U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Task 2.2: Co-optimization of Scalable Membrane Separation Processes and Materials

FY23 BETO Peer Review

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Meltem Urgun-Demirtas (ANL)

Lauren Valentino (ANL)

Argonne NATIONAL LABORATORY | BERKELEY LAB | Los Alamos NATIONAL LABORATORY | NREL NATIONAL RENEWABLE ENERGY LABORATORY | OAK RIDGE National Laboratory | Pacific Northwest NATIONAL LABORATORY

Bioprocessing Separations Challenge

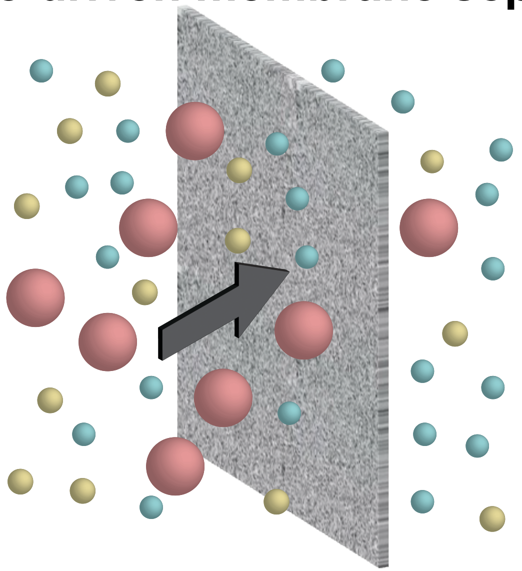
Membrane-based separation processes can provide an energy and carbon-efficient alternative separation strategy for **decarbonization of transportation and industry** (**BETO strategic goals**).

However, the technology is not currently optimized for the bioprocessing industry and has scalability issues due to lack of mechanical strength, performance stability, fouling resistance (*IAB feedback and stakeholder engagement*).

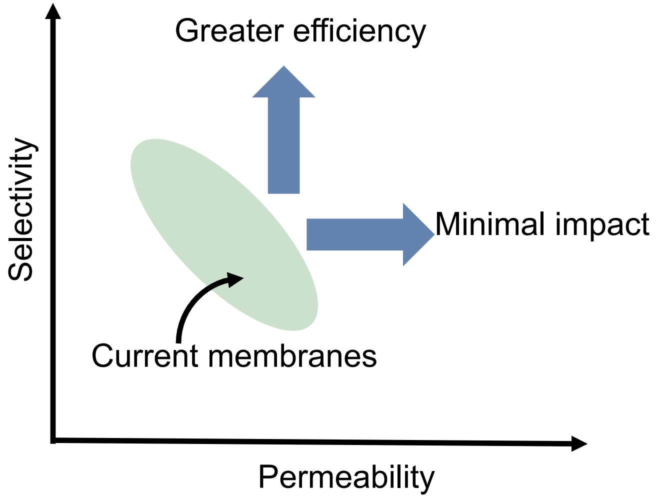
Project Overview

- Most commercially available are designed for aqueous based separations.
- Permeability and selectivity are interdependent with the upper limit constrained by current membrane materials.
- Due to similar chemistries, polymeric membranes are highly susceptible to organic solvent degradation, limited permeance of hydrocarbons, and operational problems including fouling.
- Industry is looking for low cost and carbon intensity processes for separation of biofuels and bioproducts.
- **Project focus:** Hydrocarbon separations with organic solvent nanofiltration (OSN) / reverse osmosis (OSRO)
- Project started in FY23; SepCon previously studied membrane technologies used for aqueous streams.

Pressure-driven membrane separation



Permeability / selectivity tradeoff



Adapted from Werber *et al.*, *Nature Reviews Materials*, 2016

Industry Input Refined the Scope of Work

- Met with membrane manufacturers, technology developers, and end users to identify a relevant stream with high separations needs
  - Evonik, Sulzer, ICM Inc., Exxon Mobil, Virent, Archer Daniels Midland (ADM)
- Industry highlighted the need to eliminate or minimize the use of heat integrated and chemical intensive separation processes to reduce CO_2 emissions from fossil fuels
  - Need for electrification of heat integrated processes
  - Development of new membranes to reduce carbon intensity (CI) is crucial
- Aside from fermentation product recovery, opportunities for membrane separations include the fractionation of liquid hydrocarbons and oxygenates, homogeneous catalyst recovery, removal of impurities and inhibitors (e.g., organic sulfur compounds), and decolorization
  - Require solvent-resistant membranes that preserve separation characteristics while processing a range of solvents with defect-free morphology and controlled selectivity
- Outreach highlighted the need for more general knowledge what can be separated and under what conditions

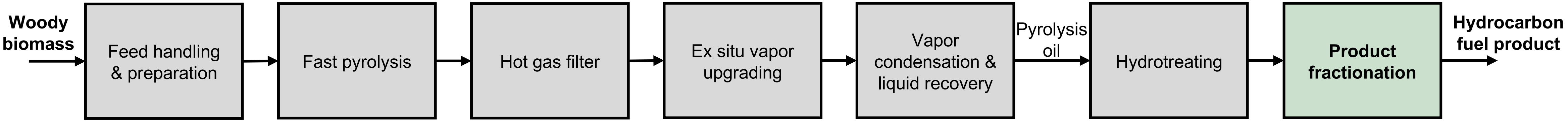
State of Technology (SOT)

- Membrane based separation technologies
  - Membrane-based processes can be an order of magnitude more energy efficient than thermal separations[1] and have been used for a broad range of applications.
  - In FY17-22, the SepCon developed membrane separation processes using commercial membranes and polymer modified ceramic membranes.
- Shortcomings of the SOT
  - Membrane-based separation processes are not optimized for bioprocessing, and improved lifetime information is needed to reduce the risk of technology adoption by industry.[2-4]
  - Membranes are applicable across the BETO portfolio; however, the *breadth and depth of data obtained from previously BETO-funded projects is not sufficient* to enable the technological and commercial maturity needed for industry.
- Application of the proposed technology
  - The proposed approach will help us understand separation needs and develop a systematic matching process for technology commercialization of bioprocesses to bring new technology out of the lab and into the market.

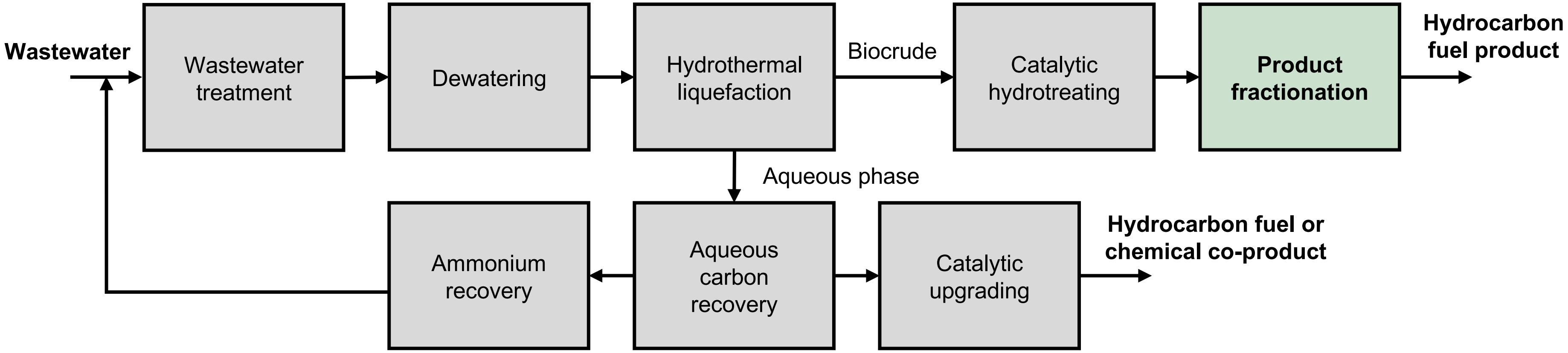
1) Sholl and Lively, *Nature*, 2016
2) Bioprocessing Separations Consortium, Summary of Industrial Listening Day, 2017
3) Bioprocessing Separations: Advancing a Research Agenda. In *ACS GC&E*, 2021
4) Bioprocessing Separations Consortium, Summary of Listening Day, 2021

Approach: Technology Application

Dry Feedstocks Converted via High Temperature and Upgrading



Wet Feedstocks to Fuels/Products via High Temperature Conversion



*Potential for co-processing these streams in a petroleum refinery replacing **distillation column***

Comparison of Distillation and OSN

Table 5 Energy requirements for solvent recovery by distillation *vs.* solvent recovery by OSN as a function of the solvent boiling point. The corresponding carbon footprint was calculated for 70% solvent recovery after Kim *et al.*[53]

Solvent	Rank[66]	Solvent generated [10^6 kg per year]	$Q_{distillation}$ [kWh]	Q_{OSN} [kWh]	$Q_{distillation}/Q_{OSN}$	CO_2 footprint [10^6 kg per year]
Methanol	1	44.8	150	0.023	6453	18
Dichloromethane	2	22.3	111	0.014	8010	3
Toluene	3	12.1	197	0.021	9278	12
Acetonitrile	4	7.9	141	0.023	6029	3
Chloroform	7	3.71	131	0.012	10 543	0.4
n-Hexane	8	2.99	149	0.028	5300	3
n-Butyl alcohol	9	2.86	223	0.023	9788	2
DMF	10	2.79	244	0.019	12 569	2
N-Methyl-2-pyrrolidone	12	2.02	303	0.018	16 930	1
Xylene	13	1.47	208	0.021	9748	1
1,1,2-Trichloroethane	15	1.23	194	0.013	15 090	0.2
Methyl *tert*-butyl ether	16	1.2	126	0.025	5062	1
Ethylene glycol	18	0.82	337	0.017	20 285	0.3

Energy requirements for distillation are much greater than for OSN

Szekely *et al.*, *Green Chemistry*, 2014

Utilization of OSN at Field-Scale

- Commercialized for use in pharmaceutical applications
- Demonstrated in petrochemical refining applications
  - OSN helped debottleneck existing thermal dewaxing units in a petrochemical refinery (36,000 barrels per day sent to membrane unit), resulting in reductions of 20% in process energy intensity, 20,000 tons of greenhouse gas emissions per year, and 4 million gallons of water per day.[1]

Solvent	Application	Membrane material
Acetone	Vegetable oil deacidification	PA
Chloroform/toluene	Removing metals and carbon residue from heavy oil	PVDF
Cyclopentane	Fractionation of hydrocarbon oils	P/carbonate
DMF	Pharmaceuticals, purification of polymers	PDMS, PI
Ethanol	Nutraceuticals, flavors, pigments, vegetable oil, proteins, amino acids	several
n-Heptane	Aromatics from heavy oil	P/propylene
Hexane	Vegetable oil refining. regeneration of used lube oils	PDMS, PI, PVA, PAN, ceramic
Lube base oil	Concentration of furfurals	PDMS
Methanol	Refining of vegetable oils, pharmaceuticals	Composites, ceramics
Methyl esters	Biodiesel, vitamins	Composites
MEK	Removal of dewaxing solvents	CA, PI
Paint solvents	Treatment of paint wastes	PI
n-Paraffins	Lube oil dewaxing	P/carbonate
Propane	Oils from organic solvents	PI
Toluene/DMF/xylene	Removal of low MW compounds in polymer manufacture	PI
Vegetable oil	Dewaxing, recovery of dewaxing aids	PES, PI

1) Gould *et al. Environmental Progress,* 2001.
Table: Priske *et al.*, *Chemie Ingenieur Technik*, 2015

Technical Approach

- The proposed technology will
  - Explore how simultaneous material and process innovations improve the performance and stability of membranes while reducing separations cost
  - Focus on paired development of membrane materials and processes by tailoring commercial OSN membrane surfaces for pressure driven membrane-based separation processes
- Project goals
  - Simultaneous membrane material and process development, targeting TRL ≥ 4 for OSN/OSRO
- Technical approach for achieving project goal(s)
  - Establish a baseline using commercially available membranes for key performance metrics: chemical stability, permeability, and selectivity
  - Conduct membrane performance testing in bench-scale test cells using a range of operating conditions with synthetic multicomponent mixtures and real bioprocessing streams – membrane flux and selectivity
  - Investigate the surface modification of commercial membranes through scalable coating techniques
  - Demonstrate scalable membrane surface modification techniques using ANL's roll-to-roll (R2R) facility
  - Evaluate performance of surface-modified membranes in a pilot scale (140 cm^2) membrane unit

Technical Approach (*continued*)

- Top challenges facing the technical approach
  - Robustness of membranes in the presence of aggressive organic feeds– introduce additional post-fabrication modifications
  - Different coating equipment may require further optimization of parameter to maintain reproducible coating quality- Identify critical process parameters and scale fabrication incrementally
- Our approach will advance the state of the art
  - Improvements in process performance (durability, flux, and selectivity) and increased scalability of membrane processes developed for biofuels and bioproduct production
- Potential innovation in application
  - Development of 2-3 OSN membrane applications at TRL≥ 4 to decrease bioprocessing separation costs and GHG emissions
  - Address gaps related to process engineering and scale up with the overall goal of transitioning membrane technology into more challenging separation environments
  - Pilot-scale data (TRL≥ 4) from evaluation of membrane materials and process conditions for applications in bioprocessing.
- Economic and/or technical metrics that will be used to measure progress
  - Process performance, cost of product, and GHG emissions to be compared to heat-based processes

Technical Approach

Project divided into 5 main tasks:

1. New surface coatings. Develop new scalable coating synthesis methodology by tailoring commercial OSN membrane surfaces to improve the performance and stability of membranes–structure characterization

2.New separation process. Test process performance (durability, flux, and selectivity) and stability with real samples at bench (40 cm^2) and pilot-scale (120 cm^2) test units- various solvent transport at different operating pressures

3. New OSN membranes production at scale. Fabricate new OSN membranes by using R2R facility for pilot-scale performance evaluation to bring new OSN technology into the market.

4. Technoeconomic Analysis (TEA). Develop a framework for new OSN membrane materials and their separation performance of biofuels and products by using an integrated systems-engineering approach

5. Lifecycle Analysis. Use the Greenhouse gases, Regulated Emissions, and Energy use in Technology (GREET) model to evaluate the environmental impacts of new OSN membranes and their separation performance of biofuels and products

Approach: Management

- Biweekly project meetings with task PIs
- Progress tracking with monthly Consortium meetings
- Meetings with Analysis team to evaluate economic and sustainability measures
- Findings published and IP generated for new concepts
- Bi-annual meeting with Industrial Advisory Board for progress updates and feedback
- Collaborate with other BETO projects and industry partners
  - BETO-funded projects related to HTL and pyrolysis pathways
  - Sulzer
  - Compact Membranes
  - ICM Inc.
  - Exxon Mobil
  - Virent

Approach: Diversity, Equity, and Inclusion

Research team
- Diverse team including scientists and engineers from STEM underrepresented groups (Meltem Urgun-Demirtas, Lauren Valentino, and Yuepeng Zhang)

Outreach activities
- Introduce a Girl to Engineering Day @ Argonne
- Science Careers in Search of Women @ Argonne
- Disseminate results at the MSI (community colleges and universities)

Student mentoring
- 2 undergraduate student internships per year from underrepresented groups

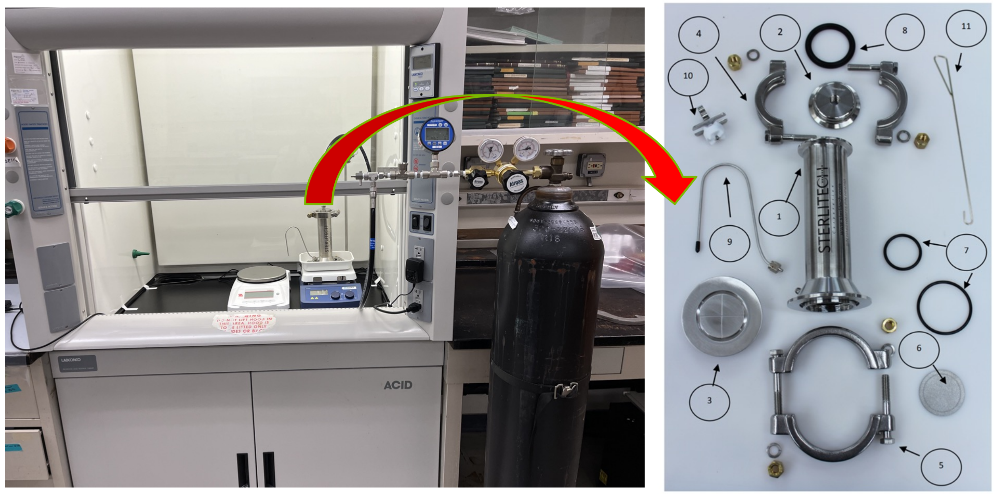
Economic development
- Utilize Argonne's vendor and procurement systems that support purchasing goods/services from veterans, women, and disadvantaged owned small businesses

FY23-FY25 Bioenergy Bridge to Career Program
- Participate in Consortium-wide program

Results and Progress

- Conducted an extensive literature search and review on utilization of the OSN at field-scale
- Engaged (and continue to engage) membrane manufacturers, technology developers, and end users
- Obtained commercially available OSN membranes and set up of bench-scale OSN membrane testing units
- Met with SepCon analysis team (Task 3.1) to discuss the pathway for TEA and LCA model development
- Reached out to NREL and PNNL (via TEA teams) to obtain pyrolysis oil and crude oil samples for baseline study
- Obtained Health and Safety approval for the experimental work

Results and Progress: Experimental Work



Bench-scale OSN membrane test unit and components

OSN MEMBRANE NAME / DESCRIPTION	Operating pressure (psi)	Pore size	Polymer
Evonik Flat Sheet Membrane, Puramem Flux, NF, 47 mm and 210 x 297mm	290 - 870 psi	300-500 Da	Silicone-coated PAN
Evonik Flat Sheet Membrane, Puramem, Performance, NF, 47 mm and 210 x 297mm	290 - 870 psi	300-500 Da	Silicone-coated PAN
Evonik Flat Sheet Membrane, Puramem Selective, NF, 47 mm and 210 x 297mm	290 - 870 psi	300-500 Da	Silicone-coated PAN
BORSIG Flat Sheet Membrane, ONF1, 47 mm and 210 x 297mm	217 - 507 psi	600 MWCO	Silicone polymer-based
BORSIG Flat Sheet Membrane, ONF2, 47 mm and 210 x 297mm	217 - 507 psi	350 MWCO	Silicone polymer-based
BORSIG Flat Sheet Membrane, ONF3, 47 mm and 210 x 297mm	217 - 507 psi	900 MWCO	Silicone polymer-based

R2R Membrane Pilot-scale Facility at ANL

Roll-to-roll screen printing and slot-die coating- Pilot-scale continuous membrane synthesis

Energy efficient membrane thermal treatment

FY24 Q4 Annual Milestone

Milestone Name/Description	Criteria	Date
Task 2.2 Co-optimization of Scalable Membrane Separation Processes and Materials [ANL]: Demonstrate coating technique and evaluate membrane performance in crossflow cell	Fabricate at least one coated membrane at pilot scale (~140 cm^2) and demonstrate stable membrane flux (<10% change over 8 h) for at least 2-3 organic solvents.	9/30/2024

Impact

- New membrane separation technology has potential
  - Eliminate or minimize the use of heat integrated separation processes to reduce CO_2 emissions from fossil fuels
- This new technology could be translated to other applications in bioprocessing
  - Fractionation of liquid hydrocarbons and oxygenates, homogeneous catalyst recovery, solvent recovery, removal of impurities and inhibitors, dewatering and decolorization
- Planned demonstrations
  - Baseline study using commercial OSN membranes
  - Surface modification of OSN membranes and synthesis of new membrane materials at Roll2Roll pilot unit (0.30 m× 1 m)
  - Performance evaluation of new OSN membranes with real samples at pilot-scale (140 cm^2)
- Industrial engagement provides project guidance
  - ADM
  - Evonik North America
  - Sulzer ChemTech
  - ICM Inc.
  - Exxon Mobil
  - Virent

Summary

Approach	Explore how simultaneous material and process innovations improve the performance and stability of membranes Focus on paired development of membrane materials and processes by tailoring commercial OSN membrane surfaces for pressure driven membrane-based separation processes at TRL≥ 4 to decrease bioprocessing separation costs and GHG emissions Integrated TEA and LCA identify research and development priorities and guide experimental work Frequent interaction and coordination among researchers to meet project goals Regular updates and feedback from the Advisory Board and ongoing collaboration with industry
Progress and Outcomes	Engaged (and continue to engage) membrane manufacturers, technology developers, and end users Obtained commercially available OSN membranes and thermochemical stream composition (NREL and PNNL) Successfully completed the set up of bench-scale OSN membrane system and obtained health safety approval for the planned experimental work Demonstrated scalable surface modification techniques using ANL's roll-to-roll (R2R) facility
Impact	New materials and OSN membrane-based separation process for the bioprocessing industry Develop a systematic matching process for technology commercialization of separations processes into the market Overcome scalability issues due to lack of mechanical strength, performance stability, fouling resistance of current membrane technologies Eliminate or minimize the use of heat integrated separation processes to reduce CO_2 emissions from fossil fuels and electrify separation processes Dissemination results via conference presentations and peer-reviewed journal articles enable technology transfer Industry engagement guides project deliverables and outcomes

Quad Chart Overview

Timeline

- Project start date: October 2022
- Project end date: September 2025

	FY22 Costed	FY23-25 Total Award
DOE Funding	$0	$1,272,000
Project Cost Share *	N/A	N/A

TRL at Project Start: 3
TRL at Project End: 4

Project Goal

The goal of this project is to conduct research towards the simultaneous membrane material and process development, targeting TRL≥ 4 for OSN/OSRO to separate pyrolysis oil and biocrude oil samples from NREL and PNNL.

End of Project Milestone

- Development of 2-3 OSN membrane applications at TRL≥ 4 to decrease bioprocessing separation costs and GHG emissions
- insight for OSN/OSRO process scale up
- Pilot-scale studies (TRL≥ 4) to evaluate membrane materials and process conditions for OSN/OSRO applications in bioprocessing.

Project Partners

- NREL and PNNL (TEA and providing pyrolysis oil and biocrude oil samples)
- Sulzer (Industry partner)
- Compact membranes (industry partner)
- Exxon Mobil (Industry partner)

Acknowledgements

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

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- Hakan Olcay

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Pacific Northwest NATIONAL LABORATORY

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Thank you!

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Technical Approach: Metrics and Risks

Technical approach

- Co-optimize of membrane materials and processes
- Demonstrate scalable surface modification techniques and evaluate membrane performance at pilot scale (140 cm^2) unit

Technical, economic, and sustainability metrics

- Reduction in energy consumption and increase in membrane membrane lifetime
- Reduction in cost of product selling price
- Greenhouse gas emissions, energy consumption, and solvent and water consumption

Risks and Mitigation

- Chemical compatibility of membrane materials- Introduce post-fabrication modifications (*e.g.*, cross linking)
- Scalability of membrane fabrication techniques- Identify critical process parameters and scale fabrication incrementally to achieve desired quality and functionality

Year	Technical metrics
1	Fabricate at least one coated membrane at bench scale (40 cm^2) and demonstrate stable membrane flux (<10% change over 8 h) for at least 2-3 hydrocarbon compounds
2	Fabricate at least one coated membrane at pilot scale (~140 cm^2) and demonstrate stable membrane flux (<10% change over 8 h) for at least 2-3 organic solvents.
3	Performance evaluation of new OSN membranes with real samples at pilot-scale (140 cm^2)

Responses to Previous Reviewers' Comments

Since this project started in FY23, there were no previous reviewers' comments.