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, 2022 (24 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

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

Synthesis: Dimethyl Carbonate (DMC)

	route	description	reactions
	~~I~~	~~methanol phosgenation~~	~~$\boxed{COCl_2} + 2\,CH_3OH \rightarrow (CH_3O)_2CO^a + \boxed{2HCl}$~~
★	II	oxidative carbonylation of methanol (Eni)	$\boxed{CO} + 2CH_3OH + \boxed{O_2} \rightarrow (CH_3O)_2CO^a + H_2O$
★	III	oxidative carbonylation of methanol via methyl nitrite (Ube)	$N_2O_3 + 2CH_3OH \rightarrow 2CH_3ONO + H_2O$ $\boxed{2CH_3ONO} + \boxed{CO} \rightarrow (CH_3O)_2CO^a + NO$
★	IV	ethylene carbonate transesterification (Asahi)	$\boxed{(CH_2)_2O} + \boxed{CO_2} \rightarrow C_2H_4O$ $C_2H_4O + 2CH_3OH \rightarrow (CH_3O)_2CO^a + (CH_2OH)_2$
?	V	urea transesterification	$2NH_3 + \boxed{CO_2} \rightarrow (NH_2)_2CO + H_2O$ $(NH_2)_2CO + \boxed{CH_3OH} \rightarrow CH_3OCONH_2 + NH_3$ $CH_3OCONH_2 + CH_3OH \rightarrow (CH_3O)_2CO^a + NH_3$
	VI	direct synthesis from CO_2	$\boxed{CO_2} + 2\boxed{CH_3OH} \rightarrow (CH_3O)_2CO^a + H_2O$

Technology Background

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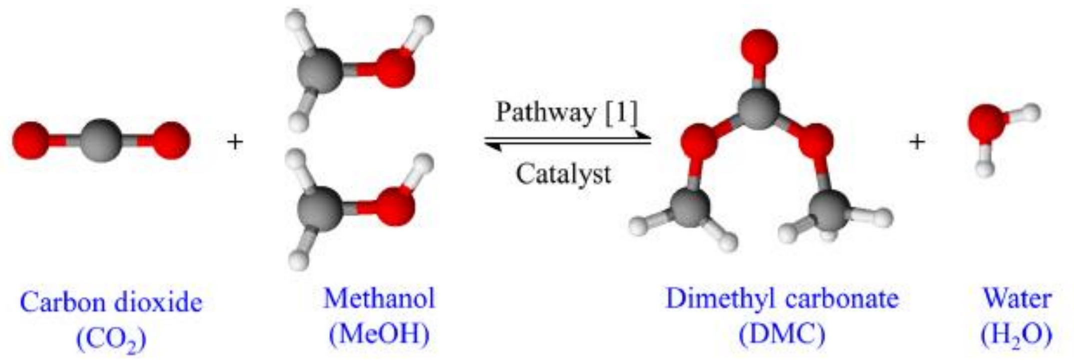
Direct Synthesis of DMC: Advantages and Challenges



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 2 to 5%
2. **Methanol/DMC Azeotrope:** Multiple column azeotropic distillation required.
3. **Energy intensive:** Combination of these problems drives production cost

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

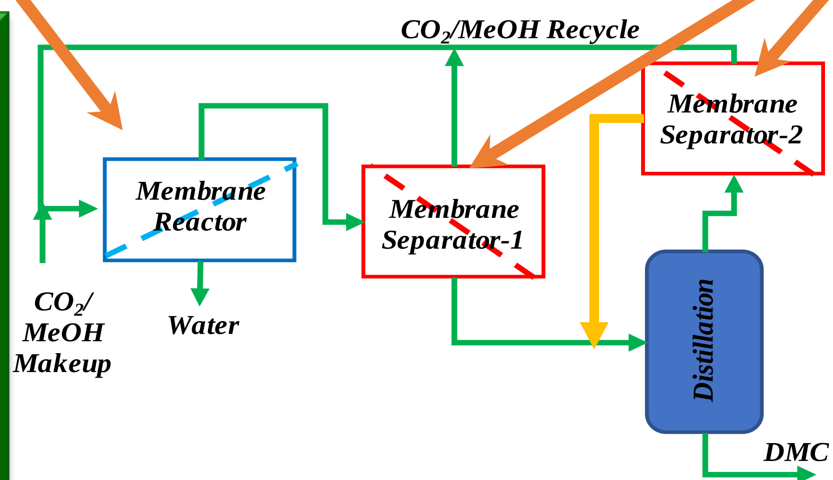
1. Operation Mode: Nanofiltration
2. Azeotrope Break: Remove MeOH (and CO_2) from DMC.
3. Reduced Energy and Cost: Eliminate multiple column azeotrope distillation.

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

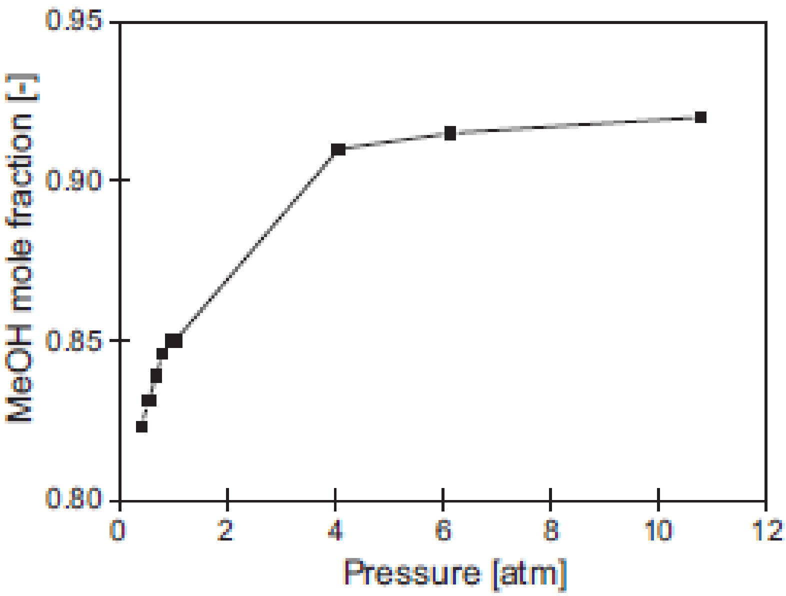
M&P TECHNOLOGY BACKGROUND

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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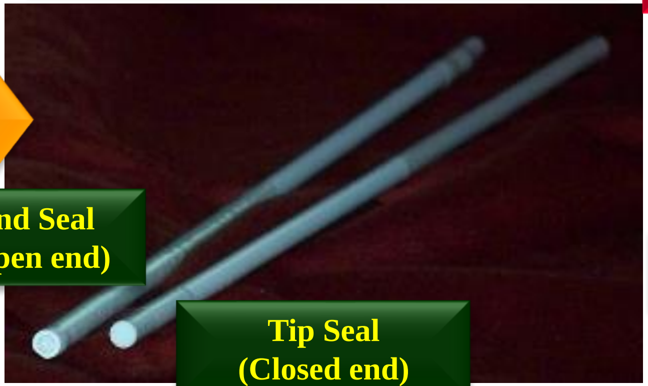
M&P TECHNOLOGY BACKGROUND

Advanced Inorganic Molecular Sieving Membranes

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

Ceramic Tube Extrusion

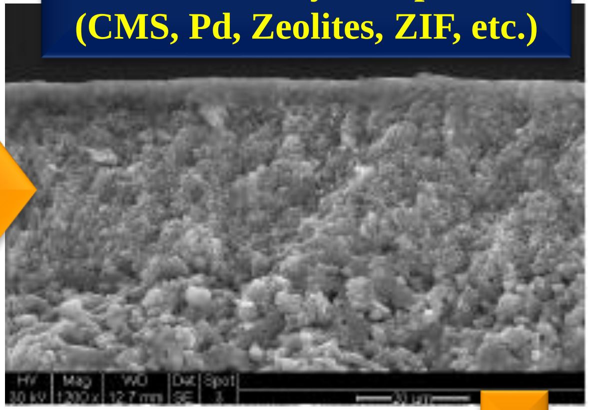
Intermediate Layer Deposition
+
Non-porous Tip and End Seals



End Seal (Open end)

Tip Seal (Closed end)

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



Package into Multiple Tube Bundle

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

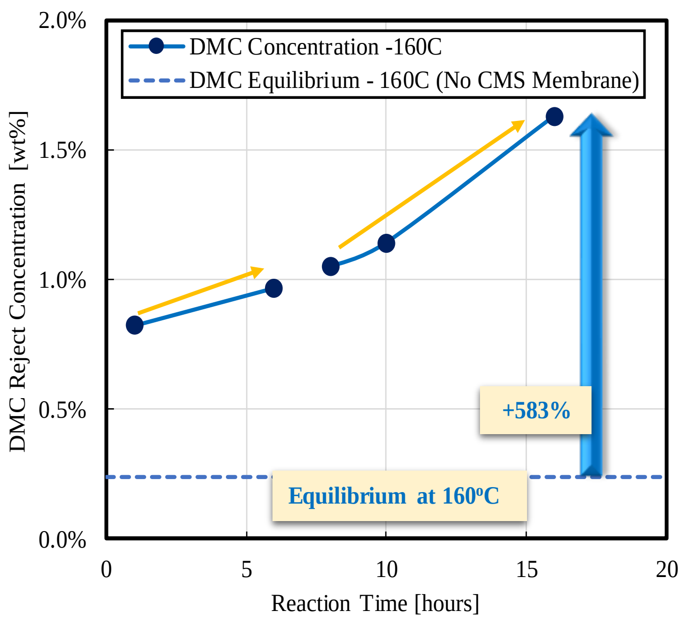
M&P TECHNOLOGY BACKGROUND

CMS Membranes in Direct Synthesis of DMC. *Proof of Concept*

Phase I Results

MR Water Separation

160ºC; 350 to 450psig

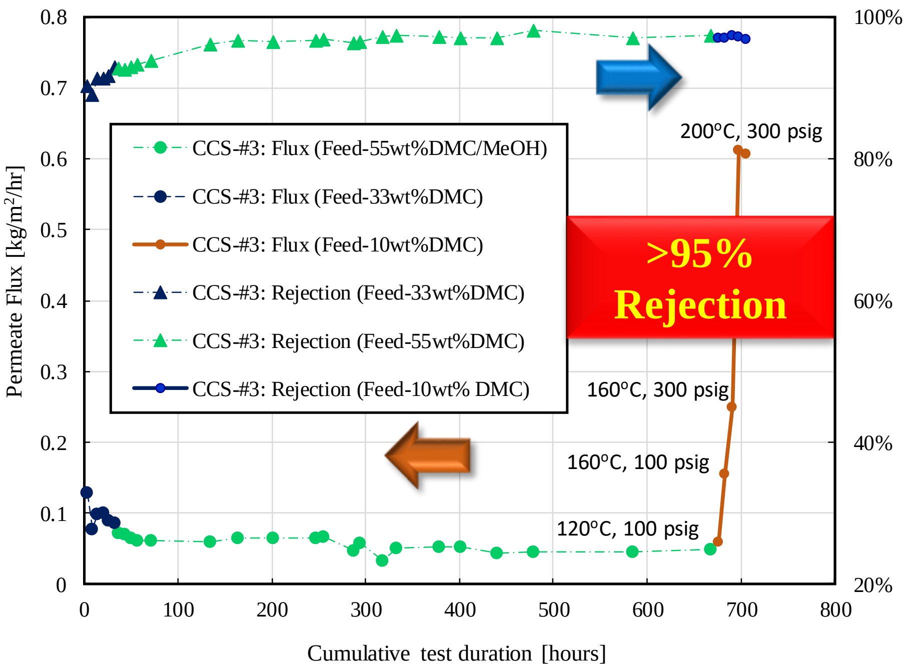


Vapor	Kinetic Diameter [Å]	Permeance [GPU]	Selectivity [H_2O/x]
Water	2.6	230 to 280	-
MeOH	3.8 to 4.1	0.55 to 1.0	>290
DMC	>4.6 to 6.3	0.26 to 0.54	>530

Phase I Results

NF MeOH/DMC Separation

120 to 200ºC; 100 to 300psig



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

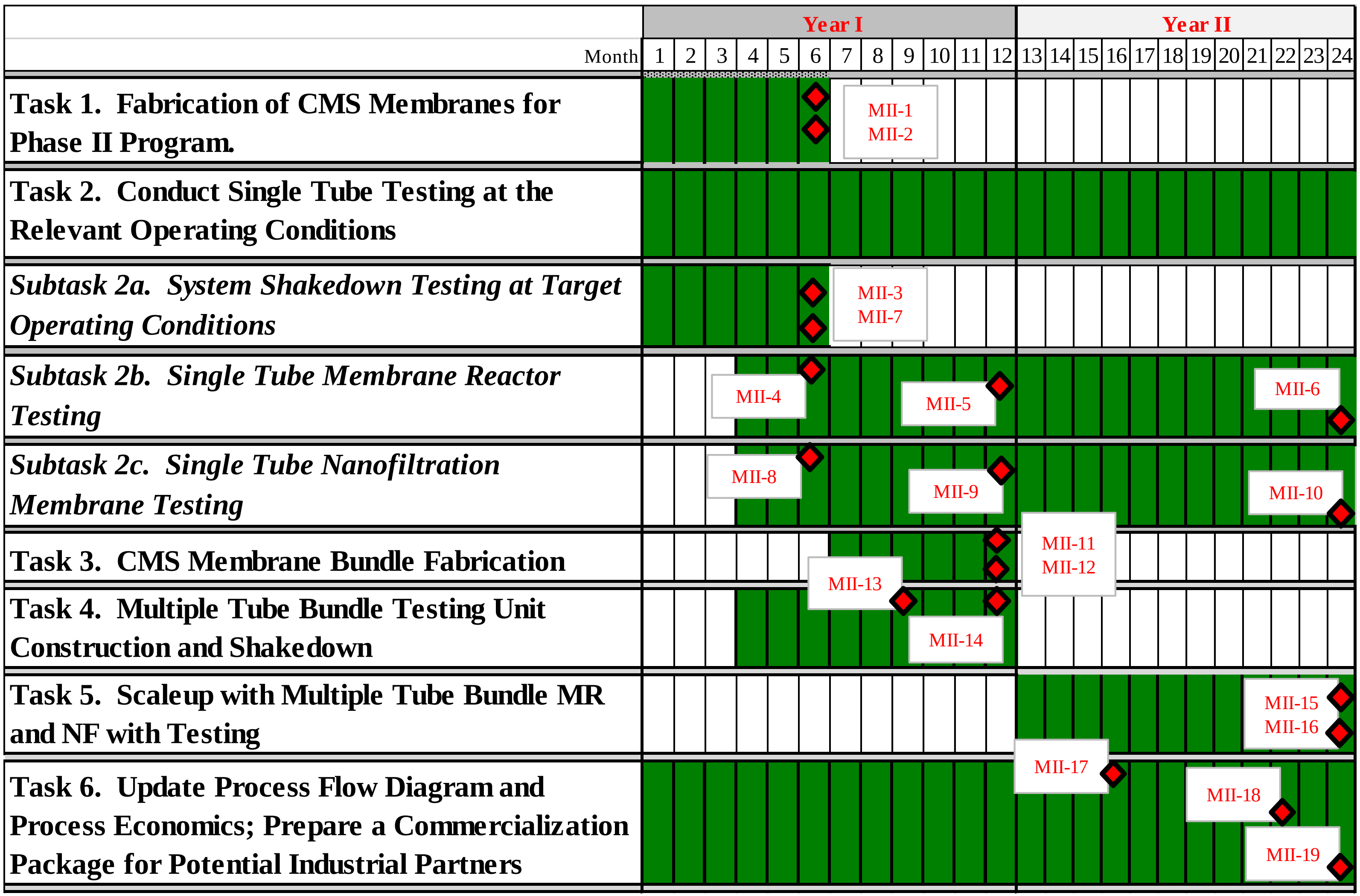
Process Scaleup at Target Operating Conditions

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^{o}C	1
#2	Nanofiltration (NF) Testing with Full length single tube membrane testing at up to 1,500 psig and 200^{o}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. CMS Membrane Preparation

Phase II Milestones
MII-01. MR Membrane Fabrication

Membrane ID [-]	Permeance at 250°C He [GPU]	N_2 [GPU]	Selectivity He/N_2 [-]
CMS-30Rg-2001	426	1.96	217
CMS-30Rg-2002	303	1.04	292
CMS-30Rg-2014	414	2.44	170
CMS-30Rg-2018	346	2.19	158
CMS-30Rg-2019	422	1.48	285
CMS-30Rg-2020	112	0.52	216
CMS-30Rg-2021	281	1.48	189
CMS-30Rg-2022	388	1.57	248
CMS-30Rg-2027	232	0.65	355
CMS-30Rg-2030	342	2.11	162
CMS-30Rg-2031	423	1.87	227
CMS-30Rg-2034	403	2.62	153
CMS-30Rg-2036	443	1.62	273
CMS-30Rg-2037	399	1.23	325
CMS-30Rg-2038	261	0.77	338
CMS-30Rg-2040	361	1.90	190
CMS-30Rg-2041	299	1.17	257
CMS-30Rg-2043	564	1.53	369
CMS-30Rg-2044	303	1.08	280
CMS-30Rg-2045	542	1.26	431
CMS-30Rg-2046	231	0.41	564
CMS-30Rg-2047	524	2.87	183

MR Target: He/N_2 >150

Phase II Milestones
MII-02. NF Membrane Fabrication

Membrane ID	Gas Permeance [GPU] He	N_2	SF_6	Selectivity He/N_2	N_2/SF_6
182NF	695	8.8	0.11	78.6	80.9
183NF	892	11.3	0.13	78.9	84.8
186NF	1024	31.7	0.09	32.3	340.9
191NF	1120	47.2	0.59	23.7	79.5
199NF	950	6.9	0.04	137.0	155.7
203NF	955	11.7	0.06	81.8	180.0
205NF	1197	12.6	0.34	94.8	37.6
206NF	832	27.8	0.17	29.9	161.4
207NF	1060	20.4	0.13	51.9	155.2
208NF	1037	12.4	0.20	83.5	62.8
209NF	911	11.3	0.33	80.6	34.6
210NF	1002	6.4	0.12	156.2	52.8
213NF	1123	15.5	0.08	72.4	204.3
215NF	1019	10.2	0.27	99.6	37.8
216NF	1036	10.1	0.05	102.5	192.2
217NF	706	18.6	0.15	38.0	124.0

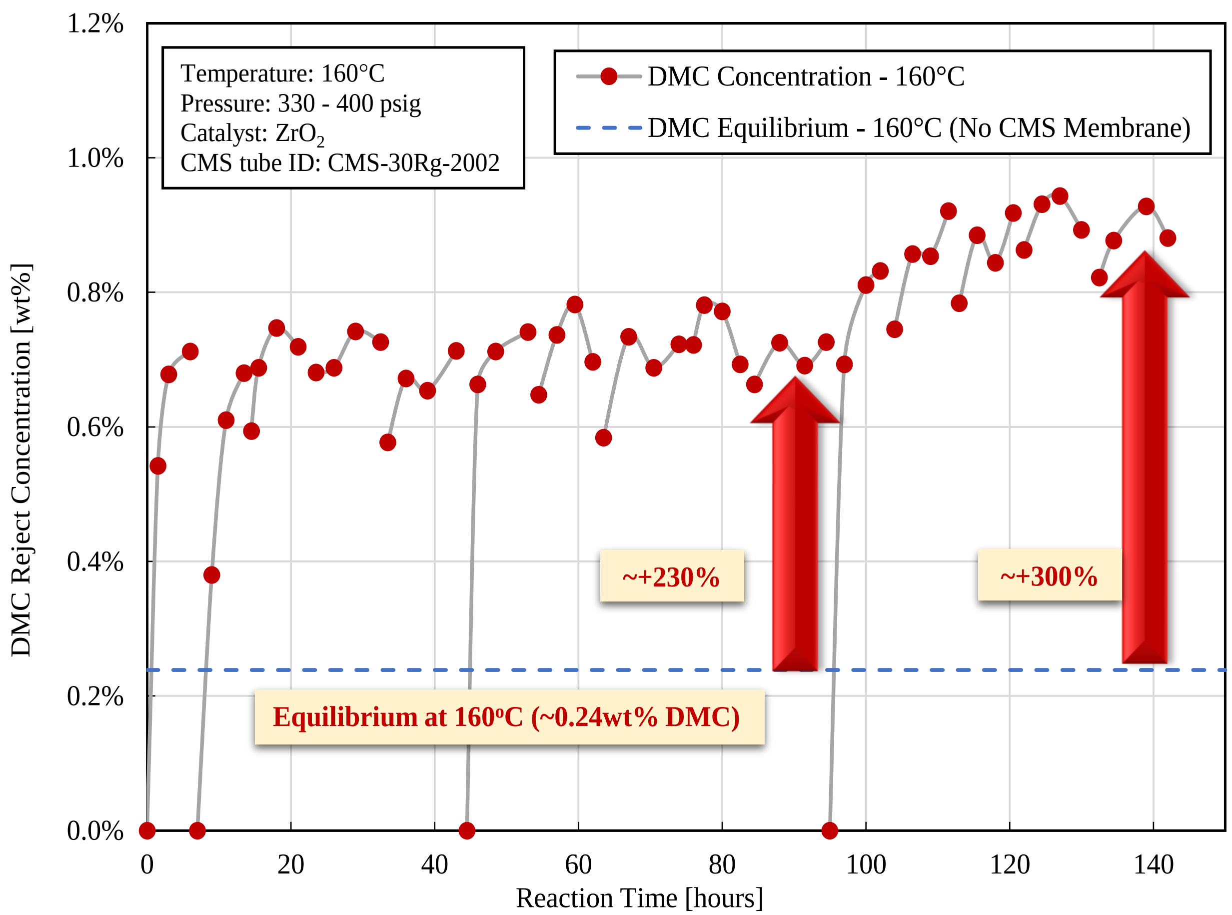
NF Target: N_2/SF_6 >30 to 50

Current Progress

Task 2. MR Membrane Performance Testing

Phase II Milestones

MII-03 to 6. Membrane Performance Verification at Target Conditions; Long Term Stability

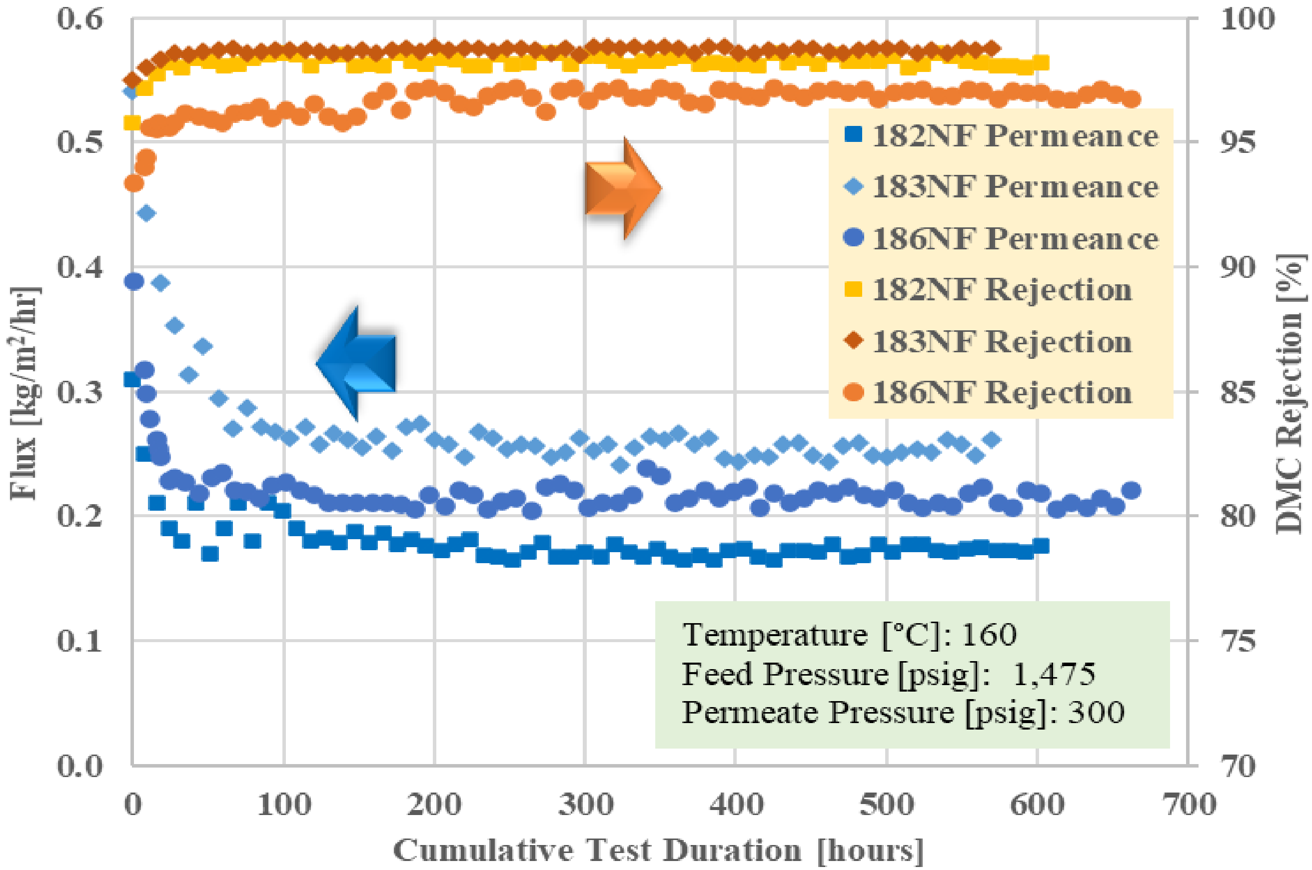


Current Progress

Task 2. NF Membrane Performance Testing

Phase II Milestones

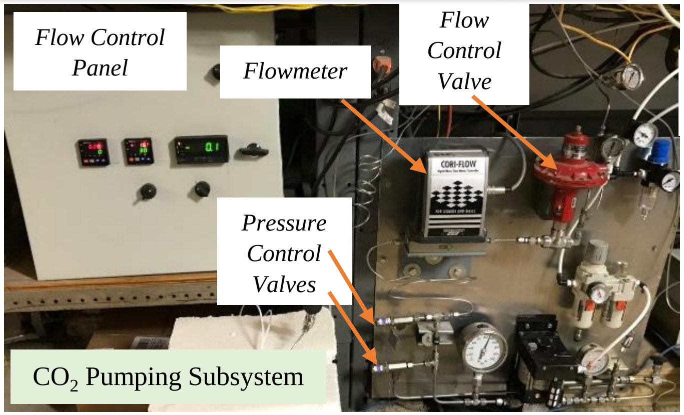
MII-07 to 10. Membrane Performance Verification at Target Conditions; Long Term Stability

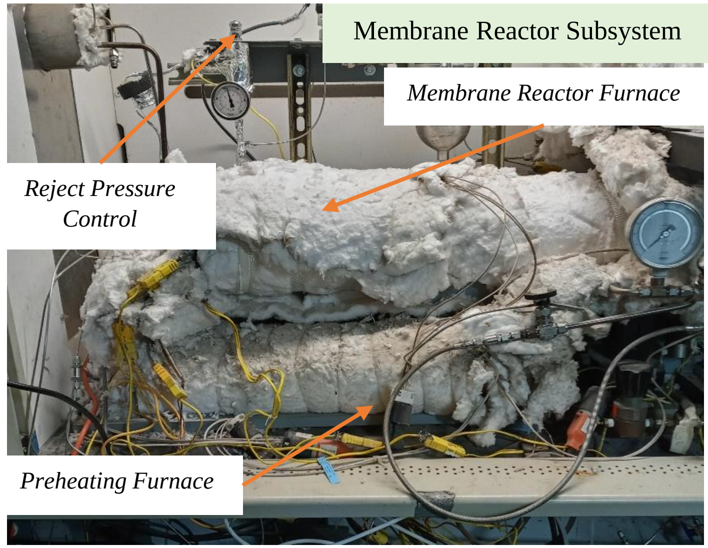


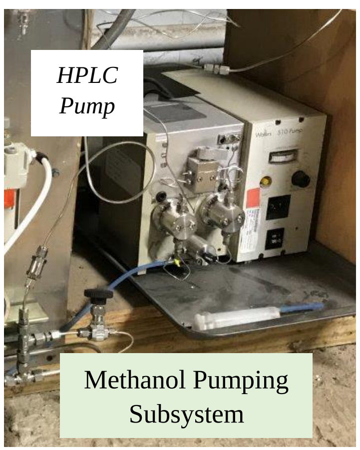
Current Progress

Task 4. System Construction and Testing

Membrane Reactor System



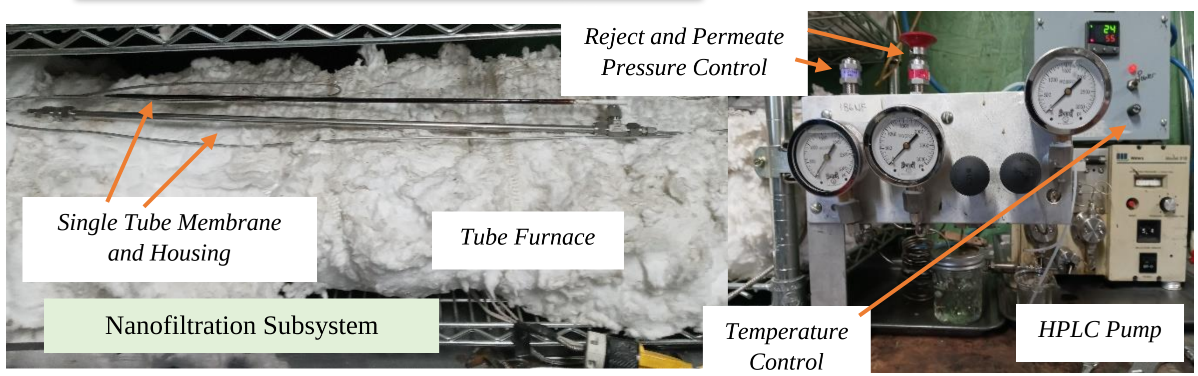




Phase II Milestones

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

Nanofiltration System



Next Step

Task 3. Multiple Tube Bundle Fabrication
Task 5. Multiple Tube Bundle Performance Testing

CMS Bundle Targets

- Full Length (>30”) CMS Tubes
- Full Ceramic Potting
- 3 and 7-Tube Full Ceramic Bundles
- Rating: <500°C; >1,500 psig

Phase II Milestones

MII-11. MR Bundle(s) Fabricated
MII-12. NF Bundle(s) Fabricated
MII-15. Complete MR Bundle Testing
MII-16. Complete NF Bundle Testing

MPT Pilot/Field Testing Modules

Rating: 2,000 psig at 200°C

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

Rating: 1,500 psig; up to 450°C

Next Step

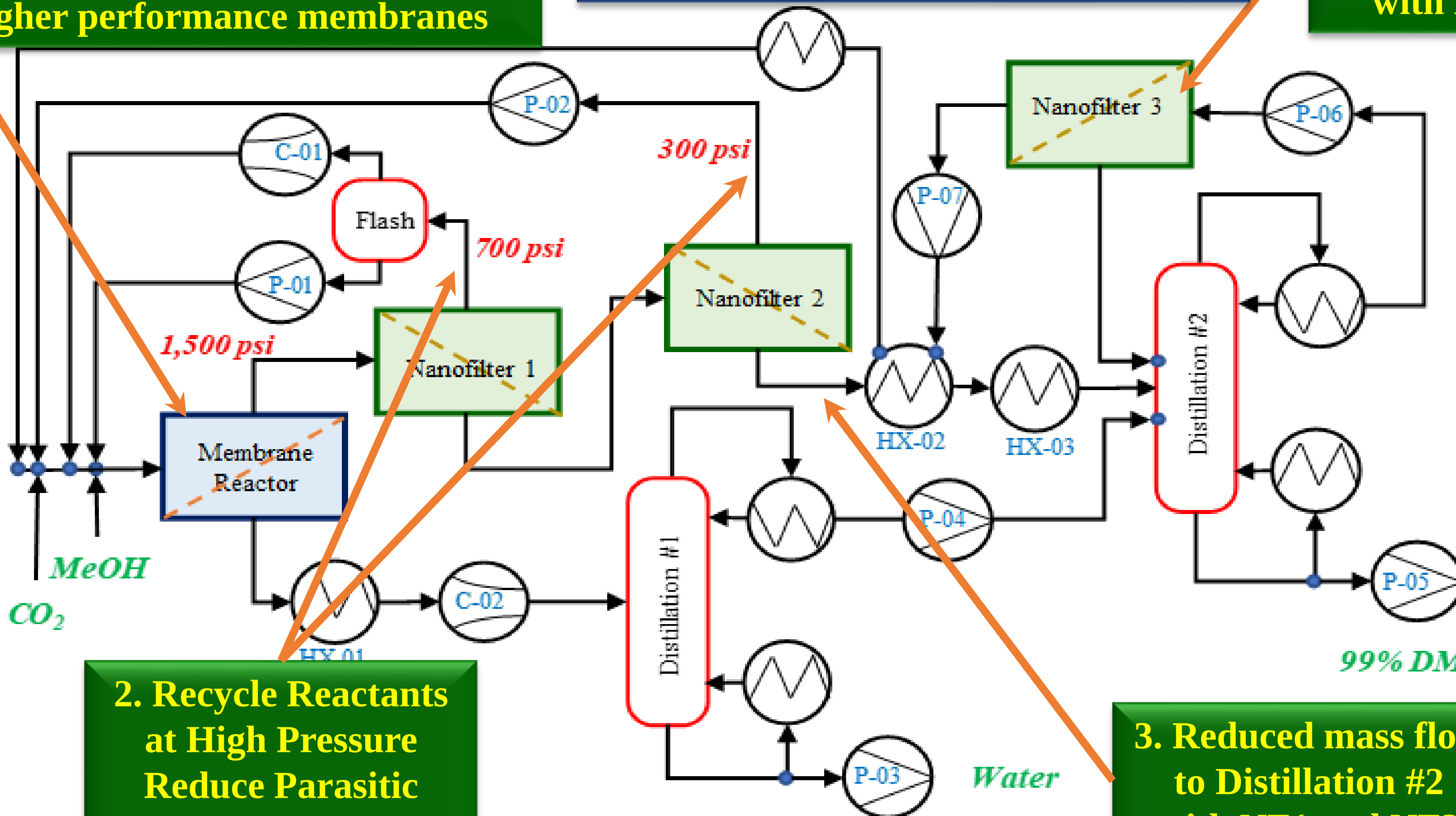
Task 6. Process Design Update; TEA Update

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

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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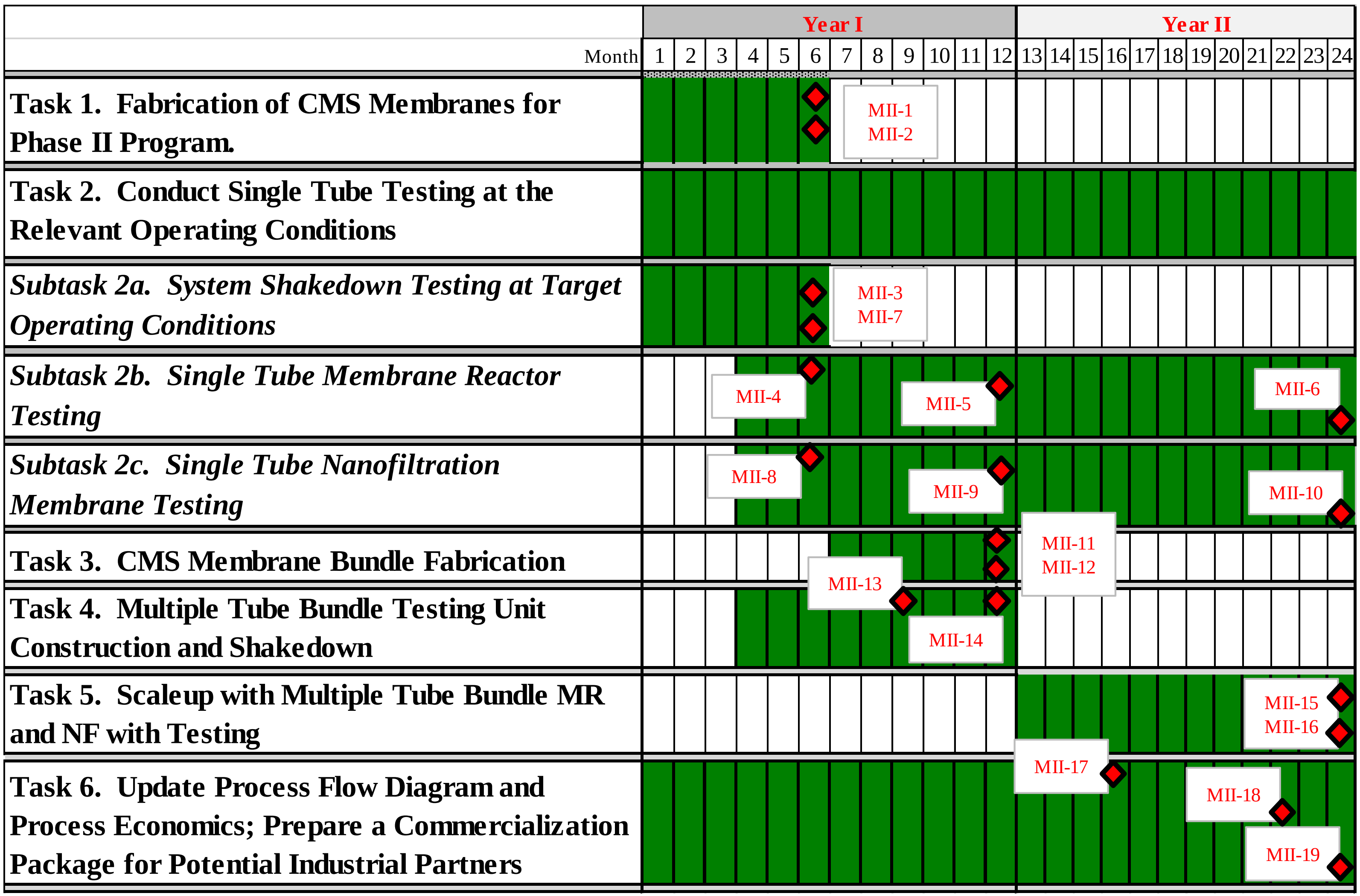
Poly-generation: Advanced Inorganic Membranes

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

Poly-generation: Advanced Inorganic Membranes

Project Timeline and Milestones



End