Inorganic Membrane-based Reactive Separation and Reactant Recycle for Direct Synthesis of Dimethyl Carbonate (DMC)

DE-SC0019556

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Media and Process Technology Inc.

M&P TECHNOLOGY BACKGROUND

Project Overview

Program: *Phase II Small Business Innovation Research (SBIR)*

Funding: *Overall project budget: $1,050,000 (including DCA funding).*

Overall Project Performance Dates: *March 19, 2020 - March 18, 2023 (36 months)*

Project Participants:

- *Media and Process Technology…Membrane manufacturer/supplier and technology developer*
- *TechOpp Consulting, Inc.…Discretionary Commercialization Assistance provider (POC: Mary Ann S. Bonadeo)*

Overall Phase II Project Objectives:

Demonstrate the proposed inorganic membrane-based DMC Production process at pilot scale at the relevant operating conditions:

(i) Improved Dimethyl Carbonate (DMC) conversion in a membrane reactor configuration

(ii) Improved DMC product recovery in a downstream membrane nanofilter.

M&P TECHNOLOGY BACKGROUND

Motivation: Carbon Capture and Reutilization

Carbon Capture and Reutilization

- ✓ *Effective means to overcome carbon storage problems.*
- ✓ *Green alternative to petroleum sources of fine chemicals*

Focus: Dimethyl Carbonate

- ✓ *Green production (CO_2 and biomass MeOH)*
- ✓ *Low toxicity*
- ✓ *Low viscosity*
- ✓ *High solvent power*

M&P TECHNOLOGY BACKGROUND

Synthesis: Dimethyl Carbonate (DMC)

route	description	reactions
~~I~~	~~methanol phosgenation~~	~~$COCl_2 + 2\,CH_3OH \rightarrow (CH_3O)_2CO^a + 2HCl$~~
★ II	oxidative carbonylation of methanol (Eni)	$CO + 2CH_3OH + O_2 \rightarrow (CH_3O)_2CO^a + H_2O$
★ III	oxidative carbonylation of methanol via methyl nitrite (Ube)	$N_2O_3 + 2CH_3OH \rightarrow 2CH_3ONO + H_2O$ $2CH_3ONO + CO \rightarrow (CH_3O)_2CO^a + NO$
★ IV	ethylene carbonate transesterification (Asahi)	$(CH_2)_2O + CO_2 \rightarrow C_3H_4O$ $C_3H_4O + 2CH_3OH \rightarrow (CH_3O)_2CO^a + (CH_2OH)_2$
V	urea transesterification	$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$ $(NH_2)_2CO + CH_3OH \rightarrow CH_3OCONH_2 + NH_3$ $CH_3OCONH_2 + CH_3OH \rightarrow (CH_3O)_2CO^a + NH_3$
VI	direct synthesis from CO_2	$CO_2 + 2CH_3OH \rightarrow (CH_3O)_2CO^a + H_2O$

Technology Background

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M&P TECHNOLOGY BACKGROUND

Solution: Membranes in DMC Synthesis and Recovery

Membrane Reactor: In-situ Dehydration

1. Operation Mode: Pervaporation/Vapor permeation.
2. Equilibrium Shift: Increase DMC yield via in-situ water removal
3. Increased Yield: Reduce downstream separation and recycle requirements.

Membrane Separator: MeOH/DMC

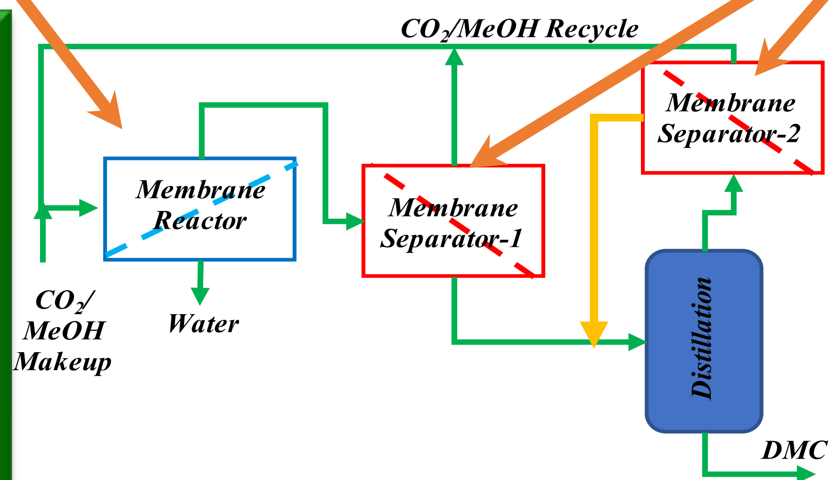
1. Operation Mode: Nanofiltration
2. Azeotrope Break: Remove MeOH (and CO_2) from DMC.
3. Reduced Energy and Cost: Eliminate multiple column azeotrope distillation.

Challenge

Operating Conditions
120 to 200°C; 300 to 1,500psig
Operating Environment
MeOH, DMC, CO_2, water

Solution

Inert Membrane
Inorganic Gas/Vapor Separation Membrane



Challenge

Operating Conditions
80 to 150°C; 300 to 1,500psig
Operating Environment
MeOH, DMC, CO_2, water

Solution

Inert Membrane
Inorganic Nanofilter

M&P TECHNOLOGY BACKGROUND

Reaction. In-situ Dehydration in Direct Synthesis

MR Configuration eliminates these problems

Dehydration Approach	DMC Yield Impact	Advantages	Barriers/Problems
Organic Dehydrating Agent	10 to >95%	a. Highest DMC yields observed. b. Continuous processing capable and demonstrated on bench. c. Very high reaction rates demonstrated in continuous versus "batch" reactors. d. High selectivity to DMC for some selected systems.	***The dehydrant yields…*** a. Byproduct formation due to dehydrant degradation. b. Catalyst deactivation. c. Limited upper operating temperature (<140°C). d. Additional separation and regeneration equipment. e. Dehydrant loss; hence makeup chemicals required.
Inorganic Adsorbent	<10 to ~40%	a. Commercial examples of cyclic "dehydration" are installed/operational (corn ethanol production, for instance). b. No byproduct formation. >99% selectivity c. No catalyst deactivation.	a. Low H_2O adsorbent capacity at reaction temperatures. b. Discontinuous highly unfavorable cyclic operation due to mismatch of the reaction and adsorption/regeneration temperatures. c. Long reactor residence times.
Membrane Reactor	Up to ~10%.	a. No byproduct formation. >99% selectivity b. No operating temperature limit in the expected range. c. Continuous processing capable. d. No chemical makeup required. e. No catalyst deactivation	a. Yields above 10% have not been laboratory demonstrated. Very low-quality membranes have been tested. b. Limited range of membrane candidates; CO_2 and MeOH are good plasticizers; T > 120C; P>>300psig

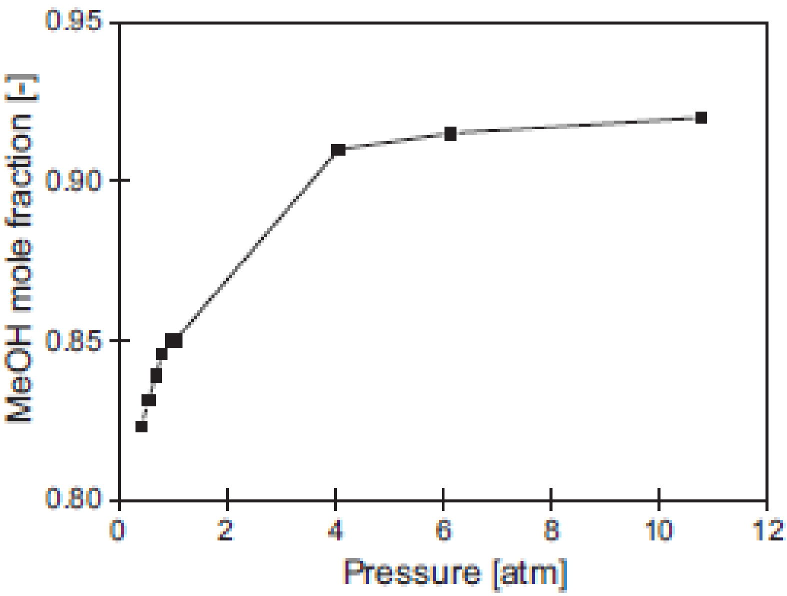
M&P TECHNOLOGY BACKGROUND

Separation: Nanofiltration for MeOH/DMC separation

Primary Cost Drivers

1. Azeotrope: Extractive Distillation Cost
2. Low DMC Conversion: Balance

MeOH/DMC Azeotrope Composition



Equipment Impact

Equipment	Code	Key specifi-cations	Height [m]	Diameter [m]
Distillation columns	Dist-01	50 stages	27.5	3.16
	Dist-02	79 stages	42.0	2.92
	Dist-03	67 stages	36.0	2.00
	Dist-04	49 stages	27.0	1.58
Flash drum	–		10.6	3.32
Compressors	C-01	1530 kW	–	–
	C-02	30 kW	–	–
Pumps	P-01	4 kW	–	–
	P-02	133 kW	–	–
	P-03	28 kW	–	–
	P-04	8 kW	–	–
	P-05	13 kW	–	–
Heat exchangers	Reboiler Dist-01	471 m^2	–	–
	Reboiler Dist-02	279 m^2	–	–
	Reboiler Dist-03	104 m^2	–	–
	Reboiler Dist-04	142 m^2	–	–
	Condenser Dist-01	1861 m^2	–	–
	Condenser Dist-02	175 m^2	–	–
	Condenser Dist-03	113 m^2	–	–
	Condenser Dist-04	326 m^2	–	–
	He-01	600 m^2	–	–
	He-02	10 m^2	–	–
	He-03	99 m^2	–	–
	He-04	92 m^2	–	–
	He-05	9 m^2	–	–
	He-06	41 m^2	–	–
	He-07	15 m^2	–	–
	He-08	5 m^2	–	–
	He-08	5 m^2	–	–

MPT Membrane Technology

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M&P TECHNOLOGY BACKGROUND

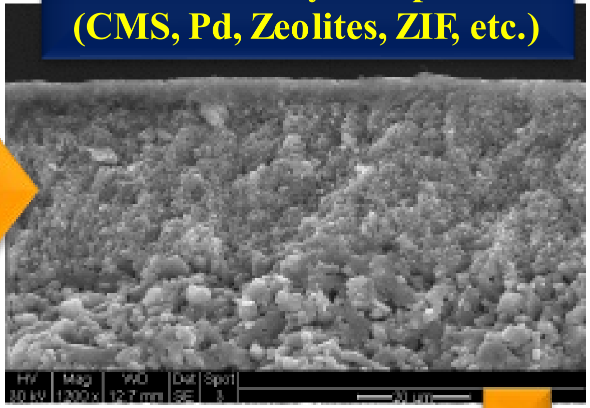
Advanced Inorganic Molecular Sieving Membranes

- Wide range of membranes technologies
- Multiple tube bundles
- High temperature (>500^{o}C)
- High pressure (>1,000psig)
- Stepping stone from the laboratory to field/commercial scales.

Ceramic Tube Extrusion

Intermediate Layer Deposition + Non-porous Tip and End Seals

Thin Active Layer Deposition (CMS, Pd, Zeolites, ZIF, etc.)



Package into Multiple Tube Bundle

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

Project Technical Scope and Approach

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M&P TECHNOLOGY Phase II Program

Phase II Project: Multiple Tube Bundle Scaleup at Target Conditions

Primary Technical Goal

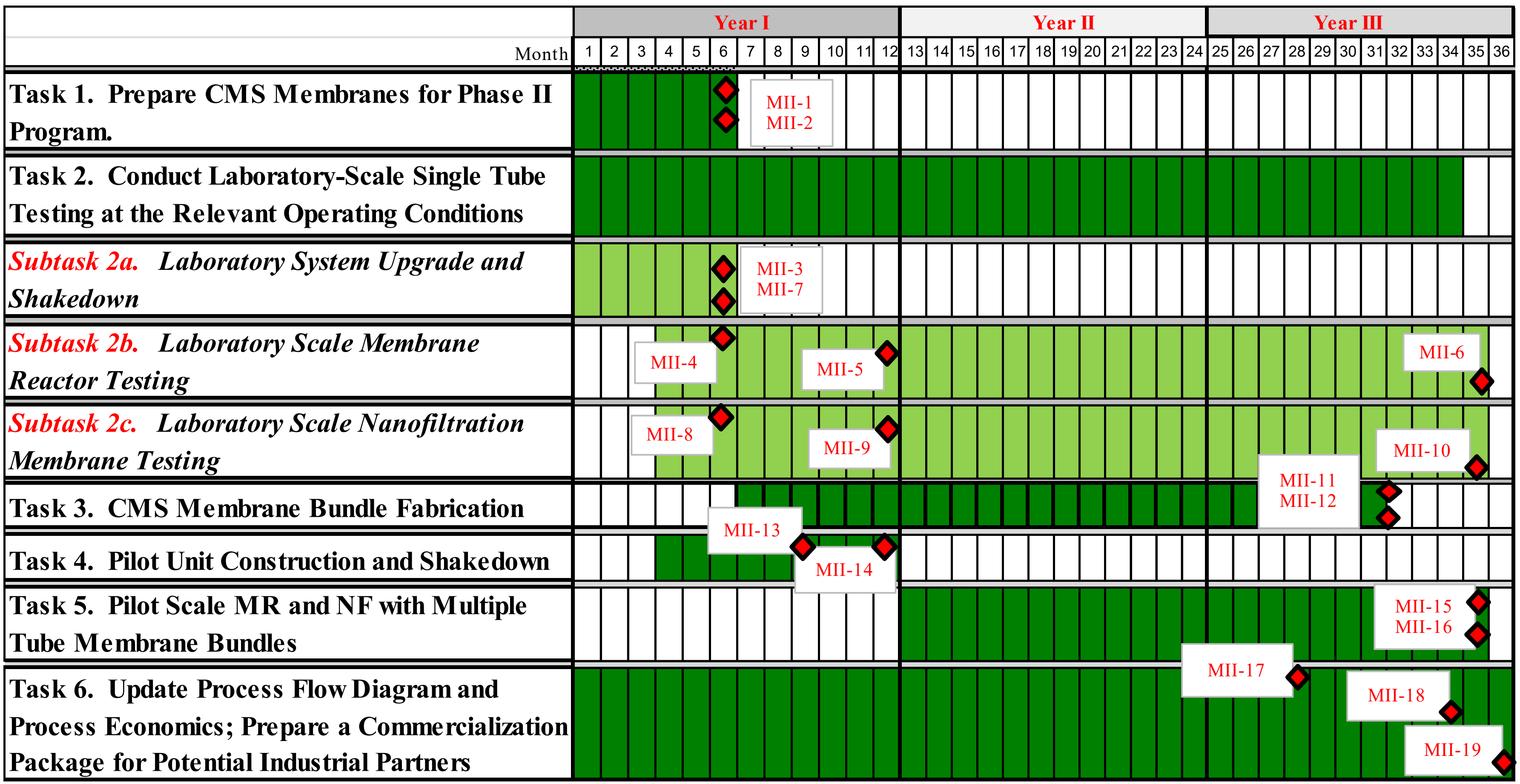
Process Scaleup at Target Operating Conditions

Demonstrate multiple tube membrane bundles in MR and NF operation at the target operating conditions.

Objective	Target/Goal	Yr
#1	Membrane Reactor (MR) Testing with Full length single tube membrane testing at up to 1,500 psig and 200°C	1
#2	Nanofiltration (NF) Testing with Full length single tube membrane testing at up to 1,500 psig and 200°C	1
#3	Multiple tube bundle fabrication (MR and NF membranes) for testing under target operating conditions.	1
#4	Multiple Tube Bundle Demonstration Unit Construction Target is ~0.1 to 1 lb/hr DMC production.	2
#5	Operation of the Multiple Tube Bundle Demonstration Unit in MR & NF modes	2
#6, #7, #8	Optimize and update process flow diagram and TEA. Continue commercialization development.	1,2

M&P TECHNOLOGY Phase II Program

Phase II Project Task Plan



Project Progress and Status

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Current Progress

Task 1. Membrane Preparation

Phase II Milestones

MII-01. MR Membrane Fabrication (30”) (Target: >30 on-spec tubes; He/N_2 >150)

Membrane ID [-]	Performance 250°C He [GPU]	He/N_2 [-]
CMS-30Rg-2001	426	217
CMS-30Rg-2002	303	292
CMS-30Rg-2014	414	170
CMS-30Rg-2018	346	158
CMS-30Rg-2019	422	285
CMS-30Rg-2020	112	216
CMS-30Rg-2021	281	189
CMS-30Rg-2022	388	248
CMS-30Rg-2027	232	355
CMS-30Rg-2030	342	162
CMS-30Rg-2031	423	227
CMS-30Rg-2034	403	153
CMS-30Rg-2036	443	273
CMS-30Rg-2037	399	325
CMS-30Rg-2038	261	338
CMS-30Rg-2040	361	190
CMS-30Rg-2041	299	257
CMS-30Rg-2043	564	369
CMS-30Rg-2044	303	280
CMS-30Rg-2045	542	431
CMS-30Rg-2046	231	564
CMS-30Rg-2047	524	183

Membrane ID [-]	Performance 250°C He [GPU]	He/N_2 [-]
CMS-30Rg-163	382	866
CMS-30Rg-164	432	319
CMS-30Rg-168	422	446
CMS-30Rg-169	428	614
CMS-30Rg-188	370	347
CMS-30Rg-189	399	188
CMS-30Rg-196	445	215
CMS-30Rg-139	460	188
CMS-30Rg-193	556	174
CMS-30Rg-199	445	412
CMS-30Rg-202	339	112
CMS-30Rg-203	589	209
CMS-30Rg-205	334	338
CMS-30Rg-208	375	336
CMS-30Rg-211	395	307
CMS-30Rg-212	456	257
CMS-30Rg-214	501	479
CMS-30Rg-215	383	213
CMS-30Rg-217	445	234

MR Target: He/N_2 >150

MR Water Separation
Typical Selectivities

Vapor	Kinetic Diameter [Å]	Permeance [GPU]	Selectivity [H_2O/x]
Water	2.6	~80% He Permeance	-
MeOH	3.8 to 4.1	0.55 to 1.0	>300
DMC	>4.6 to 6.3	0.26 to 0.54	>500

Operating Conditions
160°C; 350 to 450psig

Current Progress

Task 1. Membrane Preparation

✓

Phase II Milestones

MII-02. NF Membrane Fabrication (30”): Target: >30 on-spec tubes; >85% DMC rejection)

1st Generation NF Membranes

Membrane ID	250°C N_2/SF_6	Total Flux [kg/m²/hr]	DMC Rejection
182NF	81	0.27	97.2%
183NF	85	0.23	96.7%
186NF	341	0.31	93.3%
191NF	80	0.44	97.1%
199NF	156	0.51	97.7%
203NF	180	0.44	98.7%
205NF	38	N/A	N/A
206NF	161	0.44	94.3%
207NF	155	0.39	96.6%
208NF	63	0.33	98.8%
209NF	35	0.29	98.0%
210NF	53	0.39	98.9%
213NF	204	0.41	97.6%
215NF	38	0.45	97.7%
059NF	11	0.17	83.1%
067NF	18	0.04	87.3%
068NF	19	0.05	81.8%
070NF	35	0.08	83.8%
111NF	23	0.25	84.1%
119NF	18	0.21	47.4%
120NF	33	0.12	87.7%
122NF	16	0.19	66.7%
124NF	92	N/A	N/A
129NF	30	N/A	N/A
130NF	67	N/A	N/A
131NF	82	N/A	N/A
134NF	11	N/A	N/A

Membrane ID	250°C N_2/SF_6	Total Flux [kg/m²/hr]	DMC Rejection
135NF	46	N/A	N/A
141NF	17	0.16	75.8%
142NF	31	0.39	87.8%
143NF	14	0.21	89.3%
144NF	16	0.28	95.4%
145NF	24	0.13	90.9%
146NF	8	0.18	68.4%
147NF	21	0.16	93.1%
148NF	11	0.21	94.9%
149NF	81	0.57	87.1%
150NF	10	0.12	84.8%
151NF	20	0.16	93.9%
153NF	14	0.12	81.7%
154NF	16	0.14	84.6%
162NF	10	0.20	79.5%
158NF	7	0.11	93.1%
166NF	18	N/A	N/A
171NF	66	N/A	N/A
172NF	19	N/A	N/A
173NF	22	N/A	N/A
175NF	20	0.27	93.1%
178NF	38	0.34	89.8%
179NF	38	0.36	86.4%
184NF	0	0.19	94.1%
185NF	0	0.22	96.1%
197NF	0	N/A	N/A

2nd Generation Membranes

8- to 10-fold Increase in Flux

		30% DMC/Methanol		
		Pre-Bundle Performance		
Membrane ID [#]	Temp [°C]	TMP [psig]	Total Flux [kg/m²/hr]	DMC Rejection [%]
2nd Generation NF Membrane				
5NF	160	300	7.10	83.4
10NF	160	[illegible]	2.80	96.5
16NF	160	[illegible]	6.90	80.7
23NF	160	300	10.20	81.5
1st Generation NF Membrane				
144NF	160	650	0.28	95.4
184NF	160	[illegible]	0.19	94.1

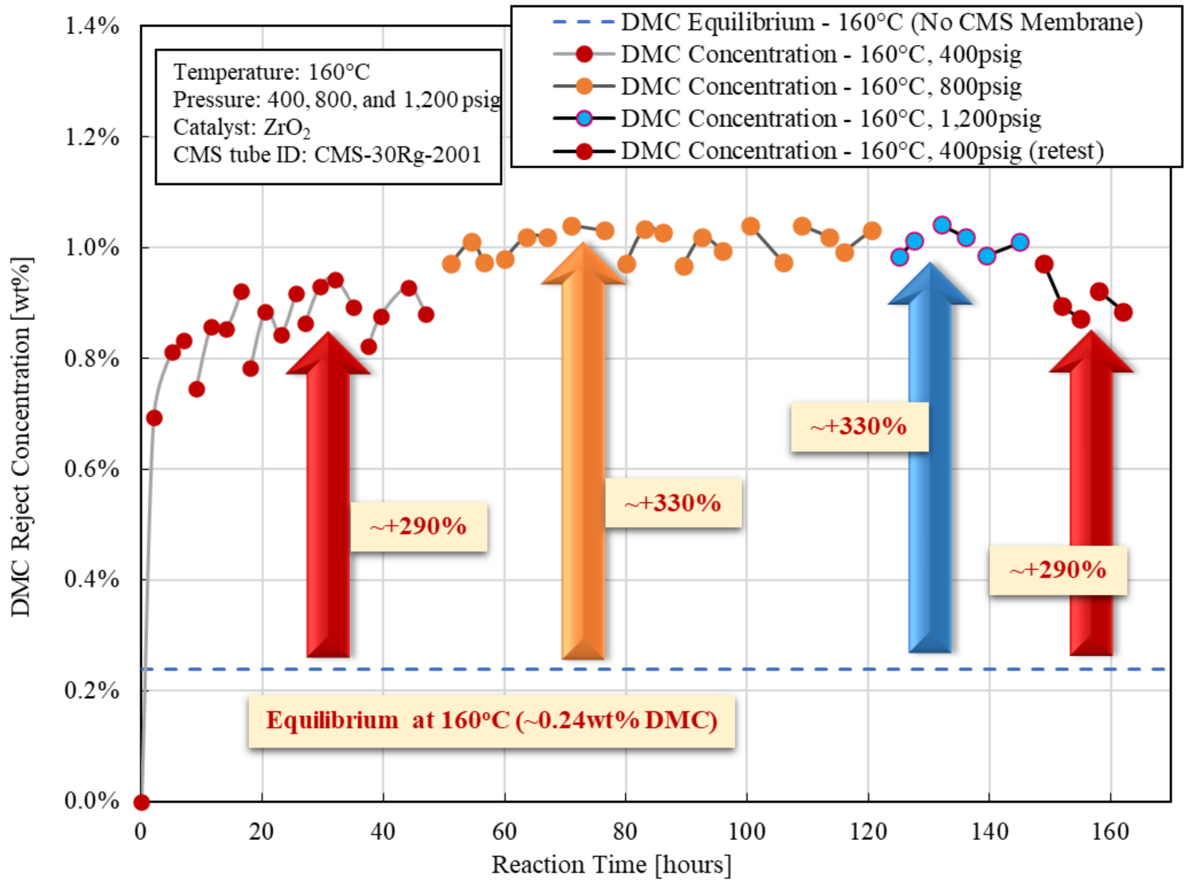
NF Target: >85% DMC Rejection

Current Progress

Task 2. MR Membrane Performance Testing

Phase II Milestones

MII-03 to -05. MR Membrane Performance Verification at Target Conditions (Single Tube)

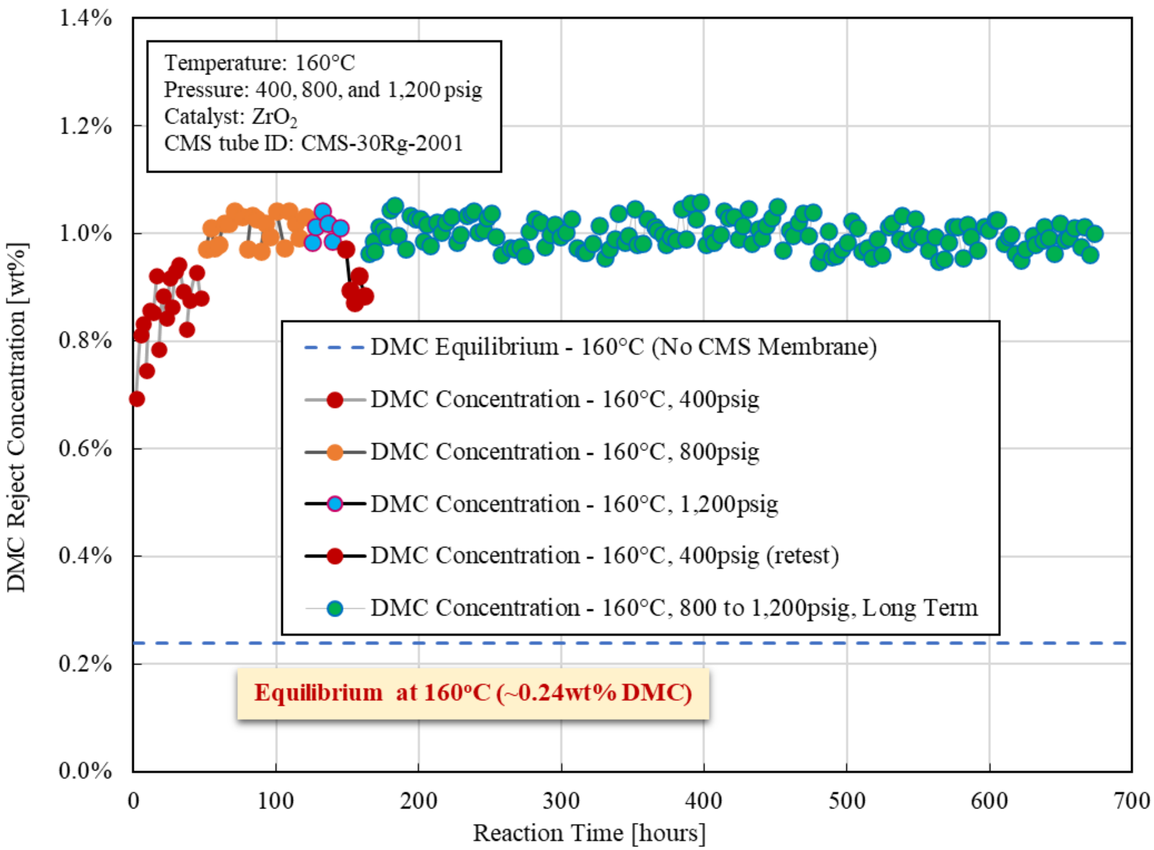


Current Progress

Task 2. MR Membrane Performance Testing

Phase II Milestones

MII-06. MR Membrane Long Term Performance Challenge Testing (Single Tube) ✓



Performance Stability Verification

Pure component He and N_2 permeance (250°C, 50psig) of the CMS-30Rg-2002 membrane before and after ca. 700 hours of membrane reactor performance stability testing.

Part ID [-]	He [GPU]	N_2 [GPU]	He/N_2 [-]
Pre-MR	426	1.96	217
Post-MR	397	1.45	274

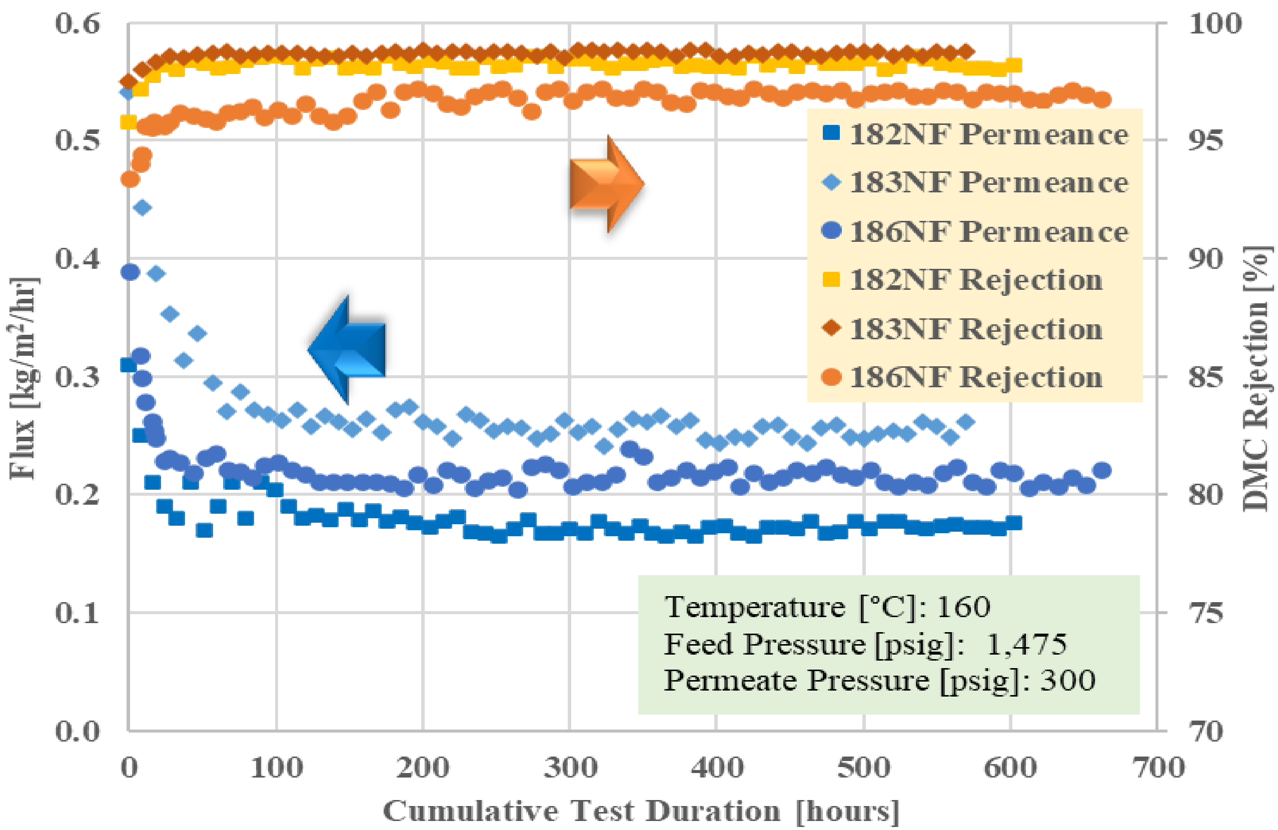
Current Progress

Task 2. NF Membrane Performance Testing

Phase II Milestones

MII-07 to 10. NF Membrane Performance Verification; Long Term Stability (Single Tube)

1st Generation NF Membranes



Current Progress

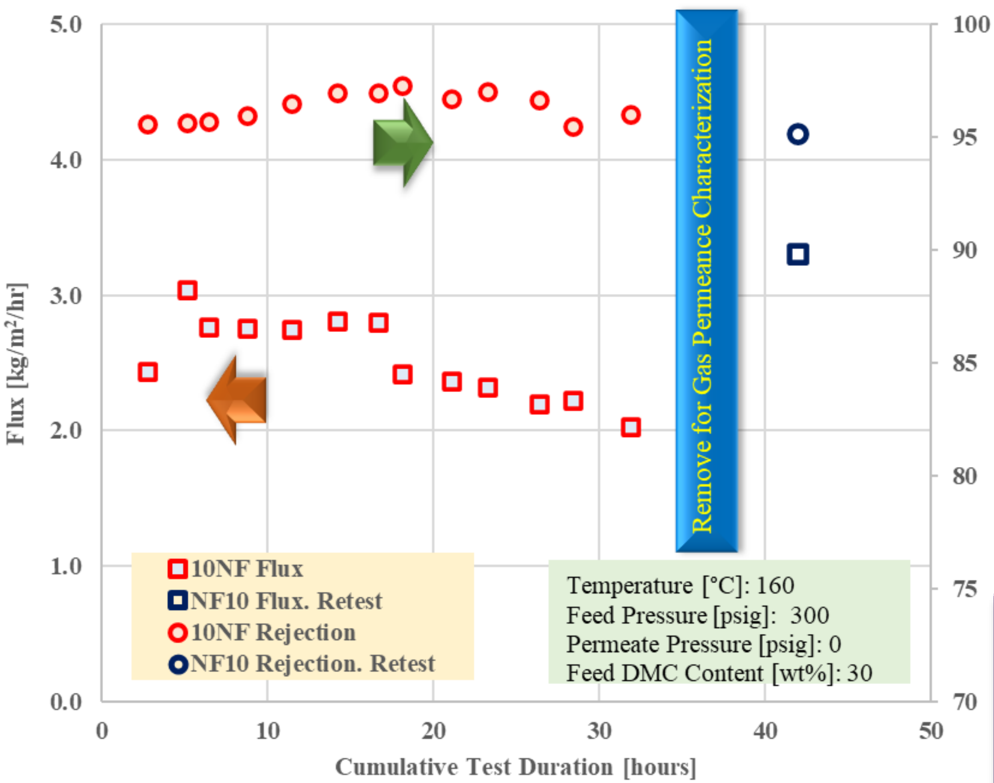
Task 2. NF Membrane Performance Testing

Phase II Milestones

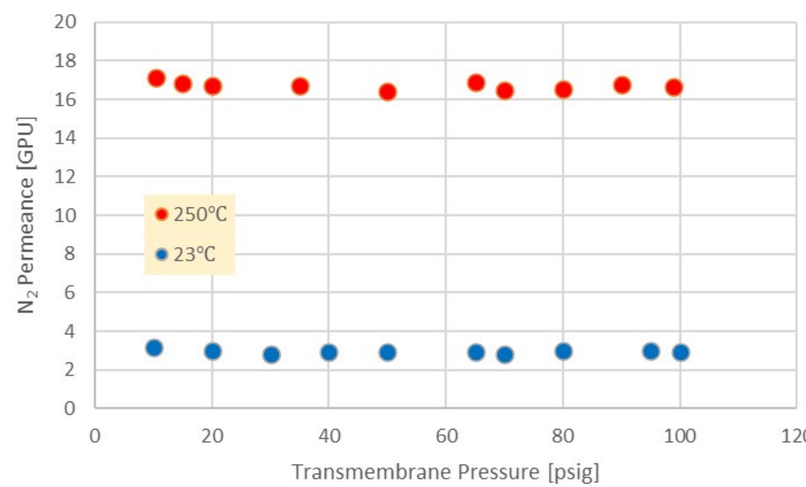
MII-07 to 10. NF Membrane Performance at Target Conditions; Long Term Stability (Single Tube)

2^{nd} Generation NF Membranes

MeOH/DCM Nanofiltration



N_2 Permeance at RT and 250°C



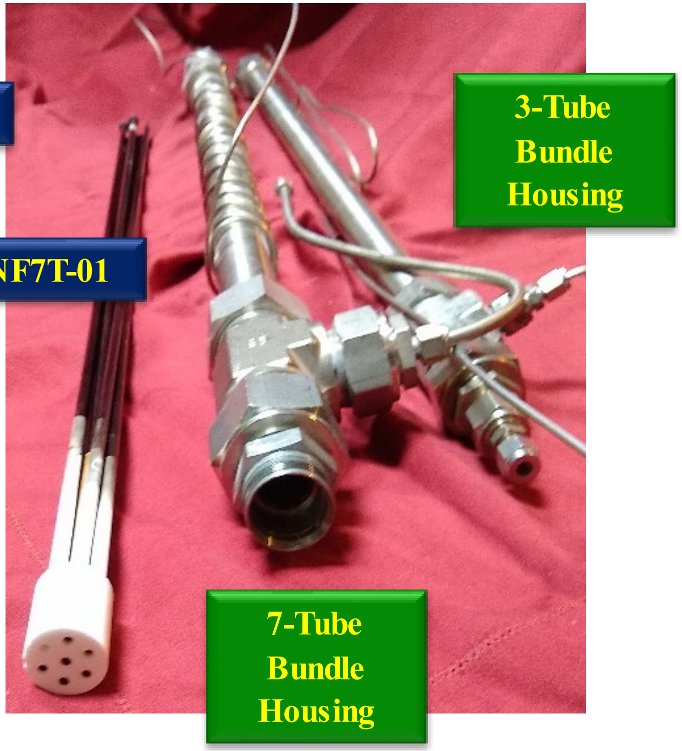
1. **No positive slope:** Minimal viscous flow defects.
2. **Very high temperature sensitivity:** Molecular sieving dominant N_2 transport mechanism versus Knudsen flow (defects)

Current Progress

Task 3. Multiple Tube Bundle Fabrication

Phase II Milestones

MII-11 and -12. Complete Fabrication of Multiple Tube MR and NF Bundles



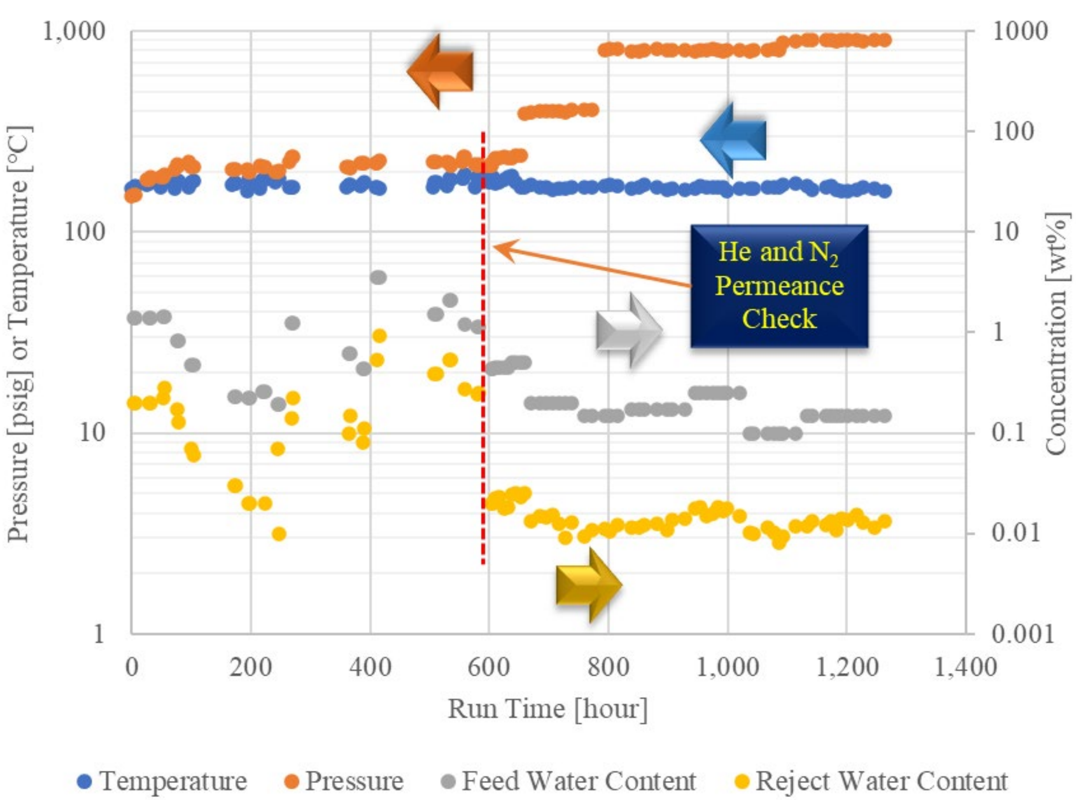
Current Progress

Task 5. Multiple Tube Bundle Performance: MR Operating Conditions

Phase II Milestones

MII-15. MR Membrane Performance and Long Term Stability (Multiple Tube Bundles)

Target: >3 to >6 months of service; performance at 80% of the single tube



Part ID: MR3T-02
3-tube Bundle

Performance Stability Verification

He and N_2 QC data for CMS membranes single tubes and the 3-tube membrane bundle MR3T-02 as-prepared and following ca. 600 hours of MR service testing. Test conditions: 250°C and 50psig.

Part ID [-]	He [GPU]	N_2 [GPU]	He/N_2 [-]
CMS-70 [2040]	360	1.76	205
CMS-82 [2001]	453	2.15	211
CMS-93 [2031]	425	2.21	193
MR3T-02 (as-prepared)	399	1.94	206
MR3T-02 (~600 hours MR service)	436	1.5	296

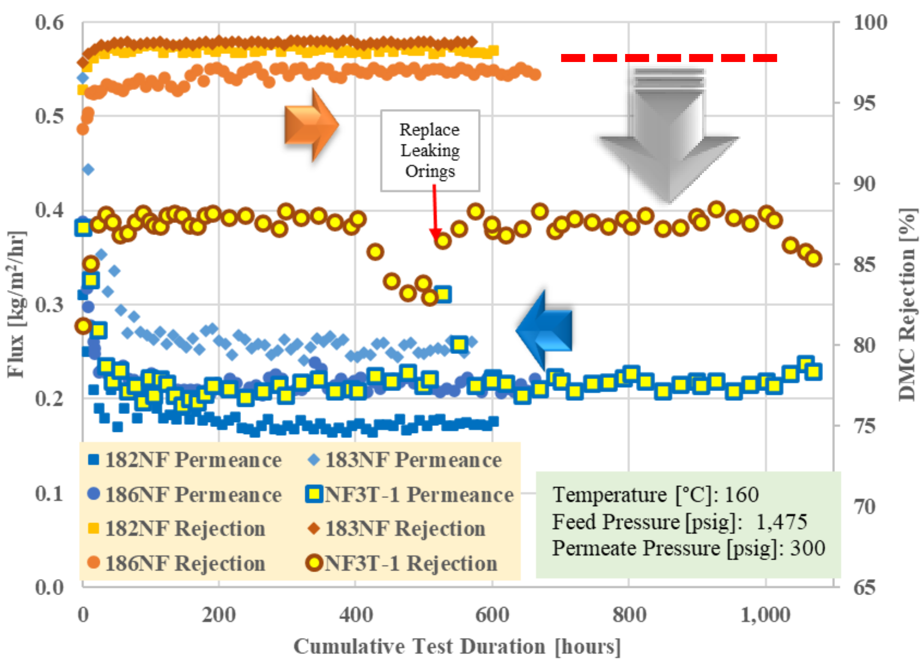
Current Progress

Task 5. Multiple Tube Bundle Performance: MR Operating Conditions

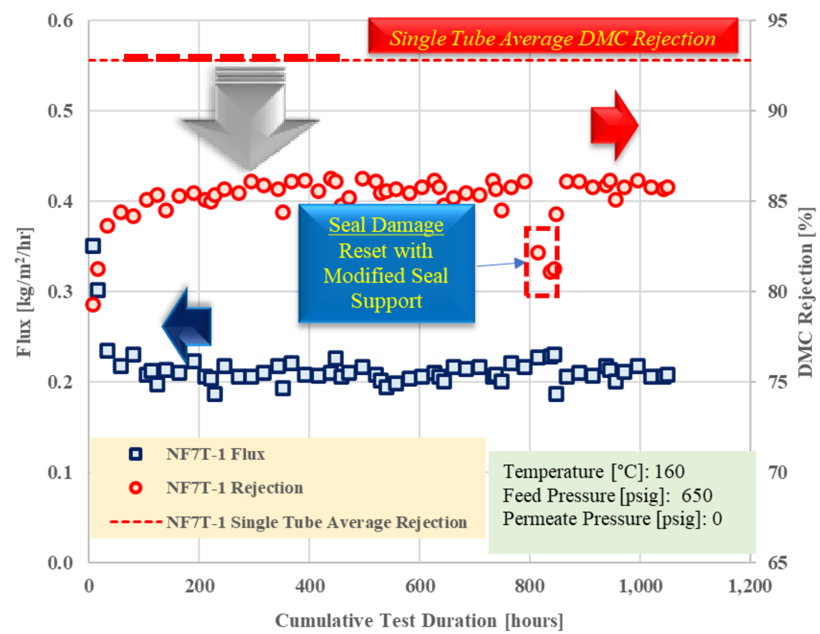
Phase II Milestones

MII-16. NF Membrane Performance and Long Term Stability (Multiple Tube Bundles)
Target: >3 to >6 months service; performance within 80% of single tube

Part ID: NF3T-01
3-tube Bundle



Part ID: NF7T-01
7-tube Bundle



Next Step

Task 6. Process Design Update; TEA Update

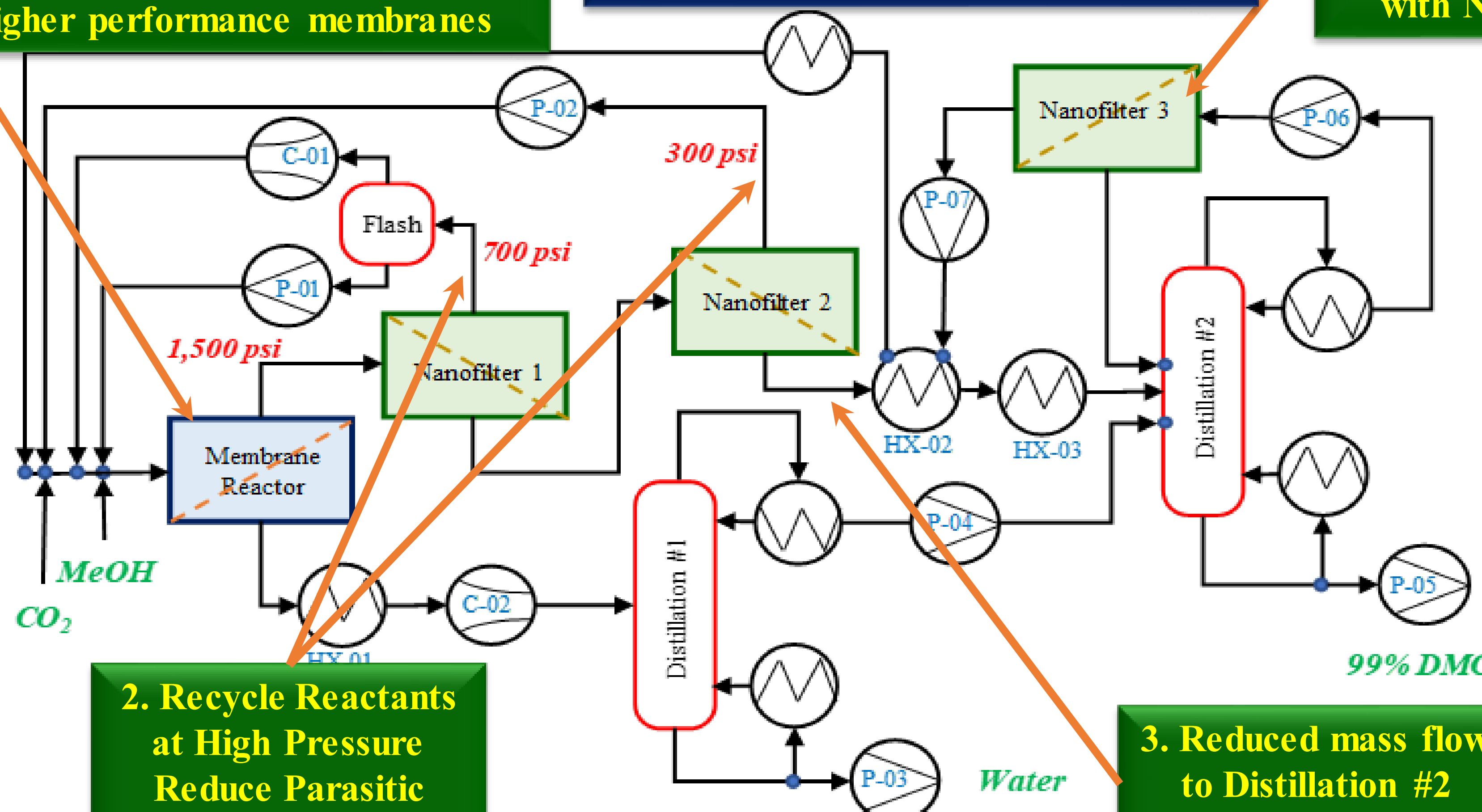
Phase II Milestones

MII-17. Process Flow Diagram Updated

MII-18. TEA Update

1. Eliminate Azeotropic Distillation with NF3

4. Improved conversion with more aggressive MR operating conditions; higher performance membranes



2. Recycle Reactants at High Pressure Reduce Parasitic Power Consumption with NF1 and NF2

3. Reduced mass flow to Distillation #2 with NF1 and NF2

M&P TECHNOLOGY Summary

Summary of MPT Process Impacts and Advantages

MPT Ceramic Membrane Enhanced DMC Production Process

Impacts, Advantages, Key Takeaway

MPT Process Features	Impacts and Advantages
Membrane Reactor subsystem operates at high temperature and pressure.	➢ Enhanced methanol conversion ➢ Enhanced DMC concentration ➢ Reduced "loads" on downstream unit operations
NF subsystem operates at the MR conditions (T and P)	➢ Direct integration with the MR without the need for thermal or pressure cycling ➢ Reagent recycle at reactor operating T and P ➢ Further "load" reduction on downstream units
NF subsystem shows excellent DMC rejection	➢ Improved reactant and product separation ➢ Azeotropic distillation eliminated
NF subsystem permeate operated at elevated pressures	➢ Substantially reduced CO_2 recycle recompression costs.
Azeotropic Distillation eliminated	➢ Significantly reduce capital cost and energy consumption.

Questions?

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Appendix

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Poly-generation: Advanced Inorganic Membranes

Project Team

Team Member	CV/Capabilities	Responsibilities
	MPT has nearly 30 years of experience in inorganic membrane materials and process development in high temperature, high pressure, aggressvive chemicals gas and liquid separations. Since 2003 MPT has been a commercial manufacturer and supplier of ceramic membrane technology into a wide range of ultrafiltration applications.	Project management; membrane bundle and housing development; performance testing; TEA update
	TechOpp Consulting has over 10 years of experience in transitioning new technologies from ideas to products by targeting the right opportunities, securing funding, establishing partnerships, and engaging with the customer to understand the application requirements.	Discretionary Commercialization Assistance provider

M&P TECHNOLOGY BACKGROUND

Markets: DMC Current and Potential Demand

Current Demand at ~$0.45/lb

Potential Demand at <$0.35/lb

Market Segment/Customer	Competing Chemical	Current DMC Demand [MM lb/yr]	Potential DMC Demand [MM lb/yr]
Polycarbonate/ Polyurethane	Phosgene; isocyanate	375	>4,500
General Solvent (Paints, coatings, resins, etc.)	Ketones such as acetone, MEK, MiBK, many others	233	3,100
Fuel Additive	MTBE; ethanol; etc.	36	15,000
Lithium Ion Battery Solvent	N/A	57	5 to 10% CAGR
Other	N/A	~100	N/A
	Total	**~800**	**22,600**

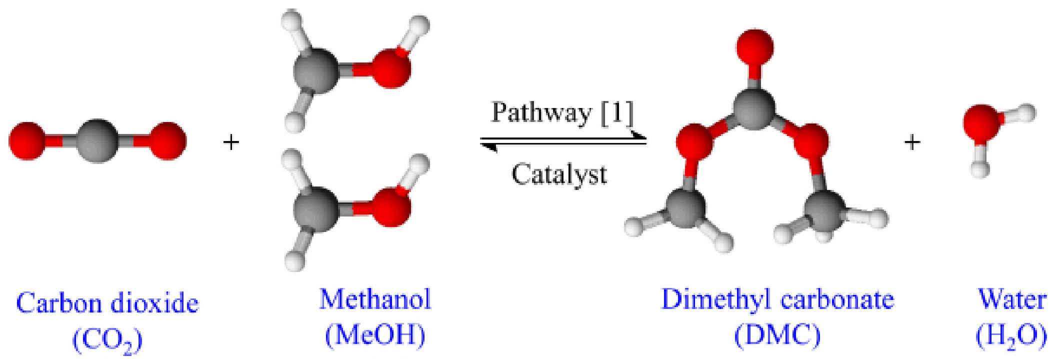
~$300MM/yr

~$6,000MM/yr

Potential ~30-fold Increase in Demand

M&P TECHNOLOGY BACKGROUND

Direct Synthesis of DMC: Advantages and Challenges



Advantages of Direct Synthesis of DMC

1. **Green Process:** Produced from CO_2 and biomass derived methanol
2. **Non-hazardous:** Reactants are non-hazardous versus other synthetic pathways.
3. **Safety:** Considerably safer operating conditions than commercial processes.

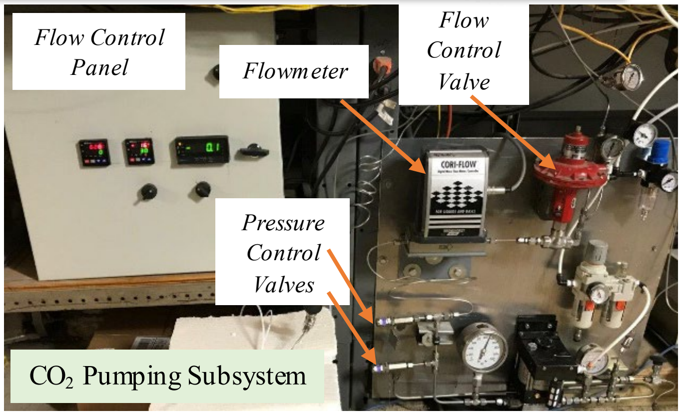
Challenges of Direct Synthesis of DMC

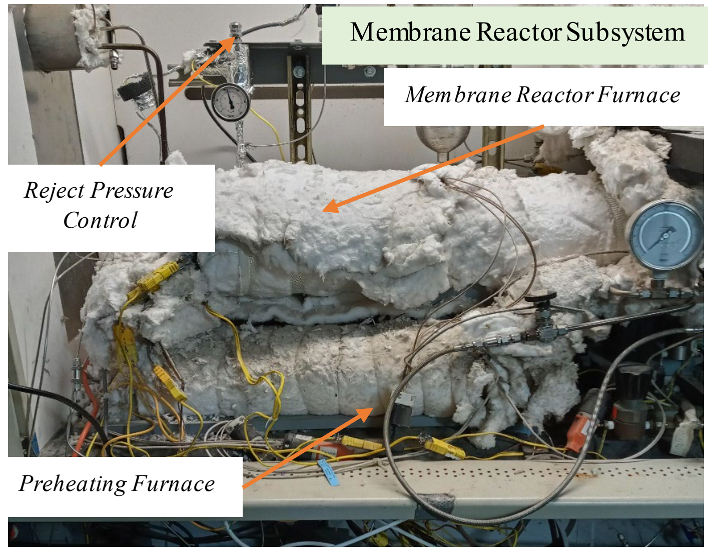
1. **Equilibrium limitation:** Conversions to DMC limited to under 1 to 3%
2. **Methanol/DMC Azeotrope:** Multiple column azeotropic distillation required.
3. **Energy intensive:** Combination of these problems drives production cost

Current Progress

Task 4. System Construction and Testing

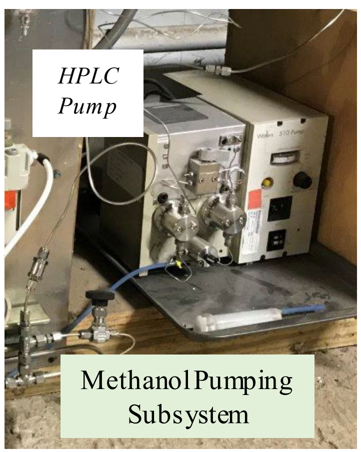
Membrane Reactor System



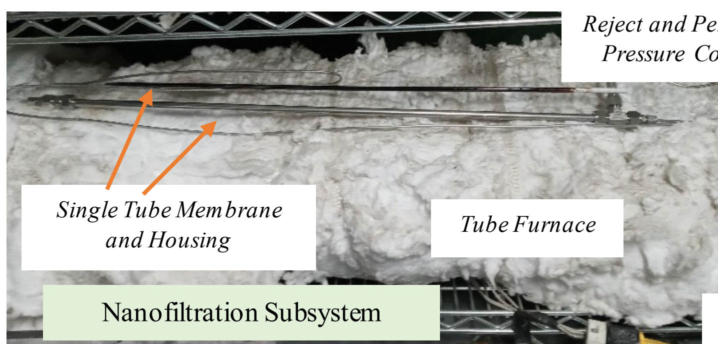


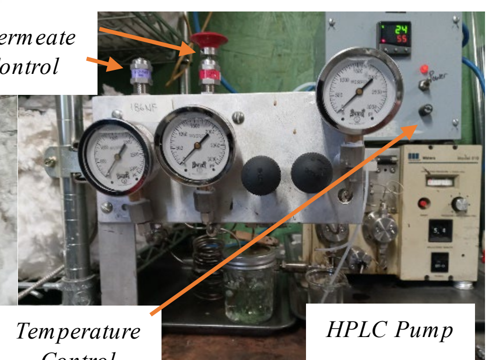
Phase II Milestones

MII-11 to 14.
System upgrade/testing.
200°C; 1,500psig
7-tube Bundles



Nanofiltration System





End