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

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Project Overview: *Funding, Participants, and Objectives*

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)*

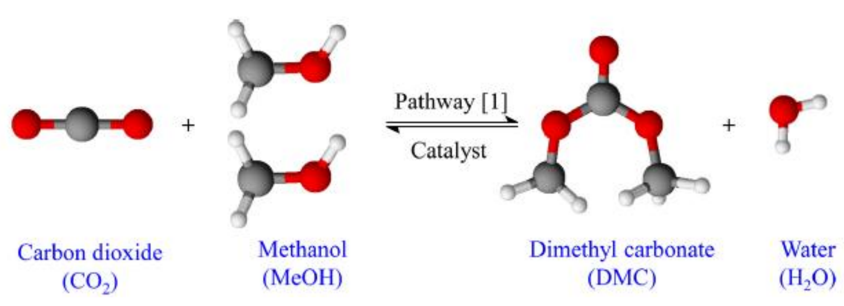
Overall Phase II Project Objectives:

Demonstrate the proposed inorganic membrane-based DMC Production process at the 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.

Background: *Direct Synthesis of DMC: Advantages & 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 yields uncompetitive cost

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

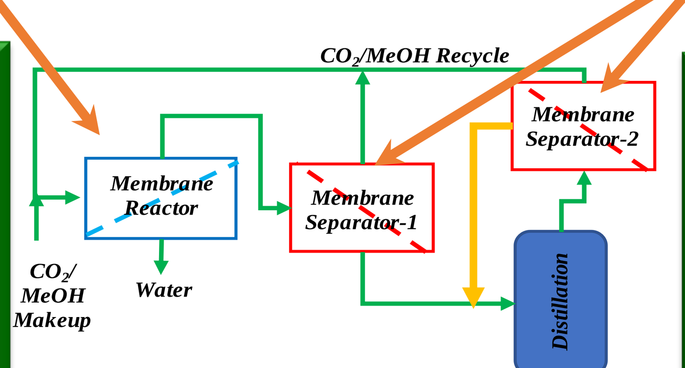
1. **Operation Mode:** Nanofiltration
2. **Azeotrope Break:** Remove MeOH (and CO_2) from DMC.
3. **Reduced Energy and Cost:** Eliminate multiple column azeotropic distillation.

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

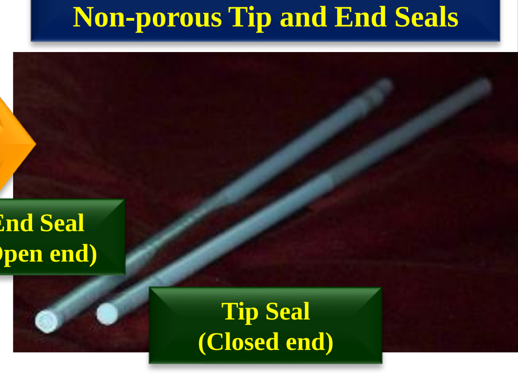
Inert Membrane
Inorganic Nanofilter

Technology: *Advanced Carbon Molecular Sieve (CMS) Membranes*

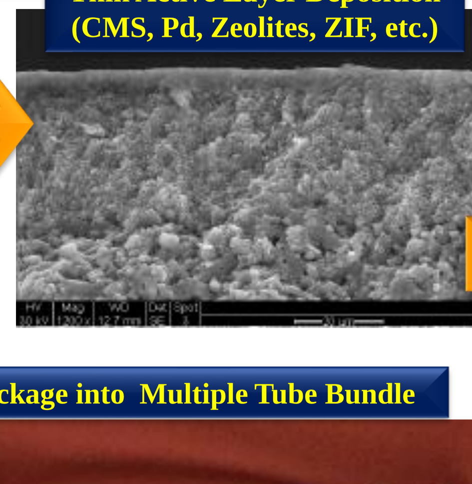
- Wide range of membranes technologies
- Multiple tube bundles
- High temperature (>500°C)
- High pressure (>1,000psig)
- Stepping stone from the laboratory to field/commercial scales.

Ceramic Tube Extrusion

Intermediate Layer Deposition + Non-porous Tip and End Seals



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

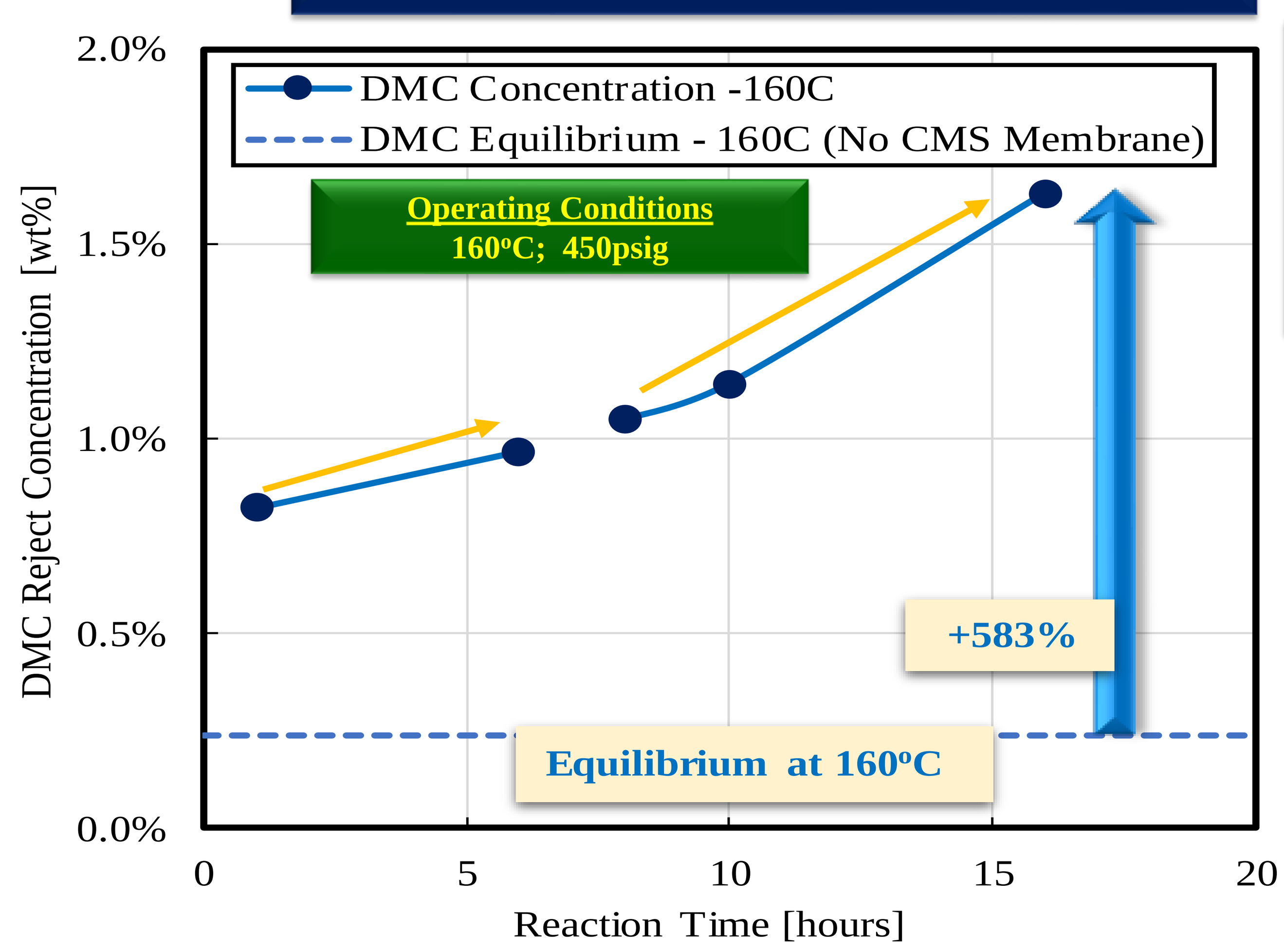


Package into Multiple Tube Bundle

MPT 57-tube Bundle (Carbon Molecular Sieve Membrane)

Results: *Membrane Reactor Subsystem:* *Enhanced DMC Conversion in MR Configuration*

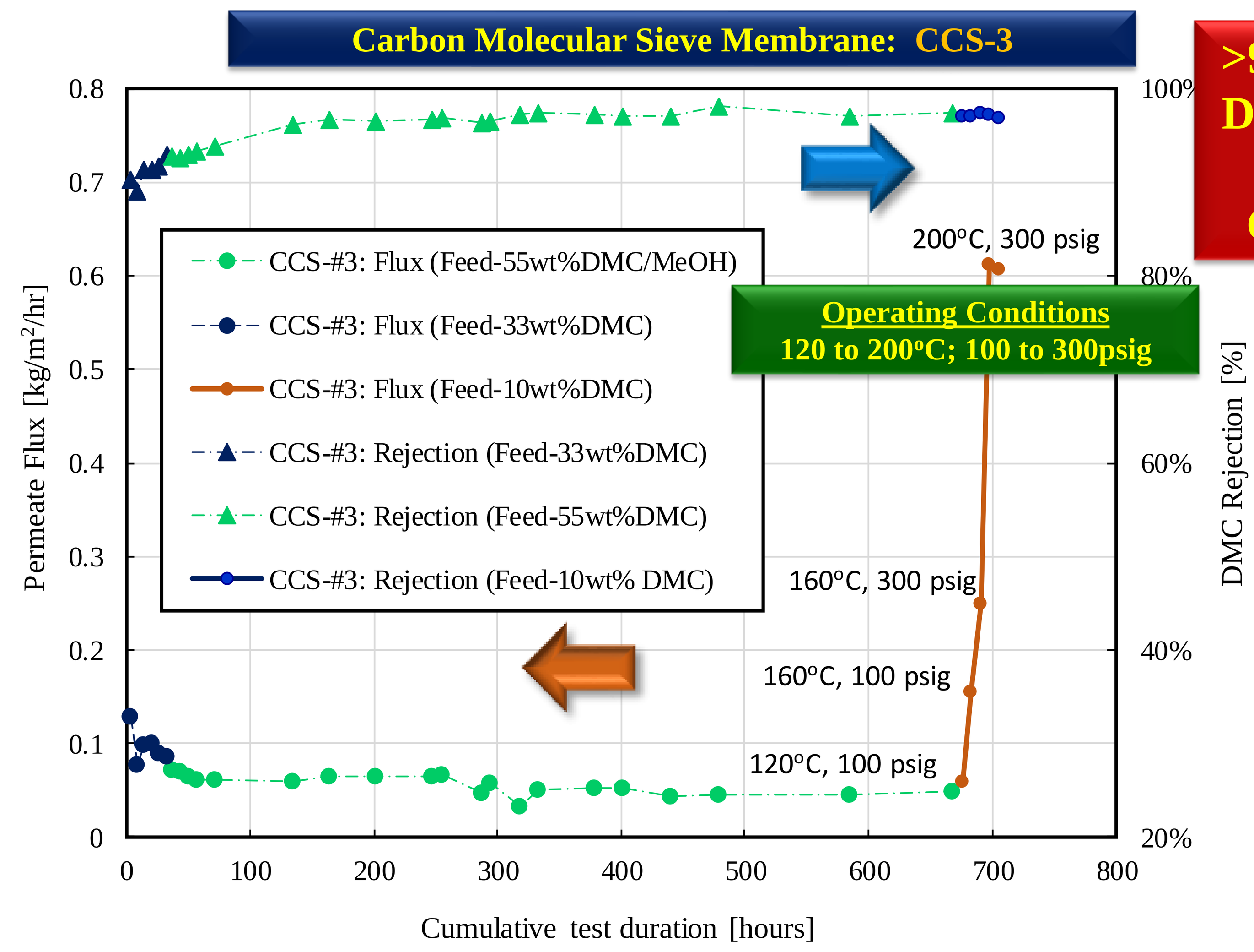
Carbon Molecular Sieve Membrane: CMS-118



~600% Increase in Conversion with Membrane Reactor Configuration

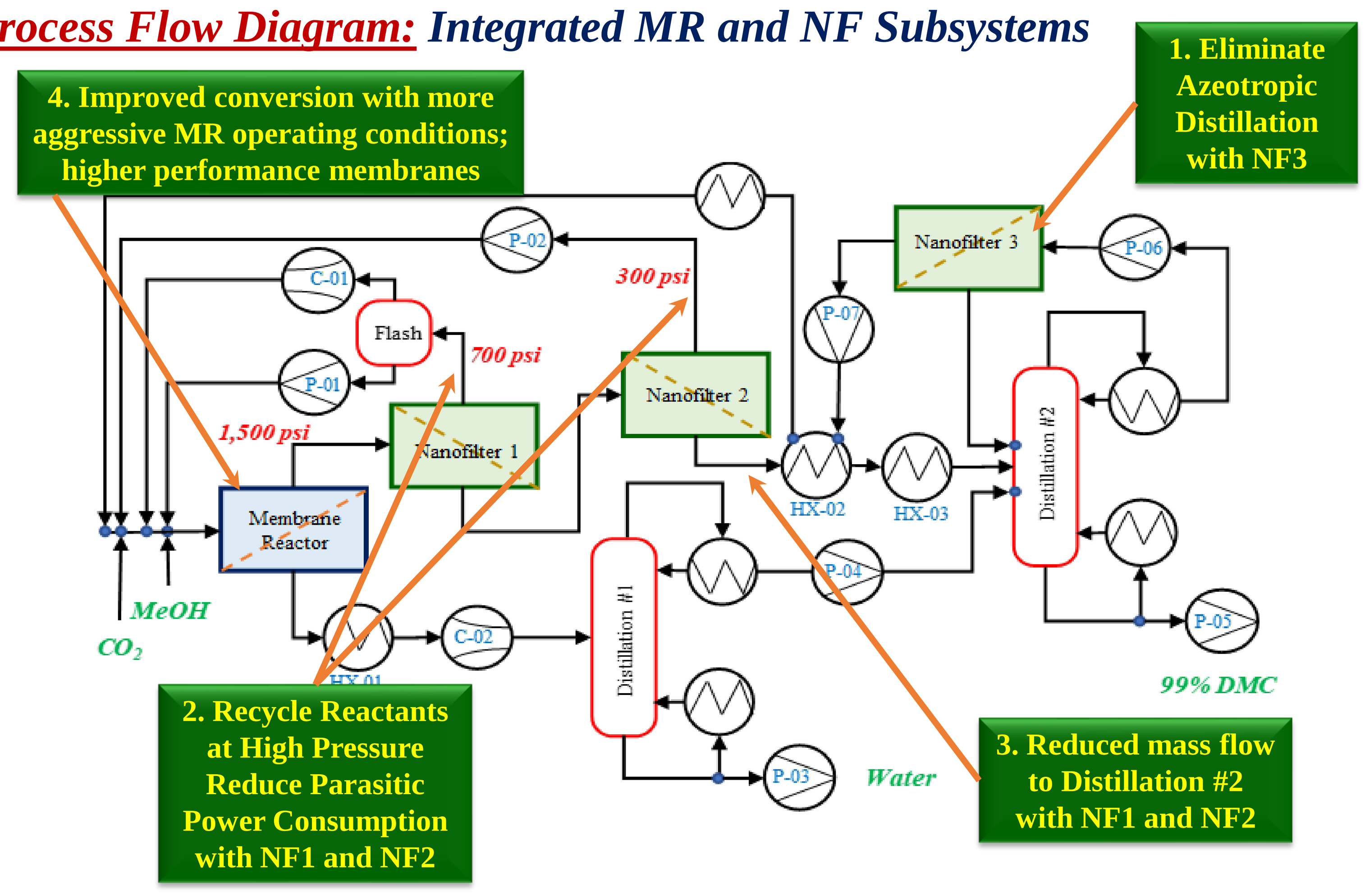
Results: *Nanofiltration Subsystem:* *Exceptional MeOH/DMC Separation*

Carbon Molecular Sieve Membrane: CCS-3



>98% Rejection of DMC from MeOH with CMS Nanofilter

Process Flow Diagram: *Integrated MR and NF Subsystems*



Accomplishments: *Demonstrated Proof of Concept*

Milestone-Objective	Target/Goal	Result
MI-01-Obj#1	MR MeOH Conversion Enhancement of >10%	***Success:*** +580% versus equilibrium
MI-01-Obj#2	Stable MR Membrane Performance	***Success:*** No change in 2,800 hours of testing.
MI-02-Obj#3a	NF DMC rejection >90%	***Success:*** DMC rejection >95 to >98%
MI-02-Obj#3b	NF flux decay <10% in long term testing	***Qualified Success:*** Initial flux decay at ~50%, then very stable during >400 to ~700 hours of testing.
MI-03-Obj#4	Develop MR mathematical model	***Success:*** In-house model available.
MI-03-Obj#5	Update process flow diagram.	***Success:*** Re-designed the PFD.
MI-03-Obj#6	Refined TEA with DMC production cost target <$0.35/lb.	***Success:*** Demonstrated DMC production cost ~$0.27/lb

MR Subsystem
Significant conversion enhancement and long term performance stability.

NF Subsystem
High rejection and long term performance stability.

Process Commercialization
Preliminary TEA shows potential for low cost DMC production.