additionally cross-thrust integration with T2P5 (non-thermal C-C coupling) and T3P4 (electrochemical methane oxidation) which also utilize electrocatalytic processes.
- **Abstract:** Electrocatalytic ethane dehydrogenation to ethylene is a promising alternative dehydrogenation technology that could substantially decarbonize ethylene production by utilizing renewably sourced electrons and by avoiding equilibrium limitations of the thermal case, thereby limiting required separations. This can be achieved either at medium temperature (450 - 600C) in solid oxide electrochemical cells, or at low/ambient temperature (<100C) with non-aqueous liquid electrolyte electrochemical cells. The technology is in very early stages of development, with only a handful of peer-reviewed articles published on the solid oxide case. Nevertheless, the results of these works are highly promising, far surpassing single pass equilibrium conversion of the thermal case with >90% selectivity. Our goal, therefore, is to optimize the catalyst to enable high selectivity and conversion at the lowest temperatures possible. We therefore plan to use relevant CISTAR catalysts and Thrust 1 knowledge of thermal reactions to optimize the solid-oxide electrocatalytic process. However the solid-oxide case has a lower temperature limit on the proton conductivity of the electrolyte, which motivates us to explore non-aqueous liquid electrolyte systems. Our goal, therefore, will be to identify the appropriate

electrolyte/electrocatalyst combination that enables selective dehydrogenation without overoxidation to unwanted products. We will also quantify fundamental kinetic parameters for both scenarios, which will establish the standard for the field, as there are no known attempts to determine these.

In Year 6, we onboarded a 1st year PhD student in the summer, who has researched the best materials and synthesis methods needed to test solid-oxide electrolysis for ethane dehydrogenation, and we have begun assembling the experimental setup. We have also researched and identified promising non-aqueous electrolytes for our preliminary studies of alkane adsorption and reaction in those systems.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
    - Preliminary results have not yet been obtained, and the main effort for this project since onboarding a new student has been establishing the experimental setup to enable the work. This involved working with T3P4 researchers to understand the appropriate equipment needed for solid oxide electrolysis material synthesis and testing, and development of a synthesis plan for initial studies.
    - For the non-aqueous liquid electrolysis, we identified acetonitrile and dimethyl ether as potential electrolyte candidates that would enable effective electrocatalytic dehydrogenation at room temperature. One of the primary selection criterion was the electrochemical stability window of the electrolyte, which we obtained from literature, such as the following figure:

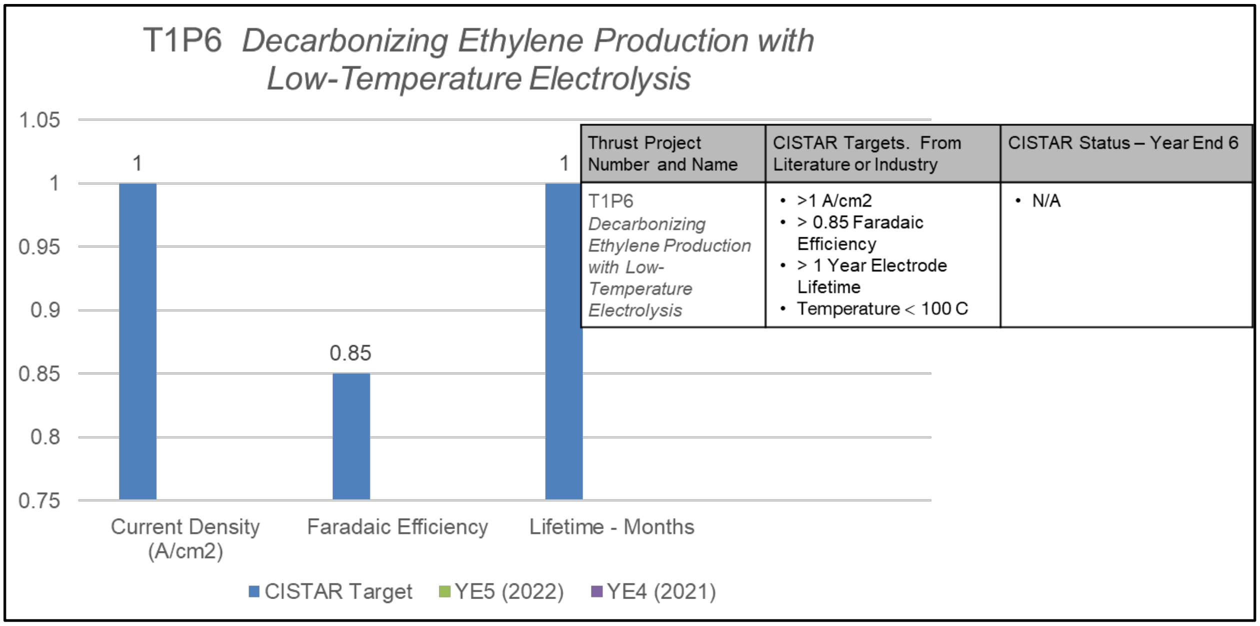


- We also conducted (along with Gary Sawyer) a preliminary techno-economic analysis of the electrocatalytic ethane dehydrogenation system based on the solid oxide electrolysis case. The results show that, at a first pass with idealized numbers, there could be substantial reduction in capex and opex, due to the reduction in downstream separations, compared to a steam cracker on a 1500 kTA ethylene basis. These results (table below) are highly preliminary but show that there is

	Steam Cracker	**Electrochemical Reactor**
Capital Cost: Reaction	Base	<< 50% of Base
Capital Cost: Recovery	Base	< 50% of Base
Energy Cost: Reaction	\$0.046/kg @ \$3/MMBTU	\$0.083/kg @ \$0.05/kWh
Energy Cost: Recovery	Base	50% of Base

reasonable promise for pursuing electrocatalytic routes.

- **Interdependence:** T1P6 officially started in the summer of Y6 with the onboarding of a new 1st year PhD student. The student on this project collaborates with Thrust 1 researchers through Thrust 1 meetings. The student has also collaborated with T3P4 researchers to help design an appropriate solid-oxide electrolysis system. Further collaborations have been identified in Thrust 2 (namely T2P5), by which unique insights into electrocatalytic activation of hydrocarbons can be mutually beneficial. We also anticipate more extensive collaborations with other Thrust 1 researchers for in-situ characterization of electrocatalyst materials.
- **Testbed Impact and Value:** This project uses nontraditional chemistries. At this stage, the exact Testbed is unknown, but based on the initial results and possibilities, T1P6 could span Testbed 1, 2, and 3
- **Technical Targets:** T1P6 is in the early stages of research and development (TRL 1). The technical targets are based on results from literature (Ding et al., "A novel low-thermal-budget approach for the co-production of ethylene and hydrogen via the electrochemical non-oxidative deprotonation of ethane", *Energy and Environmental Science*, 2018, https://doi.org/10.1039/C8EE00645H).



Thrust Project Number and Name	CISTAR Targets. From Literature or Industry	CISTAR Status – Year End 6
T1P6 *Decarbonizing Ethylene Production with Low-Temperature Electrolysis*	• >1 A/cm2 • > 0.85 Faradaic Efficiency • > 1 Year Electrode Lifetime • Temperature < 100 C	• N/A

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** We have currently identified the appropriate materials and synthesis equipment and procedures needed to synthesize and characterize the solid oxide electrolytes and electrocatalysts. We have also identified candidate electrolytes for the liquid non-aqueous electrolysis. Our overall challenges at this early stage of the project are to (1) establish any catalyst dehydrogenation performance trends (current density, faradaic efficiency, stability) for the solid oxide case as there are none in the literature, and (2) demonstrate the feasibility of ethane adsorption and reaction on electrocatalysts in non-aqueous electrolytes. The underlying challenge at this stage is to determine the fundamental molecular transformations that occur in the electrochemical system and understand how they compare to what we know about the analogous thermal systems. Answering this question will enable us to leverage CISTAR knowledge and collaborations to design effective electrocatalytic dehydrogenation processes.
- **Path to Targets Summary:** This project will utilize fundamental electrocatalytic characterization techniques available at PU to study adsorption and reaction for the non-aqueous electrolyte case. We are also in the process of purchasing and building the appropriate solid-oxide synthesis equipment needed to make relevant solid oxide electrolytes and catalyst materials. As the project matures, we may consider scaling up the electrode size to demonstrate higher reaction rates.
- **Specific Plans Organized by Challenge:** To understand adsorption and reaction at electrocatalyst surfaces in the non-aqueous liquid electrolyte case, we will utilize a sensitive and versatile electrochemical mass spectrometer (EC-MS). This will enable us to accurately calculate adsorbate coverage and to speciate products that are evolved from the

electrocatalyst surface. In this way we can use the EC-MS in an analogous manner to a temperature program desorption experiment to quantify fundamental kinetics. This will also enable us to select proper electrolytes based on performance. For the solid oxide electrolyte synthesis, we will follow published procedures of high-energy ball milling, annealing, and sintering in order to synthesize the relevant electrolyte. Characterization and testing of these materials will also be aided by collaborations in Thrust 1 as well as in T3P4.

THRUST 2:

OLIGOMERIZATION

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T2P1 Brønsted Acid-Catalyzed Olefin Oligomerization* ***Project Lead:*** *Linda Broadbelt (NU)*

F: Rajamani Gounder (PU), Justin Notestein (NU), William Schneider (ND), Fabio Ribeiro (PU)		
GS: Elizabeth Bickel (PU), Ricem Diaz Arroyo (PU), Jerry Crum (ND), Andrew Wolek (NU), Grant Marsden (NU), Thomas Hietala (NU, visiting student), Kurt Russell (PU) , Sopuruchukwu Ezenwa (PU), Diamarys Salome Rivera (PU), Hao-Ran Lei (PU)		
PD: Sai Praneet Batchu (NU)	**UG:** Gillian Simpson (NU), Geoffrey Hopping (PU), Cameron Taylor (ND)	
REU: Kaila Durden (PU), Kyla Fung (PU)	**RET:** Soren Kyale (NU)	**S:** Evan Sowinski (PU)

Project Goals

- Study the effects of zeolite material properties (Si/Al ratio, Al site proximity, Al spatial zoning in the crystallite, and crystallite size and diffusion parameter or Thiele modulus) on olefin oligomerization rate, product selectivity, and deactivation behavior
- Develop novel non-zeolite Brønsted acid materials with high activity and mitigated deactivation
- Develop synthesis methods to vary zeolite material properties independently of one another
- Develop core-shell zeolite synthesis methods to bias Al spatial distributions toward/away from external crystallite surfaces, to alter the effects of coupled reaction-diffusion phenomena and pathways that cause deactivation
- Develop characterization methods to quantify extent of Al spatial distribution and zoning, and to quantify diffusion rates of probe molecules, and apply these techniques to study CISTAR zeolite samples
- Create microkinetic models accounting for effect of Al spatial distribution and diffusion on oligomerization reactivity

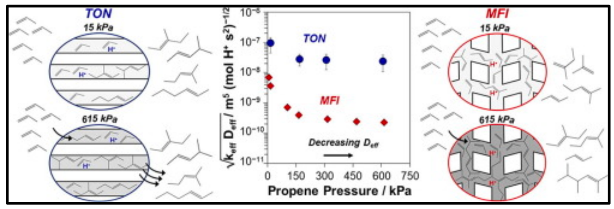


Figure: Propylene oligomerization rates and selectivities are influenced by intrazeolite diffusion restrictions caused by heavier oligomers that reside within zeolite pores during reaction. The MFI framework topology is a 3-dimensionally connected 10-membered ring zeolite, with have void spaces at channel intersections that are larger than the limiting windows for entry, allowing for growth of heavy oligomers that preferentially form at higher propene pressures and introduced more severe diffusion restrictions. Changing the framework to the TON topology, which is a 1-dimensional 10-membered ring pore, restricts the growth of larger hydrocarbons and alleviates intrazeolite diffusion limitations in the same reaction temperature and pressure range.

Barriers and Methodologies	Research Achievements
Barriers ● Identifying thermal stability and performance of SiO_2/MOx materials at catalytically relevant operating temperatures ● Developing unifying relations that can model and predict oligomerization rate and selectivity differences on all MFI zeolite samples (and other zeolite frameworks) when properties simultaneously change with synthesis procedure ● Rates and selectivities of forming heavier oligomers depend sensitively on intracrystalline diffusional constraints. ● Decoupling kinetic and transport effects on observed rates and product selectivities requires the development of a crystallite-scale, reaction-transport model, and independent validation by experiment and theory ● Product portfolio at high conversion demands large microkinetic models **Methodologies** ● Synthesis of samples of varying crystallite size and Al spatial distribution or zoning ● Estimates of effective diffusivities on CISTAR samples using rate of adsorption measurements of probe molecules ● Kinetic measurements performed on a single zeolite sample of varying diffusion parameter ● Collaboration between theoreticians (DFT, microkinetic modeling) and experimentalists to interpret and predict experimental data ● Leveraging Technology Module to collect data at high conversion and duration to collect sufficient liquid product for detailed isomer composition analysis (with Prof. Hilkka Kenttamaa, PU)	**Research Achievements** ● Microkinetic modeling framework that takes into account intraparticle diffusion effects has been developed, solved using an orthogonal collocation method summarized by Pirro. ● New material synthesis approaches developed at Northwestern (Notestein) focused on controlling the deposition of small amounts of silica on Lewis-acidic core oxides, and developing correlations between synthetic methods, acid properties, and reactivity in various acid-catalyzed probe reactions. This effort cemented a cross-thrust collaboration (w/ T1: Datye; paper published in *J. Catal.*). ● Propene oligomerization rates and selectivities in 10-MR zeolites, but not 12-MR and larger pores, are strongly influenced by intrazeolite diffusion limitations imposed by heavier hydrocarbons that build up and remain occluded within zeolite micropores during catalysis. (paper published in *ACS Catal.*) ● Intrazeolite diffusion restrictions worsen on MFI samples of higher Si/Al ratio (lower H^+ content) because this favors growth of larger hydrocarbon chains. (paper published in *ACS Catal.*) ● Intrazeolite diffusion restrictions are alleviated on TON zeolites (a 1-D 10-MR pore topology) compared to MFI (a 3-D 10-MR pore topology) because products formed are restricted to linear and mono-branched species. (paper published in *J. Catal.*) ● Diffusion-limited zeolite samples show time-on-stream deactivation as occluded hydrocarbons accumulate, and shift product selectivities toward lighter molecules (e.g., C_6 dimers), and this problem is alleviated on catalysts synthesized with smaller crystallite sizes. (provisional patent filed in Feb. 2023). ● The number of external H^+ sites on zeolite samples was varied by post-synthetic passivation treatments and core-shell synthesis methods, and quantified using a probe reaction of bulky reactants (mesitylene alkylation with benzyl alcohol). (paper submitted in Sep. 2023).

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** In support of CISTAR's research strategic plan, Thrust 2 researchers are developing new catalytic strategies to convert the olefins produced in Thrust 1 (alkane dehydrogenation) to higher molecular weight products that can be transported as a liquid and used as transportation fuels or chemicals. Thrust 2 explores different strategies to control the product distribution achieved by olefin oligomerization. This project, T2P1, focuses on the use of solid Brønsted acid catalysts as the vehicle to convert olefins into a distribution of higher molecular weight products that are primarily branched, with molecular and physical properties that are being evaluated in conjunction with Thrust 4 researchers for application as a blendstock for gasoline related to Testbed 3. The research portfolio in T2P1 focuses on novel synthesis strategies to control catalyst material properties and evaluations and predictions of reactivity using a combination of experimental kinetic studies and modeling analyses that aim to address knowledge gaps regarding control of the product distribution, catalyst lifetime, and operation at conditions compatible with the overall vision for the integrated CISTAR process. Solid acids provide a promising and diverse materials platform to develop novel olefin oligomerization technologies because these materials can be engineered with different materials properties (e.g., acid site distribution and location, pore structure and connectivity, particle and crystallite diffusion length) that influence olefin oligomerization rates, product distribution and catalyst lifetime.

- **Abstract:** Solid Brønsted acids provide an attractive materials platform for catalyzing olefin oligomerization reactions, because they can be engineered with different materials properties (e.g., active site distributions, characteristic diffusion parameter) to influence reaction rates, product selectivities, and catalyst lifetime. Current technical challenges in acid-catalyzed oligomerization are related to the broad molecular weight range of oligomer products that are generated on commercially available materials, and the short catalyst lifetimes observed during practical operation that often result from coke formation. In this reporting period, CISTAR researchers in T2P1 have made significant progress on developing new materials synthesis strategies, and on combining computational and experimental methods for materials characterization and evaluation of model solid acids with different materials properties for olefin oligomerization, including reactor-scale modeling that includes the effect of intraparticle diffusion limitations. Broader impacts of these research efforts include the development of new catalyst synthesis and characterization methods for solid acid materials, which are used for reactions and separations relevant to CISTAR and other process technologies, and the development of microkinetic modeling approaches to account for complexities in reaction networks and catalyst structures, which are broadly applicable to other reaction classes.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

Influence of reaction kinetics and diffusion on propene oligomerization on Brønsted acid zeolites: This occluded organic phase becomes heavier in composition at higher propene pressures and lower reaction temperatures, which favor the growth of higher-molecular-weight oligomers, resulting in effective diffusivities of reactant and product alkenes that systematically decrease with increasing propene pressure. MFI samples of lower H^+-site density possess higher rate constant ratios for trimerization relative to dimerization, leading to the formation of heavier alkenes within their micropores and, in turn, to a greater decrease in the effective diffusivity of alkenes with increasing propene pressure. As a result, measured dimerization rates on MFI samples exhibit an increasingly negative-order dependence on propene pressure with decreasing H^+-site density. These results are described in a manuscript published in *ACS Catalysis* in 2023. Furthermore, intrazeolite diffusion limitations are alleviated in TON zeolites, which are unidimensional 10-MR straight-channel pores that restrict the formation of highly branched and larger alkenes that otherwise form in MFI (3D, 10-MR), leading to higher rates and more selective formation of linear and monobranhed alkenes. These results are described in a manuscript published in *Journal of Catalysis* in 2023.

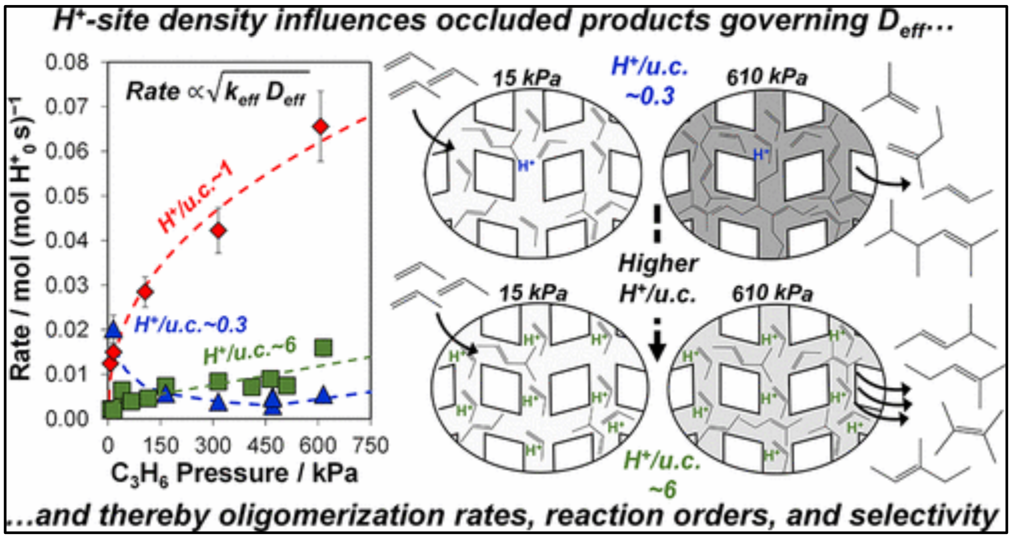


Figure 1. Propene oligomerization rates on MFI zeolites are influenced by coupled reaction-transport phenomena, and intrazeolite diffusion restrictions become more consequential on samples with increasing Si/Al ratios (lower H^+ per unit cell) that favor growth of heavier alkenes that remain occluded within pores during catalysis, leading to negative reaction-order dependences.

<u>Microkinetic modeling of effect of spatial proximity of acid sites</u>**:** Within zeolites, T-site location is a major factor for determining catalytic activity. The 12 crystallographically unique T-sites of orthorhombic MFI demonstrate significant differences that are difficult to resolve experimentally. A DFT-parameterized microkinetic model was developed that is able to capture with fine resolution the effects of each independent T-site of MFI on a test reaction of methanol dehydration to dimethyl ether. Flux analysis, surface speciation analysis, and degree of rate control analysis were used to identify that methanol tetramers are the key intermediate for the production of DME over MFI. T4, T6, T7, and T12 were identified as dominant sites to catalytically promote this reaction, matching with the lower activation barriers for the tetramer mechanism on these sites. The technique developed through this work expands the existing framework for evaluating paired sites in zeolites as catalogued in the Y6 report, creating a holistic technique able to capture both location and proximity effects.

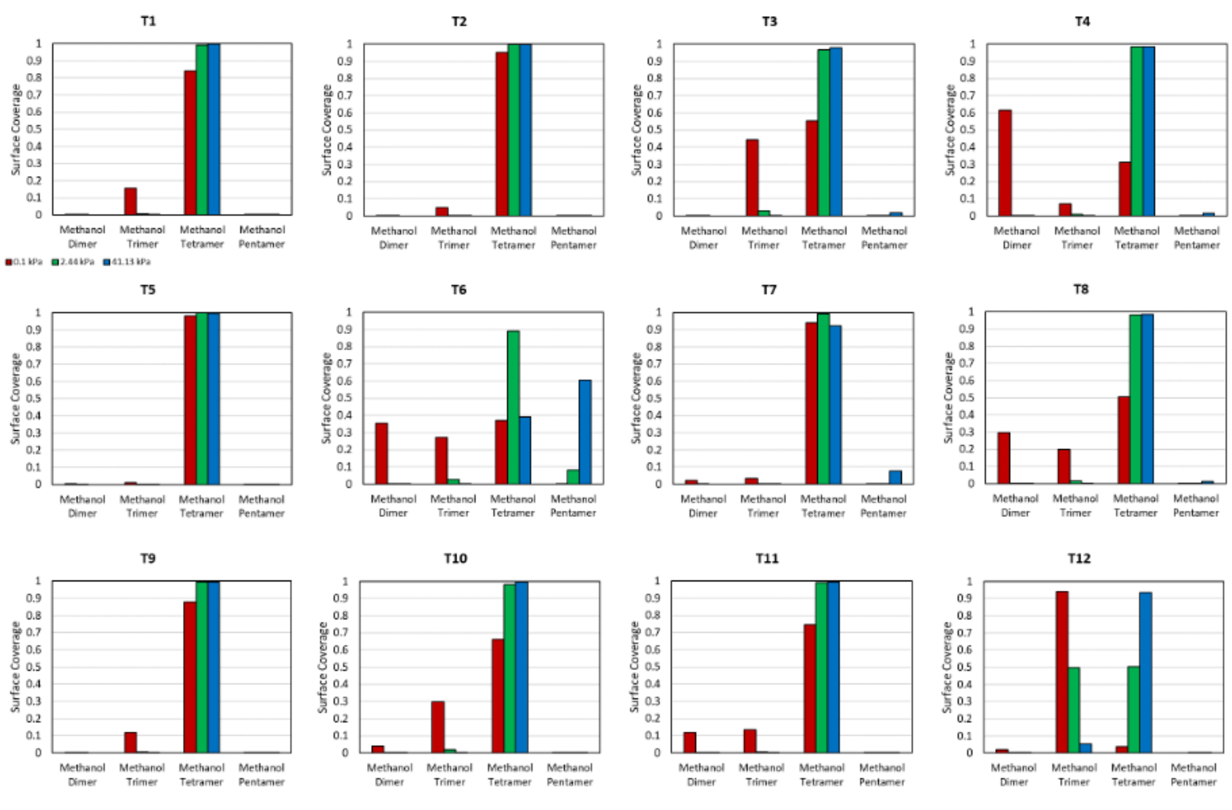


Figure 2. The surface coverage of major species for all T-sites evaluated at different methanol partial pressures, for methanol dimerization on MFI as a demonstration of the ability to model multiple active sites using microkinetic modeling. Red, left bar: 0.1 kPa. Green, middle bar: 2.44 kPa. Blue, right bar: 41.13 kPa..

<u>Microkinetic modeling of propylene oligomerization that incorporates intraparticle diffusion limitations:</u> To better connect the design of materials with tailored active site distributions, the microkinetic modeling method was extended to incorporate effects of intraparticle concentration gradients due to diffusion limitations. A visiting scholar from the group of Professor Pedro Mendes in Portugal, Thomas Hietala, implemented a reactor model that allowed for tracking of concentration/pressure gradients in the axial direction of a PFR that also incorporated concentration gradients in the pore dimension. The reactor model is solved using a finite difference method:

$$-U_s \cdot \frac{dC}{dz} = \frac{3}{r_p} \cdot D_e \cdot \left(\frac{dC_{int}}{dr}\right)_{r=r_p}$$

where the reaction rate is included as the flux at the pore mouth of the zeolite catalyst. The intraparticle concentration is solved using an orthogonal collocation method:

$$\frac{d^2 C_{int}}{d^2 r} + \frac{2}{r} \cdot \frac{dC_{int}}{dr} - \frac{r_A}{D_e} = 0$$

A simplified LHHW rate law based on our earlier work for modeling of propylene oligomerization has been incorporated to date, and inclusion of rates based on elementary steps without an assumption of a rate-determining step is in progress. Comparison to the experimental data collected in the Gounder group will be completed in Y7.

Design of Brønsted acid zeolites with tailored atomic arrangements and small crystallite sizes: Significant progress was made in the design of Brønsted acid zeolites with small crystallite sizes using surfactant-based structure directing agents (SDAs). These materials show improved time-on-stream oligomerization rates and product selectivities, and mitigated deactivation. This work was disclosed in a provisional patent filing in Feb. 2023, with a manuscript to be submitted in the near future. Additionally, different post-synthetic treatments were explored to passivate Brønsted acid sites at the external surfaces of MFI crystallites, including ammonium hexafluorosilicate treatments (AHFS; intended to replace framework Al atoms with Si) and tetraethylorthosilicate treatments (TEOS; intended to graft or "cap" exposed Brønsted acidic OH groups). Routes for the direct synthesis of core-shell materials to control active site zoning was also progressed. Research performed by six undergraduate students at PU (including two pairs of REU/REM students over the summers of 2022 and 2023) led to the development of characterization methods using a probe reaction of bulky molecules (mesitylene alkylation with benzyl alcohol) to quantify the number of external H^+ sites present in a given zeolite material. This is being written into a manuscript for submission in Sep. 2023 to *Reaction Chemistry & Engineering*. In a manuscript published in *Micro. Meso. Mater.* (Schneider) describes a strategy and software package (https://github.com/jtcrum/zse) for "fingerprinting" T sites in frameworks based on their ring membership, which is useful for constructing DFT models and for machine learning on zeolite properties.

Synthesis of novel acidic non-zeolite catalysts: Catalytically active acid sites associated with the silica-MOx interface were probed with a series of overcoated SiO_2 on Nb_2O_5, Al_2O_3, TiO_2, and ZrO_2. NH_3 TPD, pyridine DRIFTS, and ^{31}P NMR trimethylphosphine oxide chemisorption studies indicated that the speciation of acid sites in the materials evolved as a function of SiO_2 loading and the nature of the underlying metal oxide, impacting the quantity and stability of Brønsted sites. Catalyst activity was highly dependent on SiO_2 loading in the liquid phase hydroalkoxylation of dihydropyran with n-octanol as well as the vapor phase oligomerization of propylene. At SiO_2 surface densities corresponding to approximately 1 Si per surface M, the activity of these catalysts in hydroalkoxylation passed through a maximum 10-20 times higher than the activity of the core oxide. The activity of SiO_2-coated Al_2O_3 was nearly 100-fold greater than that of bare Al_2O_3 in propene oligomerizaton. All catalysts showed negligible cracking and good stability after an initial period. First-order propene oligomerization rate constants increased with core oxide acidity as measured by TMPO chemisorption, which is a good proxy for deprotonation energies. The trends followed the same pattern as for more conventional solid acids. New results across many materials reported in Wolek et al., J. Catal.

https://doi.org/10.1016/j.jcat.2023.06.008, with an additional manuscript under review specifically on the oligomerization chemistry.

- **Interdependence:** The researchers in T2P1 span three universities (Purdue, Notre Dame, and Northwestern) who work closely together to accomplish the project goals. Students collaborate closely between experimental groups and between experimental-theory groups to efficiently utilize the resources at each institution. We also hold frequent in-person day-long research update and planning meetings, to evaluate current research and guide future directions and collaborations within the Thrust, with the most recent one being held at Purdue Northwest campus (Hammond, IN) in August 2023. Most publications reflect collaboration from more than one faculty member within Thrust 2.

  Cross-thrust collaborations occur via two mechanisms: 1) direct communication with T4 contacts to identify process operation targets, and 2) via participation from PIs that reside in multiple thrusts (Schneider: T1, T2; Notestein: T2, T3). Specific examples include microkinetic models developed by Broadbelt used by Stadtherr (T4) to identify operating conditions and markets to maximize the value (e.g., octane rating) of oligomerization products, and by Dowling (T4) to develop lumped kinetic models for reactor simulation that can be used in process optimization efforts.

  CISTAR Fellow (and SLC Chair), Ricem Diaz Arroyo, participated in an internship with Chevron, a CISTAR industrial member. CISTAR undergraduate researcher, Geoffrey Hopping (PU), graduated with his BS in ChE in spring 2023 and is now a PhD student in ChBE at Georgia Tech.

  CISTAR Fellow, Grant Marsden, finished his PhD in June 2023 and has begun full-time employment at Shell. CISTAR Fellow Andrew Wolek completed his PhD studies and has begun full-time employment at Dow, a CISTAR industrial member.

- **Testbed Impact and Value:**

  This project is relevant to Testbeds 2 and 3, which make linear (diesel) and branched (gasoline) hydrocarbons. The research in T2P1 can provide new process alternatives that can undergo economic evaluation by the Testbed team. For example, the development of a catalyst that is unreactive for ethene oligomerization in the presence of propene, and another catalyst that is selective for ethene oligomerization in the presence of traces of propene, would allow designing a process with these two catalysts in series to process an ethene/propene co-feed (that is derived from dehydrogenating shale gas alkanes) and potentially remove separation units to prepare distinct ethene and propene streams. This project is also relevant to future testbeds that may be constructed to produce chemicals. Connecting the Testbeds with the Technology Module, the Micromeritics Effi reactor is fully operational, achieving Milestone 12a and supporting the realization of 12b. Novel materials including SiO_2/TiO_2 and aluminosilicate zeolites of the MFI topology (with small crystallite size)and non-MFI topologies (e.g., MEL) have been tested in the Technology

Module for extended times on stream. Typical data that can be obtained from the Effi reactor is shown in Figure 3 using propylene oligomerization over a commercial MFI zeolite (large crystallite size, ~300 nm) and over a CISTAR MFI zeolite (small crystallite size, ~20 nm) showing more stable product distribution with time-on-stream.

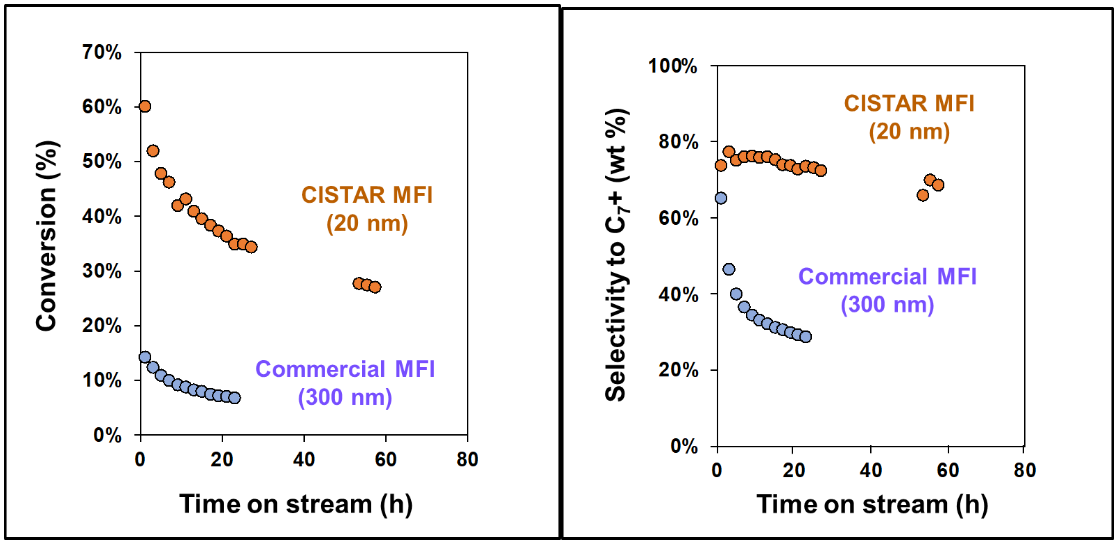
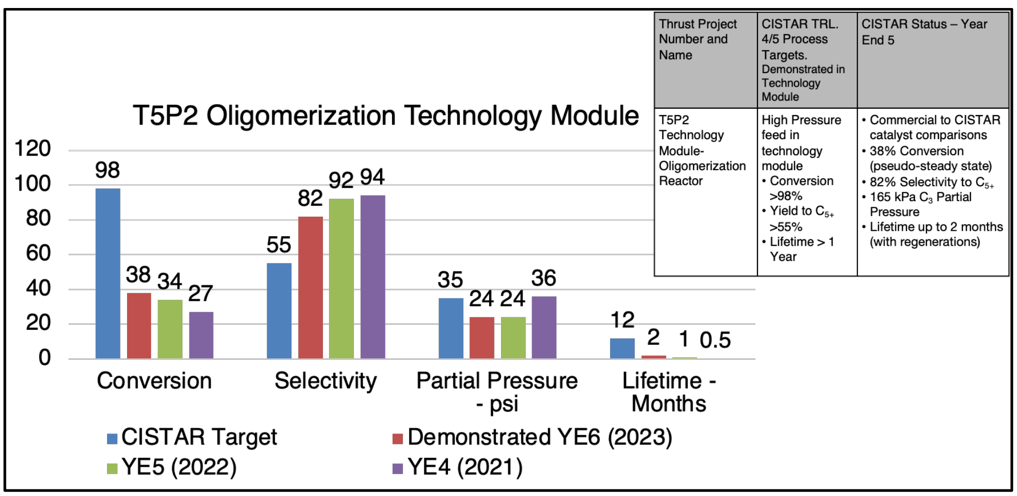


Figure 3. (left) Propene conversion measured at equivalent reaction conditions (T, P, site contact time) and (right) selectivity to liquid (C_7+) products with time-on-stream.

- **Technical Targets:**



Thrust Project Number and Name	CISTAR TRL. 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Year End 5
T5P2 Technology Module-Oligomerization Reactor	High Pressure feed in technology module • Conversion >98% • Yield to C_{5+} >55% • Lifetime > 1 Year	• Commercial to CISTAR catalyst comparisons • 38% Conversion (pseudo-steady state) • 82% Selectivity to C_{5+} • 165 kPa C_3 Partial Pressure • Lifetime up to 2 months (with regenerations)

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:**
  - Laboratory work in the Notestein group from the current year has demonstrated that reactivity in SiO_2/MOx has a strong dependence on SiO_2 surface loading and

the core metal oxide identity. Activity was not completely predictable from SiO_2 content, necessitating a thorough reaction screening. Brønsted strength was quantified for several overcoated materials, and it trends with the core metal oxide's chemical hardness. SiO_2/Al_2O_3, SiO_2/Nb_2O_5, SiO_2/TiO_2, and SiO_2/ZrO_2 materials were screened for propylene oligomerization (165 kPa, 230 °C), and reaction orders, apparent barriers, and selectivities were all determined. First-order rate constants span nearly three orders of magnitude between these materials, in a way that trends similar to that observed for zeolites and heteropolyacids. True oligomer selectivity is nearly 100% under laboratory conditions. Technology module testing confirms this observation, as well as heavies production that is lower for a given conversion than for comparable zeolite catalyst. These results are consistent with the weak acidity and lack of internal diffusional constraints in these materials.

- Developing unifying relations that can model and predict oligomerization rate and selectivity differences on all MFI zeolite samples remains a challenge. One experimental challenge arises from the fact that many material properties simultaneously change when changing the synthesis procedure used. This will be addressed by developing more purposeful synthetic approaches that allow control over changing one material property in isolation. The main variables to be studied in the following project period are: (i) local active site arrangements (isolated vs. paired Al), (ii) spatial heterogeneities and "zoning" of active sites toward external surfaces or toward internal cores, (iii) unconfined active sites at external zeolite surfaces, and (iv) small crystallite sizes.
- Rates of forming heavier molecular weight oligomers depend on intracrystalline diffusional constraints. Decoupling kinetic and transport effects on observed rates and selectivities of product formation requires the development of a crystallite-scale, reaction-transport model, and independent validation of certain properties by experimental and theoretical methods.
- Microkinetic models that take into account different site environments demand that concentration gradients within the pore be tracked to be able to calculate rates that each site environment turns over. As described above, significant progress has been made in the past year to develop more detailed reactor-scale models that take into account intraparticle concentration profiles.
- It is kinetically challenging to model high conversion and high carbon number due to the large number of isomers and isomeric reactions that make models too computationally stiff and expensive to run. Lumping techniques have been developed (see T2P2), which will be applied to modeling the testbed oligomerization experiments run on an acidic zeolite. Detailed product

composition analysis from a testbed experiment will be performed in collaboration with Prof. Hilkka Kenttamaa (PU, Chemistry).

- **Path to Targets Summary:**
  - Research in the next year will focus on scaleup of SiO_2/MOx materials of interest to the Technology Modules for ethylene/propylene oligomerization and preparing results for external dissemination. No new materials development is planned.
  - Identify mechanistic explanations for differences in dimerization rate and product selectivity across zeolites of different active site distribution, active site proximity/density, and diffusion parameter (crystallite size).
  - Quantitatively measure and compare changes in intracrystalline diffusion characteristics of CISTAR-synthesized zeolite catalysts, and advance promising materials to the Technology Module for testing under more aggressive reaction conditions.
  - Investigate ethylene oligomerization on Bronsted acid zeolites and bifunctional materials to lower temperature windows for reasonable conversion, and tuning product distributions either to suppress aromatics (for fuels testbeds) or to make more aromatics (for chemicals testbeds)
  - Collect ethylene oligomerization data on Bronsted acid-zeolites under varying reaction conditions (temperature, pressure, conversion) to complement microkinetic modeling efforts and eventual ROMK/process models (with Thrust 4)
  - Perform detailed product isomer composition analysis on liquid products from Tech Module (Kenttamaa), alongside efforts to first hydrogenate olefinic liquid products to paraffinic mixtures to improve resolution on GCxGC methods (Evan Sowinski)
  - Develop microkinetic modeling of propene oligomerization data on MFI zeolites at reaction conditions more realistic of practical operation (higher temperature, pressure, conversion ranges)
  - Develop coupled reaction-transport models (particle and bed-scale) of propene oligomerization on MFI zeolites to better model experimental data
  - Synthesize MFI zeolite materials with modified diffusion and reaction properties, measure diffusion properties using rate of adsorption of probe molecules, and model diffusion barriers of said probe molecules in defect-free, defect-containing, and acid site-containing unit cells of MFI
- **Specific Plans Organized by Challenge:**
  - Non-zeolitic SiO_2/MO_x materials: In the near term, we will address scaleup of materials of interest to the Technology Modules and preparing results for external dissemination. No new materials are planned. Catalyst behavior is now

understood as a function of temperature, pressure, and catalyst composition and is comparable to other acidic materials. Relatively low mass activity limits conversions, so further development of this system is limited to larger-scale, longer duration work in the Technology modules.

- Identify mechanistic explanations for differences in dimerization rate as material properties in MFI are varied: Perform follow-up propene oligomerization experiments at different pressures, temperatures, and space velocities, as additional sample properties of interest (such as crystallite size, Al density and Al zoning) are varied. Continue collaboration with computational groups to compare DFT predictions of free energies of species in propene dimerization mechanisms to experimental data.
- Distinguish between mechanistic influences of active site density, proximal active sites, and crystallite size on H-MFI: Study samples prepared using synthetic protocols to individually vary one material parameter, aided by using core-shell synthesis approaches. Quantitatively measure changes in diffusion characteristics of CISTAR-synthesized catalysts using transient rate of adsorption measurements with probe molecules, model diffusion barriers in zeolite unit cells (with and without defects and active sites), and develop mathematical models of measured rate data using effectiveness factor formalisms.
- Identify and optimize catalyst properties that result in high yields and selectivity to higher molecular weight olefins under testbed conditions, working with the Oligomerization Technology Module (Evan Sowinski): Catalysts with promising selectivity at the laboratory-scale will be tested at high conversion in the oligomerization testbed. Oligomerization testbed results further inform our understanding of the consequences of different zeolite active site and crystallite properties for selectivity at an industrial scale, helping focus synthetic efforts to develop catalysts with tailored active site distributions and crystallite sizes, and allowing us to make connections between observed effects of kinetic and diffusional changes in catalyst crystallites at the laboratory scale and their ultimate application in the CISTAR process.
- Develop microkinetic models of the steady-state testbed runs at high yields and high molecular weight olefins. This will require combined knowledge from previously published low conversion propylene microkinetic models as well as novel lumping and physisorption techniques to decrease computational load.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Crum, J. T., Crum, J. R., Taylor, C., and Schneider, W. F. "Characterization and analysis of ring topology of zeolite frameworks," *Microporous Mesoporous Materials*, *351*, 112466, (2023).
2. Bickel, E. E., and Gounder, R. "Hydrocarbon Products Occluded within Zeolite Micropores Impose Transport Barriers that Regulate Brønsted Acid-Catalyzed Propene Oligomerization," *JACS Au*, *2*, 2585-2595, (2022).
3. Bickel, E. E., Lee, S., and Gounder, R. "Influence of Brønsted-Acid Site Density on Reaction-Diffusion Phenomena that Govern Propene Oligomerization Rate and Selectivity in MFI Zeolites," *ACS Catalysis*, *13*, 1257-1269, (2023).
4. Bickel, E. E., McGinness, H., Zamiechowski, N., and Gounder, R., "Synthetic Methods to Vary Crystallite Properties of TON Zeolites and Their Consequences for Brønsted-Acid Catalyzed Propene Oligomerization," *Journal of Catalysis*, *426*, 189-199, (2023).
5. Lejarza, F., Koninckx, E., Broadbelt, L.J., Baldea, M., "A dynamic nonlinear optimization framework for learning data-driven reduced-order microkinetic models", *Chemical Engineering Journal*, *462*, 142089, (2023).
6. Wolek, A.T.Y, Hicks, K.E., Notestein, J.M. "Tuning acidity in silica-overcoated oxides for hydroalkoxylation," *Journal of Catalysis*, *426*, 113-125, (2023).
7. Ezenwa, S., Locht, H., Montalvo-Castro, H., Hoffman, A. J., Attebery, J., Jan, D. Y., Schmidthorst, M., Chmelka, B., Hibbitts, D., and Gounder, R., "Synthetic Placement of Active Sites in Zeolites for Selective Toluene Methylation to para-Xylene," *submitted* (2023).
8. Ezenwa, S., Hopping, G., M., Sauer, E., Scott, T., Mack, S., and Gounder, R., "Effects of Ammonium Hexafluorosilicate Treatment on External Acid Sites on MFI Zeolites Probed by Mesitylene Alkylation with Benzyl Alcohol," *submitted* (2023).
9. Kilburn, L., Salome-Rivera, D., Bickel, E. E., Gounder, R., and Hibbitts, D. "Isolating Kinetic Effects of Void Environment in MFI Zeolites on Transport-Limited Propene Oligomerization Using a Combined Computational and Experimental Approach", *submitted* (2023).

- **Disclosures, Patents Filed for the Period 10/1/2022 to 9/30/2023:**

1. Gounder, R., Bickel, E., Lee, S., Sowinski, E., "Stable Product Oligomer Selectivity From Olefin Oligomerization on ZSM-5 Zeolites and Zeotypes." U.S. Provisional Application No. 63/445,206. Filed: February 13, 2023.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T2P4: Oligomerization Catalyzed by Transition Metals Based on Non-Zeolites* ***Project Lead:*** *Jeff Miller (PU)*

F: Linda Broadbelt (NU), Jeffrey Greeley (PU), Rajamani Gounder (PU), Jason Hicks (UND), William Schneider (UND)	
GS: Ted Kim (PU), Wei-Ling Huang (PU), Christian Borrero Villabol (PU), Anik Biswas (PU), Alba Scotto D'apollonia (UND), Yoonrae Cho (UND)	**PD:** Alex Shaw (NU)

Project Goals

Production of fuels from shale gas requires activation of alkanes (Thrust 1) and conversion of the former to higher molecular weight fuels, e.g., gasoline and diesel (Thrust 2). This project is developing a new generation of conversion process and catalysts to convert olefins to high quality liquid fuel (gasoline and diesel) hydrocarbons

- Thermal conversion of olefins, e.g. ethylene and propylene, gives higher molecular weight hydrocarbon products with no coke formation
- ©-Alumina catalyst gives the same products but with much higher rate and lower temperature
- Ni ions stabilized by Mo and W oxides give stable oligomerization catalysts
- Isolated Zn and Ga main group metal ions give high temperature catalysts

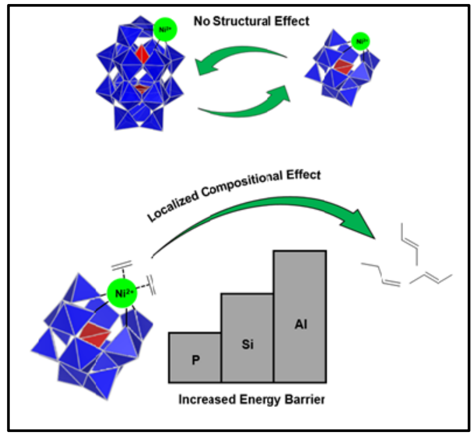


Figure 1: The size of the POM (Wells-Dawson vs. Keggin) did not influence the oligomerization kinetic behavior but variation in internal heteroatom dramatically influences the activation barrier

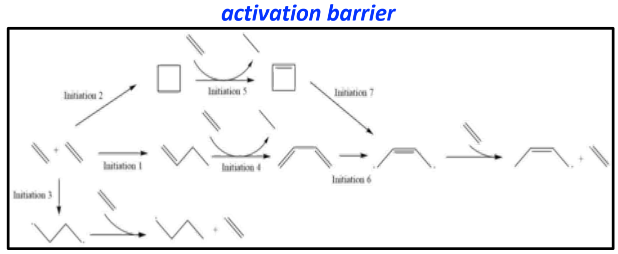


Figure 2: Non-catalytic thermal oligomerization of ethylene relies on multiple initiation pathways that were unraveled using density functional theory.

Barriers

- Existing conversion processes, for example by zeolites, suffer from rapid coke deactivation; what alternative catalysts and processes are possible?
- What is the reaction mechanism for the thermal and catalytic processes?
- How can the structure of the product hydrocarbons be controlled and optimized?

Methodologies

- Determine the reaction products, kinetics, elementary steps and reaction intermediates for the thermal and catalytic processes
- Use DFT and microkinetic modeling of the reaction pathway and reaction mechanism
- Identify the active site for the catalytic processes and identify opportunities to improve performance, e.g., rate, selectivity, life

Research Achievements

- A microkinetic model for the non-catalytic thermal oligomerization of ethylene to fuel range hydrocarbons has been developed
- The active oligomerization sites on ©-alumina and silica-supported Ga sites are low coordinate Lewis acids, as determined through a combination of detailed DFT calculations and XAS measurements.
- No structurally-induced kinetic effects were observed between Ni-modified Keggin (KG) and Ni-Modified Wells-Dawson (WD) POM structures, both of which provided the similar measured activation energy, rate order, and product selectivity.
- Ni-POMs with P, Si, and Al internal heteroatoms provided activation energies for ethylene dimerization that correlated with the electronegativity difference between Ni and internal atom.

Section 2: Project Summary Brief

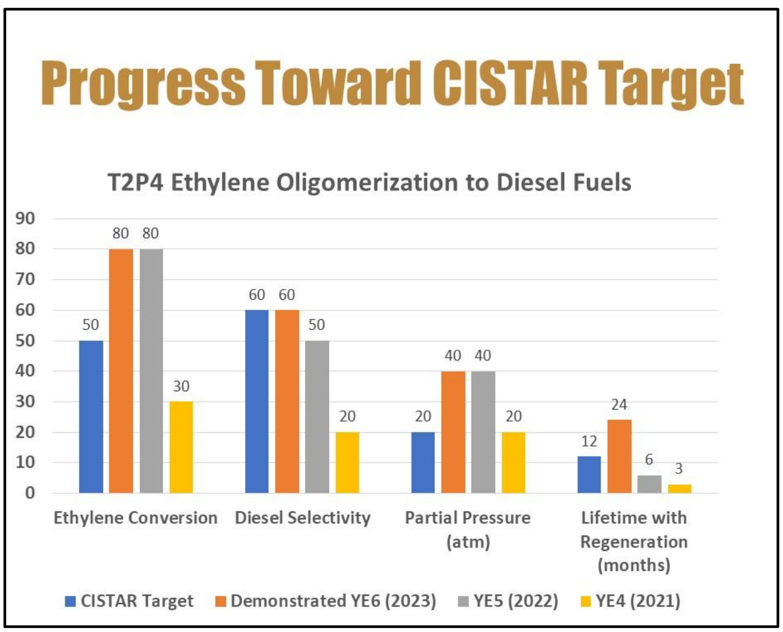
- **The Project's Role in Support of the Strategic Plan:** The CISTAR process seeks to convert shale gas alkanes, for example, ethane and propane into olefins. These will be converted to fuel and chemical products in a subsequent process step. This project seeks to develop new olefin conversion technologies to gasoline and diesel fuel hydrocarbons.
- **Abstract:** A microkinetic model of the thermal, free radical, oligomerization reaction pathway for conversion of ethylene and propylene to high yields of higher molecular weight hydrocarbons has been developed. Based on density functional theory calculations, initiation routes were unraveled, and fluxes to major products via different pathways were quantified using net rate analysis. Previously, a ©-alumina catalyst was shown to catalytically oligomerize olefins; however, additional reaction steps also occurred. The catalysis occurs on Lewis acid sites. High olefin conversions can be obtained without significant carbon deposition or catalyst deactivation. Previously, a Ni-modified phosphotungstate polyoxometalate (POM) was identified as an active catalyst for ethylene and propylene oligomerization; however, the role of the POM size and composition was unknown. Synthetic methods to incorporate different internal heteratoms (Si, P, Al) were adopted and Ni^{+2} ions were incorporated into the POM structure and supported on SBA-15 to provide a high fraction of linear dimers.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:** Previously, thermal, non-catalytic, free-radical ethylene oligomerization was investigated at temperatures between 300 and 500 ^{o}C and ethylene pressures from 1.5 to 45 bar. Non-oligomer products such as propylene and/or higher odd carbon products were significant at all reaction temperatures, pressures, and reaction extents. Methane and ethane were minor products (< 1 % each), even at ethylene conversions as high as 75 %. The isomer distributions revealed a preference for linear, terminal C_4 and C_5. The reaction order was found to be 2nd order with a temperature-dependent overall activation energy ranging from 39.4 to 58.3 kcal mol^{-1}. Four bimolecular initiation reaction steps for ethylene were calculated using DFT. Of these, simple H-transfer to yield vinyl and ethyl radicals was found to have a free energy activation energy barrier higher (about 10 kcal mol^{-1}) than the other three initiation steps forming either cyclobutane, 1-butene, or tetramethylene. The importance of diradical species in generating free radicals during a two-phase initiation process was proposed. The microkinetic model showed through flux analysis that the main driver of initiation was identified to be hydrogen abstraction from ethylene by a 1,4-butyl diradical produced from the reaction of two ethylene molecules. As conversion increased, the primary initiation mode switched to hydrogen abstraction by a butene diradical as 1-butene began to be produced in high quantities. Odd-numbered carbon species were seen to originate from the β-scission of C8 radical species, with the radical position varied due to intramolecular hydrogen shift reactions from terminal radicals formed via radical addition reactions. The significant quantity of linear terminal olefins in the experimental product distribution was

identified to originate from the formation of vinyl radicals through hydrogen abstraction reactions involving ethylene that were then propagated via radical addition reactions to ethylene. The reaction chemistry for ethylene, which has only strong, vinyl C-H bonds, starkly contrasted with propylene, which possesses weaker allylic C-H bonds and showed preference for dimeric C_6 products over C_2-C_8 non-oligomers. The resulting C_4 and C_5 non-oligomers from propylene contained more iso-olefins compared to linear C_4 and C_5. Recently, ©-alumina has been shown to give similar products but at a much higher rate. The kinetics suggest this is a catalytic free-radical reaction.

Ethylene oligomerization catalyzed by mono-Ni substituted polyoxometalate (POM) catalysts is promising due to the observed selectivity toward linear butene products and stability of these well-defined materials. In Y6, two approaches to tailor the catalytic properties of isolated Ni sites in POMs were experimentally tested, both of which perturbed the surrounding molecular environment of the active sites. This work was published in Appl. Catal. A: Gen., 2023, 119391 (https://doi.org/10.1016/j.apcata.2023.119391). First, the size of the polyoxometalates was compared by evaluating Ni-modified Wells-Dawson and Ni-modified Keggin structures while maintaining the same elemental components. It was observed that the Ni active sites were kinetically independent from the effect of POM size, which was evidenced by the identical product distributions and kinetic parameters observed with both structures. However, a localized kinetic effect was observed when Keggin POM structures containing different internal heteroatoms (e.g, P, Si, Al) were included in close proximity to the Ni active site. Specifically, a notable periodic trend was observed between the electronegativity of internal heteroatoms, and the measured apparent activation energy for the catalyzed ethylene coupling reaction to butene. These findings contribute to a better understanding of the relationship between the structure of polyoxometalates, the properties of isolated Ni active sites, and their catalytic behavior in alkene dimerization reactions. DFT calculations were initiated in this period to relate observations to molecular details of POM active sites.

Previously, amorphous, single-site, silica-supported main group metal catalysts were found to promote olefin oligomerization with high activity at moderate temperatures and pressures (~250 °C and 10-30 atm). A combination of detailed DFT-determined energetics, microkinetic modeling, and experimental XAS measurements determined that, in the case of silica-supported Ga, low coordinate sites dominate the oligomerization chemistry. An improved synthesis method has been developed to give low coordinate sites even at very high metal loadings resulting in much higher rates (per g). In addition to the expected oligomerization products, additional reactions occur leading to unexpected products. At low conversion, primary products include alkanes, which occur by H-transfer reactions. Additionally, non-oligomerization products occur, for example, propylene forms ethylene and butenes in equal molar amounts. Olefin double bond isomerization also occurs, while skeletal isomerization does not. IR spectra of adsorbed pyridine, indicate the active site is a Lewis acid. These results and understanding suggest changes in composition for controlling the rate and product distributions for improved yields.

- **Interdependence:** To better control the reaction product quality and molecular weight distribution, it is necessary to understand the reaction pathway for the thermal and catalytic pathways. In addition, for the catalytic process, we need to identify the active site to give improved catalysts with higher rates, higher yields and better product quality. Density functional theory has identified the likely radical initiation pathway (Broadbelt, NU). Additional DFT modeling (Broadbelt (NU), Greeley (PU), Schneider (UND)) will differences for the catalytic process. Characterization and quantification of the catalytic site (Miller (PU), Datye, (UNM), Gounder (PU), Hicks (UND)) will help identify other potentially more active or selective catalysts.
- **Testbed, Impact and Value:** High conversion reactions occur at pressures 10-40 atm. Thus, all studies are conducted under realistic reaction conditions. These also produce liquid products (in a few hours) in the gasoline and diesel range. There is little deactivation for the process. The product distributions change with conversion and catalyst composition. We have a method to determine the boiling point distributions to determine the optimum process conditions for each potential product, i.e., gasoline or diesel.
- **Technical Targets:**



Thrust Project Number and Name	**CISTAR TRL 4/5 Process Targets. Demonstrated in Technology Module**	**CISTAR Status: Year Ending 2023**
T2P5 Thermal and Catalytic C-C Bond Coupling to Various Products	● > 50% $C_2^=$ Conversion ● > 90% Selectivity to C_3^+ olefin products ● > 50% Selectivity to C_{10}^+ ● > 20 atm $C_2^=$ Partial Pressure ● 1-year life with regeneration	● > 75% $C_2^=$ Conversion ● > 90% Selectivity to C_3^+ olefin products ● > 65% Selectivity to C_{10}^+ ● 10-45 atm $C_2^=$ Partial Pressure ● 2+ year life with regeneration

<u>Section 3: Specific Plans for Next 12 Months</u>

- **Challenges and Current Status:** Catalysts and reaction conditions have been identified to obtain high olefin conversion, long life and gasoline and diesel products have been identified. The diesel selectivity per pass is about 60%, but with light olefin recycle, much higher diesel selectivity could be obtained. The immediate challenges are what is the octane and cetane (after hydrogenation) values of the gasoline and diesel fractions and how can one shift the product distribution from gasoline to diesel. Also, how do the products from propylene differ from those of ethylene, and which is more desirable? These would allow for a detailed techno-economic process analysis for the optimum product slate. What are the reaction pathways and mechanisms for formation of non-oligomeric products? How does the product distribution, rates and stability change with catalyst compositions?
- **Path to Targets Summary:** At 1-5 atm, propylene gives higher quality gasoline products than ethylene; however, for the latter, reaction at higher pressures are required for high conversion. At these pressures, however, propylene is a liquid, and currently we do not have reactors that can deliver liquid propylene, which likely are the optimum process conditions. For now, we can compare the products from propylene and ethylene at low pressure to determine to determine differences in the rates of individual reactions; we are limited in the data at high pressure.
- **Specific Plans Organized by Challenge:** To determine the effect of feed composition, i.e., ethylene or propylene, and process conditions, e.g., temperature and pressure, on molecular weight distribution, we can analyze all products on line. In addition, to get the boiling point distribution, which is used in industry, we can get a simulated distillation analysis of the liquid products. Obtaining an octane value for the gasoline fraction would require much larger equipment than currently available.

  We have prepared catalysts with different compositions and determined these do give different products. We are obtaining product yields, rates, and spectra on the structure of the catalyst and reaction intermediates for DFT modeling of the mechanistic steps and how these change with catalyst compositions.

We are also exploring Ni-based mesoporous supports (Ni-MCM-41) functionalized with surface organic functional groups, and operated while co-feeding solvents during ethylene oligomerization, to induce capillary condensation at higher temperatures and lower pressure conditions that can lead to stable time-on-stream operation without deactivation.

Section 4: Papers and IP

Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:

- Q. Zhao, Y. Xu, J. Greeley, and B. Savoie, "Deep reaction network exploration at a heterogeneous catalytic interface," Nature Communications **13** (2022) 4860; doi: 10.1038/s41467-022-32514-7.
- C.J. Breckner, H.N. Pham, M.G. Dempsey, M.A. Perez-Ahuatl, A.C. Kohl, C.N. Lytle, A.K. Datye, J.T. Miller, "The Role of Lewis Acid Sites in γ-Al_2O_3 Olefin Oligomerization," *ChemPhysChem*, **24** (2023) e202300244; doi 10.1002/cphc.202300244.
- Y. Cho, A.G. Oliver, J.C. Hicks, "Localized Structural and Compositional Effects on the Kinetic Performance of Ni-Modified Polyoxometalate Catalysts for Ethylene Oligomerization", *Applied Catalysis A: General,* **666** (2023), 119391, doi: 10.1016/j.apcata.2023.119391.
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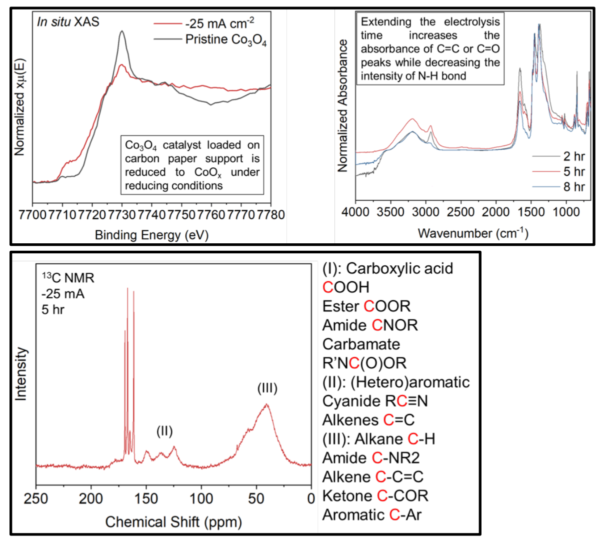
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T2P5 Non-Thermal C-C Bond Coupling to Various Products* ***Project Lead:*** *Linsey Seitz (NU)*

F: Linsey Seitz (NU), Brian Tackett (Purdue), Jason Hicks (ND), Justin Notestein (NU)
GS: Xiao Kun Lu (NU)

Project Goals

- This work aims to identify catalysts and operating conditions (pH, potential, etc.) that will enable electrochemical upgrading of C_2 with CO_2/CO at moderate conditions to form longer chain products (at higher production rates compared to pure CO_2 reduction, ex. 1-butanol and 1,2-furandiol at 1 mA cm-2.)
- Integrate electrochemical processes with other non-thermal approaches to develop tandem reactor systems.
- Leverage electrocatalytic alkane dehydrogenation processes alongside C-C coupling reactions.



Barriers

- Project represents exploration of new chemistries and unknown reactivity under electrochemical conditions (moderate temperature and pressure) as well as novel intersections among non-thermal catalytic approaches for tandem reactors. Will characterize a range of novel products as a function of tuning: catalyst active site structure, co-feed ratios, reaction environments, and probe reaction mechanisms.
- Graduate student temporarily paused this work (and funding) to complete an internship at a national lab. Another graduate student will help with this work until his return.

Methodologies

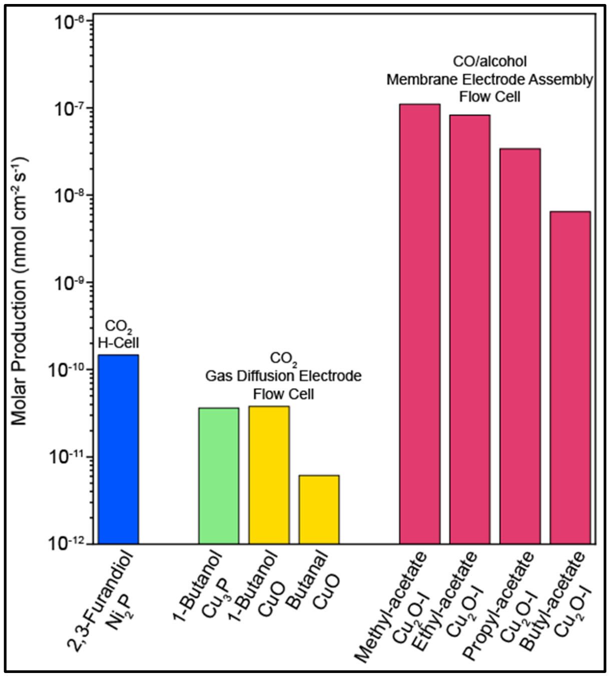
- Spray-coated catalysts on carbon paper, treated with PTFE to tune hydrophobicity
- Electrocatalytic testing in applied reactor designs with olefin and COx co-feeds
- MS, NMR, and MALDI for product identification
- Isotopic labeling and differential electrochemical MS for mechanistic insights

Research Achievements

- Electrochemical CO2 reduction with pyridine additive on Co catalyst yields solid polymeric product
- Solid state NMR, IR, and elemental analysis suggest polyurethane-like structure of solid product
- Identified operating conditions for solid product formation:
    - presence of CO2 and pyridine
    - neutral or alkaline electrolyte
    - operating current -15 to -40 mA/cm2
    - >2 hr electrolysis

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** In support of CISTAR's strategic plan, this project is investigating non-thermal routes to olefin oligomerization. Specifically, this project is currently exploring electrochemical activation of olefins produced in Thrust 1 to electrify these conversion processes and take advantage of renewable electricity sources. This project also supports decarbonization by co-feeding CO_2 with light olefins to create longer chain carbon products. Finally, this project is exploring novel tandem reactor couplings that will combine multiple non-thermal approaches or non-thermal with thermal approaches for activation and oligomerization.
- **Abstract:** Work in T2P5 aims to explore and establish electrochemical pathways for upgrading light olefins with CO_x under moderate conditions that can either replace or expand upon current thermochemical processes, such as hydrogenation and hydroformylation. Drastically different reaction conditions of electrocatalytic processes (controlled by electric potential, pH, and supporting electrolyte species) will enable unique knobs with which to tune product selectivity compared to thermochemical processes. Electrocatalytic approaches also enable isolated investigation of reduction and/or oxidation processes, as they occur at opposite electrodes, and remove need for stoichiometric additions of reductant or oxidant chemicals to drive reactions of interest. Lastly, co-reaction of olefins and CO_x provides a unique approach for introducing oxygen into products (e.g. propionic acid, propionaldehyde, etc.), while also providing a sink for captured CO_2 to contribute towards decarbonization and overall emissions mitigation.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:** Through this work we have identified a catalyst and electrolyte platform that successfully co-reacts CO_2 with C_2H_4 via electrochemical reduction at standard temperature and pressure to produce novel solid polymeric product. Solid state NMR, IR, and elemental analysis suggest a polyurethane-like structure. We have also tested a range of reaction conditions to determine that presence of CO2 and pyridine in neutral or alkaline electrolyte are required for formation of the solid product. In addition, operation at -15 to -40 mA/cm2 for over two hours consistently results in formation of solid product.
- **Interdependence:** This work is synergistic with other electrochemical projects (T1P6, T3P7, T3P8). The lead PI of T2P5 has also explored collaboration opportunities from PIs in Thrust 6 for complementary work on membrane materials. Other connections include utilization of activated ethane from plasma reactors (T1 PIs Schneider and Hicks) as the input for various oligomerization catalysts being studied in T2 (PI Hicks).
- **Testbed Impact and Value:** This project is relevant to Testbed 2, which aims to form a range of desired products using ethylene as a feed. Research in T2P5 can provide novel



routes with improved energy efficiency and potentially access novel products using electrochemical conversion.

- **Technical Targets:**
    - Stable operation for 1 hour under constant potential or constant current operation
    - Molar production rates ranging from 10^{-12} to 10^{-7} mol cm^{-2} s^{-1} of various products

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Challenges for this work include tuning selectivity towards desired products, understanding reaction mechanisms, and optimizing production rates/conversion. Other challenges include forming new, strategic connections to other (non-)thermal processes for tandem catalytic oligomerization processes. Finally, a minor note is that the graduate student that was previously working on this project is currently completing an internship at a national lab and will return in December 2023.
- **Path to Targets Summary:** When the graduate student returns to this project, near term work will involve exploring different catalyst modifications, surface treatments, and additive tuning to determine the impact on product distributions. Isotope labeling will also be used to track reactants to products and provide insights to possible reaction mechanisms. Longer term work will involve optimizing reactor conditions and design of the gas diffusion electrode microenvironment, as well as establishing and building inter-/intra-thrust collaborations to pursue tandem reactor processes.
- **Specific Plans - (i) Challenge 1:** Novel solid products have been identified using a Co3O4 catalyst, with pyridine added to the electrolyte. Reactions will be run with varied catalyst

composition, pyridine concentration, electrolyte conditions, operating potential, and CO_2/C_2H_4 co-feed ratios to tune product distributions. Catalysts will be characterized using XANES/EXAFS to determine electronic structure and potential surface deposition of pyridinic species. Reactions will be run for extended times to determine stability and probe initial degradation pathways.

- **Specific Plans - (ii) Challenge 2:** Complementary reactions will be explored in a gas-purged electrolyte cell, which enables use of attenuated total reflection infrared spectroscopy to track effects of reaction environment variables on the interaction of intermediate species bound on the catalyst surface. This will also provide further insight to the role of pyridine on the catalyst surface. Differential electrochemical MS will also be used for on stream product detection and to probe local reaction conditions.
- **Specific Plans - (ii) Challenge 3:** New opportunities for inter-/intra-thrust collaborations and connections between multiple non-thermal (or thermal and non-thermal) processes were identified during a Thrust 2 meeting. Reactant and product streams of independently run processes will be characterized to enable reproduction (i.e. using product stream of one process as reactant stream of another process) and assessment of tandem reactor feasibility (while still operating independently). This will progress towards modification of independent reactors to support future integration into tandem reactor systems.

THRUST 3:
C1 ACTIVATION

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T3P5 Dehydroaromatization of Light Alkanes* ***Project Lead:*** *Jeffrey Miller (PU)*

F: Abhaya Datye (UNM)	
GS: Shan Jiang (PU), Arunima Saxena (PU), Kurt Russell (PU), Ryan Alcala (UNM)	**UGS:** Josiah Rocky (PU), Rebecca Hanna (PU)

Project Goals

The project goal is to develop a single step process and bifunctional catalyst for conversion of propane and ethane to aromatic compounds and gasoline range hydrocarbons

- Develop highly active bifunctional catalyst for reactions with ethane
- Improve the aromatic and gasoline yields
- Determine the reaction steps and catalyst functions that limit the product yields
- Optimize the catalyst composition and process conditions to give improved yields

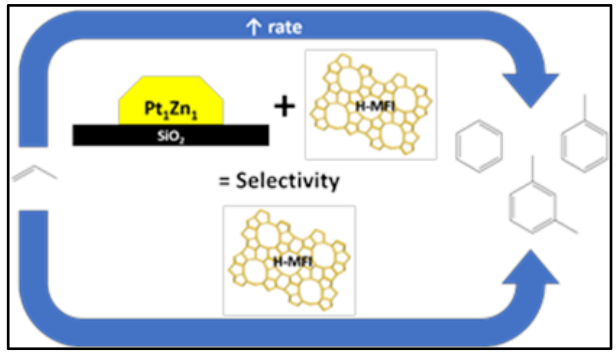


Figure: Olefin Conversion with bifunction $PtZn/SiO_2$ + ZSM-5 give similar BTX yields as ZSM-5, but with much higher rate

Barriers

- The individual steps and catalytic functions in the reaction pathway that limits product yields are unknown
- Ethane is kinetically less reactive and has a lower equilibrium conversion to ethylene thus giving poor yields with known catalysts
- Short-term and long-term catalyst stability with high selectivity to aromatics

Methodologies

- The kinetic rates and selectivities for each step in the reaction pathway for activation of the alkane and reaction of olefins to aromatics will be determined
- The activity of the individual catalytic functions will be varied to give the optimum product rate, selectivity and life
- The effect of process conditions, temperature, pressure and feed composition on product yields will be evaluated
- The pathways for converting olefins to aromatics with bifunctional catalysts will be determine to determine the optimum composition that gives the highest selectivity and rate

Research Achievements

- For ethane dehydroaromatization, high BTX selectivity can be achieved with Pt alloy + ZSM-5 catalysts
- The ethane conversion rates exceeded the ethane/ethylene equilibrium since the latter is subsequently converted to reaction intermediates and aromatics
- Ethane conversion rates were higher for bifunctional catalysts with high loadings of the Pt alloy dehydrogenation catalyst and lower amounts of ZSM-5
- The aromatics selectivity was slightly higher with lower amounts of ZSM-5 in the bifunctional catalyst
- Coking leads to cycle lengths of about 1day. Regeneration conditions were determined in T1P3 for complete recovery of initial catalytic performance
- Ethane dehydroaromatization co-produces H_2, which decreases aromatic selectivity at high ethane conversion; however, low H_2 levels have minimal effect on product selectivity or rate

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** CISTAR's goal is to convert shale gas ethane and propane into transportation fuels and chemicals. The initial process is to first dehydrogenate alkanes to olefins and subsequently convert the olefins to products in a second process operation. This project seeks to convert the shale gas alkanes to gasoline and aromatic chemicals in a single step using a bifunctional catalyst. To better understand the role of the bifunctional catalyst and how its performance is affected by its composition, the conversion of olefins with and without H_2 to aromatics was also determined.

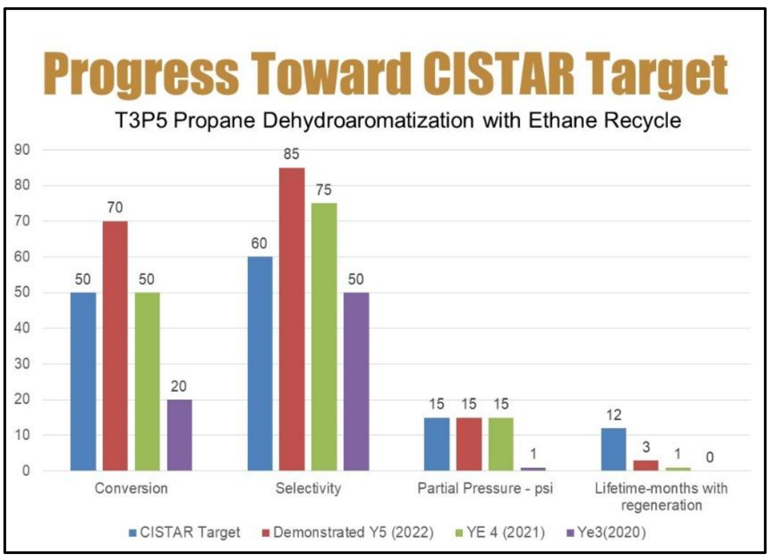
- **Abstract:** Previously, it was determined that the light gas selectivity (methane and ethane) was formed primarily by monomolecular cracking on ZSM-5 in the bifunctional propane dehydroaromatization catalyst. For catalysts containing high levels of the Pt alloy with lower levels of H-ZSM-5, the BTX selectivity was increased to about 80% at (~70% propane conversion per pass) at full recycle. The methane and ethane selectivities were about 5 and 15%, respectively. A techno-economic analysis suggested that recycle of the by-product ethane with increased aromatic yields would result in a more attractive process.

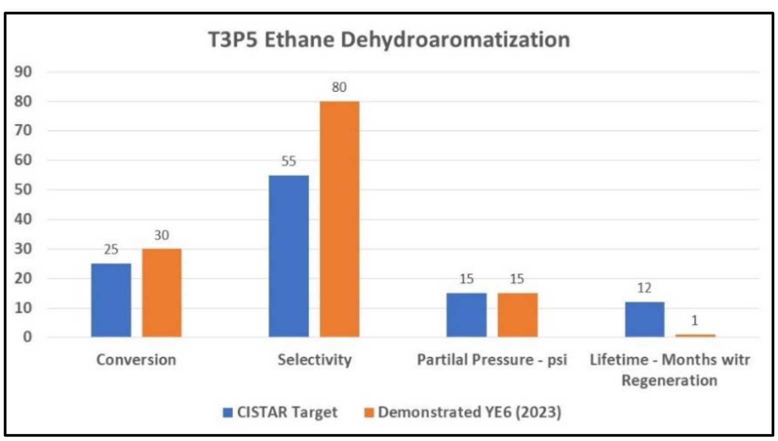
  This year, the process conditions and catalyst composition for ethane dehydroaromatization have also been determined with bifunctional Pt alloy + ZSM-5 catalysts. Unlike propane, where monomolecular cracking limits the aromatic selectivity, this reaction does not occur with ethane. While the ethane dehydrogenation equilibrium conversion is much lower than that of propane, with the bifunctional catalyst ethane conversions higher than the dehydrogenation equilibrium are possible. The aromatic selectivities are also above 80%. The rate of ethane conversion and the aromatic selectivity are higher for compositions with higher dehydrogenation activity and lower amounts of ZSM-5. Dehydroaromatization also co-produces H_2. At high conversion, i.e., high H_2, the methane selectivity significantly increases resulting in lower selectivity to aromatics.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:** Fundamental understanding of the reaction pathway for direct conversion of propane to aromatics was previously determined for Pt alloy + ZSM-5 catalysts. With the higher activity and more stable dehydrogenation catalysts developed in Trust 1, the conversion of ethane to aromatics was determined during the past year. By optimizing the process conditions and catalyst composition, the BTX selectivity can be increased to about 80% at about 30% conversion, which is significantly higher than previously reported catalysts, ca. 55%. The ethane conversion exceeds the equilibrium conversion of ethane to ethylene, since the latter is subsequently converted to aromatics.

  Ethane dehydroaromatization also produces H_2. The effect of H_2 on the product selectivity was determined for the reaction of olefins + H_2 with ZSM-5 and bifunctional Pt alloy + ZSM-5 catalysts. H_2 had a minimal effect on the rate or selectivity of BTX with ZSM-5. (These results are important for the two-step CISTAR process.) For the bifunctional catalyst, low concentrations of H_2 had little effect on the catalyst performance for ethane dehydroaromatization; while at higher levels, there was a significant increase in the methane and decrease in the BTX selectivity. The latter result suggests that to obtain high ethane selectivity, the conversion per pass will be limited to about 30-40% and that much, but not all, of the co-produced H_2 will need to be separated from the ethane recycle stream.

- **Interdependence:** Success of this project relies on development of highly active and stable dehydrogenation catalysts (T1), process evaluations under realistic conditions (TB), and technoeconomic analysis (T4). The latter (T4) has also identified process improvements, which would make the process more economically attractive.
- **Testbed, Impact and Value:** In laboratory reactors, fundamental understandings about the rates and selectivity of individual reactions in the conversion pathway of propane, ethane and co-produced H_2 to aromatics have identified opportunities for improved catalysts. The impact of these on product yield and quality, were determined in the testbed under realistic reaction conditions. The impact of the improved yields and rates were determined by a technoeconomic analysis (T4), which look attractive. Further process improvements have been identified and are in progress.
- **Technical Targets:**





Thrust Project Number and Name	CISTAR TRL 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status: Year Ending 2023
T3P5 Dehydroaromatization of Light Alkanes	● > 50% C_3 Conversion ● > 60% Selectivity to aromatics ● 1 atm C_3 partial pressure ● 1-year life with regeneration ● > 25% conversion of ethane ● > 55% Selectivity to aromatics ● 1 atm $C_{2\,p}$artial pressure	● > 70% C_3 Conversion ● > 75% Selectivity to aromatic products ● > 85% Selectivity to aromatic products with C_2 recycle ● 1 atm C_3 Partial Pressure ● > 25% C_2 conversion ● > 80% Selectivity to aromatics with ethane ● 3-month life with regeneration

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** An economically attractive single-step process for conversion of propane to aromatics with significantly improved yields has been demonstrated. Ethane has also been shown to have high selectivity to aromatics; thus, ethane formed during propane dehydroaromatization can be recycled to the process to increase yields. An ethane dehydroaromatization is also possible; however, the co-produced H_2 limits the conversion to about 30-40% conversion per pass. For both processes, catalyst lives are 1-3 days, and frequent regenerations will be required. Effective regeneration conditions have been developed in collaboration with T1P3.

- **Path to Targets Summary:** For both propane and ethane dehydroaromatization the aromatic selectivity has been significantly improved over previously reported catalysts. However, coke deactivation limits the cycle time to 1-3 days. Effective regeneration methods have been developed in T1P3 to limit sintering of the Pt alloy dehydrogenation and ZSM-5 catalysts. It is desirable to develop longer cycle lengths for less complex process designs.

- **Specific Plans Organized by Challenge:** *Extending Process Cycle Length:* Project T3P5 will collaborate with the efforts of T1P3 to determine if coking can be mitigated, significantly extending the cycle length between regenerations. This would have a major impact on the performance of CISTAR's dehydrogenation and dehydroaromatization processes. Preliminary results suggest that coking rate can be significantly reduced and cycle lengths extended by changes to the process. The effects on product quality and long-term stability for dehydroaromatization, however, are under investigation.

Section 4: Papers and IP

Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:

1. C.K. Russell, A. Saxena J.T. Miller, "Influence of Bifunctional $PtZn/SiO_2$ and H-ZSM-5 Catalyst on the Rates and Selectivity of Propene Aromatization, Catal. Res., 3 (2), 018 (2023); doi:10.21926/cr.2302018.

2. C.K. Russell, J. Rockey, R. Hanna, J.T. Miller, "Impact of Co-Fed Hydrogen on High Conversion Propylene Aromatization on H-ZSM-5 and Ga/H-ZSM-5, submitted Carbon Resources Conversion, 2023.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *Methane Dehydroaromatization* ***Project Lead:*** *Tobin Marks (NU), Raj Gounder (PU)*

F: Justin Notestein (NU), Tobin Marks (NU), Jeffrey Miller (PU), Fabio Ribeiro (PU)
GS: Ángel Santiago-Colon (PU), Xinrui Zhang (NU), Jordy Ramos-Yataco (NU)
REU: Jackson Boodry (PU), Mahagani Lasciers (PU)

Project Goals

- Improve catalyst material stability and resistance to degradation over successive reaction-regeneration cycles.
- Correlate active site (e.g. Mo) speciation with kinetic measurements of metal-zeolites over consecutive reaction-regeneration cycles.
- Develop new regeneration strategies to increase catalyst lifetime in continuous reaction-regeneration process.
- Synthesize, modify, and study catalyst supports (i.e., zeolites, core-shell structures) that have increased hydrothermal stability.
- Investigate alternate methane activation sites (e.g. Fe) that may successfully trade activity for stability

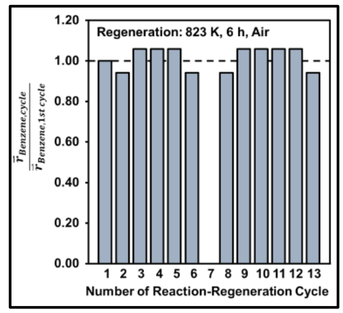


Figure: Benzene formation rates measured on Mo-nanosheet-CHA (950 K) during sequential cycles of reaction-regeneration, normalized by the rate measured during the first cycle. Rates did not decrease after 13 cycles of reaction-regeneration.

Barriers

- Determining properties of the acidic support and the metal site that improve catalyst stability.
- Stabilizing active sites and support structures (e.g., zeolites) during regeneration.
- Reliable syntheses for highly dispersed active sites and conformal external passivation.

Methodologies

- Combine kinetic measurements (950 K) with characterization methods (TPR, titration) to elucidate relations between Mo speciation, zeolite acid sites (H^+), and benzene forward rate.
- Develop synthetic strategies to encapsulate catalytically-relevant Mo-derived sites, deactivate external surfaces, and incorporate alternative metal atoms in high dispersion.
- Evaluate material properties and performance upon successive reaction-regeneration cycles.
- Develop synthetic routes of hydrothermally stable zeolite supports with smaller crystal size to increase the amount of external active sites and increase benzene formation rate and selectivity.
- Critically compare catalysts across the literature to derive new insights.

Research Achievements

- Oxidative regeneration leads to loss of H^+ sites in MFI zeolite, which anchor Mo. This causes loss of ion-exchanged Mo, which are the active site precursors for methane DHA, and formation of inactive aluminum molybdates domains.
- Adding “fresh” H-MFI with “spent” Mo-MFI catalyst after reaction-regeneration leads to transformation of aluminum molybdate into ion-exchanged Mo, which recovers DHA activity.
- Mo-zeolites with improved hydrothermal stability (e.g., CHA), was synthesized for methane DHA. Synthetic methods were developed to decrease CHA crystal size to circumvent diffusion constraints for aromatic products.
- Mo supported on nanosheet-CHA was used for several (>10) cycles of methane DHA reaction-regeneration and no decrease in rate was observed.
- ALD-coated MFI and oxide supports can improve hydrothermal stability over several cycles by reducing external acid sites and changing the coke distribution. Long term structural changes are unchanged.
- For Fe-MFI, increasing dispersion markedly decreases induction times and improves benzene yields. In framework Fe-MFI via direct synthesis may be especially promising. Related active sites that do not carburize identified for investigation.
- Synergies with the C2C program have been identified.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** In support of CISTAR's strategic plan, Thrust 3 researchers are developing new strategies to convert methane to fuels, chemicals, aromatics and hydrogen. For this specific project, non-oxidative chemistries are being studied on different catalyst materials to convert methane into aromatics and hydrogen ("turquoise" H_2) as a by-product. An important aspect of this work is to improve catalyst material stability and regenerability. Catalysts are being evaluated with regards to their tolerance to various regeneration protocols.

- **Abstract:** Non-oxidative methane dehydroaromatization (DHA) allows converting stranded methane into aromatics (Testbed 1) and generating "turquoise" hydrogen (H_2) as a byproduct. Methane and alkane dehydroaromatization have been studied on catalysts with Mo (and Fe, Re, W, etc.) on acidic supports (e.g., ZSM-5 zeolite). Mo from a variety of sources undergoes carbidization during reaction to activate methane by an unclear mechanism at relatively low temperatures (likely involving radical intermediates), while the acid sites catalyze further reactions to form higher olefins and aromatics; the relative locations of these two active site functions and how this material property influences selectivity and stability is unclear. Furthermore, co-feeding CO_2 (and other higher alkanes such as ethane) can be co-processed with methane to improve the thermodynamics of the process and the selectivity to aromatics and H_2, providing another means to lower the CO_2-footprint. The key challenge is to overcome commercial implementation is the rapid catalyst degradation that occurs during regenerations needed to remove coke on deactivated catalysts. We propose to collaboratively enhance catalyst stability using two materials strategies. First, we will prepare more intrinsically stable supports, both zeolite and non-zeolite-based. Zeolite supports include small-pore frameworks that are known to be stable under hydrothermal conditions (in automotive exhaust applications); further, small crystallite sizes will be used to maximize the external surface area available to form aromatics, and internal defect sites will be minimized as

they are a source of material instability (Gounder). Modified-zeolites and non-zeolite supports will include MoOx overcoated by porous acidic oxide layers that are subsequently carburized, which are expected to be intrinsically hydrothermally stable (Notestein). Second, we will investigate methane activation sites other than Mo where there may be beneficial trade-offs between activity and framework stability, as well as additional characterization tools available (Marks). Catalysts will be evaluated at NU (Notestein) and PU (Gounder/Ribeiro). Active and spent phases will be characterized by XAS (Miller), 1- and 2D high-resolution solid-state NMR (Marks), and in situ/operando transmission electron microscopy (Marks). Coke/precursor structures on spent catalysts will be characterized by UV-Raman (Notestein).

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
  - Flow reactor systems at Purdue and Northwestern constructed and validated for methane dehydroaromatization (DHA) experiments, as shown for a series of Fe-MFI samples, and expressed, differently, a series of Mo-based catalysts (Figure 1).

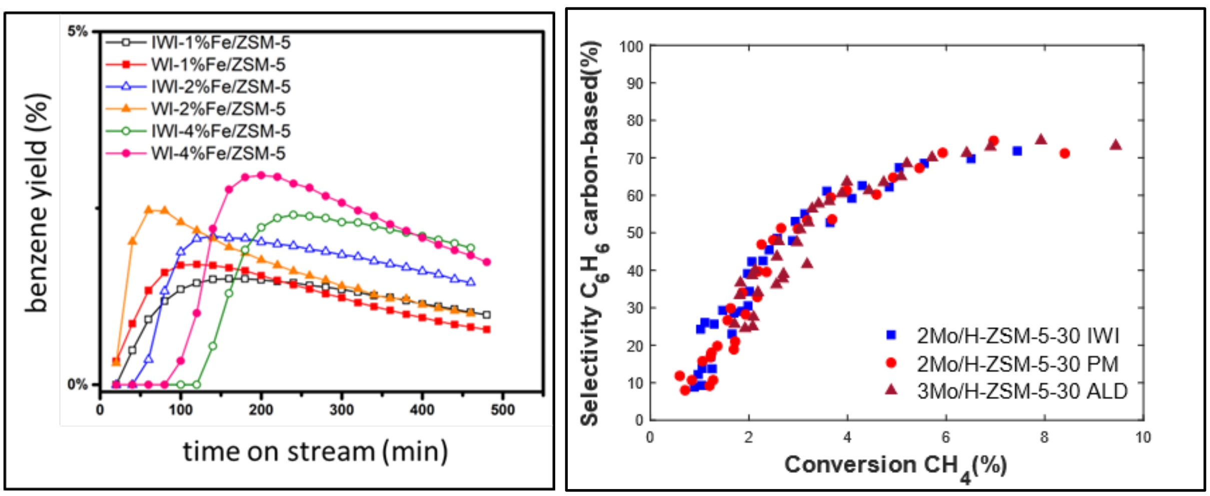


Figure 1: Typical data for Fe-MFI (left) and Mo-MFI (right). On left are time-on-stream data showing periods of induction, activation to a maximum, and deactivation via coking. Catalysts are typically tested over 3-4 reaction and regeneration cycles (not shown). On right are parametric plots of benzene selectivity (total carbon basis) vs. methane conversion. Within a family of catalyst, these curves tend to be universal, providing an excellent way to identify outlier behavior, either good or bad.

  - Some Fe- and Mo-MFI zeolite samples were synthesized with varying composition and active site density, speciation and distribution. Catalysts and supports were modified via additional SiO_2 or Al_2O_3 modification to stabilize the materials. Mo was deposited on bulk SiO_2, Al_2O_3, and mixed oxides prepared by atomic layer deposition.
  - DHA reaction experiments were performed on Fe- and Mo-MFI zeolite materials synthesized by several routes and external surface modifications and followed over

successive reaction-regeneration cycles. Baseline performance data were established. A universal trend was noticed among a given materials class (Figure 1, right) consistent with successive bed deactivation rather than loss of specific active sites. An avenue to maximize overall yield may be via maximizing time in the high-yield regime, rather than developing entirely new active sites.

- Highly-dispersed Fe-MFI has shorter induction periods and much higher yields than do analogous materials that give Fe_2O_3 domains (Figure 2). Due to its much lower volatility, Fe-MFI is much more sensitive to synthesis conditions than is Mo-MFI.

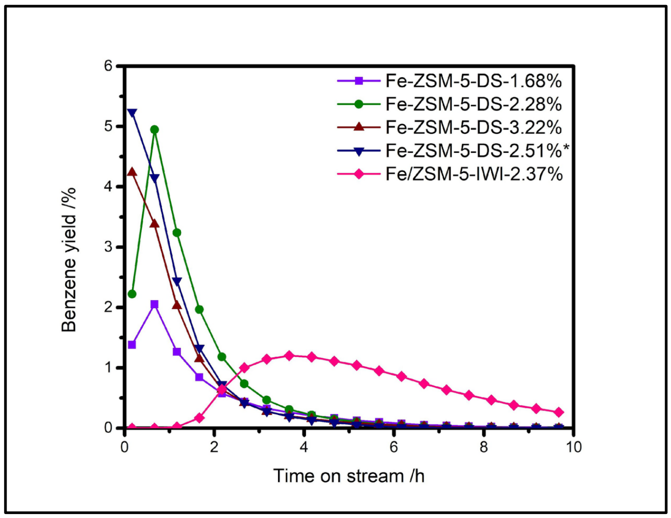


Figure 2. A comparison of two synthetic routes to 2 wt% Fe-MFI. Across a range of Fe loading, methods that give highly dispersed Fe ions in the MFI framework or at exchange sites give minimal induction periods and higher overall yields than those giving Fe_2O_3 crystallites. Findings corroborated by XAS, UV-vis, and TPR.

- A new regeneration strategy was developed by mixing spent Mo-MFI catalysts (with some Mo sites that became deactivated) with fresh H-MFI catalysts, which provided an additional reservoir of H^+ sites to recover and stabilize ion-exchanged Mo sites during high-temperature oxidation treatments, to recover initial DHA rates (Figure 3).

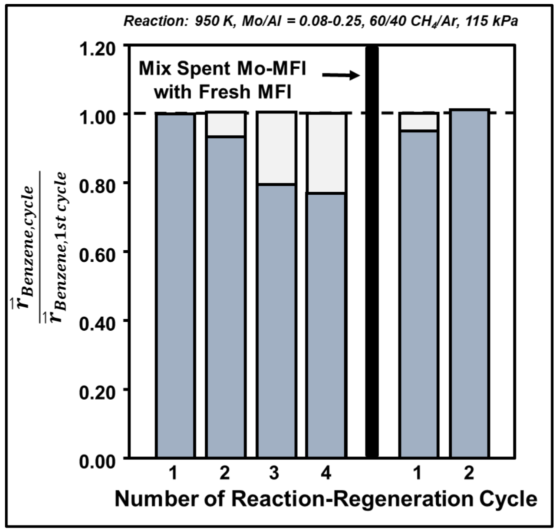
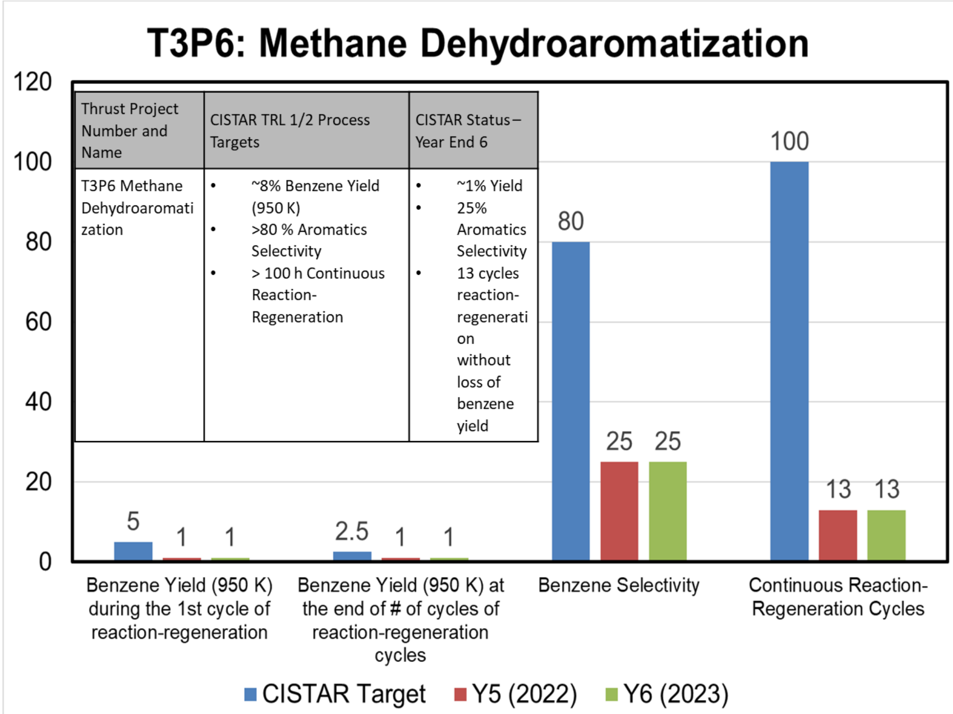


Figure 3. Benzene formation rates (950 K) measured on Mo-MFI during sequential cycles of reaction-regeneration, normalized by the rate measured during first cycle. Measured rates decrease systematically with increasing number of reaction-regeneration cycles. Spent Mo-MFI after 4 cycles was mixed with fresh H-MFI and rates recovered to values observed on the 1st cycle.

- Characterization methods based on H_2 TPR, UV-visible spectroscopy, and XAS are being developed to identify and quantify different M species (ion-exchanged sites vs. clusters or bulk MOx) on a zeolite support.
- Characterization methods based on NH_3 TPD are being developed to distinguish between different M ion-exchanged species on a zeolite support.

- **Interdependence:** The researchers in T3P6 span Purdue and Northwestern, working closely together to accomplish project goals. Students collaborate directly between experimental groups to efficiently utilize resources at each institution. This group is in frequent communication with one another so students can share recent progress or relevant papers. We also held a day-long in-person meeting at Purdue Northwest Campus (Hammond, IN) in August 2023 to have a group discussion on current progress and future work. We are also collaborating with Abhaya Datye (UNM, Thrust 1) on high-resolution STEM imaging of metal-zeolite catalysts to characterize metal dispersion and the integrity of the zeolite support after reaction-regeneration cycles.
- **Testbed Impact and Value:** This project is relevant to Testbed 1, which makes aromatic compounds useful as chemicals. The research in T3P6 can provide new process alternatives that can undergo economic evaluation by the Testbed team.
- **Technical Targets:** Technical targets will be developed in the first year of the project (Y6), informed by baseline measurements performed on representative conventional materials.



Blue bars are data obtained from Kosinov et al., J. Catal., 346 (2017) 125-133 (2 wt.% Mo-MFI).

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Conventional Mo-zeolite materials structurally degrade with successive reaction-regeneration cycles, irreversibly losing catalytic activity over time. We are making progress on using structurally stable, small-pore (CHA) zeolites that retain activity through reaction-regeneration cycles (see quad chart). However, the production of aromatics is restricted to Mo active sites at the external surface, since benzene is too large to diffuse through eight-membered ring windows. Therefore, synthesis efforts are being dedicated to shrink the crystallite size and increase external surface areas to increase benzene and H_2 formation rates (per Mo). Modification of the external surface of Mo-MFI with small amounts of an additional oxide can improve yields over a small number of reaction-regeneration cycles, but the effect decays rapidly. Alternate overcoat compositions are being explored, especially ZrO_2. A systematic literature scan and re-xanalysis of data has identified several non-standard active site compositions worth investigating.

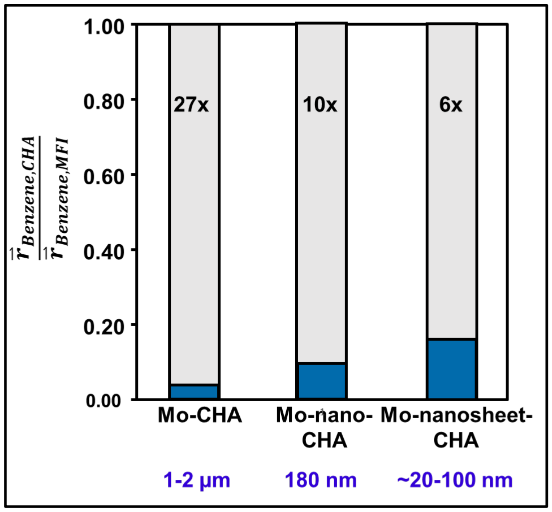


Figure 4. Benzene formation rates (950 K) measured on Mo supported on CHA zeolites with varying crystallite size (blue numbers) normalized by the rate measured on Mo supported on MFI zeolites. Decreasing CHA crystal size increases the observed benzene formation rate and it ranges from 27x to 6x lower than rates measured on Mo-MFI.

- **Path to Targets Summary:** New synthesis methods are being studied to improve zeolite/support material stability. Also, alternative (milder) regeneration strategies are being explored to minimize the severity of conditions the catalyst is exposed to (namely high-temperature steam) during regeneration (eg, coke removal) of spent catalysts.
- **Specific Plans Organized by Challenge:** The materials synthesis and regeneration strategies being explored both address the technical challenge associated with insufficient material stability through successive reaction-regeneration cycles.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Arinaga, A.M.; Biswas, A.; Zhang, X.; Greeley, J.; Marks, T.J.; Origin of Rate and Selectivity Trends and Exceptional Yield in Sulfur-Oxidative Propane Dehydrogenation Over Supported Vanadium Catalysts, *ACS Catal.* **2023**, in press.(CISTAR)
2. Ahn, S. Littlewood, P.; Liu, Y.; Marks, T.J.; Stair, P.C.; Stabilizing Supported Ni Catalysts for Dry Reforming of Methane by Combined La Doping and Al Overcoating using Atomic Layer Deposition, *ACS Catal.* **2022**, *12*, 10522–10530. **DOI**: 10.1021/acscatal.2c02599. (Associated)
3. Ramos-Yataco, J.; Notestein, J. Assessment of catalysts for oxidative coupling of methane and ethylene. *Catalysis Today*, *416*, 113770 (2023).
4. Wang, D.; Littlewood, P.; Marks, T.J.; Stair, P.C.; Eric Weitz, E.; Coking Can Enhance Product Yields in the Dry Reforming of Methane, *ACS Catal.* **2022**, *12*, 8352–8362. **DOI**: 10.1021/acscatal.2c02045. (Associated)

- **Disclosures, Patents Filed for the Period 10/1/2022 to 9/30/2023:**

1. Gounder R., Santiago-Colón, A. 2023. “Process for Extending Mo-Zeolite Catalyst Lifetime During Methane Dehydroaromatization.” US Provisional Patent Application No. 63/521,517
2. Gounder R., Santiago-Colón, A., Lee, S. 2023. “Method for Making CHA Zeolites and Zeotypes.” US Provisional Patent Application No. 63/529,264
3. Gounder R., Santiago-Colón, A. 2023. “Preparation of Nanosheet Zeolites and Applications for Methane Dehydroaromatization.” US Provisional Patent Application No. 63/529,189

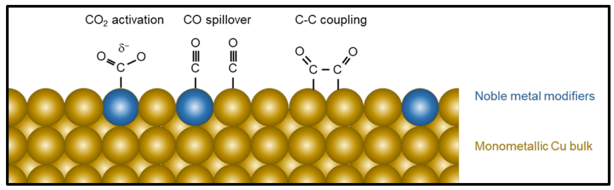
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T3P7 Electrochemical CO2 Reduction to Multi-carbon Products using Single Atom Alloys*
Project Lead: *Joaquin Resasco (UTA)*

F: Jeff Greeley (PU), Christina Li (PU)
GS: Joel Graves (UTA)

Project Goals

- Design and synthesize bimetallic catalysts that generate ethylene from electrochemical CO_2 reduction. These bimetallics will be in the form of single atom alloys, where isolated reactive metal atoms (Pt, Pd, Rh) are doped into a pure Cu surface.
- The first goal is to develop methods for synthesis and characterization of single atom alloy catalysts as thin films. We will characterize the active site structure in the pristine material and under working conditions with operando spectroscopy.
- Then, insights from model thin film catalysts will be to dispersible, high surface area nanoparticle catalysts for testing in membrane electrode assembly devices.
- Experimental measurements will be supported by density functional theory calculations to describe site stability and reaction mechanisms.



Barriers

- It is challenging to ensure that site isolation is achieved. This is critical as small clusters of dopant atoms will yield very different performance than isolated sites.
- Catalyst structure must be assessed under operando conditions, as the structure of the catalyst is known to be dynamic under CO_2R conditions.

Methodologies

- A suite of spectroscopic techniques including probe molecule infrared spectroscopy, x-ray absorption spectroscopy, and aberration corrected electron microscopy will be used to understand catalyst structure.
- Density functional theory calculations will be used that incorporate explicit solvents and accurately model electrochemical reactions at constant potential.

Research Achievements

- Benchmark activity data has been collected for model thin film Cu catalysts which compares well with previous reports on single crystal electrodes.
- A system for conducting probe molecule CO infrared spectroscopy during electrochemical testing has been developed. This is invaluable for operando structural characterization.
- Methods for experimental kinetic analysis (temperature dependence of rates, partial pressure dependence of rates, isotopic labelled studies) have been developed in our lab.
- Synthesis of bimetallic Cu-Pt, Cu-Pd, and Cu-Ni catalysts have been developed for both thin film and nanoparticle catalysts.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** This project is focused on the discovery of novel materials for the efficient electrochemical conversion of CO_2. The target product is ethylene (Testbed 2), which is the multicarbon product generated with highest selectivity over Cu catalysts. Ethylene produced from electrochemical reduction can be fed to oligomerization processes, helping to decarbonize the process by replacing energy intensive cracking processes. Furthermore, sourcing of carbon from CO_2 helps to produce less carbon intensive fuels and chemicals, supporting CISTAR's overall decarbonization efforts.

- **Abstract:** The electrochemical conversion of CO_2 provides a means for generating low carbon intensity fuels and useful chemicals. Currently, the electrocatalysts available for mediating this chemistry are not sufficiently active or selective to make this process economically feasible. Here, we aim to develop novel bimetallic *Cu-based single atom alloy* catalysts that can efficiently generate ethylene from CO_2 electrochemically. This is in contrast to a number of previously studied Cu bulk bimetallics, which suffer from surface segregation and consequently low selectivity to desired products.

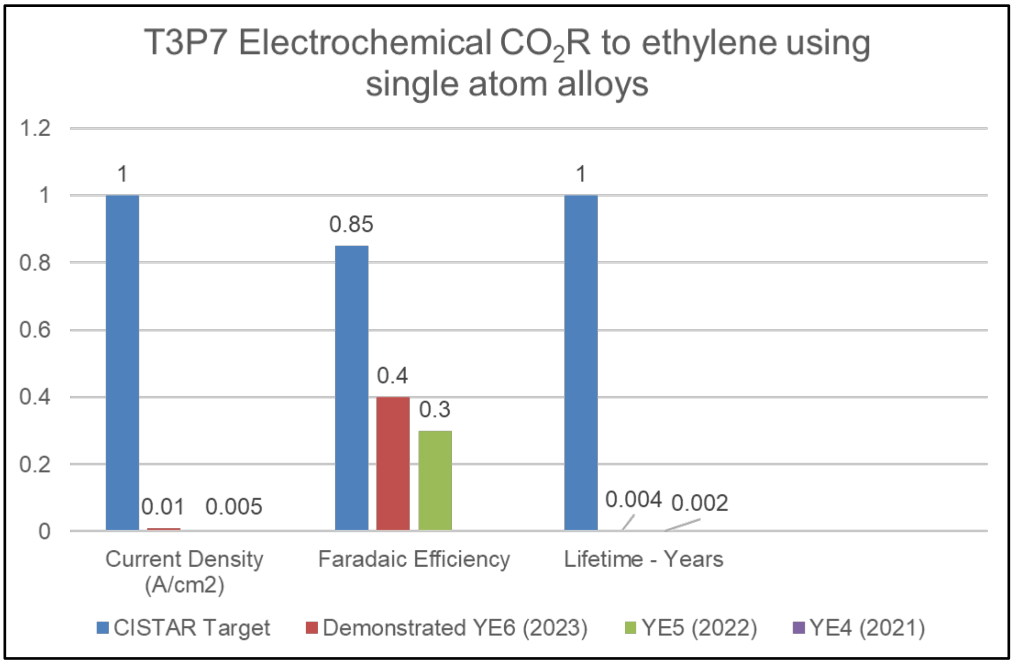
  Technical summary: The electrochemical conversion of CO_2 provides a means for generating low carbon intensity fuels and useful chemicals. Currently, the electrocatalysts available for mediating this chemistry are not sufficiently active or selective to make this process economically feasible. A number of catalysts (e.g. Ag, Au) selectively generate carbon monoxide while others generate formic acid in reasonable yields (e.g. Sn, Bi). Cu catalysts are unique in their ability to form carbon-carbon bonds and therefore produce molecules with higher energy density and value. But Cu is neither sufficiently active nor selective for practical application of this technology. As a result, extensive efforts have been aimed at modifying Cu with the goal of increasing its activity or selectivity to a desired multicarbon product (e.g. ethylene). Unfortunately, despite decades of research, no reported catalysts show intrinsic activity that meaningfully exceeds that of Cu.

  Alloying metals is a common method for influencing the activity of catalytic sites. The addition of a second metal can influence reactivity through ensemble or ligand effects. Therefore, it is surprising that Cu based bimetallics have not yielded more promising results. Recently, we demonstrated that this is likely due to changes in the surface structure and composition of these catalysts under operating conditions. During CO_2R, adsorbates such as carbon monoxide can drive segregation of reactive metals to the surface, resulting in a surface enriched in this metal relative to the intended bulk composition.

  To overcome this limitation, we plan to use single atom alloy catalysts featuring a bulk material composed of elemental Cu with the modifying metal present only as isolated atoms doped into the surface of the catalyst. As the second metal is limited to the surface, this will avoid the migration of reactive atoms from the bulk to the reactive interface and prevent formation of a monometallic "skin". We hypothesize that incorporation of reactive metals (Pt, Pd, Ni) will aid in the activation of CO_2 to produce CO, which can then spill over onto Cu sites and undergo C-C coupling reactions. This will allow formation of ethylene at lower potentials that what would be observed over pure Cu.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:** This project has been led by a graduate student at UT Austin, Joel Graves, and began on 03/01/2022. In the last year, Joel has synthesized well-defined oriented thin films on Si single crystal electrodes to serve as model catalysts for investigating single atom alloys. He has characterized the activity and selectivity of these materials as a function of potential and finds excellent agreement with prior work on single crystal electrodes. Joel has also developed experimental methods for carrying out electrochemical measurements while changing reactor temperature, partial pressure of reactants, and isotopic identity, which are critical for mechanistic understanding of observed reaction rates. We have also recently developed the ability to perform in-situ electrochemical CO probe molecule infrared spectroscopy measurements in our lab. These experiments are carried out in the attenuated total reflectance (ATR) mode using a beveled Si wafer as an ATR prism. The working electrode is deposited as a thin film on the surface of the Si wafer. These experiments will allow for operando characterization of catalyst structure and composition, including characterizing site isolation of reactive metals. Finally, Joel has developed synthetic protocols for producing Cu-Ni, Cu-Pd, and Cu-Pt bimetallic catalysts both as thin films and supported nanoparticles for use in membrane electrode assemblies.
- **Interdependence:** This project combines experimental electrochemical measurements in the Resasco lab at UT Austin with computational work at Purdue with PI Jeff Greeley. The Greeley group has extensive experience simulating catalytic reactions in electrochemical media. This is critical as it is necessary but quite challenging to accurately simulate the electrochemical environment (liquid solvent, surface charging, electrolyte ions). To support synthesis of single atom alloys in nanoparticle forms, collaborative work will be performed between the Resasco lab at UT and PI Christina Li's group at Purdue. The Li group has demonstrated expertise in the synthesis of controlled bimetallic nanocrystalline materials. While thin film catalysts are optimal for understanding the structure and behavior of Cu bimetallics, these nanoparticle catalysts are well suited to use in gas-diffusion electrodes/membrane electrode assemblies that supply gaseous CO_2 and can thus operate at significantly higher rates. Finally, this project will interface with technoeconomic analysis and life cycle analysis in Thrust 7 to understand how electrochemical CO_2 reduction can be most practically employed to maximize cost effectiveness and environmental impact.
- **Testbed Impact and Value:** This project is important to Testbed 2 as it is focused on producing ethylene. The ethylene produced from electrochemical reduction of CO_2 could reduce carbon intensity as it replaces ethylene from steam cracking and sources the carbon from atmospheric carbon dioxide.

- **Technical Targets:**



Performance for YE4 is not shown as project began in Y5.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Current challenges include (1) phase segregation of reactive metals during synthesis procedures, (2) increased competition from hydrogen evolution with increased reactive metal loading, and (3) demonstration of Cu catalysts in membrane electrode assembly devices that operate at higher rates. Thus far, we have demonstrated that monometallic Cu catalysts show a maximum current efficiency to ethylene of ~40% (40% of charge passed goes to forming ethylene) and the total current density is ~7 mA/cm^2.

- **Path to Targets Summary:** In the next 12 months, we will focus on development of new synthesis methods that maintain site isolation for Cu bimetallic catalysts. We have begun trials of atomic layer deposition to controllably deposit Pd onto Cu electrodes. The linearity and saturating nature of ALD growth of Pd has been confirmed. We will also perform parallel tests of Cu bimetallics in membrane electrode assembly devices that are available in the Resasco lab at UT Austin. We expect peer reviewed publications to result from this project in the next reporting year.

- **Specific Plans – (i) Catalyst synthesis:** Thus far, catalyst synthesis has been carried primarily using co-physical vapor deposition of Cu and secondary elements for thin film catalysts and using incipient wetness impregnation or strong electrostatic adsorption methods for supported nanoparticle catalysts. These synthesis methods have resulted in the formation of islands or segregated particles of the reactive metal. To avoid this, we will explore new synthesis methods in the coming 12 months. These include atomic layer deposition for thin films and electroless deposition onto colloidal Cu for nanoparticle catalysts. Both of these methods separate the steps for formation of Cu catalysts and modification, which we believe will allow for greater control.

- **Specific Plans – (ii) Catalyst characterization:** CO probe molecule infrared spectroscopy in the diffuse reflectance mode (DRIFTS) has been invaluable for characterizing single atom alloys ex situ. We now have developed the capability of characterizing catalysts in operando using ATR FTIR, and we will employ these methods in the coming year.
- **Specific Plans – (iii) Catalyst testing:** Thin film catalysts will be tested in liquid phase batch reactors, while parallel studies will be conducted in membrane electrode assemblies that are supplied with gas phase CO_2 and operate at higher rates and energy efficiencies. We have thus far validated the performance of benchmark Ag catalysts in our membrane electrode assemblies which selectively produce CO at rates up to 100 mA/cm^2.

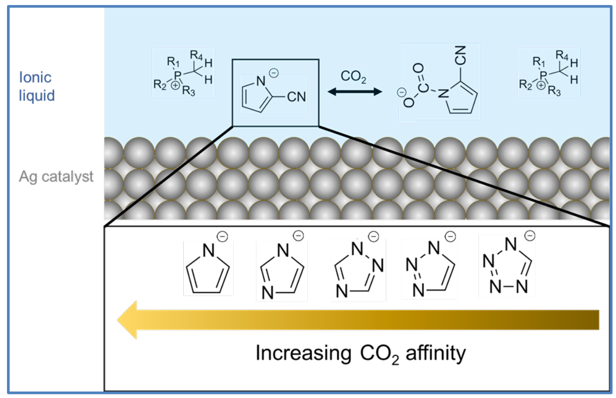
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T3P8 CO_2 Capture and Electrochemical Reduction in Azolide Ionic Liquids: Experimental Studies and Systems Integration* ***Project Lead:*** *Joaquin Resasco (UTA))*

F: Joan Brennecke (UTA), Mark Stadtherr (UTA)	
GS: Jon-Marc McGregor (UTA)	
PD:	**UG: Yasemin Dundar (UTA)**

Project Goals

- Create a system based on azolide ionic liquids that can capture and efficiently convert carbon dioxide electrochemically
- Here, azolide anions are chosen as they complex reversibly with CO_2 with an interaction strength that is systematically tunable.
- Our goal is to understand the relationship between the interaction strength of the ionic liquid and CO_2 and the activity of Ag catalysts for CO_2 reduction. Silver is known to selectively generate CO during CO_2R but is too weakly binding to effectively activate CO_2. Our hypothesis is that complexed CO_2 enabled by the IL will be more readily reduced than uncomplexed CO_2.
- Synergistic to these goals, we plan to describe how the composition of the electrolyte (cations, anions, solvent) influence CO_2 reduction rates and selectivity in aprotic media.



Barriers

- It is possible that the complexation of the IL occurs reversibly in the solvent without cooperative interaction with the surface. In this case, physically dissolved CO_2 would remain the relevant reactant species. We will understand whether this is the case with comparative studies using non-coordinating anions.
- Ionic liquids can form CO_2 complexes beyond the carbamate structure (e.g. ylides). We will use in situ IR and NMR to understand the structure of any complexes formed.

Methodologies

- To understand the role of ILs and the electrochemical environment on CO_2R rates, we will use a combination of kinetic, spectroscopic, and computational methods.

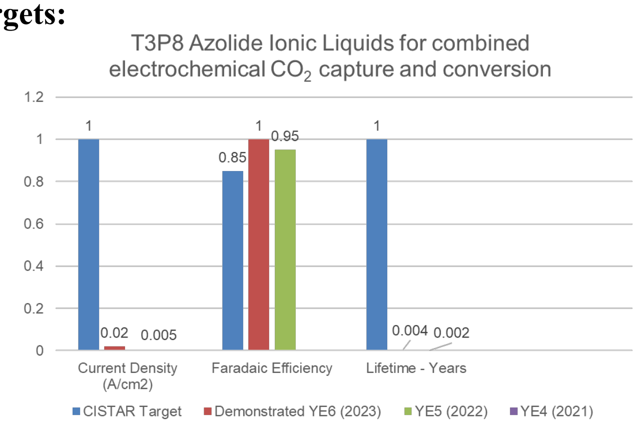
Research Achievements

- The electrochemical performance of a series of tetra-alkyl ammonium based azolide ILs have been synthesized and characterized.
- It was observed that the nature of the electrolyte cation has a dramatic influence on electrochemical CO_2R rates.
- The cation effect has been described as being due to differences in the double layer thickness and consequently the strength of the electric field at the catalyst surface with changing cation size.
- Spectroscopic data demonstrates that ILs using these cations form ylides in addition to carbamates, making interpretation of anion effects challenging. New studies have been started using phosphonium cations to understand the influence of the azolide anions.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** The goal of this project is to create systems that can carry out both the capture and electrochemical conversion of CO_2 using tailored ionic liquids. If successful, this project would impact all testbeds as it would help eliminate emissions from each part of the CISTAR process. The project is a collaboration between Joan Brennecke, who is an expert in ionic liquids and carbon capture, Joaquin Resasco, an expert in electrochemical CO_2 reduction, and Mark Stadtherr, an expert in systems modeling and optimization.
- **Abstract:** The electrochemical conversion of CO_2 to fuels and chemicals is an attractive process. Typically, it is assumed that reactors for electrochemical conversion of CO_2 will be fed gas that has been captured (from air or a flue gas stream) and released. Therefore, the development of a system that could combine the steps of CO_2 capture and conversion could circumvent the requirement of releasing and compressing the CO_2 after capture. This could significantly reduce the energy requirements on the entire process and improve both its cost and emissions impact. To realize this idea, we will use ionic liquids (ILs) featuring azolide anions. Our hypothesis is that by complexing with CO_2, these azolide anions can facilitate its activation and enhance rates of CO generation over Ag catalysts. More broadly, we seek to describe how changes to the electrolyte composition, including the choice of aprotic solvent, anion, and cation, can influence performance for electrochemical CO_2 conversion. This work will be supported by systems level analysis that will focus on how electrochemical processes can be integrated with the CISTAR technology. This analysis will describe the cost and emissions impact of using renewable electricity sources to drive the electrochemical reaction, and choice of different chemicals that can be produced from the syngas generated by the electrochemical process. This work will further aid in accelerating CISTAR’s decarbonization efforts.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:** This project is led by a graduate student, Jon-Marc McGregor, who is co-advised at UTA by Resasco and Brennecke. Jon-Marc began research on this project at UT Austin on 3/1/2022. The most significant results in the past year have been the observation that changing the alkyl ammonium cation paired with the azolide anion can dramatically impact CO2 reduction rates. Through a series of experimental studies, we have determined the physical reason behind these effects, yielding important new scientific insights for the field. The insights of how the electrochemical medium and interfacial electric fields influence rates will be generally applicable across all electrocatalytic projects in CISTAR.
- **Interdependence:** This is a collaborative project that combines expertise from CISTARs different conceptual areas of catalysis, separations, and systems engineering. This project has also included collaboration outside of CISTAR. This has included density functional theory and ab-initio molecular dynamics simulations that have helped describe the nature of these complex electrocatalyst interfaces. Further collaborative work including atomistic simulations will be done working with experts within CISTAR (e.g. Jeff Greeley, PU and Bill Schneider, NDU).

- **Testbed Impact and Value:** The primary product of our process is CO. CO can be upgraded through a large number of electrochemical and thermochemical processes to products such as ethylene (Testbed 2) which can be integrated with CISTAR's existing oligomerization processes. For instance, Cu catalysts can electrochemically convert CO to ethylene with good selectivity (T3P7). As ethylene generated in this way is sourced from CO_2, this process advances CISTAR's decarbonization efforts, and provides a low carbon intensity route to ethylene for Testbed 2.
- **Technical Targets:**



Performances for YE4 is not shown as this project began in Y5.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** We observed that changing the alkyl ammonium cation in the electrolyte dramatically influenced CO_2R rates. Through extensive kinetic, spectroscopic, and computational studies a consistent physical model has been developed to describe these effects. These results are currently being written up for a peer reviewed publication. We have observed that alkyl ammonium cations paired with azolide anions lead to complexes beyond the desired carbamate structure, complicating analysis. We will therefore study comparative electrolytes where carbamates alone are present, along with non-complexing electrolytes. Finally, we have observed significant differences in reactivity when the nature of a supporting solvent (e.g. acetonitrile, dimethyl sulfoxide, propylene carbonate) is changed. We are currently investigating the reasons behind these effects. Finally, we will couple these experiments with systems level analysis that will guide the design and integration of electrocatalytic processes within CISTAR.
- **Path to Targets Summary:** In the next year we will continue kinetic, spectroscopic, and computational studies aimed at assessing the role of solvents and CO_2-IL complexes on CO_2 reduction rates.
- **Specific Plans: i) Understanding speciation of CO_2 complexes.** An expansive library of ammonium and phosphonium azolide ILs have been synthesized for use as potential electrolytes. To understand how these cations and anions interact with CO_2 in situ attenuated total reflectance infrared spectroscopy will be used. Here, we can observe

whether the carbamate is the only structure formed or whether unwanted ylide complexes are also present. These infrared measurements will be corroborated by nuclear magnetic resonance measurements. Once we have demonstrated electrolyte compositions where only the carbamate is formed, we will conduct comparative electrokinetic measurements with these compositions and anions where no complexation with the CO_2 is observed (e.g. $TFSI^-$). If differences are observed with complexed CO_2 and physically dissolved CO_2, systematic measurements will be performed with varying CO_2-IL interaction strength, which is known from DFT calculations and CO_2 uptake measurements.

- **Specific Plans: ii) Understanding the role of solvent on CO_2R.** We have observed that kinetic rates of CO_2R depend strongly on the choice of solvent to support the IL electrolyte. We will run kinetic studies including CO_2 partial pressure dependent studies, temperature dependent studies, and isotopic labeling studies, to elucidate the reasons behind these effects. These insights will help design optimal systems for combined CO_2 capture and conversion.
- **Specific Plans: iii) Systems analysis.** This work will be supported by systems analysis aimed at integrating electrocatalytic processes with the CISTAR technology. We will examine how electricity mix or product output impacts emissions and process economics. These insights will help design systems that optimally pair with the CISTAR process.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T3P9: Carbon-based Catalysts for Non-oxidative Coupling of Methane*
Project Lead: *Jeff Greeley (PU)*

F: Jeffrey Greeley (PU), Rajamani Gounder (PU)	
GS: Luke Pretzie (PU), Justin Rosa-Rojas (PU)	
REU: Jackson Boodry (PU)	**REM:** Mahagani Lasciers (PU)

Project Goals

- Elucidate the kinetics and mechanisms of methane non-oxidative conversion (NOCM) on carbon-based surfaces, which are believed to be the working state of heterogeneous catalysts under reaction conditions
- Synthesize high surface area carbons, with varying densities of defects, to assess the impact of structure and morphology on NOCM performance
- Identify and quantify active sites in carbon surfaces for NOCM
- Develop theoretical models of NOCM kinetics on defected graphene and amorphous carbon surfaces to quantify elementary kinetic parameters

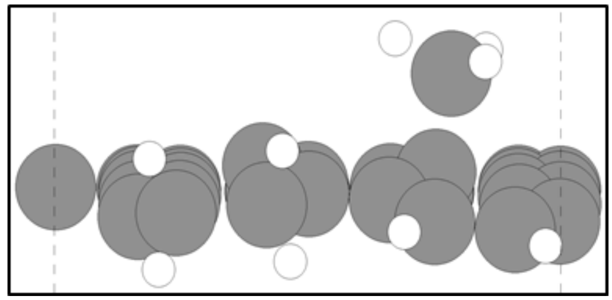


Figure 1. Activation of methane at the armchair edge of a graphene nanosheet. DFT calculations suggest that, as soon as the C-H bond is activated, a CH_3 radical is immediately rejected to the gas phase. This step is likely rate-limiting for NOCM on spent, carbon-based catalyst structures. Gray = carbon, white = hydrogen.

Barriers

- NOCM rates on spent heterogeneous catalysts scale with the spent, carbon-covered surface area of the material, but the molecular structure of the active sites is unknown
- Characterization methods to accurately quantify defect sites in carbons is lacking
- Synthesis methods to tailor the structure and density of defect sites in carbons are lacking

Methodologies

- Synthesis of carbons with varied material properties (e.g. , zeolite-templated carbons)
- Development of characterization techniques (e.g., chemisorption, temperature-programmed desorption) to identify and quantify defect sites in carbons
- Experimental reaction kinetics studies
- Combined Density Functional Theory, ab-initio thermodynamic, and microkinetic model development to establish robust relationships between active site structure and kinetic properties

Research Achievements

- Flow reactor and on-line analytical (eg, gas chromatography) unit has been redesigned, built, and commissioned for methane non-oxidative reactions and chemisorption experiments at high temperatures (1400 K)
- Zeolite-templated carbons with high surface area and carbon defects have been successfully synthesized for catalytic testing
- Computational models of several well-known graphene defects, including vacancies, armchair edges, and zigzag edges, have been developed as candidate active site structures for NOCM
- Adsorption energies and activation barriers for hypothesized elementary reaction steps in NOCM have been calculated on the candidate active site structures. Graphene terraces are found to be inert for NOCM, while edges exhibit higher activity.
- Mechanistic analysis suggests that hydrogen-passivated graphene edges will be excited to produce bare carbon atoms, which then dissociate methane and immediately reject CH_3 radical to the gas phase. This last step is rate-limiting for the selective (non-coking) process.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** This project seeks to advance the science and technology of non-oxidative conversion of methane (NOCM) to higher order hydrocarbons, including significant fractions of C2's, on supported carbon-based catalysts. This effort directly supports Thrust 3's focus on methane activation and conversion.
  Abstract: Recent work in CISTAR has determined that carbon deposits, formed during the initial stages of non-oxidative methane activation on transition metal and carbon substrates, can directly catalyze NOCM. These results motivate direct studies of how various allotropes of carbon, supported on metal substrates, catalyze methane coupling. These studies, in turn, seek to determine both the specific structural features of model carbon moieties that are active for methane conversion and the extent to which the interaction of these carbonaceous species with the metal substrate influences the reactivity. A combination of synthesis of high surface area and templated carbons, molecular-level characterization, and theoretical modeling will be deployed for this purpose. As the fundamental aspects of the active site structure and chemistry are elucidated, additional screening studies, utilizing a combination of computational and experimental analysis, will also be undertaken to identify catalysts and reaction conditions that maximize the NOCM reactivity.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
  - Flow reactor and on-line analytical (eg, gas chromatography) unit has been redesigned, built, and commissioned for methane non-oxidative reactions and chemisorption experiments at high temperatures (1400K)
  - Zeolite-templated carbons (ZTC) with high surface area and carbon defects have been successfully synthesized (with help of REU/REM students) for future catalytic testing

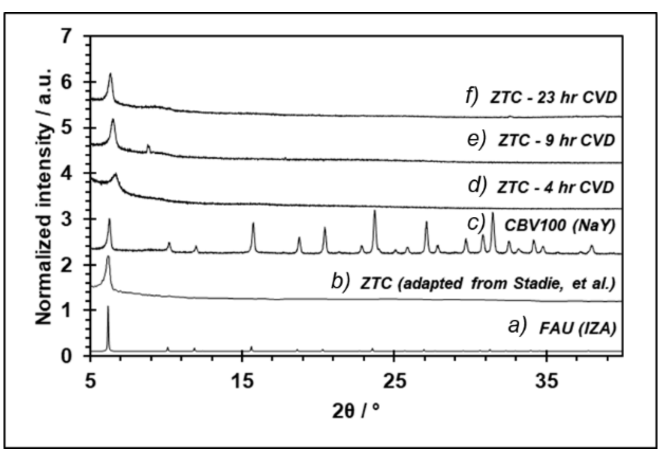


Figure 2: XRD patterns on ZTC samples a) faujasite framework obtained from the International Zeolite Association (IZA) database, b) ZTC reported from Stadie, N. P., et al. Langmuir 2012, 28 (26), 10057–10063, c) CBV100 commercial zeolite template, d)-f) ZTCs synthesized with different propylene chemical vapor deposition (CVD) durations (4-23 hr).

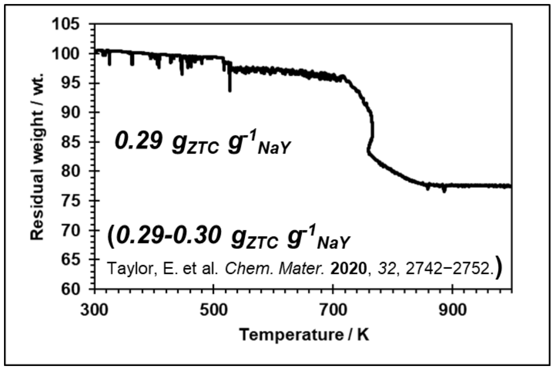


Figure 3: Combustion thermogravimetric analysis of ZTC + NaY composite after 23 hr propylene CVD.

- Computational models of several well-known graphene defects, including vacancies, armchair edges, and zigzag edges, have been developed as candidate active site structures for NOCM
- Adsorption energies and activation barriers for hypothesized elementary reaction steps in NOCM have been calculated on the candidate active site structures. Graphene terraces are found to be inert for NOCM, while edges exhibit higher activity.
- Mechanistic analysis suggests that hydrogen-passivated graphene edges will be excited to produce bare carbon atoms, which then dissociate methane and immediately reject CH_3 radical to the gas phase. This last step is rate-limiting for the selective (non-coking) process.

- **Interdependence:** Our team has extensive expertise relevant to the project. Gounder is an expert in synthesis of zeolites and carbon-containing materials, as well as materials characterization and kinetic measurements. Greeley has extensive experience in DFT calculations of the stability and thermodynamics of graphene and transition metal nanostructures, as well as in making predictions of reaction kinetics based on combined DFT and microkinetic models. These experimental and computational efforts are highly synergistic and will permit comprehensive elucidation of active site/reactivity relationships in carbon-based NOCM catalysts.
- **Testbed Impact and Value:** This project has direct relevance to the methane conversion to alkenes, achieved by high temperature dehydrogenation, testbeds.
- **Technical Targets:** An important component of the proposed work is the effort to understand the true active site of NOCM on transition metal-based catalysts. Literature presents a confusing and often conflicting picture of these active site features, and has not recognized the dominant role of surface carbon species (that form during early stages of reaction) on NOCM performance. Based on previous CISTAR results, combined with state-of-the-art experimental and computational methods available to our team, it will be possible to resolve these discrepancies and develop new directions to tailor the structure of carbon-based catalysts to promote methane NOCM. This basic knowledge will, in turn, form a solid basis for the development of enhanced NOCM catalysts.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Current methane non-oxidative reactions efforts are focused on validating the flow reactor and on-line analytical unit operation. Validation is needed before detailed reactivity and site quantification measurements can begin. Computational models have been developed for selected model graphene defects, and kinetic and thermodynamic energies for NOCM have been determined. Full microkinetic modeling of the associated mechanisms, as well as development of rigorous models for templated carbons, remain to be carried out, as the requisite unit cell size is extremely large.
- **Path to Targets Summary:** the program in the next year will focus on (i) measurement of NOCM turnover frequencies on carbon-covered heterogenous catalysts and zeolite-templated carbons, (ii) chemisorption experiments for carbon defect site quantification, (iii) synthetic and/or post-synthetic methods for changing defect site quantity of zeolite-templated carbons, (iv) continued DFT modeling of templated carbons, including zeolite-templated carbon structures, and (v) calculation of NOCM kinetic parameters and refinement against corresponding experimental values
- **Specific Plans Organized by Challenge:** Synthetic efforts will focus on zeolite templated carbons and graphene nanosheets with varying defect site quantity, while chemisorption techniques to determine active site densities will be pursued in parallel. Computational analysis will focus on continued development of models for graphene defects and templated carbons, as well as completion of thermodynamic and kinetic analysis of NOCM mechanisms on these structures. The computational models will be refined against the experimental data, and resulting kinetic rate expressions will be used to identify compact descriptors to characterize the rates and selectivities of NOCM on the various carbon structures. Intrathrust collaborations with T1, possibly involving investigation of the templated carbon materials for ethane and propane dehydrogenation, are also envisioned.

THRUST 6:
MEMBRANE SEPARATIONS

Section 1: General Information & Quad Chart for the Period 10/1/2021 to 9/30/2022

Project Title: *T6P1 Supported Ionic Liquid Membranes (SILMs) for Olefin/Paraffin Separations*
Project Lead: *Joan Brennecke (UTA)*

F: Benny D. Freeman (UTA), Jeffrey Brinker (UNM)
GS: Sejoon Park (UTA), Matthew Davenport (UTA), Leonard (L.J.) Ruggiero (UNM)
UG: Taylor McClung (UTA)

Project Goals

- Supported ionic liquid membranes (SILMs) with stable gas permeance in which an ionic liquid is filled in the pores of a support membrane
- Ag^+-based facilitated transport membranes whose separation performance is stable to exposure to reducing gases, such as H_2, H_2S, and C_2H_2.
- Polymeric electrolyte membranes with dissolved Ag (I) salts, stable to reducing gases, and developed based upon results from the SILM membranes.
- Ag^+-based facilitated transport membranes possessing separation performance and lifetime above target thresholds informed by other membranes from the literature and collaborative process modeling through CISTAR
- Mixed-gas permeation experiments to evaluate membranes under industrial separation conditions

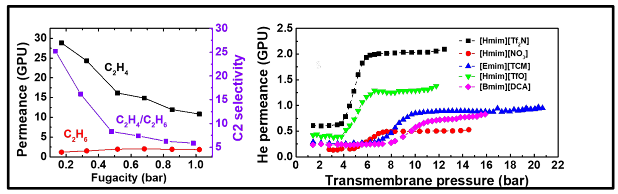


Figure 1: Supported ionic liquid membranes; C_2 mixed gas separation performance as a function of feed pressure (left) and high-pressure stability performance of the SILM prepared with a support modified with mesoporous silica

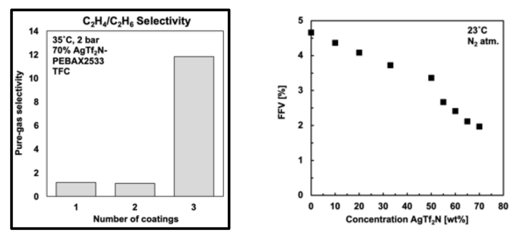


Figure 2: Polymeric membranes; C_2 selectivity of a 70 wt% $AgTf_2N$-PEBAX2533 TFC coated on MTR PEI support vs. number of coatings (left) and fractional free volume of $AgTf_2N$-XLPEGDA vs. $AgTf_2N$ concentration via PALS.

Barriers	Research Achievements
● Ag^+ is highly reactive and can be easily degraded by poisoning gases such as H_2, H_2S, and C_2H_2. ● Polymeric Ag^+ facilitated transport membranes have low gas permeability ● SILMs can experience blow-out of the ionic liquid at high transmembrane pressures **Methodologies** ● Ionic liquid and polymer electrolyte membranes with large, weakly-coordinating anions stabilize Ag^+ in solution ● Development of high-flux thin film composites (TFCs) ● Development of support membranes for SILMs with smaller pore size and enhanced adhesion to increase capillary forces and prevent blowout ● Process modeling in collaboration with Thrust 4 to identify suitable process conditions	● Developed the silica-alumina hybrid membrane, which results in SILMs with high-pressure stability (>20 bar) ● Demonstrated high C2 selectivity (>20) of $AgTf_2N$ based SILM for both pure gas and mixed gas ● Development of promising and relatively defect-free TFC membranes with an $AgTf_2N$-PEBAX2533 coating with C_2H_4/C_2H_6 selectivity approaching that observed in dense films. ● Achieved reproducible characterization of $AgTf_2N$-XLPEGDA membrane stability to H_2S through a continuous exposure cell ● Characterized the fractional free volume of $AgTf_2N$-XLPEGDA solid polymer electrolytes using Positron Annihilation Lifetime Spectroscopy (PALS)

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** The goal of this project is to develop stable, long-lifetime olefin-paraffin separation membranes which separate olefinic products from paraffin reactants following dehydrogenation of natural gas feedstocks. Membranes could lower capital and energy costs, are more scalable, and have lower physical footprints than the currently practiced cryogenic distillation, and thus, are key to the strategic goal of decentralized chemicals production.

- **Abstract:** A chemically specific coordination complex between solvated Ag^+ ions and double-bonded olefin molecules, such as ethylene or propylene, results in a facilitated transport mechanism and increased olefin-paraffin selectivity. However, previous studies on Ag^+-containing facilitated transport membranes report poor stability of the Ag^+ carrier, especially in the presence of reducing gases, such as H_2, H_2S, and acetylene. Ionic liquid can solubilize and stabilize Ag^+ ions by forming a metal complex structure with anions. In our studies, the ion aggregation effectively attenuates the reactivity with hydrogen gas showing no significant olefin-paraffin selectivity loss over long periods of pure hydrogen permeation. In addition to the chemical stability of carriers, we are also focused on achieving physical stability of the liquid membranes such as preventing blow-out of the liquid from the pores, which leads to no separation. Using nanoconfinement of the ionic liquid in mesoporous silica structures that have modified alumina membranes, we have been able to stabilize the liquid under high pressure conditions. To extend the exciting stability results of the SILM membranes to a more scalable embodiment, solid polymer electrolyte facilitated transport membranes consisting of crosslinked

poly(ethylene glycol) diacrylate (XLPEGDA) and high loadings of $AgTf_2N$ and AgTfO salts were synthesized and characterized for ethylene-ethane selectivity. The $AgTf_2N$-containing membranes are stable to long-term pure- and mixed-gas H_2 permeation as well as C_2H_2 gas mixtures. However, H_2S exposure leads to Ag_2S formation on the surface of the membrane and reduced gas permeability. Currently, efforts are ongoing to reproducibly fabricate high flux and defect-free TFC membranes with a PEBAX 2533-based coating matrix and Ag salts through a scalable process.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

  SILMs:

  - Reproducible preparation of mesoporous silica-alumina hybrid membranes as porous supports for high-pressure stability of SILMs has been achieved.
  - SILMs prepared with the modified membranes show superior high-pressure stability, with no IL blow-out even at pressures higher than 20 bar, significantly expand the feasible operating pressure of SILMs for olefin/paraffin separation.
  - To maintain high olefin/paraffin selectivity of the SILM at high flux under high pressure we have explored how modification of the cation can enhance Ag salt solubility in the IL.
  - The SILM at high Ag^+ concentration showed mixed C2 gas selectivity greater than 20.

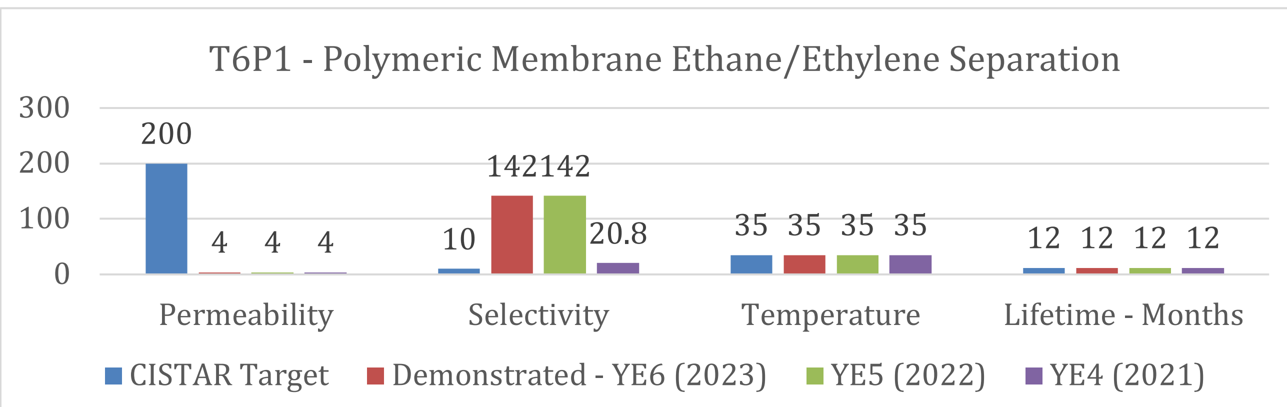
  Polymeric Membranes:

  - In collaboration with Membrane Technology and Research (MTR), Inc., various commercial membrane support materials were evaluated for compatibility with $AgTf_2N$-PEBAX 2533 coatings to form TFCs, and polyetherimide (PEI) was found to have lowest strikethrough. Spin-coating, brush-coating, dip-coating, doctor blade draw-down coating, and wire-wrapped rod draw-down coating were evaluated, and a multi-layer wire-wrapped rod draw-down process was found to be most reproducible.
  - Pure PEBAX 2533 TFCs with C_2H_6/N_2 selectivity >85% of dense film values and 70% $AgTf_2N$ PEBAX 2533 TFCs with a pure-gas C_2H_4/C_2H_6 selectivity of approximately 10 and an active layer of c.a. 1 μm thickness were demonstrated.
  - Building upon preliminary results from Y5, H_2S tolerance of the H_2-stable $AgTf_2N$-XLPEGDA membranes has been reproducibly characterized through the use of a custom continuous flow sweep cell to fix the H_2S concentration in the upstream and prevent concentration polarization.
  - In collaboration with the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia, the fractional free volume of

$AgTf_2N$-XLPEGDA solid polymer electrolytes has been characterized and was found to decrease with increasing salt concentration.

- **Interdependence:** To guide further development of these membranes and design of experiments to evaluate the effect of different process conditions, this project is interdependent with Thrust 4 to provide target process conditions. In addition, Thrust 4 can interface with researchers in this project and throughout Thrust 6 to identify the limits of the materials under investigation in order to yield realistic process flow sheets. As an interdependence work of the project, to break through the operating pressure limit of liquid membrane due to the blow-out at high transmembrane pressure, UT Austin and UNM have collaborated to develop ceramic mesoporous structures to enhance the adhesion between ionic liquid and the support. This development provides a wider window of possible operating pressures and can lead to higher productivity per unit membrane area.
- **Testbed Impact and Value:** This project is relevant to Testbeds 2 and 3 which aim to develop processes for generating high-value ethylene and propylene, with potential further conversion to linear and branched hydrocarbons. This project is essential for each testbed by enabling purification of the target products.
- **Technical Targets:**

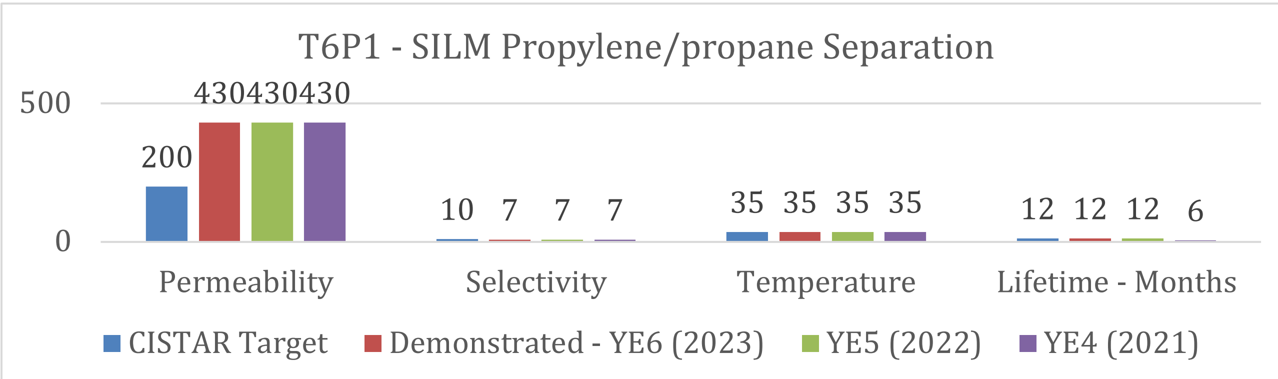
Polymeric membranes:



Thrust Project Number and Name	CISTAR TRL 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Year End 6
T6P1: SILMs for Olefin/Paraffin Separations - Ethylene/Ethane	• >200 Barrer Permeability • > 10 Ethylene/Ethane Selectivity	• 4.0 ± 0.2 Barrer C_2H_4 • 140 ± 2 C_2H_4/C_2H_6 Selectivity • 35 ˚C Temperature

	• > 35 ºC Temperature • > 1 Year Lifetime	• > 10 week lifetime (with pure 4 atm H_2 exposure) We expect it would also be stable for 12 months.

SILMs:



Thrust Project Number and Name	CISTAR TRL 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Year End 6
T6P1: SILMs or Olefin/Paraffin Separations – Ethane/ethylene Propane/propylene	• >200 Barrer Permeability • > 10 Ethylene/Ethane Selectivity • > 10 Propane/propylene selectivity • > 35 ºC Temperature • > 1 Year Lifetime	• 430 Barrer C_3H_6 • 1800 Barrer C_2H_4 • 7 C_3H_6/C_3H_8 Selectivity • 25 C_2H_4/C_2H_6 Selectivity (@ 0.2 bar, 50/50 mixed gas) • 35 ˚C Temperature • > 1 week lifetime (with pure 2 atm H_2 exposure)

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:**

  SILMs:

  Alumina anopore disc that are structurally modified with mesoporous silica allow SILMs to be operated under high transmembrane pressure (> 20 bar). Under high pressure conditions silver ion carriers are added in the IL for facilitated transport can become saturated, leading to lower selectivity than observed at lower pressures. To maintain high selectivity under high pressure, we plan to explore ways to dissolve higher concentrations of carriers in the IL.

Polymeric Membranes:

The key challenges currently facing the solid polymer electrolyte facilitated transport membranes ($AgTf_2N$-XLPEGDA and AgTfO-XLPEGDA) are fabricating high-flux, defect-free thin-film composite (TFC) membranes with minimal strikethrough, overcoming reduced mixed-gas selectivity relative to pure-gas resulting from plasticization, and synthesizing membranes with both high permeance and high selectivity despite high cohesive energy density due to solvation of Ag salts. Only membranes with high $AgTf_2N$ content (at least 50 wt%) show useful pure gas selectivity, and due to plasticization, mixed-gas C_2H_4/C_2H_6 selectivity has been observed to be approximately half that of pure-gas selectivity, further incentivizing increased Ag^+ content to maximize the selectivity. However, increasing the salt content increases the cohesive energy density and reduces the permeability of all gases, and thus development of suitable TFC membranes with a high selectivity active layer is critical. High-quality dense films of XLPEGDA can be easily fabricated, however, it has proven to be a challenging coating material for forming TFCs due to low molecular weight prior to cross-linking and oxygen sensitivity of the cross-linking process. Synthesizing thin film composites with minimal defects is inherently challenging due to the necessity of very thin coating layers.

- **Path to Targets Summary:**

  To increase silver salt solubility in the IL, some oxygen functional groups that are known to coordinate with silver ions will be incorporated in the cation structure. To move towards and beyond lifetime, permeability, selectivity, and temperature targets, research on polymeric facilitated transport membranes over the next 12 months will focus on evaluating the stability of AgTfO-PEBAX 2533 membranes, developing repeatable, high-selectivity, and scalable TFC fabrication procedures, and further characterization of the mixed-gas performance of promising TFCs in the context of process models developed by Thrust 4.

- **Specific Plans – SILMs**
  - Cation structure modification for high silver salt solubility in IL: Based on our previous study on the molecular structure of Ag ion complexes in IL mixtures, additional coordinating ability in the system is required to dissociate or dissolve the $AgTf_2N$. We are currently designing cations that can associate with Ag ions and further increase the Ag solubility to improve olefin selectivity.
  - High pressure mixed gas separation test on high [Ag^+] containing SILM prepared with the modified porous structure: To finally demonstrate the separation performance by the pore size reduction and higher carrier concentration, mixed gas

separation tests will be conducted using the mesoporous silica modified membranes in the mixed gas technology module (T5P1).

- **Specific Plans – Polymeric membranes:**
  - Stability of higher selectivity materials: We found that increasing the concentration of Ag^+ through use of AgTfO vs. $AgTf_2N$ in an XLPEGDA matrix improves selectivity. However, the permeability is so low that H_2 stability experiments are too time-consuming. Thus, we will evaluate the H_2 stability of AgTfO membranes as dense films in a higher-permeability PEBAX 2533 matrix, both as dense films and also as a TFC.
  - TFC synthesis and characterization: Procedures for fabricating $AgTf_2N$ and AgTfO PEBAX 2533 TFC membranes with high flux (i.e., as thin a layer as possible) and defect-free gas transport (C_2H_4/C_2H_6 selectivity at least 90% of the dense film values) will be further optimized such that a selective, pilot-scale membrane module could be created from a large sheet of membrane area (e.g., 0.1 m^2).
  - Mixed-gas performance: Building upon promising pure-gas TFC results, mixed-gas properties of $AgTf_2N$-PEBAX 2533 TFC membranes will be characterized using the CISTAR membrane technology module and compared with CISTAR benchmarks and optimized process conditions in collaboration with Thrust 4.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T6P2 High Temperature Membranes for Hydrogen Separation*
Project Lead: *Jeffrey Brinker (UNM)*

F: Hiroki Nagasawa (Hiroshima University), Abhaya Datye (UNM), Joan Brennecke (UTA), Benny Freeman (UTA), Ruilan Guo (ND), Justin Notestein (NW), Jeff Miller (PU), John Nogan (CINT)
GS: Isabel Ibarra (UNM), Ryan Alcala (UNM), Ayrton Jordan (UNM), Leonard Ruggiero (UNM), Sejoon Park (UTA)
UG: Aiden Littleton (UNM), Ian Alsobrook (UNM)

Project Goals

- The overall project goal is the development of new classes of thermally stable, ultra-thin hydrogen separation membranes exhibiting high hydrogen flux combined with high H_2/alkane selectivity to promote catalytic dehydrogenation reactions.
- A second goal is to use our uniform mesoporous silica films to stabilize ionic liquid membranes to high pressures (UTA collaboration) and to stabilize polymeric membranes to high temperatures and avoid swelling (ND collaboration).
- A third goal is to develop a catalytic membrane reactor (CMR) to promote catalytic dehydrogenation and achieve higher than equilibrium conversions, while reducing coke formation.

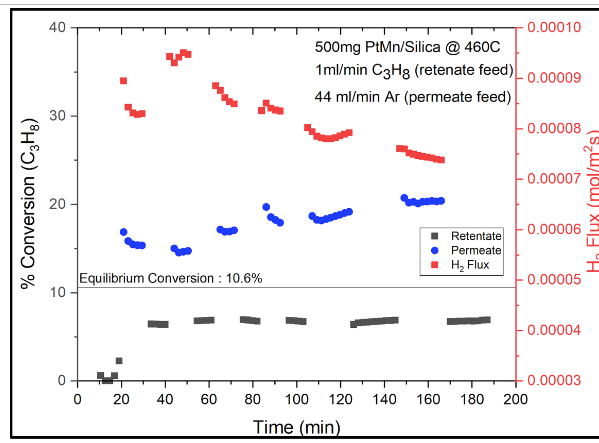


Figure 1: PDH reaction at 460 ℃ and 1mL/min propane feed. Conversions above equilibrium can be seen on the permeate side. A significant number of products can be seen on the permeate side due to loss of integrity of the membrane before reaction was conducted.

Barriers

- (Technical) There is no fundamental understanding of atomic layer deposition confined within nanoporous channels, and the achievement of ultra-thin defect-free membranes is extremely challenging. To address this challenge, we will develop fundamental processing-structure-property (separation) relationships for these new classes of ultra-thin membranes to optimize performance and stability.
- (Institutional) As in the previous year, we have had several levels of complete personnel turnover during the past year. This of course necessitates extensive training of new personnel in chemical synthesis, processing, characterization, and permeation analysis.

Methodologies

- Combine sol-gel processing and molecular self-assembly to create mesoporous silica films composed of ordered arrays of uniformly sized 2-

Research Achievements

- In the CMR experiments conducted at 460˚C, we achieved higher than equilibrium conversions due to extraction of hydrogen with a high flux from the reactor through the membrane (See **Fig.1**). The reactor is envisioned to be stable to temperatures at or above 600˚C, depending on the specific membrane. A PtMn/silica catalyst prepared in T1 was used in the CMR.
- Working with the Sandia/Los Alamos Center for Integrated technologies (CINT), we prepared nominally dense, amorphous SiO_2 membranes via plasma-assisted ALD using $H_2Si[N(C_2H_2)_2]_2$ (supplied by Air Liquide under the product name SAM.24) as the Si precursor. SAM.24 was developed in the microelectronics industry to deposit ultra-thin, defect-free dielectrics, suggesting its use to prepare ultra-thin, defect-free SiO_2 membranes. SiO_2 ALD was performed on TiO_2 nanoparticle modified porous alumina tubes used in the CMR.

8 nanometer diameter pores within the pore channels of disc or tubular alumina substrates.

- Perform ALD, plasma-assisted ALD, plasma-assisted CVD (SiO_2) or sol-gel processing (SiO_2) to form ultrathin silica or hybrid nanoporous SiO_2 membranes confined within the ≡Si-OH-modified nanopore volume.
- Conduct H_2 and alkane permeation studies as a function of temperature and determine H_2 flux and H_2/alkane selectivity factors.
- Deposition of atomically dispersed Sr on á-alumina to poison Lewis acid sites and prevent further reaction of propylene to coke.

- We have evaluated membrane materials that can be used to achieve coke resistance and observed Sr modification of ⟨-alumina particles decreased coke deposition by an order of magnitude. We also established silica substitution or modifiction reduce coke deposition (See **Table 1**).
- We have obtained preliminary permeance results for silica membranes deposited via the aerosolization of sol gels. The membranes span pores between 20-100 nm in diameter and have high coverage after only one second of deposition time (See **Table 2**).

Table 1: BET surface area, weight % coke deposition, and grams of coke per surface area for bare and Sr modified ⟨-alumina particles, Davisil 646, and quartz sand. All materials saw 40mL/min of 10% propylene in nitrogen for 18.5 hours at 460℃. All materials were regenerated via temperature programmed oxidation in 10% oxygen in nitrogen and the resulting carbon dioxide curves were integrated to determine coke content per unit area.

Sample	Surface Area m^2/g	Coke wt%	g C/m^2	
Bare α-Al_2O_3 (200 nm)	7.01	0.103	1.47E-04	
1wt% Sr on α-Al_2O_3 (200 nm)	7.01	0.113	1.64E-04	
10wt% Sr on α-Al_2O_3 (200 nm)	7.01	0.069	9.87E-05	
Davisil 646	277.86	0.025	9.15E-07	
Quartz Sand	2.44	0.0005	2.11E-06	

Table 2: Aerosol spraying distance in mm and N_2 permeance in MPU for spray samples 3-9 and blank alumina anodiscs 1-4. The permeances of blank anodiscs were recorded as controls. Spray samples 1 and 2 broke during the preparation process.

Sample	Spray Distance (mm)	MPU
Blank Anodisc 1	-	528.24
Blank Anodisc 2	-	525.81
Blank Anodisc 3	-	549.51
Blank Anodisc 4	-	553.45
Spray Sample 3	15	126.24
Spray Sample 4	15	176.04
Spray Sample 9	19	398.40
Spray Sample 5	23	388.79

Spray Sample 6	23	395.67
Spray Sample 7 **	26	1607.18
Spray Sample 8	26	148.92

**Spray sample 7 had a N_2 permeance more than three times that of a blank anodisc. Even though the anodisc was not physically broken it is possible there may be small cracks present.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** Alkane dehydrogenation, which is the first step in test bed TB2 (NGL Conversion to Linear Hydrocarbons) and test bed TB3 (NGL Conversion to Branched Hydrocarbons) can be promoted by H_2 removal. Our project aims to create hydrogen separation membranes that selectively remove H_2 and operate at the dehydrogenation reactor temperature (400–800˚C) thereby increasing conversion efficiency, improving thermal management of the reactor system, decreasing operation costs, and mediating coke formation. Ultimately, we propose to integrate alkane dehydrogenation and hydrogen separation in a catalytic membrane reactor (see Path to Targets Summary). The challenge is the development of ultra-thin, thermally stable membranes that exhibit high H_2 flux combined with high H_2/alkane selectivity.

- **Abstract:** Our high risk/high pay-off, high temperature, ultra-thin dehydrogenation membrane project is based on dense amorphous silica or microporous silica membranes deposited on porous alumina supports via sol-gel deposition, atomic layer deposition (ALD), aerosol, or plasma-assisted CVD processes. The integration of these silica membranes into a catalytic membrane reaction for propane dehydrogenation has demonstrated that conversions above equilibrium conversions can be achieved at 460°C . The increased conversions are promoted by H_2 extraction through the membrane. The sol-gel derived membranes have demonstrated hydrogen fluxes as high as 8.0×10^{-5} mol/m^{2}s. Hydrogen deficient conditions seen by the dehydrogenation catalyst within the membrane reactor promote coke formation on the catalyst and on the membrane. Coke formation on the membrane is being studied to determine modifications or substitutions that need to be made in order to develop a coke/fouling-resistant membrane reactor.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:** During this period, we demonstrated that the integration of a sol-gel derived silica membrane with a tubular catalytic membrane reactor (CMR) promotes higher than equilibrium conversions in propane dehydrogenation (PDH) reactions at 460°C. Hydrogen deficient conditions within the membrane reactor, due to hydrogen separation, increase the rate of coke formation on the catalyst and on the membrane. We have begun testing for membrane reactor component modifications or substitutions to develop a coke/fouling-resistant membrane. In parallel, we have been investigating the different silica membrane deposition methods (sol-gel processing, aerosol, and ALD) that can give us ultra-thin, high flux, and highly selective membranes for hydrogen separation from PDH.

- In the membrane reactor tests, 1 mL/min of propane is fed to the annulus of the tubular membrane reactor that is filled with a catalyst bed (See **Fig. 2**). A sweep gas flow of 44mL/min of Ar is fed in counter-current to the propane feed stream. Prior to the reaction the CMR is heated to 200°C and held for an hour to prevent rapid desorption of absorbed water vapor that may damage the integrity of the membrane via rapid outgassing of micropores. The temperature is then increased to 460°C before the feed gas flows is started. GC injections are started at the same time the flows are directed towards the CMR. Since we only have one micro-GC, we are only able to sample from either the retentate or the permeate one at a time. The breaks in the data shown on **Fig.1** show which side was being sampled at any point in time. The conversion calculations are broken down between permeate and retentate sides to reflect the conversion that is sampled. UNM has purchased a new micro-GC that will be dedicated only to the membrane reactor experiments. We will sample from both sides at the same time using the new and the current micro-GCs to obtain a full data set whenever necessary. Propane conversions above equilibrium were achieved and sampled from the permeate side alone. If we consider that the conversion in the retentate is constant, we can assume that the conversion will be the same even when we are sampling from the permeate side. Therefore, the overall conversion is the sum of both sides. For example, at 70 mins on stream the overall propane conversion would be about 24% (17% from the permeate and 7% from the retentate).

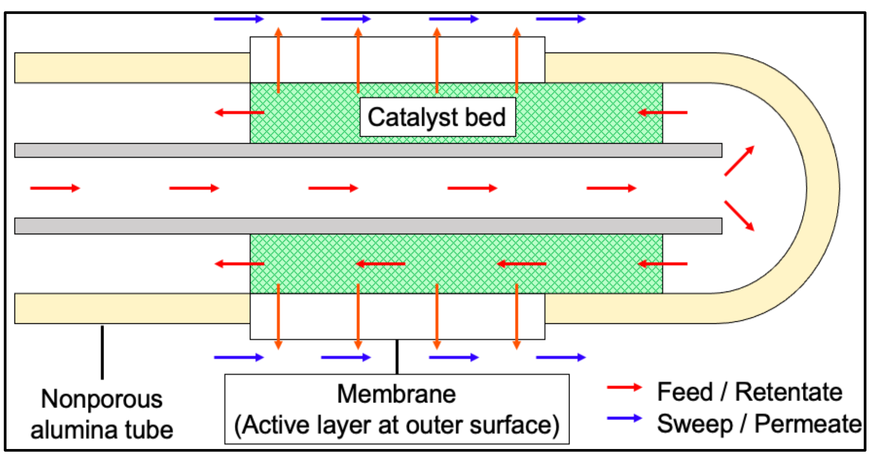


Figure 2: Schematic of catalytic membrane reactor configuration with material flows. The sol-gel derived microporous silica membrane, the active layer, sits on the outer surface and is not in contact with the catalyst bed.

- We removed the CMR from its chamber after one of the reactions and noticed the formation of coke on the outer surface. We used a separate membrane reactor to test the membrane in coking conditions. We fed 10% propylene in nitrogen to the membrane for 17.3 hours at 460°C. Coke formed on the membrane without a catalyst present and in the presence of propylene (See **Fig.3a.**). A temperature programmed oxidation (TPO) was conducted of the fouled membrane. Coke came off in the form of CO_2 and was monitored by a micro-GC. A CO_2 mole flow was determined and the resulting curve (**Fig.3b.**) was integrated to determine that approximately 1.12mg of carbon were deposited. Since silica is transparent the coke deposition may be occurring on any of the layers beneath the silica.

a. b.

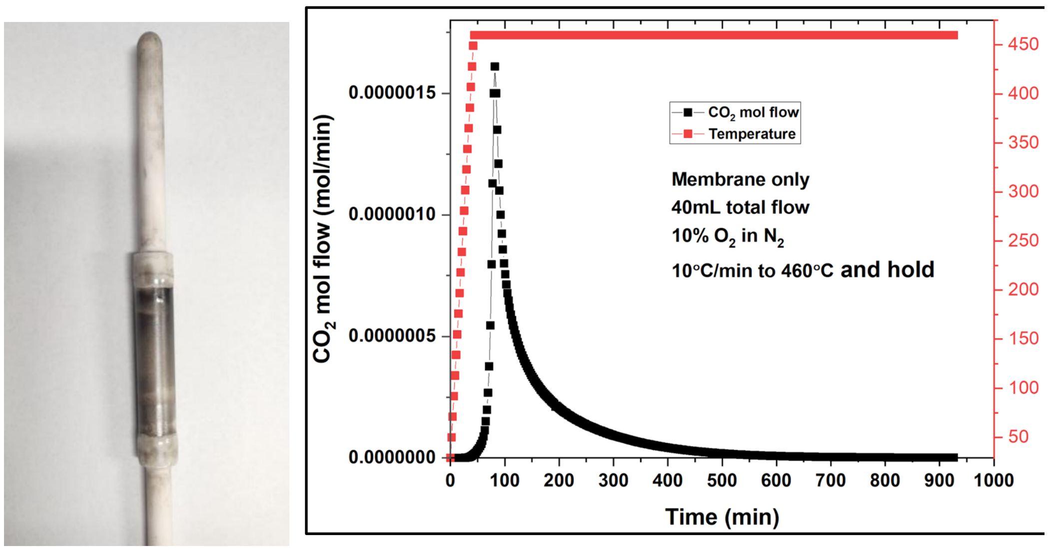


Figure 3: Membrane only H_2 depleted environment results a. coke formation of the outer surface of the membrane reactor and b. CO_2 coming off the membrane over time during a temperature programmed oxidation.

- We conducted a series of coking experiments on the alumina particles used in the membrane as well as several other materials to study the formation of coke that occurs in these materials. Bare ⟨-alumina particles 200nm in diameter, 1wt% Sr doped ⟨-alumina, and 10wt% Sr doped ⟨-alumina were tested to study the effect of Sr poisoning had on coke formation. Strontium is known to poison the Lewis-acid-sites where propylene reactions occur. By poisoning those sites, we are looking to reduce the rate of coke formation on the ⟨-alumina. Other methods for mitigating coke formation we are considering include the substitution of alumina with silica or a silica coating on the membrane support and intermediate layers. A common Davisil 646 silica and quartz sand were tested under the same conditions and reaction duration as the ⟨-alumina samples to compare the rate of coke formation to the materials currently used in the membrane reactor. The results are summarized in **Table 1.** where coke wt% and coke mass normalized to surface area are reported. The 10wt% Sr on ⟨-alumina sample had reduced amounts of coke compared to the bare ⟨-alumina. However, overall, the Davisil silica performed significantly better than everything else based on the surface area. An optimized Sr doped 〈-alumina sample or silica coatings look promising.

- Preliminary aerosol-silica membrane depositions were made on alumina anodiscs with 20nm pore sizes. We started with a one second spraying time to allow the evaporation in EISA to occur properly. N_2 permeance was recorded before and after deposition (See **Table 2.**) to monitor deposition effectiveness at different spraying distances. A spraying distance of about 15mm showed the most reduction in N_2 permeance and will be used for future depositions. We looked at the surface of the anodiscs that were sprayed from a distance on 13 mm in the SEM (See **Fig.4.**). After a one second spraying time the surface coverage is significantly high. A few areas where the pores were not covered were found. We will be testing a second cycle of spraying and determine if there is a significant improvement in the number of defects present and N_2 permeance.

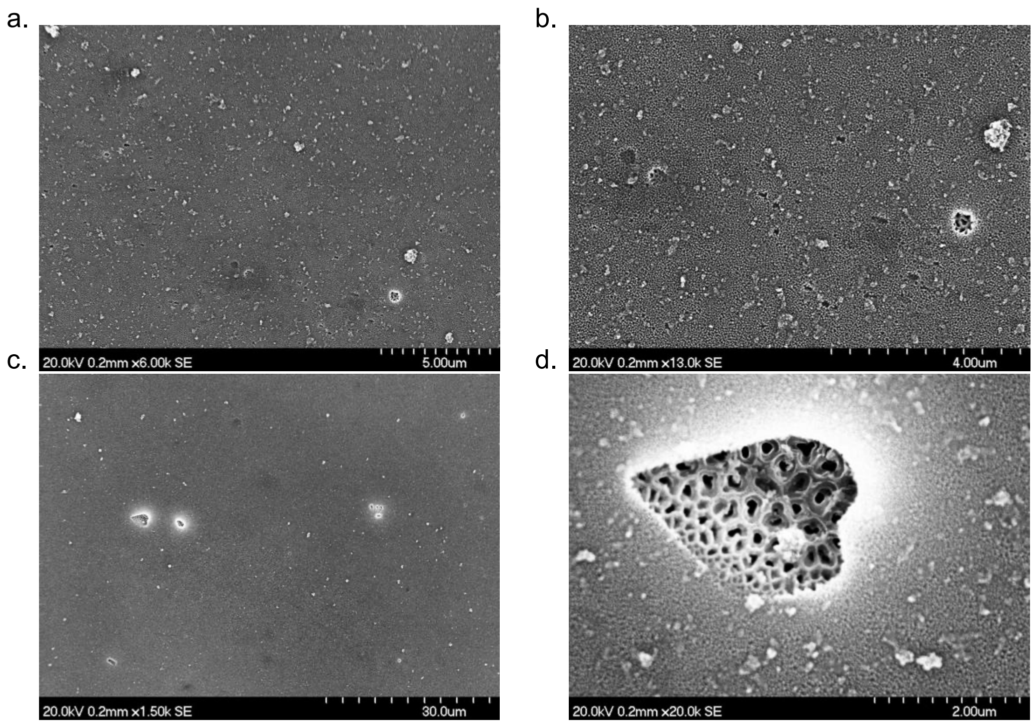
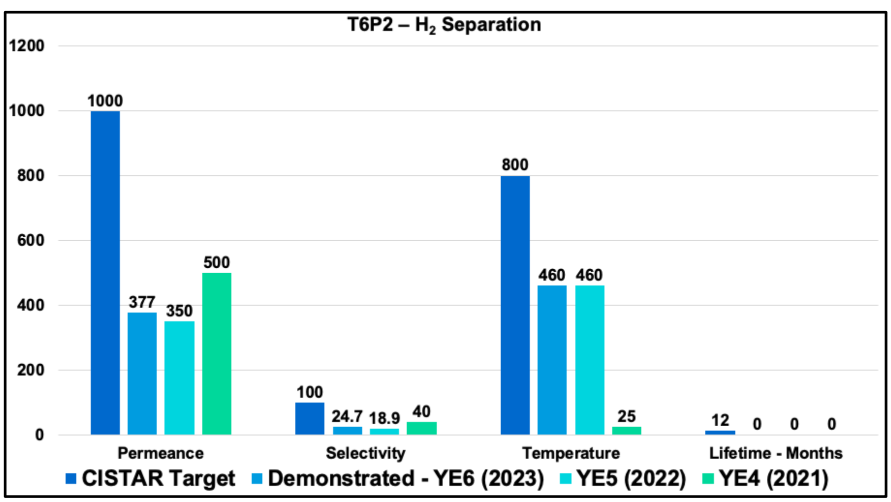


Figure 4: SEM images of defects on aerosol silica coated anodiscs. Sprayed with sol gel solution for 1 sec at room temperature. Aged for an hour at room temperature, five hours at 150°C, then ramped 1°C/min to 450°C and held for two hours.

- **Interdependence:** Since we do not have ALD facilities at UNM to perform SiO_2 ALD, we have continued a project with Dr. John Nogan at the Sandia/Los Alamos Center for Integrated Nanotechnologies (CINT), where we are using Bis(diethylamino)Silane as the Si precursor based on its use in the microelectronics industry to prepare ultrathin, defect free amorphous silica dielectrics. The ultrathin dense silica membranes should selectively transport H_2 at the CMR reactor temperature. In a new collaboration with the Garzon group in thrust 3, same SiO_2 ALD membranes are being used to provide H_2 selectivity to H_2 sensors.

Finally working with Ryan Alcala and Abhaya Datye in Thrust 1, we have tested our catalytic membrane reactor (see Fig 1) for performing catalytic dehydrogenation of propane at an operating temperature of 460˚C, employing their CISTAR-developed Pt-Mn/silica catalyst. We observed that hydrogen extraction from the reactor increased the conversion efficiency above that at equilibrium.

- **Testbed Impact and Value:** As discussed above selective hydrogen removal will promote catalytic dehydrogenation, which is relevant to test beds TB2 (NGL Conversion to Linear Hydrocarbons) and TB3 (NGL Conversion to Branched Hydrocarbons). Development of a catalytic membrane reactor has the potential to achieve higher conversion efficiencies and selectivities, reduce temperature and coke formation, improve thermal management, and reduce cost.
- **Technical Targets:** In order to be successful, high temperature dehydrogenation membranes must simultaneously satisfy the multiple criteria of high H_2 flux, high H_2/alkane selectivity, and high temperature stability. To meet these criteria, we are exploring the formation of ultra-thin membranes having the potential to increase flux by over a factor of ten compared to state-of-the-art membranes. The challenge is to develop defect-free ultra-thin membranes, and, to address this challenge we are exploring multiple materials (dense amorphous silica and microporous amorphous silica) and deposition approaches (ALD, plasma-assisted ALD, plasma-assisted CVD, aerosol, and sol-gel processing). So far, we have been successful in demonstrating a high temperature dehydrogenation membrane using sol-gel processing of microporous amorphous silica, and the results are presented in the following chart.



Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Although high temperature H_2 membranes have been demonstrated, their thicknesses often greatly exceed 200-nm. Our goal is to reduce the membrane thickness to 20-nm and thereby increase flux (and reduce membrane area and cost) by a factor of 10 compared to state-of-the-art membranes. To achieve this, we need to reduce and unify the pore size of the support so that deposition of the final membrane by ALD can be accomplished with as few ALD cycles as possible. Our approach is to use evaporation induced self-assembly (EISA) to modify the support (so far Anodiscs) with a mesoporous silica layer exhibiting a *uniform* ~8-nm pore size. So far, in the hands of multiple students, EISA has been shown to work on Anodiscs (as evidenced by high pressure stabilization of IL membranes by UTA), but there have been reproducibility issues that need to be rectified. Sejoon Park (UTA; GS) is carrying out a fundamental synthesis/structure/properties study to perfect EISA deposition on Anodiscs by spin-coating. However, spin-coating is not amenable to tubular supports used in the catalytic membrane reactor (due to shape), so we will use aerosol-assisted EISA (Lu, Brinker et al *Nature* 1999) in which aerosolized droplets dry and self-assemble in the vapor phase into silica/surfactant mesophase droplets that upon deposition on a surface coalesce into a coherent and conformal mesoporous silica film. Beyond being adaptable to tubular supports (which will be the focal point of future research), aerosol-assisted EISA has the further advantage that, due to their size, aerosol droplets should have minimum penetration into the Anodisc, or tubular alumina supports, resulting in thin support layers that exhibit a minimum decrease in flux.

- **Path to Targets Summary:** As Stated above our target is to increase the flux by a factor of 10 over state-of-the-art membranes while achieving requisite H_2/alkane separation factors and high temperature stability (400-600˚C). Due to the cost of Pd and challenges in deposition of continuous and conformal films, we will focus on preparation of dense or microporous silica membranes in the near term. Furthermore, due to their scalability and their ability to be filled with catalyst, we will transition from Anodiscs to tubular alumina supports. The tubular supports will be integrated into a membrane reactor *Technology Module* configured to enable determination of permeance and separation factors in situ to temperatures of 600˚C and to be loaded with catalyst, where we can conduct catalytic membrane reactor studies as we have demonstrated this year. Here in the near term, we will employ Pt/Mn dehydrogenation catalysts developed in Thrust 1 by the Miller and Datye groups. Longer term studies will aim at optimizing membrane properties to achieve high conversion efficiencies, low coke formation, and long-term stability combined with the ability to easily regenerate the catalyst.

- **Specific Plans Organized by Challenge:**

  Challenge 1: Reduce and unify the pore size of tubular alumina supports used in the catalytic membrane reactor. Alumina reactor tubes used to date have a nominal pore diameter of 8µm, and we have used a multi-stage TiO_2 and Al_2O_3 nanoparticle deposition process to reduce the pore diameter to ~40-nm prior to membrane deposition. However, the size and polydispersity of these pores requires a rather thick membrane (>100-nm) to form a continuous, defect-free separation layer. To develop ultra-thin membranes, we will purchase tubular alumina supports with a smaller pore size and use aerosol-assisted evaporation induced self-assembly to create a support surface with uniform 4-8 nm diameter silica mesopores.

<u>Challenge 2:</u> Prepare ultra-thin, dense, thermally stable, dense or microporous amorphous SiO_2 membranes on tubular alumina supports that exhibit the requisite H_2 flux and H_2/alkane selectivity. Here due to the ability to deposit highly dense SiO_2 in a controlled monolayer-by-monolayer fashion on arbitrary supports, we will focus on using SiO_2 ALD and depositing films with thicknesses ranging from 5-50-nm on mesoporous silica-modified tubular alumina supports. The membranes will be tested in situ at 200˚C (the ALD deposition temperature) in the reactor to establish initial H_2 flux and H_2/propane selectivity (membranes can be removed from the reactor and re-coated if necessary). Flux and selectivity will then be determined at elevated temperatures equal to or exceeding the catalytic dehydrogenation reactor temperature (>400˚C) for times up to 24h. With the membrane performance fully characterized, we will load the reactor with catalysts and conduct catalytic membrane reactor studies. Based on these results we will optimize membrane performance to achieve maximum reaction yields at lowest possible temperatures with minimal coke formation.

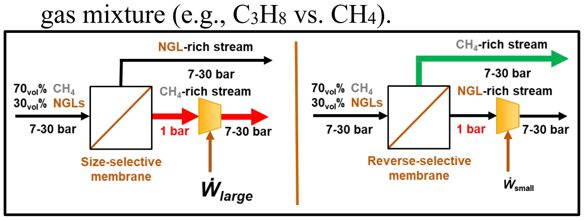
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T6P3 Paraffin Separations with Reverse Selective Membranes* ***Project Lead:*** *Benny Freeman (UTA)*

F: Joan Brennecke (UTA)	
GS: Justin J. Rosenthal (UTA)	**RET:** Heidi Roop-Morland, Joseph Savoldi

Project Goals

- Prepare robust, reverse-selective, highly permeable supported ionic liquid membranes (SILMs) for natural gas light paraffin separations (e.g., C_3H_8/CH_4, C_2H_6/CH_4, C_3H_8/C_2H_6).
- Develop SILMs capable of operating at industrially relevant conditions by manipulating the pore size and pore size distribution of the supports.
- Use reverse-selective ILs from literature to selectively permeate the larger components in the gas mixture (e.g., C_3H_8 vs. CH_4).



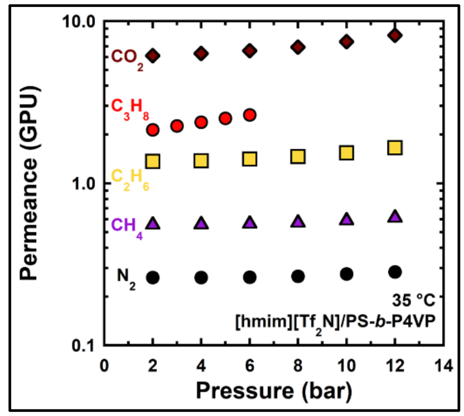


Figure 1 (above): Pure-gas permeances for an [hmim][Tf$_2$N]/PS-b-P4VP isoporous SILM. Displayed is the superior operating pressures of this membrane (when compared to conventional SILMs) while maintaining C_3H_8/CH_4 selectivity around 4.

Barriers

- Plasticization of the polymer support by the incorporated IL.
- Blowout of the IL at pressures below realistic operating conditions (e.g., 7-30 bar).
- Nanoconfinement effects which lead to deviations from ideal transport behavior when using supports with small pores.

Methodologies

- Exploration of SILMs for light hydrocarbon removal from natural gas.
- Use of gas permeators to investigate pure gas permeabilities.

Research Achievements

- Measured sorption isotherms of CH_4 and C_2H_6 in [hmim][Tf$_2$N] at 35 °C.
- Measured sorption isotherms of CH_4, C_2H_6, and C_3H_8 in [P_{2228}][TMPP] at 35 °C.
- Measured pure-gas permeances of N_2, CH_4, C_2H_6, C_3H_8, and CO_2 in both [hmim][Tf$_2$N]/PES and [P_{2228}][TMPP]/PES SILMs.
- Validated the Young-Laplace (YL) equation and matched YL predictions to experimental data.
- Developed the most stable SILM in the literature when using a commercial support capable of operating up to 18.5 bar of pressure.
- Linked deviations from ideal transport behavior of the most stable SILMs to nanoconfinement effects.
- Developed isoporous SILMs with both high-pressure stability and good selectivity.

Section 2: Project Summary Brief

This project aims to create novel SILMs for CISTAR separations. Here, reverse-selective SILMs will be used to preferably separate C_3H_8 and C_2H_6 from natural gas feedstocks near ambient temperature. This approach eliminates energy-intensive refrigeration associated with conventional condensation-based strategies while simultaneously avoiding the need to recompress the CH_4 (~70% of the total mixture) for further use or processing.

- **The Project's Role in Support of the Strategic Plan:** Light paraffin separations (e.g., C_3H_8/CH_4, C_2H_6/CH_4, C_3H_8/C_2H_6) are required for CISTAR-based pathways that convert these hydrocarbons into liquid fuels and chemicals. Typically, these separations are accomplished by energy-intensive cryogenic condensation/distillation approaches which are not suitable at smaller scales. Commercial membranes do not currently exist for such paraffin separations and therefore novel membranes must be created to support the CISTAR strategic plan for modular, distributed, and small-scale processing of shale gas.
- **Abstract:** This project focuses on designing and testing novel reverse-selective membranes which permeate larger hydrocarbons (e.g., C_3H_8 and C_2H_6) faster than CH_4. We started by synthesizing ILs which are known to be solubility-selective towards the larger hydrocarbons. Then, we evaluated the IL uptake of potential polymers for the SILM porous supports (i.e., PVDF, PSF, PAN, CA, PEI, and PES) with [hmim][Tf_2N] to determine compatibility. After choosing PES as the most compatible polymer because it sorbed the lowest amount of IL, we began preparing SILMs to overcome the low selectivities typically associated with conventional polymer membranes. Our current SILMs have displayed stability up to 18.5 bar (the second highest in literature) but lose their reverse-selectivity as a result of nanoconfinement. A recently developed SILM using an isoporous support displayed stability up to 14 bar while maintaining its reverse-selectivity. In year 6, we will evaluate isoporous polymeric supports, new ILs, and possibly explore other polymer/IL combinations such as poly(ionic liquid) membranes.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:**

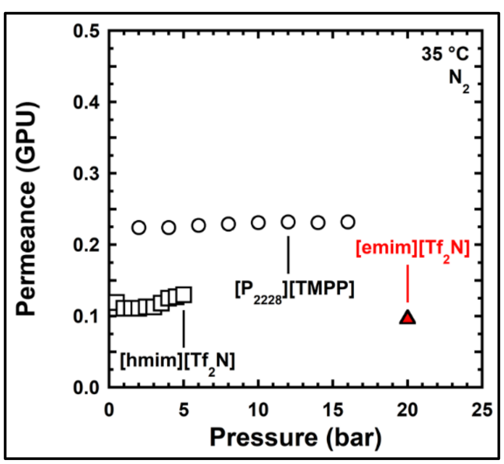


***Figure 1.** N_2 permeance for three selected SILMs. The black [P_{2228}][TMPP] and [hmim][Tf_2N] curves represent SILMs synthesized in our lab using PES as the support. The red [emim][Tf_2N] represents the most stable SILM in literature which utilized an isoporous support.*

- To our knowledge, we developed the most stable SILM in the literature while using a commercially available support. This SILM was composed of the IL [P_{2228}][TMPP] immobilized in PES and can operate consistently up to 16 bar of pressure. This result is shown in Figure 1 and directly compared to a similar [hmim][Tf_2N] SILM along with the most stable SILM in the literature (20 bar) which utilizes an isoporous support made with PS-*b*-P4VP.

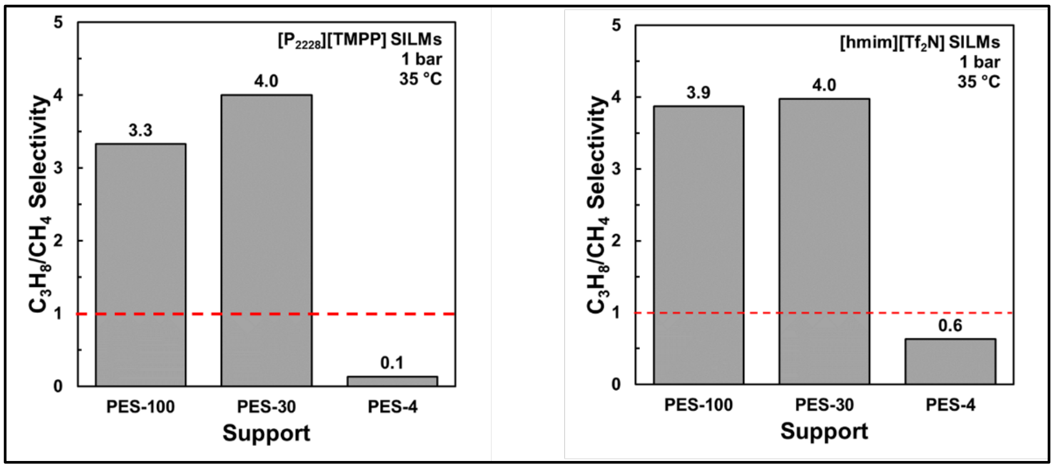


Figure 2. Pure-gas C_3H_8/CH_4 selectivity for [P_{2228}][TMPP] (left) and [hmim][Tf_2N] (right) SILMs made with various supports. Moving from left to right the supports have nominal pore sizes of 100 nm, 30 nm, and 4 nm.

- Despite the unprecedented stability of our membranes, they showed undesirably low C_3H_8/CH_4 selectivity. This effect was observed for both ILs tested, and the results are represented above in Figure 2. The supports with nominal pores sizes of 100 nm and 30 nm show the desired reverse-selectivity, but it is lost when using the support with a nominal pore size of 4 nm. Literature and DSC confirm that this phenomenon is likely a result of nanoconfinement.

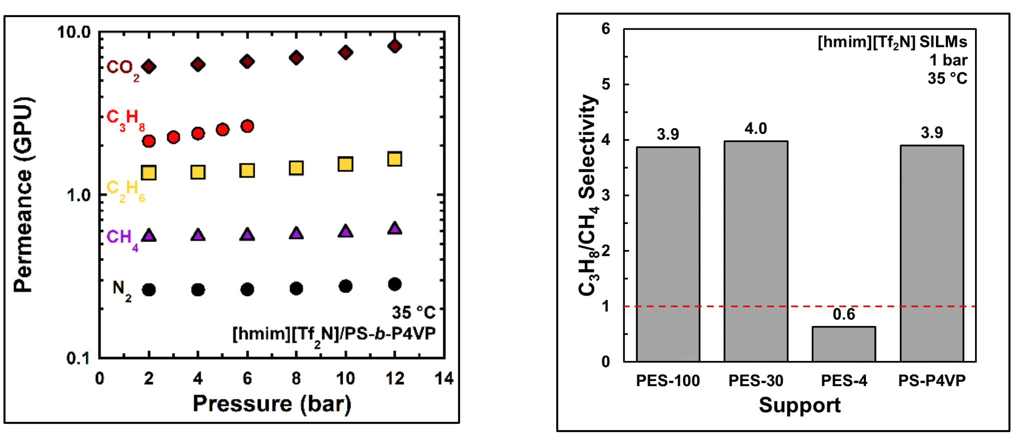
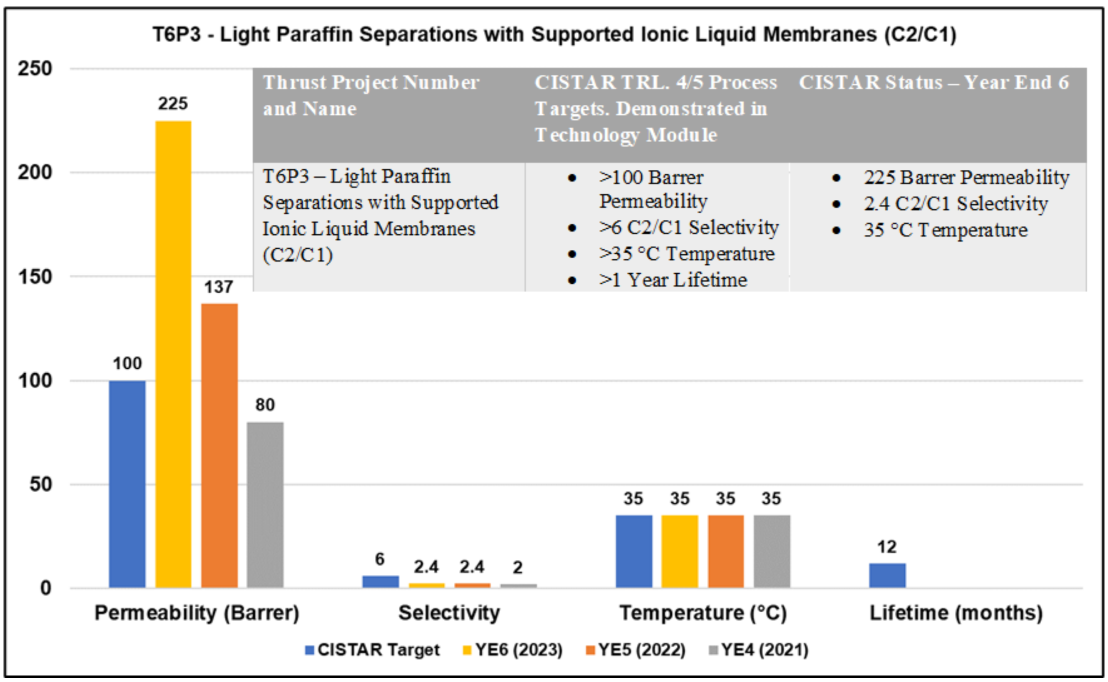


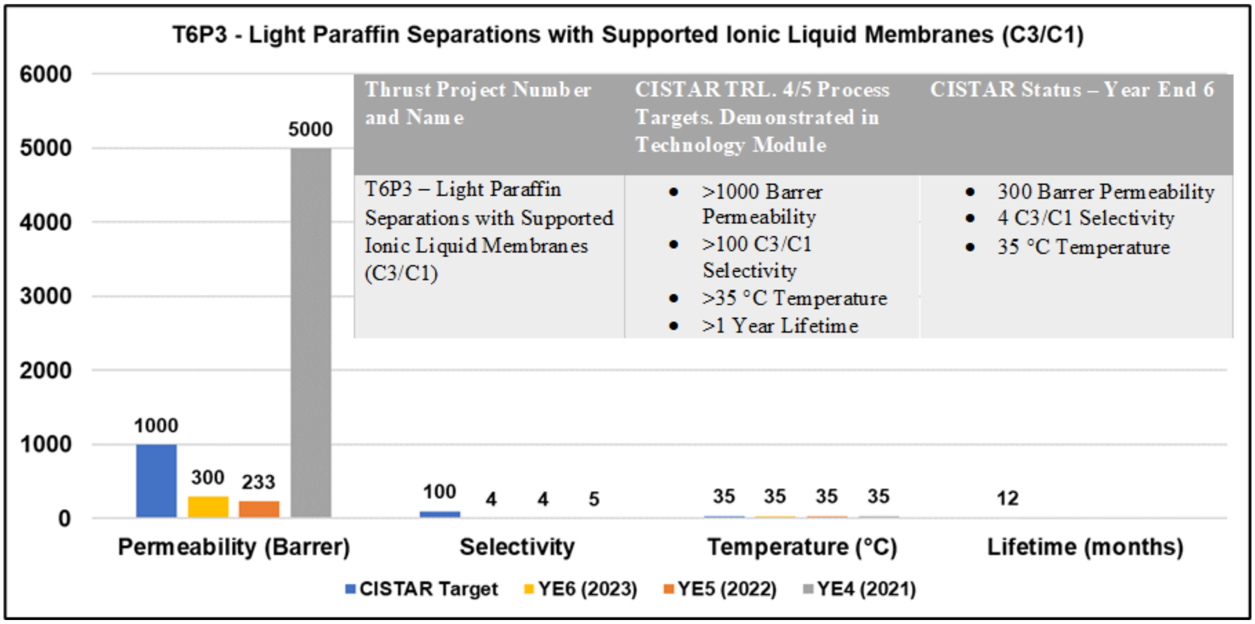
Figure SEQ Figure * ARABIC 3. Left: Pure-gas permeance results for our [hmim][Tf_2N] SILM made with an isoporous support. Right: Pure-gas C_3H_8/CH_4 permeances for all of the tested [hmim][Tf_2N] SILMs.

  - Isoporous supports made from PS-*b*-P4VP were then synthesized and utilized due to their uniform pore size and high surface porosity. These characteristics allowed for high stability SILMs capable of operating up to 14 bar and that also displayed the desired reverse-selective behavior. These results are shown above in Figure 3, where the pure-gas permeances follow the same trends observed with the PES-100 and PES-30 supports. Additionally, it can also be seen from Figure 3 that the C_3H_8/CH_4 pure-gas selectivity is the same as was observed when using the PES supports with larger nominal pore sizes.

- **Interdependence:** Future results from this project will emphasize the important interplay and feedback between the Thrusts and the Technology Modules (e.g., T5P1). Additionally, process modeling from Thrust 4 confirms the benefits of reverse-selective membranes where CH_4 (the retentate) remains at higher pressure.
- **Testbed Impact and Value:** This project is relevant to Testbeds 1, 2, and 3. Separating propane and ethane from methane is a desired "up front" separation to allow processing of the C_2+ hydrocarbons into olefins which will subsequently be converted into linear or branched hydrocarbons (Testbeds 2 and 3). Activation of the methane will also be used to produce aromatics (Testbed 1).
- **Technical Targets:**



Thrust Project Number and Name	CISTAR TRL. 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Year End 6
T6P3 – Light Paraffin Separations with Supported Ionic Liquid Membranes (C2/C1)	• >100 Barrer Permeability • >6 C2/C1 Selectivity • >35 °C Temperature • >1 Year Lifetime	• 225 Barrer Permeability • 2.4 C2/C1 Selectivity • 35 °C Temperature



Thrust Project Number and Name	CISTAR TRL. 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Year End 6
T6P3 – Light Paraffin Separations with Supported Ionic Liquid Membranes (C3/C1)	• >1000 Barrer Permeability • >100 C3/C1 Selectivity • >35 °C Temperature • >1 Year Lifetime	• 300 Barrer Permeability • 4 C3/C1 Selectivity • 35 °C Temperature

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** The main challenge for SILMs is their propensity to "blowout" at higher operating pressures. SILMs developed to date are largely only capable of operating at pressures below 3 bar, while the separation of light paraffins industrially occurs at 7-30 bar. With isoporous supports, we have prepared SILMs that operate up to 14 bar.
- **Path to Targets Summary:** The path to reaching the target operating pressures and selectivity largely involves developing defect free isoporous supports that are compatible with our chosen ionic liquids. Existing equipment (membrane fabrication tools, sorption equipment, pure gas permeators, and the T5P1 Advanced technology Module mixed gas permeation systems) will be used for these investigations.
- **Specific Plans Organized by Challenge:** The plans for this project include:
    - IL uptake experiments will be completed with dense membranes made from the block copolymers used to create our isoporous supports. This will allow us to determine if our ILs will swell the polymer support.
    - If favorable results are obtained, SILMs will be developed and subjected to blowout tests to determine the maximum operating pressure.
    - Pure- and mixed-gas permeance experiments will be performed using [hmim][Tf_2N], [emim][SCN], and [P_{2228}][TMPP].
    - Efforts will also be directed at developing poly(ionic liquid) membranes which should not be limited to low operating pressures.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *T6P4 Microporous Polymer Membranes for CISTAR Gas Separations* ***Project Lead:*** *Ruilan Guo (UND)*

F: Ruilan Guo	
GS: Agboola Suleiman (UND), Sandra Weber (UND)	
UG: Gabe Pennington (UND)	**RET:** Kyle Dybing, Assoc. Prof. at Ivy Tech Community College (South Bend, IN) Jeff Kindelan, Physics Teacher at Adams High School (South Bend, IN)

Project Goals

Develop microporous polymeric membranes with ultrahigh selectivity and permeability for CISTAR relevant gas separations, focusing on H_2 separations:

- Establish synthesis protocols of microporous polymers with well-controlled microporosity
- Identify thermal protocols for the fabrication of defect-free, robust polymer thin films
- Evaluate separation performance via pure-gas and mixed-gas permeation tests at ambient and realistic conditions
- Establish structure-property relationship for new membranes, especially at conditions away from ambient temperature (i.e., up to 250 °C)

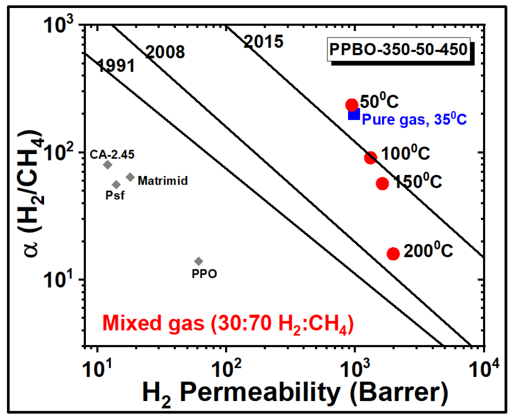


Figure 1: Pentiptycene-based PPBO film showed highly promising H_2/CH_4 separation performance in mixed-gas, high-temperature permeation tests.

Barriers

- Permeability-selectivity tradeoff for polymer membranes
- Lack of microporosity control in crosslinked polymeric membranes
- Role of thermal fabrication parameters affecting membrane microstructure and properties
- Lack of fundamental knowledge about gas transport in polymer membranes at high temperatures with multicomponent feeds

Methodologies

- Synthesize iptycene-based microporous polymers with tailorable microporosity
- Prepare crosslinked model network membranes via end-linking enabling precisely controlled microstructure
- Comprehensive examination of parameters of thermal protocols for membrane fabrication
- Perform gas permeation tests under various conditions (temperature, feed composition, feed pressure)

Research Achievements

- Scaled up by 4 times of the synthesis of triptycene- and pentiptycene-based dianhydride monomers to allow for scaling up the synthesis of polyhydroxyimide (PHI) precursors
- Scaled up by 6.5 times of the polymerization of pentiptycene PHI (PPHI) precursors from corresponding monomers
- Obtained and validated H_2/CH_4 pure-gas permeation data at high temperatures (up to 200 °C) for thermally rearranged (TR) triptycene- and pentiptycene-based polybenzoxazoles (PBO), i.e., TPBOs and PPBOs
- Obtained and validated H_2/CH_4 mixed-gas permeation data at elevated temperatures for TPBO and PPBO films, both exceeding the 2015 upper bound at ambient conditions and exceeding the 2008 upper bound at high temperatures
- Established procedures for pure-gas permeation tests of separating H_2 from C2 and C3 hydrocarbons
- Obtained preliminary pure-gas permeation data for H_2/propane and H_2/propylene gas pairs, both of which showed extraordinary selectivity

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** Development of energy efficient and modular membrane-mediated separation processes is at the core of CISTAR's mission to create a transformative engineered system for shale resources conversion in *smaller*, *modular*, *local*, and *highly networked* processing plants. The new polymeric membrane materials developed from this project directly address the H_2/alkanes separation needs demanded by the CISTAR process. In particular, research efforts within this project have been directed to identify innovative polymer membrane to address current performance gaps (i.e., permeability-selectivity tradeoff, high temperature tolerance, plasticization resistance) enabling the integration of catalytic reactions and gas separation.

- **Abstract:** The project focuses on the development of innovative polymeric membrane materials for H_2/C1-C3 separations involving complex feeds and high temperatures. In Year 6, our focuses have been to: (1) further scale up the synthesis of iptycene-based monomers as well as the polymerization of precursor polymers, (2) perform comprehensive permeation tests under high temperatures and mixed feeds, (3) initiate benchtop asymmetric membrane fabrication. Specifically, we scaled up the monomer synthesis by 6 times and the polymerization by 4 times from our original protocols. Monomers with high purity and polymers with high molecular weight can be consistently produced with the established new protocols. Comprehensive gas permeations tests were completed for both TPBO and PPBO series focusing on high temperature (up to 200 °C) pure-gas and mixed-gas permeation measurements. Both TPBO and PPBO membranes showed excellent H_2/CH_4 mixed-gas separation performance at 200 °C exceeding 2008 upper bound. Preliminary pure-gas permeation data of a PPBO membrane showed excellent H_2/C3 separation performance as well as propylene/propane selectivity of ~9-11 though membrane plasticization is evident in all tested samples. Preliminary work has initiated on benchtop preparation of asymmetric membranes.

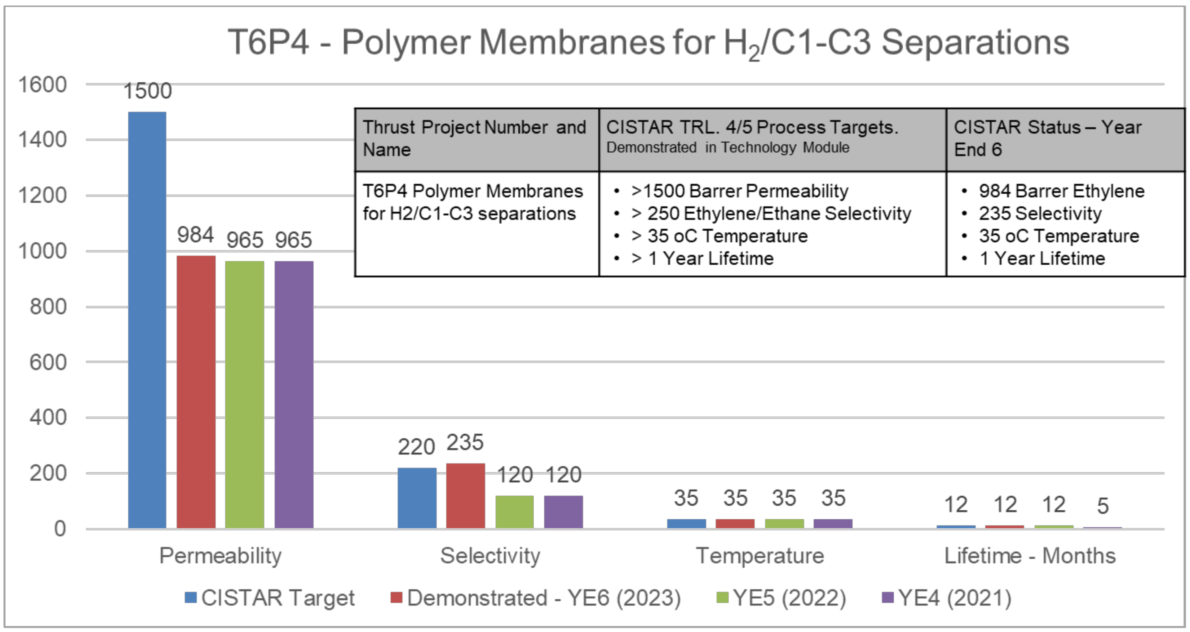
- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
  - The synthesis of triptycene- and pentiptycene-based dianhydride monomers has been scaled up significantly (by 4 times) from prior protocols, which consistently produced high-purity (>99%) products. The largest single batch monomer synthesis can produce ~24g of iptycene-dianhydride monomers. We also achieved much shorter turnover time (i.e., 50% less time) for the monomer synthesis via refining the hydrolysis conditions and post-synthesis workup procedures. This achievement in monomers synthesis has enabled the synthesis of corresponding polyhydroxyimide (PHI) precursors in much larger batch size.

- The polymerization of both triptycene-PHI (TPHI) and pentiptycene-PHI (PPHI) precursors has been scaled up significantly (by 3.5 times for TPHI and by 6.5 times for PPHI), which consistently produced high molecular weight polymers. The largest single batch polymer synthesis can produce ~7-7.5 g of high molecular weight PHI precursors. This has facilitated comprehensive investigation of gas permeation properties under various conditions.
- H_2/CH_4 permeation data for thermally rearranged (TR) triptycene- and pentiptycene-based polybenzoxazole (PBO) membranes, i.e., TPBO and PPBO, were obtained and validated with repeat experiments using both pure-gas and mixed-gas feeds over a wide range of feed pressure (up to 230 psi) and temperature (up to 200 °C). Increased H_2 and CH_4 permeabilities and decreased H_2/CH_4 selectivity with increasing temperature were observed as expected. Both TPBO and PPBO membranes displayed superior H_2/CH_4 separation performance over the full temperature range in the mixed-gas permeation tests (30:70 H_2:CH_4), with their performance at 35 °C surpassing the 2015 upper bound and high-temperature performance even at 200 °C surpassing the 2008 upper bound as shown in the figure in the table of section 1.
- We established procedures for pure-gas permeation tests of separating H_2 from C2+ hydrocarbons and obtained preliminary pure-gas permeation data on H_2/propane and H_2/propylene separations. While plasticization is evident, ultrahigh selectivities were achieved, i.e., 170-200 for H_2/C_3H_6 and 1050-1460 for H_2/C_3H_8, which also implicates pure-gas C3 gas selectivity in the range of 9-11.

- **Interdependence:** Within T6, six research groups across three universities (UND, UTA, and UNM) are working together to enable membrane separation systems under CISTAR-relevant conditions. Close inter-institutional collaborations have resulted in samples exchange for new membrane development, materials characterization and performance evaluation purposes. UND team and UTA team exchange film samples for cross-checking and validating permeation tests; UND team provides polymer samples to UTA team to prepare asymmetric flat sheet membranes for pilot-scale membrane fabrication study. Across CISTAR, membrane separation teams work with T4 to define the target flux/selectivity and realistic operating conditions required for both technical and economic success, which provides guidance on refining membrane material design. Membrane research teams also participate in Testbed meetings, where additional guidance is provided on research direction and direct connection between catalysis and separation research is made.
- **Testbed Impact and Value:** This project is relevant to all three CISTAR testbeds (Testbed 1 - the conversion of shale gas to aromatics; Testbed 2 - the conversion of natural gas liquids to linear alkanes; and Testbed 3 - the conversion of natural gas liquids to branched alkanes), where membrane separations represent a critical component. This project creates new polymeric gas separation membrane materials with highly tunable

separation performance (permeability and selectivity) and excellent stabilities. This will allow various separation needs (e.g., complex feed, high temperature tolerance) determined by overall techno-economic assessments in the CISTAR processes to be met by these specifically designed membrane materials.

- **Technical Targets:**



Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** The main challenges currently facing T6P4 are overcoming the permeability-selectivity tradeoff at elevated temperatures and lack of large-scale synthesis of iptycene monomers and corresponding PHI precursors to allow for the fabrication of asymmetric membranes from these high performance PBO membrane materials. While we have scaled up the monomer synthesis by 4 times, the use of strong base along with the requirement of long reaction time impose challenges to current lab-scale synthesis setup (e.g., corrosion of glassware). Further scaling up the synthesis of PHI precursor polymers is in need to allow for fabricating defect-free asymmetric membranes for thermal rearrangement, which will consume a lot of polymer materials based on past experience. In addition, large-scale polymerization will minimize sample variation issues in small batch synthesis.
- **Path to Targets Summary:** Over the next year, we plan to: (1) further refine and scale up the monomer and polymer synthesis, potentially with additional industry support; (2) continue to evaluate iptycene-based PBO films using mixed feeds of H_2 and C1-3; (3) explore the new design of soluble PPBOs membranes; and (4) initiate fabrication and

testing of PPHI asymmetric membranes and corresponding PPBO membranes. The specific plans are as follows, which will be executed in parallel.

- **Specific Plans Organized by Challenge:**
  - *Monomer and polymer synthesis:* We will seek alternative approaches (e.g., acidic catalysts) to perform the hydrolysis reaction to avoid the use of corrosive bases in the monomer synthesis. If such new approach is identified, we will scale up the monomer synthesis using the new approach with a goal to reach our lab's maximum capacity based on existing synthesis facilities. Synthesis of PPHI precursor polymers will be further refined via optimizing the concentration, reaction temperature, reaction time, as well as polymer purification procedure to ensure high molecular weight products. We are seeking additional industry support to facilitate the scale-up efforts of both monomers and polymers.
  - *Pure-gas permeation tests at high temperatures:* We will continue to test select TR-PPBO membranes using high-temperature gas permeation system at elevated temperatures ranging from 50 °C to 200 °C). The testing will focus on H_2/C2+ since we have completed the testing for H_2/CH_4.
  - *Mixed-gas permeation tests:* We will continue to test membrane candidates that have been identified with promising pure-gas separation performance using the Advanced Membrane Technology Module to evaluate their separation performance under CISTAR-relevant conditions. The testing will focus on H_2/C2+ since we have completed the testing for H_2/CH_4.
  - *Preparation of new soluble PPBO membranes:* To address the challenges in membrane fabrication of TR-PBO polymers that requires high temperature treatment and are insoluble, we will explore a new synthetic route to prepare organo-soluble PPBO polymers directly. The new approach will involve silylation facilitated/catalyzed in-situ cyclodehydration of polyhydroxyamide precursors in solution.
  - *Bench-scale asymmetric membrane fabrication:* We plan to initiate the effort to fabricate asymmetric flat-sheet membranes from PPHI precursor using phase inversion method at bench scale. We will start with the recipes that have been formulated for TPHI in project T6P5 to determine feasible dope solution compositions for PPHI system to achieve ideal membrane morphology, which will be examined using SEM. The prepared PPHI asymmetric membranes will then be converted into PPBO asymmetric membranes using the same thermal protocols as those applied on PPHI dense films. Gas permeation tests will then be performed to evaluate the permeance and selectivity of these asymmetric membranes to correlate with membrane morphology.

Section 4: Papers and IP

- **Papers Published or Submitted for the Period 10/1/2022 to 9/30/2023:**

1. Liu, M.; Seeger, A.; Guo, R., "Crosslinked Polymer Membranes for Energy-Efficient Gas Separation: Innovations and Perspectives", *Macromolecules*, in press, (2023) https://doi.org/10.1021/acs.macromol.3c01196.
2. Luo, S.; Han, T.; Wang, C.; Sun, Y.; Zhang, H.; Guo, R.; Zhang, S., "Hierarchically Microporous Membranes for Highly Energy-Efficient Gas Separations", *Industrial Chemistry & Materials*, *1,* 376-387, (2023).

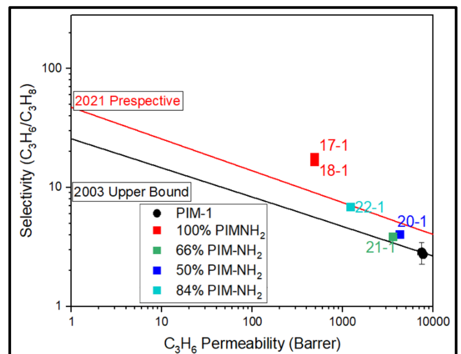
Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

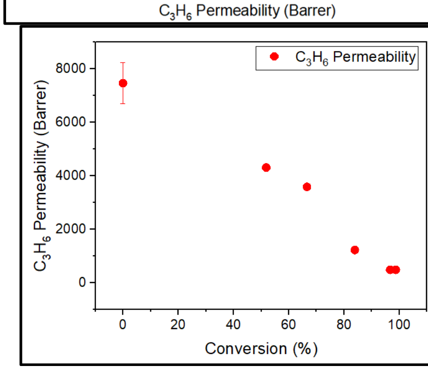
Project Title: *T6P6 Ligand Protected Clusters Embedded in Polymer Membranes for Olefin-Paraffin Separation*
Project Lead: *Casey O'Brien (UND)*

F: Casey O'Brien (UND)	
GS: Bo Wei Cynthia Chen (UND)	**RET:** Thomas Adams, David Lawrence

Project Goals

- Synthesize amine-modified PIM-1 membrane ($PIM\text{-}NH_2$)
- Develop method of controlling percent of amine conversion
- Demonstrate propylene/propane separation efficiency correlation with percent amine conversion
- Demonstrate membrane performance can be tuned by modifying PIM-1 polymer backbone structure
- Preliminary aging study of $PIM\text{-}NH_2$ membrane
- Preliminary method proposal of material modification for aging mitigation





Barriers

- Understanding of intrinsic polymeric material property and its influence towards gas transport
- Current study limited to pure gas permeabilities

Methodologies

- Synthesize amine-modified microporous membrane
- Characterization study of amine-modified microporous membrane
- Synthesize microporous polymers with tailored functional group for separation optimization
- Perform gas permeation tests with light hydrocarbon gas of interest

Research Achievements

- Synthesize amine-modified microporous membrane with controlled conversion percentage
- Demonstration of higher preferential selectivity toward olefin than unmodified PIM-1
- Preliminary result of direct relationship of amine modification amount to olefin/paraffin selectivity

Section 2: Project Summary Brief

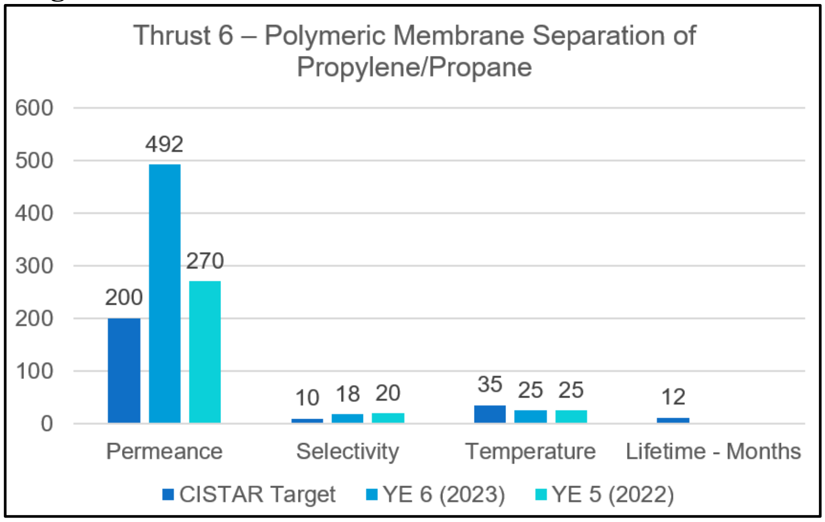
- **The Project's Role in Support of the Strategic Plan:** In order to efficiently utilize current shale resources with minimal environmental impact, CISTAR has dedicated its research effort to developing a novel transformative engineered system. The development of a new membrane separation module focuses on the purification of higher hydrocarbon species from treated shale gas streams. The focus of this project is to eliminate much of the energy- and capital-intensive cryogenic distillation steps associated with current gas separation applications. At the same time, the result of this project will support dehydrogenation research, by achieving better separation performance for its feed and product. This project investigates the potential of novel microporous polymers as robust and stable membranes for olefin-paraffin separation.
- **Abstract:** Polymeric membranes are attractive alternatives to energy-intensive distillation methods for gas separation because they do not require external energy input. However, the performance of polymeric membranes is typically limited by permeability-selectivity tradeoffs. This project aims to develop a membrane separation system to overcome this limitation and selectively separate hydrocarbon gases by designing a polymeric membrane with modified functional groups on the polymer backbone. Specifically, the project will introduce amine groups onto the PIM-1 polymer backbone. Preliminary results indicated amine modified PIM-1 (PIM-NH_2) has better gas separation performance than PIM-1. The project expands this study further by analyzing separation efficiency with controlled modification, lifetime and aging performance study, and future material design for aging mitigation.
- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
  - Synthesis of PIM-NH_2 membrane: Following previous literature studies, PIM-NH_2 membranes have been successfully synthesized in this current study. Through experiment, the percent of nitriles converted to amine has a direct correlation to reaction time, and can be controlled to synthesize specific PIM-NH_2 materials with desired amine conversion. Synthesis of PIM-NH_2 materials with varying degrees of amine conversion was confirmed through ATR-FTIR analysis.
  - Characterization of PIM-NH_2 membranes: Physical characteristics, such as density and d-spacing, of PIM-NH_2 membranes were measured to understand why PIM-NH_2 materials outperformed unmodified PIM-1 membranes.
  - Propylene/Propane separation performance study of PIM-NH_2 membrane: In comparison to unmodified PIM-1 membrane, PIM-NH_2 shows significantly higher separation efficiency of propylene/propane gas pair. A fully converted PIM-NH_2 membrane has a propylene permeability of 491 Barrer and a propane permeability of 28 Barrer, resulting in gas selectivity of 18. While PIM-NH_2 is

less permeable than PIM-1, its propylene/propane selectivity was six times higher than PIM-1.

- Preliminary result of amine conversion amount affecting gas separation efficiency: By controlling the percent amine conversion in the PIM-1 backbone, initial gas permeation result shows a relatively linear relationship between the extent of amine conversion and permeability. A 50% converted PIM-NH_2 membrane has a propylene permeability up to 4310 Barrer and a propane permeability of 1070 Barrer, resulting in a selectivity of 4. The less converted PIM-NH_2 has higher permeability but lower selectivity compared to the fully converted PIM-NH_2, clearly demonstrating the effect of permeability/selectivity trade-off. At the same time, this result provides an opportunity for performance optimization, where gas permeation and separation performance can be fine-tuned by controlling material composition.
- Aging study of PIM-NH_2 membrane: Aging studies of PIM-NH_2 have shown a loss of gas permeability up to 50% within 4 days. Extended life time study shows loss of propane permeability up to the permeation cells detection limit, where no significant gas permeation was observed for over 24 hours. This highlights the importance of the need for an aging mitigation method to extend the life time of this material.

- **Interdependence:** This project has intra-thrust collaboration with many of the Thrust 6 research groups. In collaboration with Dr. Benny Freeman and Dr. Joan Brennecke's research group at the University of Texas – Austin, the project has received guidance in regards to gas separation and material design. Dr. Ruilan Guo and her research group at University of Notre Dame has provided significant guidance towards PIM-polymer material development and the gas permeation equipment.
- **Testbed Impact and Value:** This project is directly related to the Higher Hydrocarbon (C_2+) Separation Unit within the Testbed Flow Plans, and can introduce synergy with the Dehydrogenation Unit. While not directly employed to the three testbeds, the results of this project can provide performance improvement by better purification of testbed inlet and outlet materials. Current status of this project is still at an early development stage, but will contribute to testbed studies after establishing a robust and stable membrane material.

- **Technical Targets:**



Thrust Project Number and Name	CISTAR TRL. 4/5 Process Targets. Demonstrated in Technology Module	CISTAR Status – Y6 End
T6P6: Ligand Protected Clusters Embedded in Polymer Membranes for Olefin-Paraffin Separation	• >200 Barrer Permeability • 10 Propylene/Propane Selectivity • 35 °C Temperature • > 1 Year Lifetime	• 492 Barrer Permeability • 18 Propylene/Propane Selectivity • 25 °C Temperature • Lifetime study in progress

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Preliminary results with PIM-NH_2 membranes have shown promising olefin separation performance. However, there is still a limited understanding of the influence of the amine functional group on the fundamental gas transport mechanism. Future studies will focus on elucidating interactions between different gas species and the amine functional group of PIM-NH_2 membranes, and optimizing membrane performance by varying membrane structural parameters, such as the extent of amine conversion. Finally, lifetime studies of PIM-NH_2 have shown substantial loss of permeability in the initial stages, and approach complete loss of propane permeability over time. It is crucial to develop means of aging mitigation to prolong the lifetime of this material. Common methods for mitigating aging of membranes include crosslinking and adding fillers.

- **Path to Targets Summary:** With the exception of lifetime analysis, initial results have surpassed the current CISTAR permeability and selectivity targets. However, we still lack fundamental understanding of this newly developed material. Therefore, we would like to focus on the characterization of the relationship between membrane structure and separation performance. This will be conducted through synthesis of membrane with varied structures, detailed characterization, and performance evaluation in a constant-volume, variable-pressure gas cell. Long-term lifetime studies will be accompanied by development of aging-resistant materials. The project will primarily focus on pre-modification of PIM-NH_2 to avoid the insolubility of the material. The material will be manipulated through different methods of crosslinking, and material structure will be compared to its gas permeability performance.
- **Specific Plans Organized by Challenge:**

  Specific Plan – Thermal Crosslink Partially Converted PIM-NH2: Literature has shown PIM-1 can self-crosslink at high temperatures, and the material is prepared in the form of a dry membrane. By partially converting the nitrile group to amine, the remaining nitriles can be utilized as crosslinking sites. However, thermogravimetric analysis shows that amine degradation can occur at around 300 ˚C. Therefore, structure and chemical composition characterization will first be performed to confirm the presence of amine and crosslinked species. Then, the material can be evaluated for its gas separation performance and aging. At the same time, it is important to distinguish the effect of the amount of nitrile sites used for crosslinking and amine modification towards gas permeation performance.

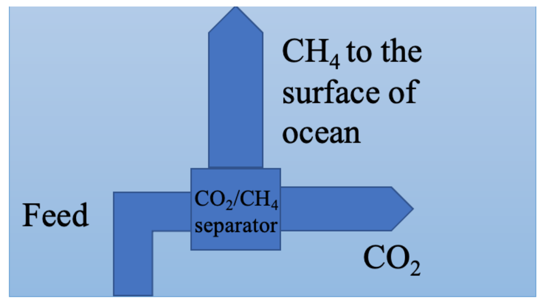
  Specific Plan – PIM-NH2 Conversion of Ester Crosslinked Partial PIM-COOH: Due to the insoluble nature of PIM-NH_2, it is most suitable to conduct any manipulation to the chemical structure prior to the amine modification. One commonly referenced method of crosslinking involves the use of the esterification reaction, where an alcohol group thermally reacts with an acid group to form an ester. This project proposes a crosslinking method of pre-modifying the PIM-1 to a partial PIM-COOH, followed by the esterification reaction with the presence of a diol linker. Any remaining nitrile groups will be utilized for amine modification. Similarly, the structure and chemical composition of this material must first be analyzed prior to any gas permeation study. Furthermore, the gas permeation study must be properly designed to include methods to distinguish the effects of crosslinking structure and amount of amine present towards gas separation performance. This method can be further expanded to investigate the impact of crosslink and conversion percentage or different diol linker structure.

C 2 C
PROJECTS

Section 1: General Information & Quad Chart for the Period 10/1/2021 to 9/30/2023

Project Title: *C2C-5* Undersea Separation of CO_2 from Natural Gas ***Project Lead:*** Joan F. Brennecke

F: Joan F. Brennecke (UT), Benny D. Freeman (UT)	
GS: Mariam Balogun (UT)	**UG:** Isabella Soares (UT)

Project Goals ● Development of a system based on CO_2 selective ionic liquids to separate CO_2 from natural gas on the seafloor. ● Develop an ionic liquid/polymeric membrane that is capable of performing separations at high pressures (i.e., > 100 bar). ● Measurements of pure and mixed gas sorption and permeabilities at high pressures.	
Barriers ● High pressure operation may accentuate polymer plasticization. ● Mixed gas solubility and permeability selectivity likely will be less than suggested by pure gas measurements, especially at high pressures. **Methodologies** ● COSMO-RS screening of ionic liquids. ● Gravimetric pure component gas solubility measurements. ● Development and use of a mixed gas sorption system. ● Development and use of high pressure pure gas permeation apparatus. ● Mixed gas permeability testing using the T5P1 Advanced Membrane Technology Module.	**Research Achievements** ● Through COSMO-RS screening and literature information, we have identified several ionic liquids that should have high CO_2/methane selectivity. ● CO_2 and CH_4 solubility measurements in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N] have been performed, at pressures up to 140 bar. ● A methodology for including the liquid sample volume expansion in the buoyancy correction of the gravimetric microbalance data, which is needed for the high pressure investigated here, has been developed and implemented. ● Initial modifications of a mixed gas polymer sorption apparatus to allow handling of liquid samples and validation with pure gas CO_2, and CH_4 measurements in [bmim][Tf_2N] complete. ● Permeability measurements in SILMs using polyethersulfone (PES) and [bmim][Tf_2N] yield a CO_2/CH_4 perm-selectivity of 10. ● Due to low mechanical stability of PES (< 2 bar), isoporous membranes are being explored to withstand transmembrane pressures up to 10 bar while maintaining high CO_2/CH_4 perm-selectivity.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** This project is part of the Center-to-Center (C2C) supplement grant to CISTAR. The strategic role of the C2C grant is to promote collaboration with researchers in Brazil who have intersecting interests with CISTAR researchers. This particular project is being done in collaboration with Professors Cláudio Augusto Oller do Nascimento (oller@usp.br) and Andressa Mota-Lima (abmlima@gmail.com) at DEQ - Escola Politécnica da Universidade de São Paulo in Brazil.
- **Abstract:** Brazil has substantial natural gas assets located offshore. Currently, to recover such natural gas, wells are drilled from the sea surface, and the gas obtained is transported to the surface in pipelines for either offshore treatment or via pipelines directly to shore. When the gas contains high concentrations of CO_2, transporting the gas from the seafloor to the surface or shore adds substantially to the cost of recovering the gas. As CO_2 content increases, the need to use special corrosion-resistant alloys for the piping increases. Since most of the CO_2 in the gas must be removed before the gas can be used, any CO_2 coming up from the seabed introduces additional cost due to larger pipes being required to transport the natural gas. The petroleum industry is exploring seafloor natural gas processing as a form of process intensification. If CO_2 can be removed undersea, the cost of piping to transport the gas to shore can be reduced. Seafloor separations technology must be compact, reliable, and low maintenance. Traditional acid gas removal technologies, such as amine scrubbing, are unsuitable for such applications. Here we propose to explore the use of ionic liquids (ILs) for this separation. We envision a supported IL membrane (SILM) system to perform this separation. The project is divided into two parts: *IL development/testing* and (supported IL) *membrane development/testing*.

  a) *Ionic Liquid Development and Testing*

  This project aims at validating the promising ability of ILs to separate CO_2 from mixtures of CO_2 and CH_4 (and, potentially, C_2H_6) at pressures up to 150 bar, temperatures between 20 and 100 °C, and a broad range of initial CO_2 content (10 to 70 mol % CO_2). Of critical importance is the gas solubility and selectivity. Most CO_2 and CH_4 solubility data in ILs in the literature is at low pressures and limited to pure gas solubilities. However, several high pressure (up to about 140 bar) and mixed gas studies point to 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) as an excellent candidate. 1-ethyl-3-methylimidazolium diethylphosphate ([emim][DEP]) also shows promise, with mixed gas CO_2/CH_4 selectivities as high as 12. Other intriguing possibilities are ILs with a dicyanamide ([DCA]) anion. These ILs exhibit much lower CO_2 and

CH_4 solubilities than the previous two, but have potentially higher selectivities, up to 26.4. We are measuring pure and mixed gas solubilities (necessary to determine selectivities) using gravimetric (Rubotherm and HidenXemis) and custom built volumetric apparatuses at the University of Texas at Austin (CISTAR) and that are being constructed at Universidade de São Paulo (RCGI). The degree of viscosity and density reduction upon dissolution of CO_2 and CH_4 at high pressure will be measured with high pressure viscometry and densitometry systems available at RCGI. Higher viscosity ILs (e.g., ([emim][DEP]) may be needed to maintain stability in SILMs.

b) *Supported Ionic Liquid Membrane Development and Testing*

We propose to explore the fundamental CO_2/CH_4 separation properties of membranes for subsea natural gas purification. We will use CISTAR's Supported Ionic Liquid Membrane (SILM) platform to tailor membranes for this application. Relying on project (a) to identify attractive ionic liquids (ILs) for this separation, we will develop polymeric support membranes to immobilize the ILs and present them to the natural gas mixture to be separated. Based on results from T6P3 that show excellent compatibility between polyethersulfone (PES) and ILs, we have developed and tested some PES/ionic liquid SILMs for CO_2/CH_4 separation. We are characterizing pure and mixed gas diffusivity and permeability (in addition to the solubilities measured in (a)) of representative natural gas mixtures to validate this concept. We are using the experimental conditions set forth in (a) for the membrane diffusivity and permeability tests, to help keep the overall effort well-focused and coordinated. Finally, for the SILMs based on polymeric membrane supports, we plan to eventually use our flat sheet membrane manufacturing facility to manufacture a SILM prototype and test it with relevant CO_2/CH_4 mixtures.

- **Significant Results for the Period 10/1/2022 to 9/30/2023:**
    - Previous work (10/1/2021 to 9/30/2022): Through COSMO-RS screening and literature information, we have identified several ionic liquids that should have high CO_2/methane selectivity as shown in Figure 1.

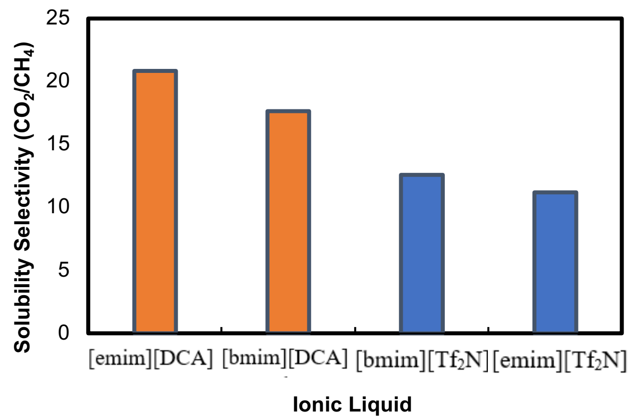


Figure 1: Pure gas selectivity of imidazolium-based cations paired with [DCA] and [Tf_2N].

- Previous work (10/1/2021 to 9/30/2022): CH_4 solubility measurements in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) have been performed, at pressures up to 140 bar, as shown in Figure 2. The solubility of CH_4 in [bmim][Tf_2N] is independent of temperature, indicating no enthalpic interactions (ΔH_{abs} = -1.5 ± 0.03 (kJ/mol)) between the IL and methane.

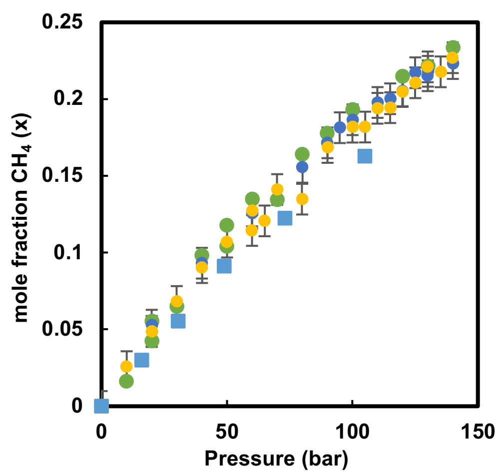


Figure 2: CH_4 solubility in [bmim][Tf_2N] using gravimetric apparatuses (HidenXemis and Rubotherm).

- This year, initial CO_2 solubility measurements in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) have been performed, at pressures up to 140 bar, as shown in Figures 3a and 3b. Solubility measurements obtained from gravimetric apparatuses take into account the buoyancy correction which includes the density of gas being measured. At pressures greater than the critical pressure of CO_2 (>73 bar), the gas is in its supercritical region. There is a large uncertainty in the density of gas as we approach the supercritical state as shown in Figure 3c, which has a significant impact on the buoyancy correction in solubility data obtained gravimetrically rather than volumetrically. As a result, the solubility at pressures greater than 73 bar is not corrected despite taking into account the liquid molar volume expansion.

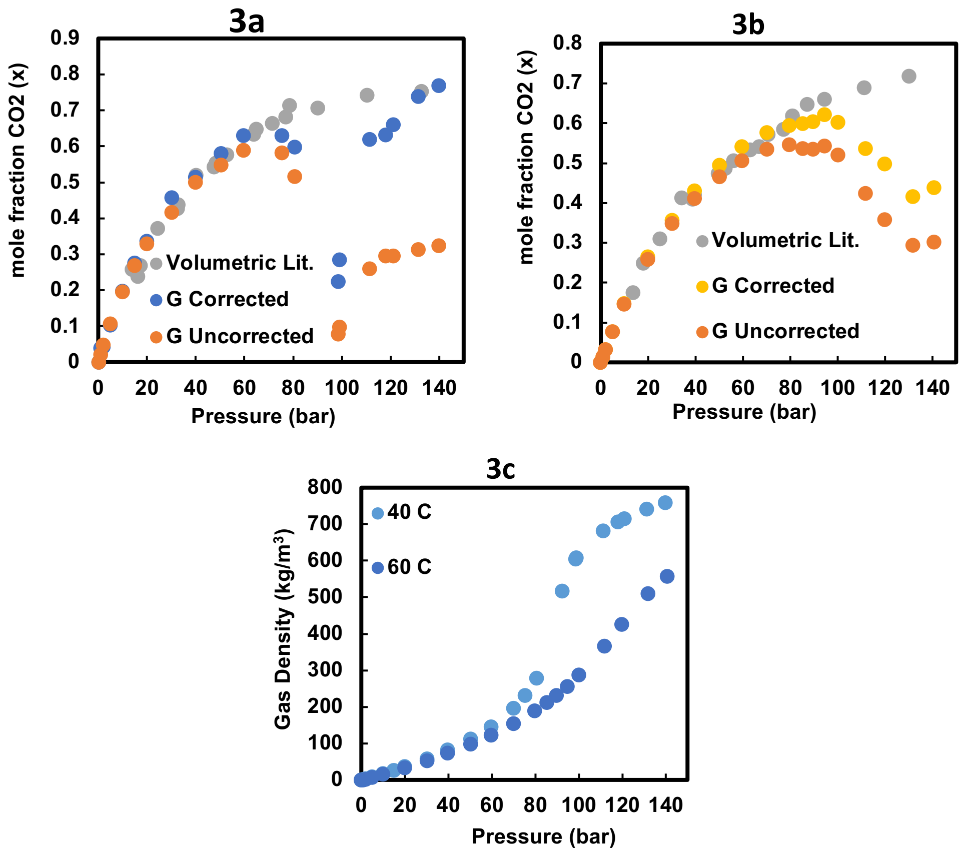


Figure 3: Preliminary CO_2 solubility data in [bmim][Tf$_2$N] using gravimetric apparatuses (Rubotherm) with liquid molar volume expansion correction measured at 40 and 60 ˚C as seen in 3a and 3b, respectively.

- CO_2 solubility in [bmim][Tf$_2$N] reduces as temperature increases due to enthalpic interactions ($\Delta H_{abs} = -17.9 \pm 0.3$ (kJ/mol)) between the gas and IL. This can be seen in the Van't Hoff plot shown in Figure 4.

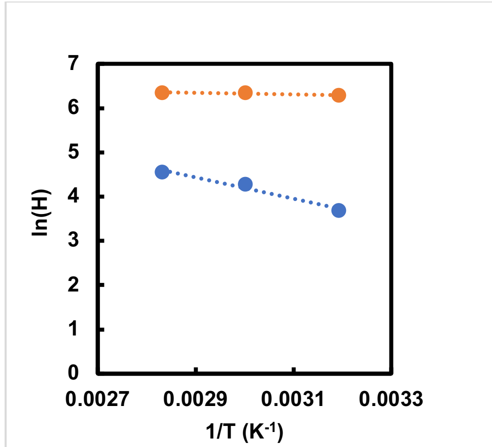


Figure 4: Van't Hoff plot of CO_2 (blue) and CH_4 (orange)

- Initial modifications of a mixed gas polymer sorption apparatus have been undertaken to allow for liquid samples, which included construction of a solid bucket to hold the liquid, with a metal frit cap to prevent spilling/loss of the liquid during the expansion step. A schematic of the mixed gas sorption apparatus is shown in Figure 5.

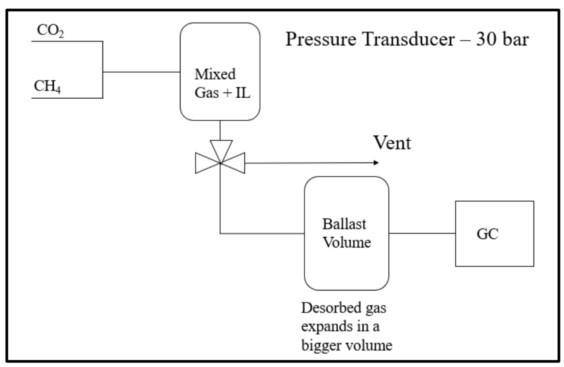


Figure 5: Schematic of the mixed gas sorption analyzer.

The mixed gas solubilities in the ionic liquid are obtained by analyzing the number of moles of gas that are desorbed from the IL in a 5 cm^3 sample chamber that expands into a 500 cm^3 ballast volume, with the compositions attained through gas chromatography.

The mixed gas solubility apparatus has been validated by comparing the pure gas solubility measurements (volumetric) obtained with the instrument to gravimetric results. This confirms that the custom-built apparatus is compatible with liquid samples as seen in Figure 6.

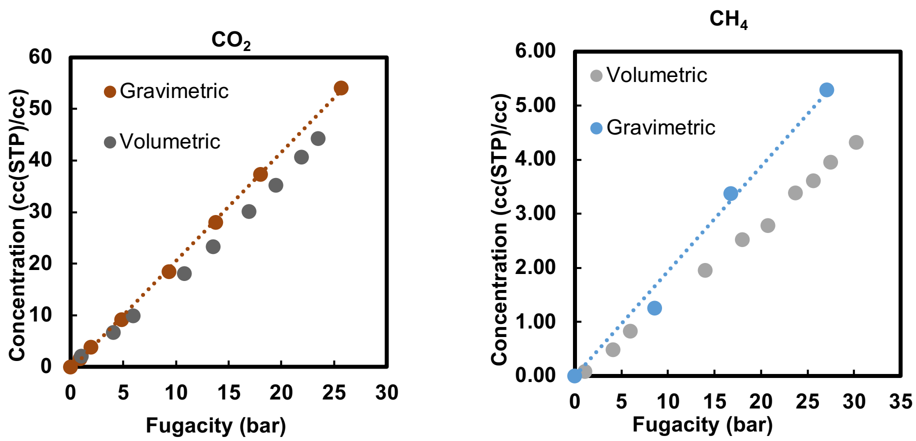


Figure 6: Volumetric pure gas solubility in [bmim][Tf$_2$N] at 40 ˚C (measured in mixed gas solubility apparatus) compared with gravimetric results.

- Based on IL/polymer compatibility tests from T6P3, polyethersulfone was chosen as a non-selective membrane support to produce SILMs for CO_2/CH_4 separation. The gas permeance results are shown in Figure 7, where we demonstrate a pure gas CO_2/CH_4 perm-selectivity of 10.

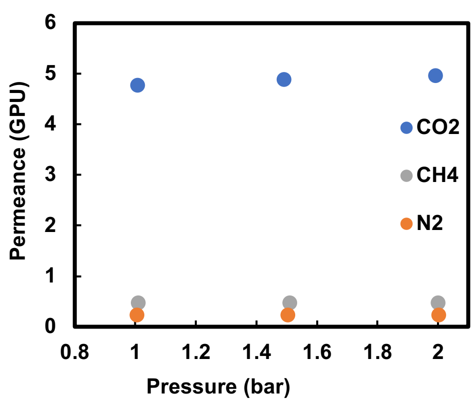


Figure 7: Pure gas permeance in PES/[bmim][Tf$_2$N] SILM at 40 ˚C

Unfortunately, the blow out pressure for [bmim][Tf$_2$N] in this polyethersulfone membrane is just 2 bar. T6P3 showed that PES membranes with smaller nominal pore sizes exhibited nanoconfinement and loss of selectivity. Hence, alternative choices of a non-selective membrane were explored that may exhibit better mechanical stability.

- Isoporous membranes has been preliminary tested as an alternative choice of a non-selective membrane to make SILMs. The isoporous membrane tested in this work are made out of a tetrablock co-polymer SISV and they exhibit pressure stability up to 6 bar. The gas permeance results are competitive with PES, having a pure gas CO_2/CH_4 perm-selectivity of 10, but the SISV isoporous membranes allow operation up to a transmembrane pressure of 6 bar.

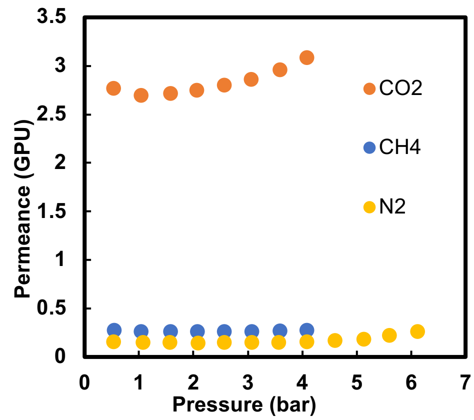


Figure 8: Pure gas permeance in SISV/[bmim][Tf_2N] SILM at 40 ˚C

- **Interdependence:** This C2C project significantly benefits from several CISTAR projects. Specifically, guidance on appropriate support materials for the SILMs comes from T6P1 and T6P3. The Advanced Membrane Technology Module (T5P1) will be used to test the SILMs developed with mixed feeds over a range of technologically important operating conditions.
- **Testbed Impact and Value:** Separation of CO_2 from CH_4 is not a component of any of the three CISTAR testbeds. However, it is of critical importance for our Brazilian collaborators, as explained in the abstract.
- **Technical Targets:**The technical targets for this C2C project are still in development. Key targets identified at this point are high pressure (>100 bar) operation and high CO_2/CH_4 selectivities (>10). The transmembrane pressure requirement is still under investigation.

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** A key challenge for year 3 of the project is collecting mixed gas sorption data at pressures up to 30 bar and modifying the instrument for pressures up to 100 bar. Another key challenge is selecting the right membrane support for high pressure stability with minimal plasticization effects from IL and CO_2, and retrofitting one of the existing permeability apparatuses for high pressure operation.

  A post-doctoral researcher from Universidade de São Paulo had initially planned to spend most of the next year here at the University of Texas at Austin. Unfortunately, it looks like this will not occur due to unforeseen circumstances.
- **Path to Targets Summary:** The mixed gas sorption apparatus has been validated for pure gas measurements, thus mixed gas solubility results in selected ionic liquids will be obtained at pressures up to 30 bar and temperatures ranging from 40 – 80 ˚C. Mixed gas selectivity will be compared to the pure gas selectivity to further guide the selection of

ionic liquid for the SILMs. Pure gas permeabilities in polyethersulfone (PES) as a membrane support for [bmim][Tf_2N] has been measured using existing permeability apparatuses. However, due to IL blowout at pressures >2 bar, alternative membrane supports are being explored and tested. Isoporous membranes have been preliminarily tested to have good pressure stability up to 6 bar while maintaining a competitive perm-selectivity compared to PES and will be further explored in year 3. Additionally, one of the membrane permeation systems will need to be modified to allow for high pressure feed and permeate operation. Mixed gas permeabilities will be performed with the T5P1 technology module. However, it will also need to be modified for higher pressure operation. We anticipate that this will be done in year 3.

- **Specific Plans Organized by Challenge:**
    - Mixed gas sorption apparatus and measurements: The mixed gas apparatus also has the ability to measure pure gas solubilities and has been validated to be leak-free and compatible for liquid measurements. A gas chromatography unit will be incorporated into the system to perform preliminary mixed gas measurements, confirming that the apparatus is fully operational for mixed gas studies. Currently, the mixed gas apparatus is rated for pressures up to 30 bar. Mixed gas CO_2/CH_4 measurements in [bmim][Tf_2N] and [bmim][DCA] will be performed at pressures up to 30 bar at temperatures at 40, 60, and 80 ^oC.
    - Pressure modifications to mixed gas sorption apparatus: We plan to make appropriate modifications that includes the addition of an ISCO pump for delivery of CO_2 at elevated pressures and the integration of new high-pressure transducers to perform measurements at pressures up to 100 bar.
    - Mixed gas solubilities: We will perform low- and high-pressure mixed gas (CO_2/CH_4) solubilities in selected ionic liquids at relevant mixed gas compositions and temperatures. The ideal selectivity will be compared to the real selectivity obtained from these measurements.
    - Permeability measurements: Polyethersulfone (PES) has been used to produce SILMs with [bmim][Tf_2N]. However, due to very low IL blow out pressures of ~2 bar, isoporous membranes are the next choice of a non-selective membrane to produce SILMs using the selected ionic liquids. Pure CO_2 and CH_4 permeability will be measured at low pressures. Following the optimization of the permeator apparatus for higher pressures, we will transition measurements to those conditions, as we work towards the targeted goal of improved CO_2/methane selectivity at high pressures.

Section 1: General Information & Quad Chart for the Period 10/1/2022 to 9/30/2023

Project Title: *C2C-6 Integrated Process Synthesis and Lifecycle Assessment* ***Project Lead:*** *Alexander Dowling (ND)*

F: Alexander Dowling (UND)	
GS: Madelynn Watson (UND)	**UG:** Yan Saltar (UND/University of Puerto Rico; UND Slatt Fellowship)

Project Goals

- Overall: Combine superstructure modeling framework with modern portfolio theory for economic and environmentally friendly sustainable aviation production under market uncertainty.
- Review state-of-the-art technologies for sustainable aviation fuel production analyzing costs, emissions, market conditions, and policies.
- Develop a superstructure model for an integrated sugarcane mill in Brazil that can produce sugar, ethanol, electricity, and sustainable jet fuel. Determine the optimal operation under market uncertainty.
- Incorporate life cycle analysis and generalize modeling framework to hydrocarbon conversion

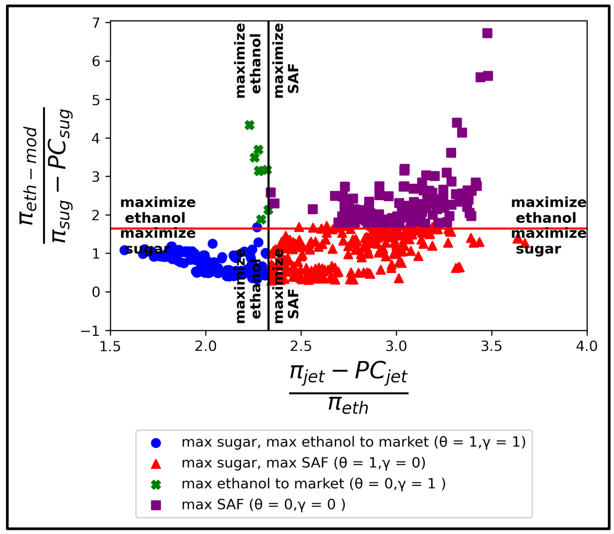


Figure 1: Scatter plot showing optimal operation (indicated by color of the point) of the integrated sugarcane mill at different historical price scenarios bounded by analytically determined ratios (black and red lines)

Barriers

- Often the best design for “average” conditions is suboptimal in uncertain real world
- New superstructure optimization approaches are needed to systematically identify sustainable and economic process alternatives while considering uncertainty and market risk

Methodologies

- Develop decision making superstructure model composed of surrogate models for the integrated sugar mill
- Use stochastic programming to optimize under uncertainty
- Perform multi-objective optimization to understand the risk reward trade-off

Research Achievements

- Analytically determined rules to determine four operation modes for the integrated sugarcane mill based on relationships between sugar, ethanol, and SAF prices..
- Test the analytically determined rules by running the integrated sugarcane mill model using historical price data in Brazil from (2013 - 2022)
- Quantitatively show the impact of premium SAF prices on frequency of operation modes
- Manuscript in preparation to be submitted in December 2023 with collaborators from Brazil as co-authors.

Section 2: Project Summary Brief

- **The Project's Role in Support of the Strategic Plan:** This project facilitates an international collaboration between CISTAR and University of São Paulo
- **Abstract:** Sustainable aviation fuels (SAF) are "taking off" in academia but are commercially "still on the ground" due to unfavorable economics. To improve SAF economics, we leverage superstructure process synthesis formulated as a mixed integer linear program (MILP) to describe integrated sugarcane mills in Brazil that produce sugar, ethanol, SAF, and electricity. Using historical price data to de-risk decisions, we show that the integrated sugarcane mill operates in four production regions based on the relationship between ethanol, sugar, and SAF prices. Furthermore, through sensitivity studies, we quantify the impact of SAF prices (e.g., price premiums airlines may pay for SAF compared to conventional jet fuel to meet industry/government decarbonization goals). As ongoing work, we are investigating integration of optimal mill operation with regional supply chains to understand the impact of policies and subsidies.
- **Significant Results for the Period 10/1/2021 to 9/30/2022:** For the relevant term we developed a superstructure model for an integrated sugarcane mill in Brazil that can produce sugar, ethanol, electricity, and SAF to determine optimal operation under market uncertainty. We analytically solve an simplified unconstrained optimization problem maximizing the profit of the sugarcane mill to determine rules for four operation modes based on the relationship between prices of sugar, ethanol, and SAF. Using historical price data, we show the constrained optimization problem follows these four operation regions (Figure 1). Furthermore, we show increasing the premium price paid for SAF from 1 USD/L to 3 USD/L increases the frequency of operation modes that maximize SAF production. Results from this year will be included in a manuscript to be submitted in December 2023.
- **Interdependence:** Collaboration with Celma de Oliveira Ribeiro at the University of São Paulo department of Industrial Engineering (Faculty), Claudio Augusto Oller do Nascimento at the University of São Paulo department of Chemical Engineering (Faculty), Aline Veronese da Silva at the University of São Paulo department of Industrial Engineering (Postdoc), and Pedro Gerber Machado at the University of São Paulo department of Industrial Engineering (Postdoc).

Section 3: Specific Plans for Next 12 Months

- **Challenges and Current Status:** Our work to date has determined optimal operation for sustainable aviation fuel production for a single sugarcane mill in Brazil under market uncertainty. Additionally to progress the collaboration this year, also resulted in GS: Madelynn Watson visiting the University of São Paulo. The next steps are to analyze the impact of mill operation in regional supply chains.

- **Path to Targets Summary:** Program in the next year will focus on three components: 1. Developing surrogate models for the ethanol-to-jet upgrading; 2. Integrate optimal mill operation with regional supply chains in Brazil; 3.Quantify the impact of policies and subsidies on regional SAF capacity development in Brazil.
- **Specific Plans – (i) Develop Surrogate Models:** Moving forward with this project we will improve the accuracy of the sugarcane mill model by developing a surrogate model for the ethylene oligomerization step in the ethanol-to-jet upgrading process. We plan to leverage CISTAR's expertise in ethylene oligomerization by collaborating with members in Thrust 2. Experimental data from Thrust 2 will be used to establish the input-output relationships for this step.
- **Specific Plans – (ii) Integrating Regional Supply Chains:** For the Brazilian sugarcane industry to increase global SAF capacity, we must think beyond a single integrated sugarcane mill. The objective of this aim is to develop an optimal supply chain for SAF production from integrated sugarcane mills in Brazil. For our supply chain optimization, we consider a 2-stage design. The supply chain starts at the sugarcane mills (Stage 1), where each existing sugarcane mill in Stage 1 has the opportunity to invest in SAF capacity. Stage 2 consists of local airports with some required fuel demand SAF production must satisfy (e.g.10% of total fuel demand). All modeling will be done in Python's modeling and optimization software, Pyomo.
- **Specific Plans – (iii) Quantify the Impact of Policies and Subsidies:**The future of SAF is highly dependent on monetary incentives from policy to overcome the economic barriers associated with existing technologies. By testing different incentive structures on our supply chain model, we can quantify the impact of monetary incentive structures on SAF supply chains in Brazil and make recommendations on optimal policy strategies for the region. This will, in return, allow us to develop a framework to inform policy design from SAF economic analysis and guide policy-makers in efficient global SAF capacity development.

Section 4: Papers and IP

1. Watson MJ, da Silva AV, Machado PG, Rivera YS, Dowling AW, Ribeiro CO, Nascimento CAO. Sustainable aviation fuel technologies, costs, emissions, policies, and markets: a critical review. Under review/under revision (2023).