Dehydration Membrane Reactor for Direct Production of Dimethyl Carbonate (DMC) from CO$_2$ and H$_2$

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Project overview

- **Background**: Membrane reactor DME production successfully developed through an ARPA-E project (DE-AR0000806)

- **Current project objective**: Develop membrane reactor for production of dimethyl carbonate (DMC) from CO₂ and H₂
  - DMC’s market projected to grow from $895 million in 2019 to $1,207 million by 2024, at a CAGR of 6.2% from 2019 to 2024

- **Performance period**: 1/1/21 – 9/30/23

- **Total funding**: $1,269,664 (DOE: $1.0 MM, cost share: $269,664)

- **Goal**: CO₂ conversion >50%, DMC selectivity >60%

- **Team**:
  - **Member**
  - **Roles**
    - Project management and planning
    - Parametric and deactivation tests
    - Techno-economic and life-cycle analyses
    - Membrane and membrane reactor development
    - Catalyst development

DME: dimethyl ether; DMC: dimethyl carbonate

- **Equation**: \[2\text{CO}_2 + 6\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O}\]

- **CO₂ conversion and DME yield significantly greater than packed bed reactors reported in the literature**
One-step process intensifies a process that would otherwise require multiple steps:

- Methanol synthesis: $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ \quad $\Delta H^0 = -49 \text{ kJ/mol}$  
  Catalyst 1: CuO/ZnO/Al$_2$O$_3$ based

- DMC synthesis: $2\text{CH}_3\text{OH} + \text{CO}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}$ \quad $\Delta H^0 = -17.3 \text{ kJ/mol}$  
  Catalyst 2: CeO$_2$ based

- Combined reaction: $3\text{CO}_2 + 6\text{H}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + 3\text{H}_2\text{O}$

Catalyst Development
Palladium-CuO/ZnO/Al$_2$O$_3$ (CZA) developed for the first reaction – methanol synthesis

**TEM image:** uniform nanoscale particles (~15 nm)

**EDX mapping:** elements of Cu, Pd, O, Al, Zn homogeneously dispersed

TEM: Transmission Electron Microscopy; EDX: Energy-dispersive X-ray Spectroscopy
0.9 wt.% Pd/CZA shows the best methanol synthesis performance in a packed bed reactor

Reaction conditions: T = 140-240°C, P = 2.8 MPa, H₂/CO₂ molar ratio = 3:1, GHSV = 2,880 mL/(g cat·h)

GHSV: Gas Hourly Space Velocity; CZA: CuO/ZnO/Al₂O₃
CeO$_2$-based catalyst developed for the second reaction – methanol dehydration

- TEM image: nanorods catalyst

- Liquid phase reaction at 140°C for DMC synthesis:
  - DMC selectivity: 100%
  - Methanol conversion: 0.48%
  - DMC yield: 8.1 mmol DMC/g$_{\text{catalyst}}$

TEM: Transmission Electron Microscopy
Removal of H₂O using a dehydration agent boosts methanol dehydration

- Dehydration agent 2-cyanopyridine (2-CP) reacts with H₂O to form 2-picolinamide

\[
\text{2-CP} + \text{H₂O} \rightarrow \text{2-picolinamide}
\]

- DMC synthesis at 140°C:

<table>
<thead>
<tr>
<th>Methanol (g)</th>
<th>2-CP (g)</th>
<th>CeO₂ (g)</th>
<th>Pressure (MPa)</th>
<th>Methanol conversion (%)</th>
<th>DMC yield (mmol\textsubscript{DMC}/g\textsubscript{cat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0</td>
<td>0.1</td>
<td>3</td>
<td>0.48</td>
<td>8.1</td>
</tr>
<tr>
<td>6.4</td>
<td>1.04</td>
<td>0.1</td>
<td>3</td>
<td>5.5</td>
<td>28</td>
</tr>
<tr>
<td>6.4</td>
<td>10.4</td>
<td>0.3</td>
<td>3</td>
<td>73</td>
<td>240</td>
</tr>
<tr>
<td>6.4</td>
<td>10.4</td>
<td>0.3</td>
<td>5</td>
<td>87</td>
<td>290</td>
</tr>
</tbody>
</table>
Membrane and Membrane Reactor Development
Breakthrough development of Na\(^+\)-gated, nanochannel membrane for dehydration

**Science**

*Na\(^+\)-gated water-conducting nanochannels for boosting CO\(_2\) conversion to liquid fuels*
Huazheng Li, Chenglong Gius, Shoujie Ren, Qiaobei Dong, Shenxiang Zhang, Fanglei Zhou, Xinhua Liang, Jianguo Wang, Shiguang Li and Miao Yu

*Science 367* (6478), 667-671,
DOI: 10.1126/science.aaz6053

Na\(^+\) neutralizes the negatively charged NaA framework and position inside zeolite nanocavities, allowing fast transport of small H\(_2\)O molecules, whereas blocking the permeation of larger molecules, such as H\(_2\), CO\(_2\), CO, and methanol

**Kinetic diameters:**
- H\(_2\)O: 0.265 nm
- H\(_2\): 0.289 nm
- CO\(_2\): 0.33 nm
- Methanol: 0.36 nm
- DMC: 0.63 nm
Membrane shows high flux and selectivity for dehydration of $\text{H}_2\text{O}/\text{CO}_2/\text{CO}/\text{H}_2$/methanol mixture

- **Other selectivities**
  - $\text{H}_2\text{O}/\text{H}_2 > 190$
  - $\text{H}_2\text{O}/\text{CO} > 170$
  - $\text{H}_2\text{O}/\text{MeOH} > 80$
  - $\text{H}_2\text{O}/\text{DMC}$: not tested yet, but expected to be $> 200$

**Kinetic diameters:**
- DMC: 0.63 nm
- Methanol: 0.36 nm
- $\text{CO}_2$: 0.33 nm
- $\text{H}_2$: 0.289 nm
- $\text{H}_2\text{O}$: 0.265 nm
Membrane also showed good dehydration capability at even lower water concentrations

- Tested with CO₂/H₂O mixtures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Feed water</th>
<th>Retentate water</th>
<th>Water permeance (mol/m²/s/Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Partial pressure (psi)</td>
<td>Concentration (vol%)</td>
<td>Partial pressure (psi)</td>
</tr>
<tr>
<td>120</td>
<td>1.76</td>
<td>0.35</td>
<td>1.35</td>
</tr>
<tr>
<td>150</td>
<td>0.95</td>
<td>0.19</td>
<td>0.95</td>
</tr>
<tr>
<td>180</td>
<td>0.94</td>
<td>0.19</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Membrane reactor methanol synthesis (first reaction): superior performance to packed bed

- Compared to a traditional packed bed reactor without membrane, both CO$_2$ conversion and methanol yield increased 3 times in membrane reactor.
Methanol synthesis (first reaction): good stability during 100-h testing
Technical challenge – low methanol conversion for the second reaction

Testing conditions:
- Catalyst: CeO₂
- Pressure: 500 psig
- Temperature: 150-180 ºC

Testing results:

<table>
<thead>
<tr>
<th>Temp. (ºC)</th>
<th>Methanol/CO₂ molar ratio</th>
<th>Methanol conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>2.2</td>
<td>0.66</td>
</tr>
<tr>
<td>180</td>
<td>2.2</td>
<td>0.86</td>
</tr>
<tr>
<td>180</td>
<td>4.4</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Future plan:
- Optimize operating conditions to improve performance
# State-point data

<table>
<thead>
<tr>
<th>Synthesis Pathway Steps</th>
<th>Units</th>
<th>Measured/Current Performance</th>
<th>Projected/Target Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1 (based on CO₂)</td>
<td>mol⁻¹</td>
<td>CO₂ + 3H₂ ⇌ CH₃OH + H₂O</td>
<td></td>
</tr>
<tr>
<td>Step 2</td>
<td>mol⁻¹</td>
<td>2CH₃OH + CO₂ ⇌ (CH₃O)₂CO + H₂O</td>
<td></td>
</tr>
<tr>
<td>Source of external intermediate 1</td>
<td></td>
<td>H₂ from reforming of natural gas or electrolysis</td>
<td>No external intermediate</td>
</tr>
<tr>
<td>Source of external intermediate 2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Reaction Thermodynamics

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total: 3CO₂ + 6H₂ ⇌ (CH₃O)₂CO + 3H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°rxn</td>
<td>KJ/mol</td>
</tr>
<tr>
<td>ΔG°rxn</td>
<td>KJ/mol</td>
</tr>
</tbody>
</table>

| Conditions | Captured CO₂ from coal-, natural gas-fired or industrial flue gases |
|           | [range] | [range] |

| CO₂ Source | Step1: CZA-based catalyst,; Step2: CeO₂ catalyst |
|           |                                                  |

| Catalyst   |                                                  |
|           |                                                  |

| Pressure   | Bar | Step 1: 28; Step 2: 4-16 | 25-35 |
|           | Bar | Step1: 7; Step 2: 1.3-5.3 | 1.5-7 |
| CO₂ Partial Pressure | °C | Step 1: 160-260; Step 2: 100-160 | 140-220 |
| Temperature | °C | Step 1: 2,240; Step 2: 1,180 | ~4,480 |

| Performance | Sec | Step 1: 50-65; Step 2: 60-90 | 60.4 |
|            |     | (range) | (minimum) |

| Selectivity to Desired Product | % | Step 1: 50-65; Step 2: 60-90 | 60.4 |
|                               |   | (range) | (optimal) |

| Desired Product-DMC | mol% | ~0.1 | 18.0 |
| Desired Co-Products-MeOH | mol% | ~32.3 | 10 |
| Desirable Co-Products-CO | mol% | ~17.5 | 0 |
| Unwanted By-Products-H₂O | mol% | ~50.1 | 70.0 |
| Unwanted By-Product-DME | mol% | 0 | 2.0 |
| Grand Total | mol% | --  | 100% |
Membrane reactor technology development path

DME: \(2\text{CO}_2 + 6\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O}\)

DMC: \(3\text{CO}_2 + 6\text{H}_2 \rightleftharpoons (\text{CH}_3\text{O})_2\text{CO} + 3\text{H}_2\text{O}\)
We are developing a membrane reactor for production of DMC.

- Na⁺-gated membrane removes water \textit{in situ}, shifting equilibrium towards product formation.

- First reaction (methanol synthesis): membrane reactor CO₂ conversion and methanol yield are 3 times greater than packed bed reactor.

- Second reaction (methanol dehydration): methanol conversion is low; approaches to resolve this technical challenge are ongoing.
Acknowledgements

- Financial and technical support

DOE NETL: Andy Aurelio, Andrea McNemar and Andrew O’Palko
Appendix – Organization chart

DOE NETL
Project Manager
*Project oversight*

GTI Energy
Ms. Kate Jauridez
*Contract administrator*

GTI Energy
Dr. Shiguang Li- PI
- Coordinate project activities
- Project management

Missouri S&T
Dr. Xinhua Liang
*Catalyst development*

UB
Dr. Miao Yu
*Membrane reactor design, testing, and optimization*

GTI Energy
Mr. Travis Pyrzynski
*Parametric and deactivation tests*

GTI Energy
Dr. Sekar Darujati
*TEA and LCA*

GTI Energy
Mr. Howard Meyer
*Project QA/QC*
Appendix – Gantt chart
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