

Advanced Membrane Separations Technology Module- POSTER #30



T5P1
Poster #: 30



Advanced Membrane Separations Technology Module

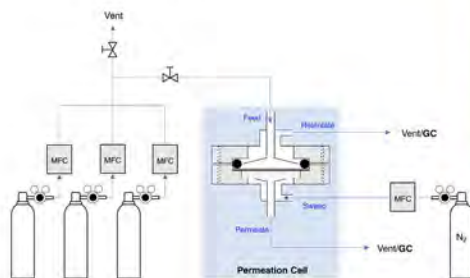
Maggie Tangqiumei Song¹, Joan F. Brennecke¹

¹McKetta Department of Chemical Engineering, University of Texas at Austin



GOALS

- Develop mixed-gas technology module with the ability to test ternary mixtures at any compositions under field conditions.

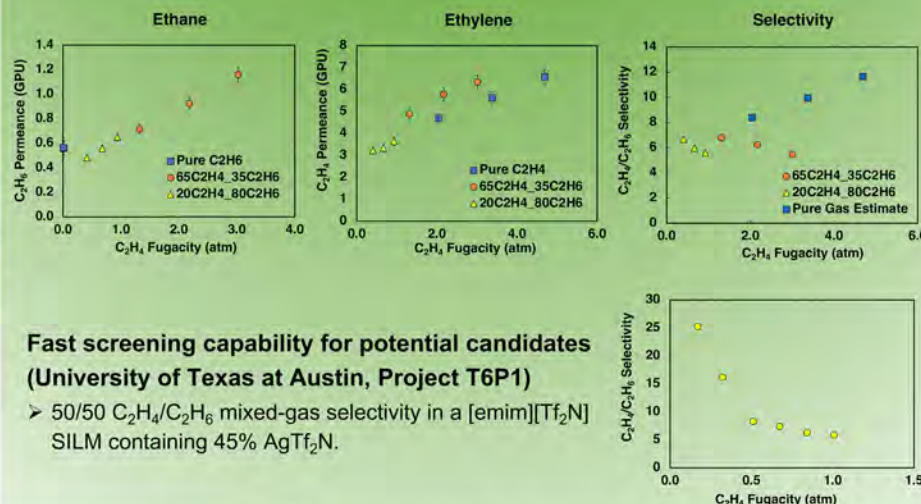


- Provide fast screening capabilities for materials developed by Thrust 6.

MAIN FINDINGS

C₂H₄/C₂H₆ mixed-gas separation performance in 70% AgTf₂N-PEBAX thin-film composite membrane (University of Texas at Austin, Project T6P1)

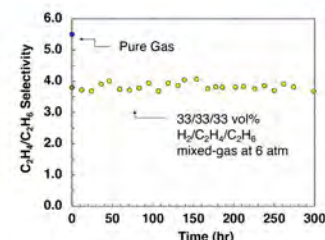
- The TFC has great permeance with a C₂H₄/C₂H₆ mixed-gas selectivity around 6.5.
- C₃H₆/C₃H₈ mixed-gas permeation experiment in progress.



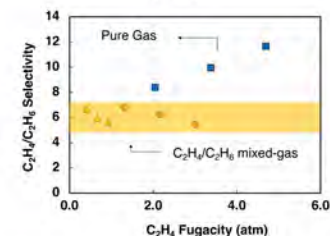
Fast screening capability for potential candidates (University of Texas at Austin, Project T6P1)

- 50/50 C₂H₄/C₂H₆ mixed-gas selectivity in a [emim][Tf₂N] SILM containing 45% AgTf₂N.

OUTCOMES

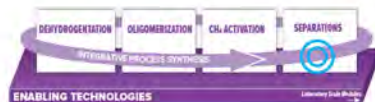


Demonstrated great hydrogen stability in AgTf₂N-XLPEGDA developed at UTA (T6P1).

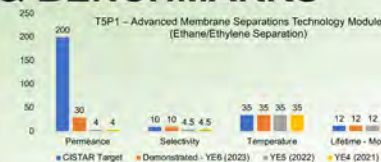
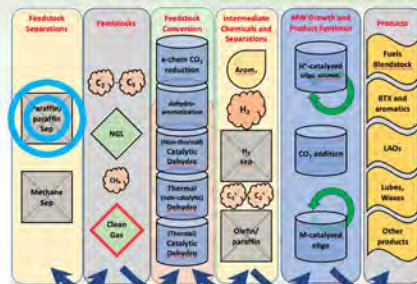


Demonstrated great mixed-gas C₂H₄/C₂H₆ selectivity in AgTf₂N-TFC developed at UTA (T6P1).

IP & INNOVATION



SYSTEM DESIGN & BENCHMARKS



Thrust Project Number and Name	CISTAR TRL 4/5 Process Targets, Demonstrated in Technology Module	CISTAR Status - Year End 6
T5P1: Advanced Membrane Separations Technology Module (Ethylene/Ethane)	>200 Barrer Permeability >10 C ₂ H ₄ /C ₂ H ₆ Selectivity >35 °C Temperature >300 hours lifetime (we expect it would be stable for 12 months)	30 Barrer C ₂ H ₄ 6.7 C ₂ H ₄ /C ₂ H ₆ mixed gas selectivity 35 °C Temperature >300 hours lifetime (we expect it would be stable for 12 months)

IMPACT & FUTURE

IMPACTS

- Enable evaluation of membrane performance using mixed-gas feeds under simplified field conditions.
- The equipment can reliably provide:
 1. temperature control between 5° and 250°C
 2. pressure control between 1.2 and 30 bar
 3. mass flow control between 20 and 1000 sccm

FUTURE WORK

- Olefin/paraffin separation in highly selective thin film composite membrane developed in UTA (Project T6P1).

Reactor Oligomerization Technology Module- POSTER #31



T5P2
Poster #: 31



Technology Module – Oligomerization Reactor High-Conversion Propylene Oligomerization on CISTAR- Developed Catalyst

Evan Sowinski, Songhyun Lee, Rajamani Gounder, Fabio Ribeiro
Charles D. Davidson School of Chemical Engineering, Purdue University

CISTAR™
NSF Engineering Research Center
Center for Innovative and Strategic
Transformation of Alkane Resources

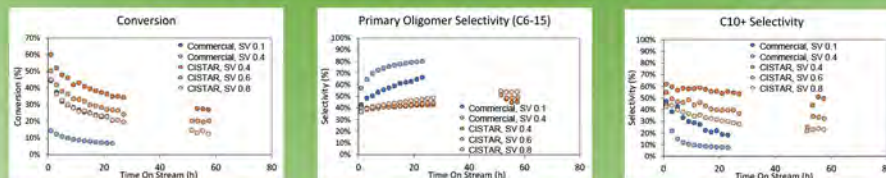
GOALS

- Select Thrust 2 CISTAR oligomerization catalysts that show promising performance in low-conversion experiments, assess at high conversion and long time-on-stream (>1 week)
- Determine product slate produced at high conversion and over long time-on-stream

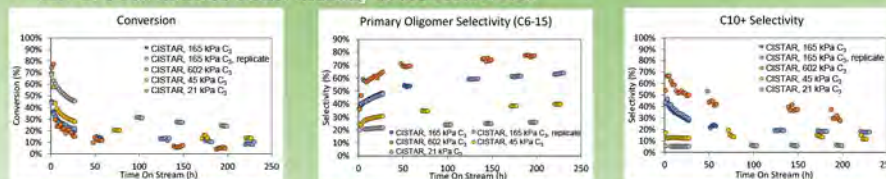


MAIN FINDINGS

CISTAR-developed small-crystallite MFI zeolite catalyst SL1-070 displays significantly higher rates and product stability compared to commercial catalyst



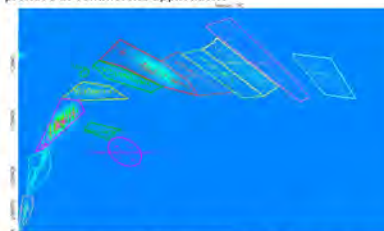
- Reaction conditions: 260 °C, 165 kPa C₃, space velocity in mol C₃/mol H₂/s
- SL1-070 had significantly higher conversion and product stability at identical reaction conditions compared to CBV2314 commercial catalyst
- SL1-070 still showed better stability at iso-conversion



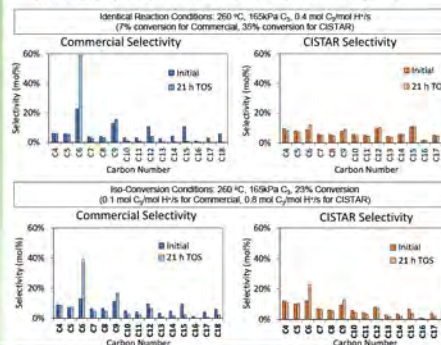
- Reaction conditions: 260 °C, 0.8 mol C₃/mol H₂/s
- Selectivity trends were still consistent at very long times-on-stream (>1 week)
- Changing pressure changes the selectivity to primary oligomers and heavier, allowing for process optimization of the product slate

OUTCOMES

- Small-crystallite MFI zeolite oligomerization catalysts may show promise in commercial applications



- In collaboration with Dr. Kentamaa at Purdue, detailed GCxGC/FID and EI-TOF composition analysis of the liquid product can yield estimates of fuel and/or chemical quality



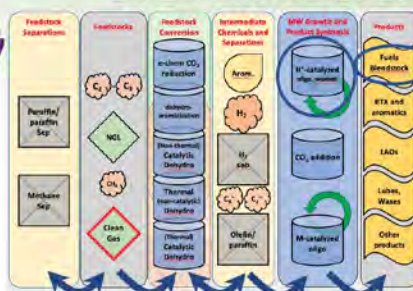
IP & INNOVATION

Provisional patent filed

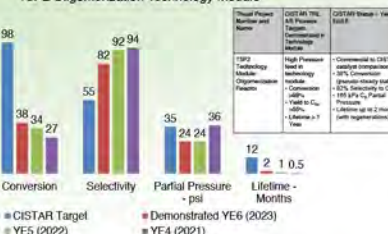
- Title: "Stable Product Oligomer Selectivity From Olefin Oligomerization on ZSM-5 Zeolites and Zeotypes"
- Filing number: 63/445,206
- Filing date: Feb 13, 2023
- For more information on the provisional patent, please see Peter Keeling



SYSTEM DESIGN & BENCHMARKS



T5P2 Oligomerization Technology Module



IMPACT & FUTURE

- The technology module connects fundamental research from Thrust 2 with the overall goals of the Testbeds, advancing the TRL of Thrust 2 projects
- Similar experiments are planned on other promising Thrust 2 catalyst technologies, such as core-shell and additional small-crystallite samples

Reactor Dehydrogenation Technology Module- POSTER #32



T5P3
Poster #: 32



Technology Module – Dehydrogenation Reactor Propane Dehydrogenation: Comparison of CISTAR Catalysts

Evan Sowinski, Fabio Ribeiro
Charles D. Davidson School of Chemical Engineering, Purdue University

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Transformation of Alkane Resources

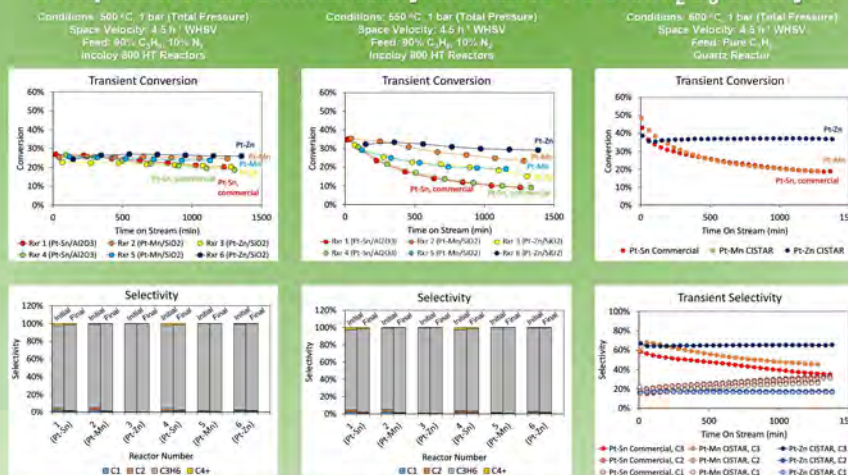
GOALS

- Comparison of CISTAR catalysts to commercial catalysts at high conversion and industrial-like WHSV
- Determine selectivity and stability with time-on-stream



MAIN FINDINGS

CISTAR-developed Pt-Mn/SiO₂ and Pt-Zn/SiO₂ propane dehydrogenation catalysts displayed greater stability compared to a commercially available Pt-Sn/Al₂O₃ catalyst



- At 500 °C, all catalysts were reasonably stable, and selectivity did not change significantly with time on stream
- At 550 °C, the commercial Pt-Sn catalyst experienced significantly more deactivation than either of the CISTAR catalysts
- At 600 °C, the Pt-Sn commercial and Pt-Mn catalysts experienced similar deactivation, but the Pt-Zn CISTAR catalyst displayed significantly less deactivation
- Selectivity for the entire experiment (selectivity for all catalysts at this temperature was not as stable and selectivity to C₃H₆ was significantly lower than at lower temperatures

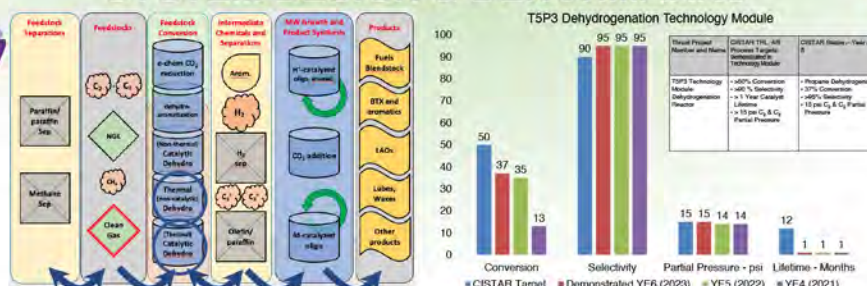
OUTCOMES

- All catalysts showed similar performance at 500 °C
- CISTAR developed Pt-Zn and Pt-Mn catalysts showed enhanced stability at 550 °C
- CISTAR Pt-Zn catalyst showed great stability even at temperatures as high as 600 °C
- At 600 °C, selectivity was less ideal than at lower temperatures
- Temperatures higher than 550 °C caused severe coking in stainless steel reactors, so quartz was used for 600 °C experiments

IP & INNOVATION

- Pt-Zn/SiO₂ catalyst in particular displays great stability for ~24 hours at temperatures up to at least 600 °C, compared to a commercially available Pt-Sn/Al₂O₃ catalyst

SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- Continued testing and comparison of CISTAR catalysts to commercial
- Modification of the technology module unit as necessary to allow for expanded reaction conditions, namely changing reactor material of construction to lessen coking at elevated temperatures

T6P1 - POSTER #33



T6P1
Poster #: 33



Scalable and Hydrogen-stable Thin Film Composite Membranes for Olefin/Paraffin Separations

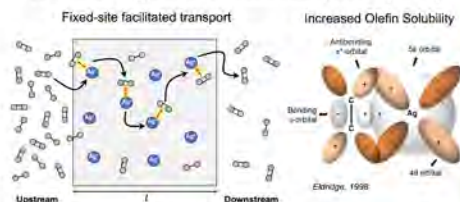
Matthew N. Davenport¹, Tangqiumei Song¹, Joan F. Brennecke¹, and Benny D. Freeman¹

¹John J. McKetta Jr. Department of Chemical Engineering, The University of Texas at Austin



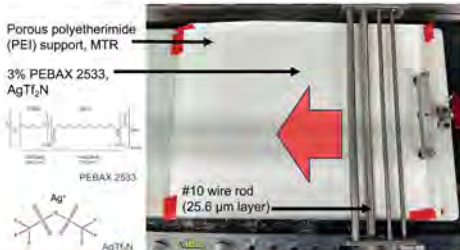
GOALS

- Ag⁺ facilitated transport membrane with high olefin-paraffin selectivity and resistance to poisoning by reducing gases, such as H₂.
- Mixed gas testing in technology module
- Scalable high-flux thin film composite (TFC)



$$\text{Permeability: } P_A = \frac{N_A \times l}{\Delta P} = D_A \times S_A, \text{ Selectivity: } \alpha_{A/B} = \frac{P_A}{P_B}$$

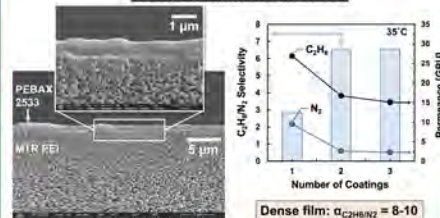
Successive coatings via automatic draw-down machine



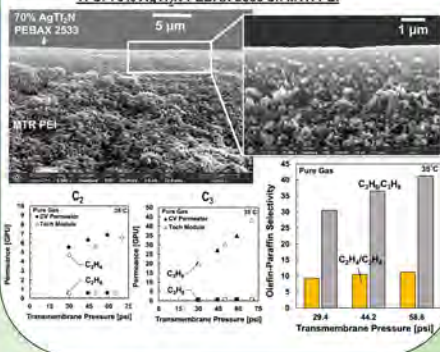
MAIN FINDINGS

Utilizing the draw-down process previously described, defect-free TFCs of neat PEBAX 2533 and 70% AgTf₂N-PEBAX2533 coated on MTR PEI were synthesized. 3 coatings was found to be sufficient.

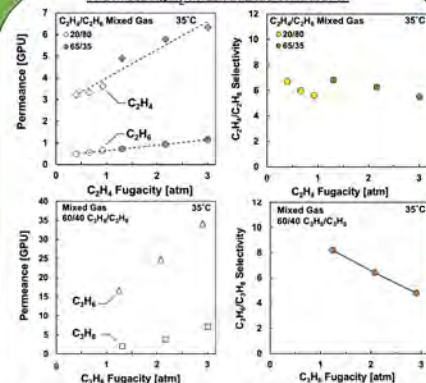
TFC: Neat PEBAX 2533 on MTR PEI



TFC: 70% AgTf₂N-PEBAX 2533 on MTR PEI

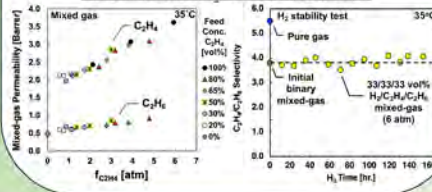


TFC: 70% AgTf₂N-PEBAX 2533 on MTR PEI



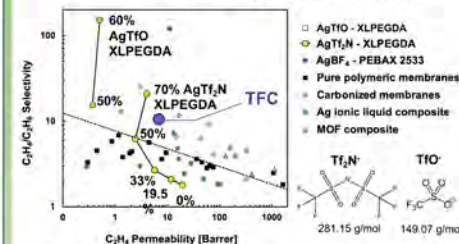
- Previously-studied dense films (ca. 50 μm) of AgTf₂N in XLPEGDA, a crosslinked polyether, also show C₂H₄ plasticization in mixed-gas testing
- AgTf₂N-XLPEGDA performance is stable to one week of H₂ mix, permeation

Dense film: 50% AgTf₂N-XLPEGDA80 ca. 50 μm

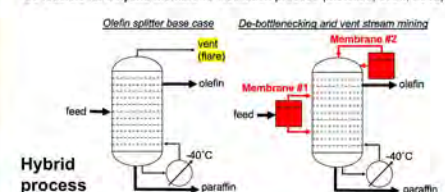


OUTCOMES

- Defect-free AgTf₂N-PEBAX 2533 TFC
- Mixed-gas C₂H₄/C₂H₆ and C₃H₆/C₃H₈ testing on CISTAR technology module
- Selectivity surpasses C₂ upper bound
- Demonstrated stability to H₂ and C₂H₂.



- 70% AgTf₂N-PEBAX2533 TFC shows lower pure-gas C₂ selectivity than dense 70% AgTf₂N-XLPEGDA film potentially due to substructure resistance
- Tech-economic analysis shows C₂H₄/C₂H₆ Selectivity (α_{C2H4/C2H6}) = 10 would be feasible for a hybrid membrane-distillation process (Motelica, et al., 2012)

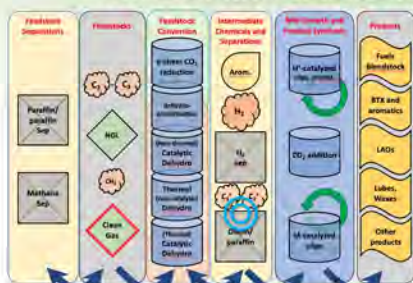


IP & INNOVATION

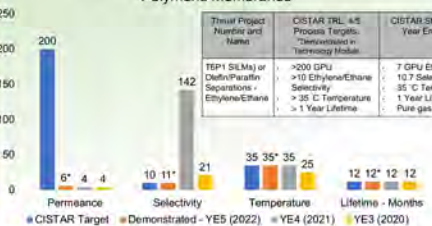
- H₂- and C₂H₂-stable Ag⁺ facilitated transport membrane with good selectivity (patent filed)
- Defect-free AgTf₂N-PEBAX 2533 TFC coating for scale-up and mixed-gas testing
- TRL 3/4



SYSTEM DESIGN & BENCHMARKS



T6P1 - SILM Ethane/Ethylene Separation - Polymeric Membranes



IMPACT & FUTURE

- The TFC morphology is readily scalable into pilot-scale spiral-wound modules
- Development of TFC membranes with other Ag salts to improve α and H₂-stability testing
- Optimization of support membrane to reduce sub-structure resistance
- Testing of 'live' mixed-gas sample from partner plant on CISTAR technology module

T6P2 - POSTER #34



T6P2 Poster #34

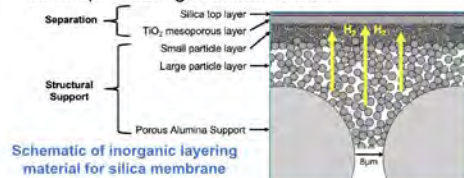
Strategies for Mitigating Membrane Fouling Via Coke Formation During PDH in a Catalytic Membrane Reactor

Isabel Ibarra¹, Ryan Alcalá¹, Ayrton Jordan¹, Aiden Littleton¹, Hiroki Nagasawa², Abhaya Datye¹, C. Jeffrey Brinker¹
¹Department of Chemical & Biological Engineering and the Center for Micro Engineered Materials, The University of New Mexico
²Chemical Engineering Program and Graduate School of Advanced Science and Engineering, Hiroshima University



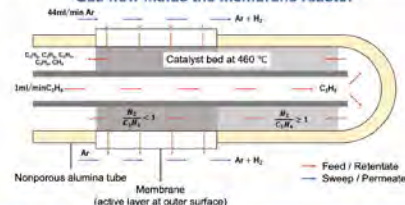
GOALS

- Develop and integrate a thermally stable, high flux membrane for the selective removal of H₂ from C₂-C₅ alkanes in a high temperature catalytic membrane reactor.
- Modify or substitute membrane components to develop a fouling resistant CMR.



Amorphous silica membrane on a porous alumina support

Gas flow inside the membrane reactor



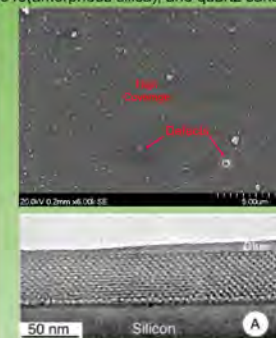
MAIN FINDINGS

Sample	Surface Area m ² /g	Coke wt% g C/m ²
Bare α-Al ₂ O ₃ (200 nm)	7.01	0.103
1wt% Sr on α-Al ₂ O ₃ (200 nm)	7.01	0.113
10wt% Sr on α-Al ₂ O ₃ (200 nm)	7.01	0.089
Davissil 646 (amorphous)	277.86	0.025
Quartz Sand	2.44	0.0005

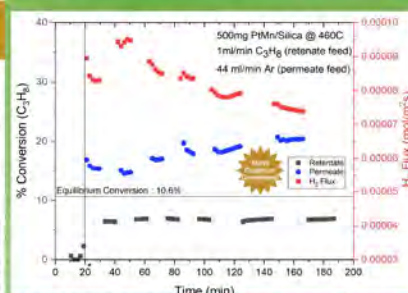
BET surface area, weight % coke deposition, and grams of coke per surface area for bare and Sr modified α-alumina particles, Davissil 646(amorphous silica), and quartz sand.



Aerosol assisted evaporation induced self-assemble silica layer with uniform 3nm pores can potentially replace intermediate particle layers reducing coking and increasing flux.

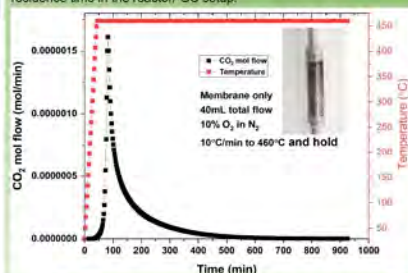


Aerosol assisted EISA mesoporous silica films. Top image from 2023 and bottom image from 1999 (Lu et al)



PDH reaction at 460 °C and 1ml/min propane feed. Conversions above equilibrium conversions can be seen on the permeate side.

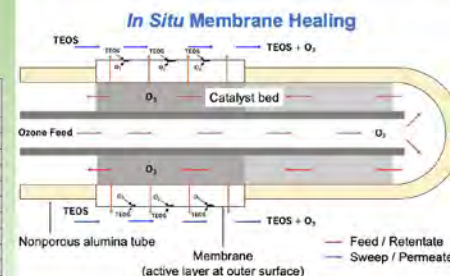
* A transient reaction can be observed in the first 20 min due to a long residence time in the reactor/ GC setup.



Temperature programmed oxidation performed on the membrane after seeing 10% C₂H₆ in N₂ for 17.3 hrs at 460 °C. Approximately 2mg of coke came off in the form of CO₂.

OUTCOMES

- Above-equilibrium conversions can be obtained
- Provides promising platform for tandem catalysis
- Mapped out material modifications and substitutions that can be made to prevent fouling.
- Redox cycling generates defects. Defects can be healed by secondary membrane formation.

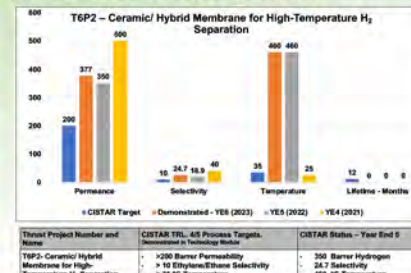
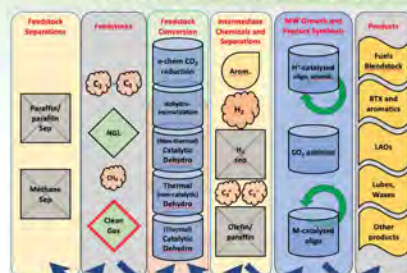


IP & INNOVATION

- Exceeds equilibrium for a given T and P
- Provides a unique platform for tandem catalysis to further improve conversion and reduce need for separation
- Patent application in progress



SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- CMR reduces needed energy input for a given conversion
- Reduction of membrane fouling increases the time between regenerations.
- Tandem catalysis offers to provide a direct route for propane to liquid fuels
- In Situ membrane healing

T6P3 - POSTER #35



T6P3 Poster #: 35



Improving the Pressure-Stability of Supported Ionic Liquid Membranes (SILMs) for the Fractionation of Light Paraffins

Justin J. Rosenthal¹, Joan F. Brennecke¹, Benny D. Freeman¹

¹ John J. McKetta Jr. Department of Chemical Engineering, The University of Texas at Austin



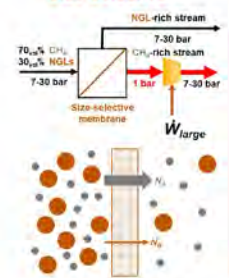
GOALS

- Light paraffin fractionation with reverse-selective supported ionic liquid membranes (SILMs)
- Membrane stability (i.e., "blowout resistance") at industrial operating pressures of 7-30 bar
- SILMs suitable for large-scale manufacturing and incorporation into low-footprint modules for decentralized natural gas processing

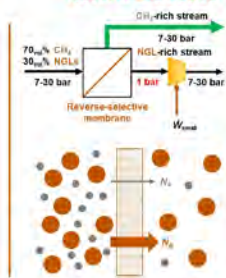
Benefit of Reverse-Selectivity

Solubility-selective ionic liquids (ILs) are reverse-selective which helps to avoid costly recompression

Size-Selective



Reverse-Selective



Supported Ionic Liquid Membrane Synthesis



MAIN FINDINGS

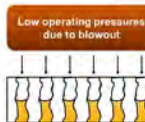
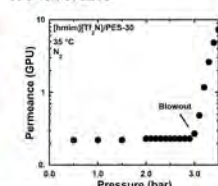
Limitations of SILMs

Plasticization of the support by the IL and high operating pressures are common challenges:

Incompatibility between the IL and the support

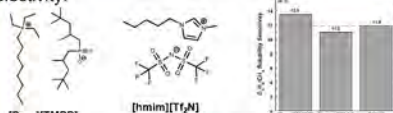


The IL can swell the polymer support if their interactions are too favorable

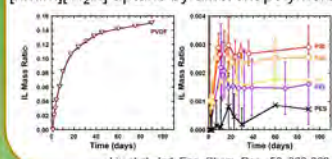


Selection of IL and Polymer Support

ILs were chosen based on their C₃H₈/CH₄ ideal solubility-selectivity:



[hmim][Tf₂N] uptake by different polymers:



PES shows lowest IL uptake

Liu et al., Ind. Eng. Chem. Res., 53, 363-368, (2014)

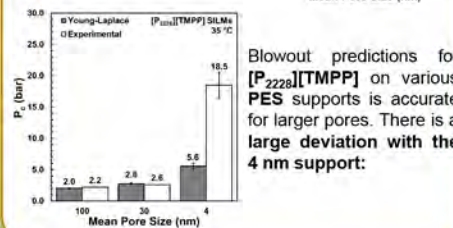
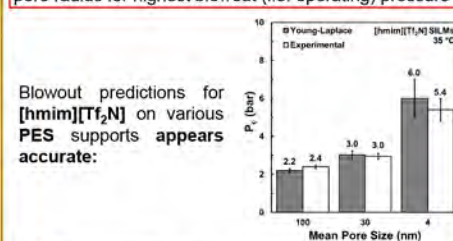
Predicting Blowout Pressures

The Young-Laplace (YL) equation is a helpful predictor of possible operating conditions:

$$P_c = \frac{2\gamma \cos(\theta)}{r}$$

P_c = Blowout Pressure (Pa)
 γ = Surface Tension (N/m)
 θ = Contact Angle (radians)
 r = Pore Radius (m)

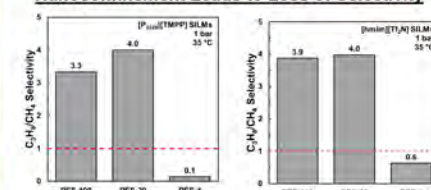
Want high surface tension, low contact angle, and small pore radius for highest blowout (i.e. operating) pressure



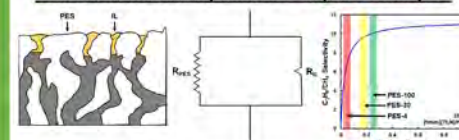
Blowout predictions for [P₂₂₂][TMPP] on various PES supports is accurate for larger pores. There is a large deviation with the 4 nm support:

OUTCOMES

Nanoconfinement Leads to Loss of Selectivity

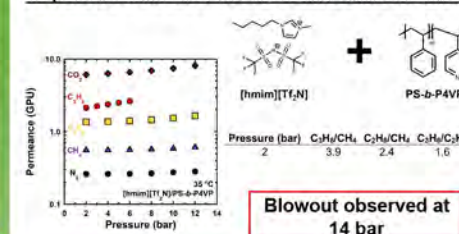


Low Surface Porosity Hinders Propane Transport



Henis, J.; Tripodi, M. J. Membr. Sci. 1981

Isoporous SILMs are Pressure-Stable and Selective



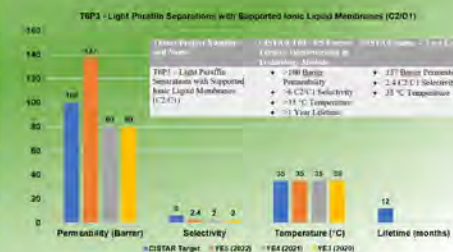
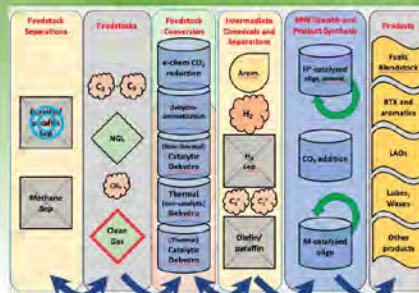
Blowout observed at 14 bar

IP & INNOVATION

- Most stable SILM utilizing commercially available supports
- Isoporous SILMs provide the necessary pressure-stability and reverse-selectivity for this separation



SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- Evaluation of the IL interactions with the support are necessary for a stable SILM
- Nanoconfinement can improve stability but leads to a loss in reverse-selectivity
- Isoporous SILMs offer both good pressure-stability and the desired reverse-selectivity
- Future: Characterize isoporous SILMs with [hmim][Tf₂N], [P₂₂₂][TMPP], and [emim][SCN]
- Future: Develop poly(ionic liquid) membranes

This paper/poster is based upon work supported primarily, OR in part by the National Science Foundation under Cooperative Agreement No. A23-116472-2.

Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.



T6P4 - POSTER #36



T6P4
Poster #:37

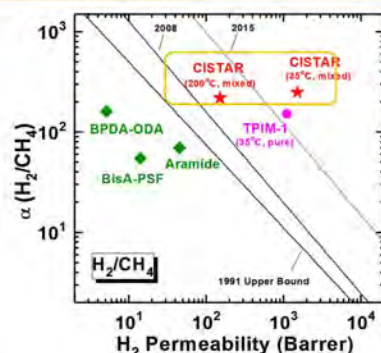


Microporous Iptycene-based Polybenzoxazole Membranes for H_2/C_1-C_3 Separations

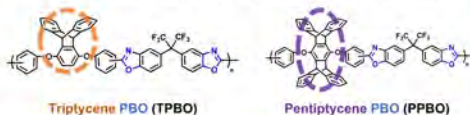
Agboola Suleiman, Zihan Huang, Ruilan Guo
Department of Chemical & Biomolecular Engineering, University of Notre Dame



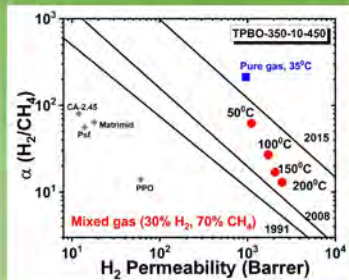
GOALS



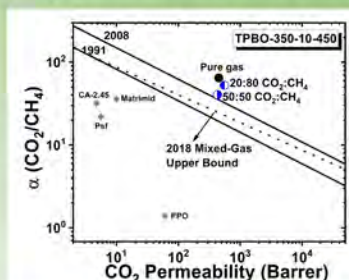
- Develop polymeric membranes tailored for H_2/C_1-C_3 separations.
- Investigate their performance with increasing temperatures (up to 200°C).
- Hypothesis: Iptycenes should minimize selectivity losses at high temperatures due to their configuration-free volume.



MAIN FINDINGS



- The Iptycene – PBOs have exceptional performance at 35°C for single gas.
- Both polymers show a similar performance α (PPBO) > α (TPBO).
- High selectivities at 200°C for binary gas mixtures confirm the hypothesis.



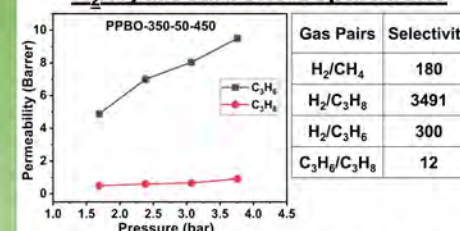
- Iptycene units mitigated the selectivity losses at high temperatures – configuration free volume are less sensitive to the high temperatures.
- Excellent plasticization resistance in mixed-gas conditions for CO_2 .



QR Code for Full Paper

OUTCOMES

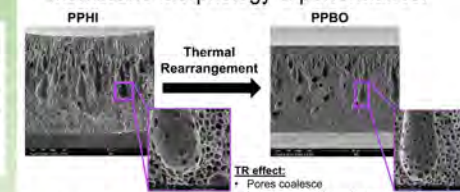
H_2 /Hydrocarbons Separations



- PPBO shows promising selectivities for C_3H_8 , C_2H_6 , and CH_4 .

Asymmetric membrane fabrication

- A complex process: simultaneous occurrence of different mechanisms on membrane morphology & performance.



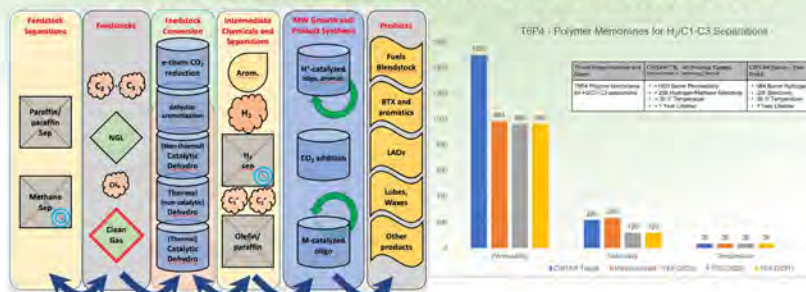
- An optimum dope composition that gives similar dense film selectivity is being studied.

IP & INNOVATION



- Developing first-of-its-kind high-performance polymer membranes for separations up to 200°C.

SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- Better heat integration of CISTAR process and separation conditions.
- Promising performance for H_2/C_3H_8 , H_2/C_2H_6 .
- Asymmetric fabrication of these materials is ongoing.
- Novel non-fluorinated materials are being investigated.

T6P6 - POSTER #37



T6P6
Poster #: 37



Olefin/Paraffin Separation Performance of Amine-modified PIM-1 Membrane

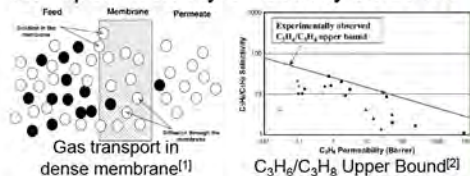
Bo Wei Cynthia Chen¹, Casey P. O'Brien¹

¹Department of Chemical and Biomolecular Engineering,
University of Notre Dame

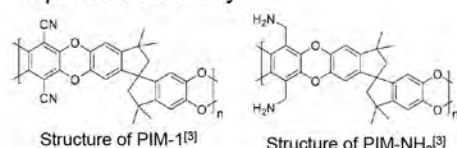


GOALS

- Gas separation using polymeric membrane reduce energy consumption
- Simple polymeric membrane suffer from permeability/selectivity trade-off



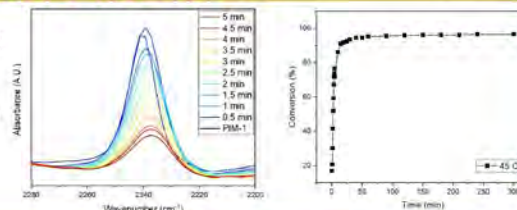
- Polymer of Intrinsic Microporosity (PIM) are known for high permeability
- Modification of polymer design can improve selectivity



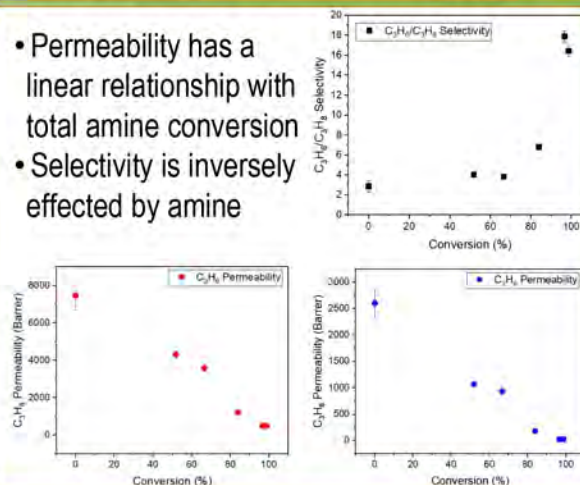
Reference [1] Farsi, A. (2015). Mass transport in inorganic meso- and microporous membranes, [2] J. Membr. Sci. 2003, 211, 299-309, [3] Rodriguez, K. M., et al. Angew. Chem. Int. Ed. 2021, 60, 6593-6599.

MAIN FINDINGS

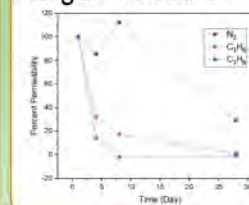
- Synthesized of PIM-NH₂ confirmed using FT-IR
- Reaction is controlled to produce PIM-NH₂ at different conversions



- Permeability has a linear relationship with total amine conversion
- Selectivity is inversely effected by amine

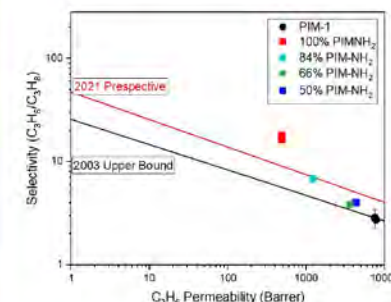


- Membrane aging is observed at initial testing day
- Nitrogen tested as comparison showing slower aging than larger molecules



OUTCOMES

- C_3H_6/C_3H_8 separation performance using PIM-NH₂ is above upper bound
- Gas separation performance can be optimized by manipulating polymer design
- Fast membrane aging occurs during initial time period

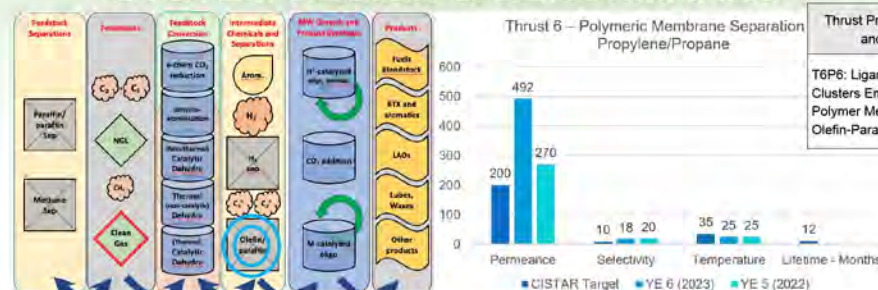


IP & INNOVATION



- PIM-NH₂ is a promising novel material for high efficiency separation
- Characteristic study of PIM-NH₂ to understand gas transport and separation properties

SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

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

- Fundamental study polymer property to optimize gas separation efficiency using molecular design
- Aging mitigation study in the future

T6P7 - POSTER #38



T6P7
Poster #: 38



Engineering Mechanically Tough Poly(ethylene oxide) Membranes for Olefin/Paraffin Separations

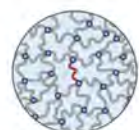
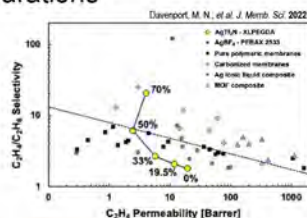
Tiffany Jeng¹, Gabriel E. Sanoja¹

¹McKetta Department of Chemical Engineering, The University of Texas at Austin

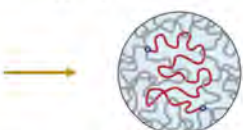


GOALS

- Engineer polymer membranes of high fracture toughness
- Understand the relationship between membrane structure and bulk mechanical and transport properties for olefin/paraffin separations



Highly crosslinked, low M_n polymer chains

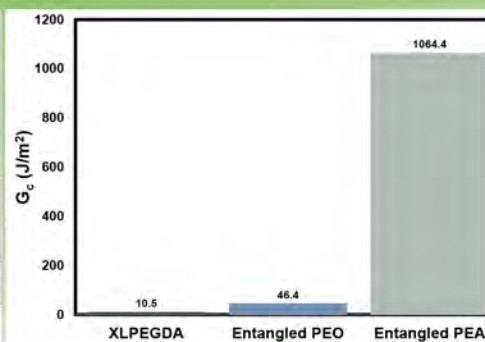
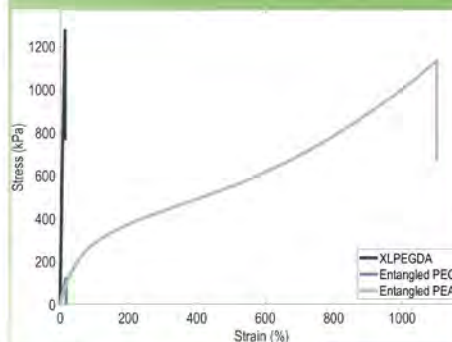


Highly entangled, high M_n polymer chains

Nian, G. et al. Adv. Mater. 2022.

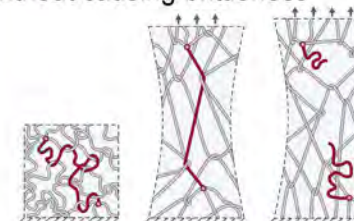
MAIN FINDINGS

- XLPEGDA/AgTf₂N membranes are stiff ($E \sim 10$ MPa) and brittle ($G_c \sim 10$ -100 J/m²)
- Highly entangled polymers yield elastic, yet tough membranes

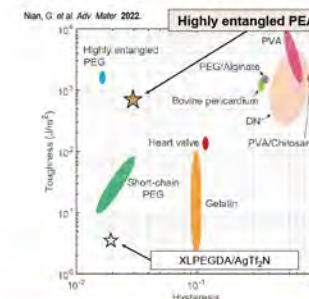


OUTCOMES

- Alternative polymer network architectures toughen membranes
- Entanglements dissipate energy without causing brittleness



Kim, J. et al. Science. 2021.

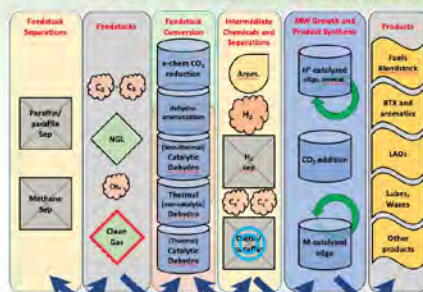


IP & INNOVATION

- Molecular understanding of the mechanical properties of PEO/AgTf₂N membranes



SYSTEM DESIGN & BENCHMARKS



IMPACT & FUTURE

- Longer-lasting, mechanically tough membranes
- PEO/AgTf₂N requires refined molecular design
- Toward highly entangled polymer membranes utilizing alternative chemistries