Plasma Assisted Catalysis for CO$_2$ Utilization
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Project Overview (1/2)

– Funding and Performance Dates
  • Source: DOE
  • Phase I: $149,998  (02/2019 – 11/2019)
  • Phase II: $1,049,923  (04/2020 – 04/2022)

– Project Participants
  • Advanced Cooling Technologies, Inc (ACT):
    Yue Xiao (PI), Chien-Hua Chen, Jay Uddi, Patryk Radyjowski, Josh Kintzer
  • Lehigh University:
    Prof. Jonas Baltrusaitis
– Overall Project Objectives

• Plasma-Assisted Dry Methane Reforming (PADMR)
  \[ \text{CO}_2 + \text{CH}_4 = 2\text{H}_2 + 2\text{CO} \]
• Improve reactor performance
• Evaluate coking formation and decoking
• PADMR modeling
• Scaling analysis and scaled-up reactor design
• Industrial process flow analysis
Technology Background (1/2)

- Current: Steam Methane Reforming (SMR)
  \[ H_2O + CH_4 \rightarrow 3H_2 + CO; \ H_2/CO=3, \Delta H=206 \text{ kJ/mol} \]

- Dry Methane Reforming (DMR)
  \[ CO_2 + CH_4 \rightarrow 2H_2 + 2CO; \ H_2/CO=1, \Delta H=247 \text{ kJ/mol} \]

- DMR advantages:
  - Consumes two greenhouse gases
  - Better and tunable H_2/CO ratio

- DMR disadvantages:
  - High temperature
  - Coking

\[ \Delta G < 0 @ 600 ^\circ C \]

Species Concentrations

Always has carbon

Severe Coking
Technology Background (2/2)

- Plasma-Assisted Dry Methane Reforming (PADMR)
  - Non-thermal plasma to sustain reactions
  - Electrons obtain energy from electric field
    \[ \rightarrow \text{High energy electron (~}10^4\text{ K scale) but room temperature gas (300–400 K)} \]

- Electrical energy consumed by non-thermal plasma
  \[ (E) = \text{Electron energy (}\Delta G\text{)} + \text{Energy loss} \]
  \[ \Delta G \text{ passed from electron to molecules} \]
  \[ \text{CH}_4 + e \rightarrow \text{CH}_3 + H^- \]
  \[ \text{CH}_3 + \text{H} + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \]
- Enables low temperature DMR reactions
- Catalysts for synergetic effects

Technical Approach/Project Scope (1/2)

– Dielectric barrier discharge (DBD) plasma reactor
  • Low temperature and atmospheric pressure
  • High conversion (>90%)
  • Suitable for industrial scale
  • Catalysts: Efficiency ↑


Source: SUEZ – Water Technologies & Solutions

DBD Ozone Generator

– Project Scope
  • Achieve high conversion and syngas production
  • Increase energy efficiency
  • Scaled-up reactor design
  • Plasma chemistry modeling $\rightarrow$ Reactor and process condition optimization
  • Industrial process modeling $\rightarrow$ Economic analysis

– Goal
  • Develop a economically viable PADMR-involved process

– Risks and Mitigation Strategies
  • Lower initial efficiency
    – Catalysts
    – Reactor and process optimization
    – Utilize waste heat and cheap electricity
Progress and Current Status of Project (1/8)

Upgraded DBD plasma reactor: Parallel plate → Cylindrical

Phase I: Parallel plates reactor

- Reduced bypass flow
- Uniform electric field
- Flexible reactor configuration

Phase II: New cylindrical reactor

- Reduced bypass flow
- Uniform electric field
- Flexible reactor configuration
Progress and Current Status of Project (2/8)

Testing Setup

![Testing Setup Diagram]

- **GC-TCD**: Gas Chromatography – Thermal Conductivity Detector
- **MS**: Mass Spectroscopy
Further improved conversion and syngas production

DMR: \( \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2 + 2\text{CO} \)

- Flow rate ↓, Conversion & production concentration ↑
- Compared with Phase I:
  - \( \text{CO}_2: \) 54% \( \rightarrow \) 70%, \( \text{CH}_4: \) 65% \( \rightarrow \) 84%.
  - \( \text{H}_2: \) 27% \( \rightarrow \) 34%, \( \text{CO}: \) 35% \( \rightarrow \) 39%. 

Progress and Current Status of Project (3/8)
Further improved conversion and syngas production

**DMR: CO$_2$ + CH$_4$ → 2H$_2$ + 2CO**

**SEI:** Specific energy input

\[
SEI = \frac{\text{Power (kJ)}}{\text{Vol. Flow Rate (L)}}
\]

- SEI ↑, conversion & production ↑
- CO selectivity insensitive to flow rate / SEI
- Flow rate ↑ (or SEI ↓), H$_2$ selectivity ↓
Progress and Current Status of Project (5/8)

Parametric studies:
Alumina catalyst and varying CO$_2$:CH$_4$ ratio

- 20% Ni/γ-Al$_2$O$_3$ tested
- Concentration crosses at ~45%
- Selectivity crosses at ~65% CO$_2$.
- Low initial concentration → higher conversion
- CH$_4$ promotes CO$_2$ conversion → Tunable syngas ratio
- No significant performance improvements for catalysts
  - Reduced residence time
  - Low temperature
Progress and Current Status of Project (6/8)

Plasma chemistry modeling: 1D CO\(_2\) conversion

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>Rate coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>e(^-)+CO(_2)→CO(_2)(^+)+2e(^-)</td>
<td>5.4 \times 10(^{-11})</td>
</tr>
<tr>
<td>2</td>
<td>e(^-)+CO(_2)→CO+O+e(^-)</td>
<td>5.8 \times 10(^{-11})</td>
</tr>
<tr>
<td>3</td>
<td>e(^-)+CO(_2)→CO+O(^-)</td>
<td>7.0 \times 10(^{-12})</td>
</tr>
<tr>
<td>4</td>
<td>e(^-)+O(_3)→O+O(_2)+e(^-)</td>
<td>2.0 \times 10(^{-9})</td>
</tr>
<tr>
<td>5</td>
<td>e(^-)+O(_2)→O+O+e(^-)</td>
<td>2.0 \times 10(^{-9})</td>
</tr>
<tr>
<td>6</td>
<td>e(^-)+O(_2)→O+O(^-)</td>
<td>4.0 \times 10(^{-11})</td>
</tr>
<tr>
<td>7</td>
<td>e(^-)+O(_2)+M→O(_2)+M</td>
<td>3.0 \times 10(^{-30})</td>
</tr>
<tr>
<td>8</td>
<td>O(^-)+CO→CO(_2)+e(^-)</td>
<td>5.5 \times 10(^{-10})</td>
</tr>
<tr>
<td>9</td>
<td>O(^-)+O(_2)→O(_3)+e(^-)</td>
<td>1.0 \times 10(^{-12})</td>
</tr>
<tr>
<td>10</td>
<td>O(^-)+O(_2)→O(_2)+O(_2)</td>
<td>3.0 \times 10(^{-10})</td>
</tr>
<tr>
<td>11</td>
<td>e(^-)+CO(_2)(^+)→CO+O</td>
<td>6.5 \times 10(^{-7})</td>
</tr>
<tr>
<td>12</td>
<td>O(_2)(^-)+CO(_2)(^+)→CO+O(_2)+O</td>
<td>6.0 \times 10(^{-7})</td>
</tr>
<tr>
<td>13</td>
<td>O+O+M→O(_2)+M</td>
<td>5.2 \times 10(^{-35}) exp(900/T[K])</td>
</tr>
<tr>
<td>14</td>
<td>O+O(_2)+M→O(_3)+M</td>
<td>4.5 \times 10(^{-34}) (T[K]/298)(^{-2.70})</td>
</tr>
<tr>
<td>15</td>
<td>O+O(_3)→O(_2)+O(_2)</td>
<td>8.0 \times 10(^{-12}) exp(-17.13/T[K])</td>
</tr>
<tr>
<td>16</td>
<td>O+CO+M→CO(_2)+M</td>
<td>1.7 \times 10(^{-33}) exp(-1510/T[K])</td>
</tr>
<tr>
<td>17</td>
<td>O(_3)+M→O(_2)+O+M</td>
<td>4.1 \times 10(^{-10}) exp(-11430/T[K])</td>
</tr>
</tbody>
</table>


After 0.3 s:
- CO 10\(^{16}\) /cm\(^3\) scale → Match with previous study
- Longer residence time to be performed
Progress and Current Status of Project (7/8)

Reduced CO$_2$ modeling $\rightarrow$ Detailed DMR Modeling

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Charged Species</th>
<th>Radicals</th>
<th>Excited Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$, C$_3$H$_6$, C$_2$H$_6$, C$_2$H$_4$, C$_2$H$_2$, CH$_4$</td>
<td>C$_2$H$_6^+$, C$_2$H$_5^+$, C$_2$H$_4^+$, C$_2$H$_3^+$, C$_2$H$_2^+$, C$_2$H$^+$, CH$_5^+$, CH$_4^+$, CH$_3^+$, CH$_2^+$, CH$^+$</td>
<td>C$_4$H$_2$, C$_3$H$_7$, C$_3$H$_5$, C$_2$H$_5$, C$_2$H$_3$, C$_2$H, CH$_3$, CH$_2$, CH</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CO, CH$_3$OH, CH$_3$CHO, CH$_3$OOH, C$_2$H$_5$OH, C$_2$H$_5$OOH, CH$_2$O</td>
<td>C$_2$O, C$_2$H$_2$OH, CH$_3$O, CH$_3$O$_2$, C$_2$HO, C$_3$CO, CH$_2$CHO, C$_2$H$_5$O, C$_2$H$_5$O$_2$</td>
<td>CHO, CH$_2$OH, CH$_3$O, CH$_3$O$_2$, C$_2$HO, C$_3$CO, CH$_2$CHO, C$_2$H$_5$O, C$_2$H$_5$O$_2$</td>
<td></td>
</tr>
<tr>
<td>O$_3$, O$_2$</td>
<td>O$_3^-$, O$_4^-$, O$_4^+$, O$_2^-$, O$_2^+$, O$^+$, O$^-$</td>
<td>O</td>
<td>O(1D), O(1S), O$_2$(a1), O$_2$(b1)</td>
</tr>
<tr>
<td>H$_2$</td>
<td>H$_2^+$, H$^+$, H$^-$, H$_3$+</td>
<td>H</td>
<td>H(2P), H$_2$(V), H$_2$(E)</td>
</tr>
<tr>
<td>CO$_2$, CO</td>
<td>CO$_2^+$, CO$^+$, CO$_3^-$, CO$_4^-$, CO$_4^+$, C$_2$O$_4^+$, C$_2$O$_3^+$, C$_2$O$_2^+$</td>
<td>C$_2$O</td>
<td>CO$_2$(E1), CO$_2$(E2)</td>
</tr>
<tr>
<td>H$_2$O, H$_2$O$_2$</td>
<td>H$<em>2$O$</em>+$, H$<em>3$O$</em>+$, OH$^-$, OH$_2$, OH, OH$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Includes hydrocarbons and many excited species
- Total 75 species and >1000 reactions
- Data collected from multiple sources
- Currently tuning for convergence

Progress and Current Status of Project (8/8)

Process Flow Analyses: SMR case as baseline

- Conventional and hybrid SMR modeled
- Low electricity cost need to be economically competitive
- Results published on King et al., *Fuel* 304, 121328 (2021).
- Currently developing DMR analysis model.
Plans for Future Testing/Development/Commercialization

- Further improvement of efficiency under high conversion
  - Achieved through reactor configuration, catalysts, and power source setup

Nanosecond Pulse Source

Ru/CeO$_2$ nanocubes


Nanosecond Pulse Source

Burst Signal

Reactor Configuration

Conventional and Nanoscale Catalysts
Plans for Future Testing/Development/Commercialization

Scale-up design:

- Twin reactor for consecutive production and decoking
- Currently designing scaled-up reactors
**Summary**

**PADMR:**
- Consumes two greenhouse gases → Produces syngas
- Demonstrates high conversion and syngas production
- Efficiency can be further improved

1) The new reactor, compared with Phase I effort:
   - Total conversion 59% → 70%
   - Maximum CH$_4$ conversion: 78% → 92%
   - Efficiency improved by 35%

2) 1D and 2D Plasma chemistry modeling
   - Predict the experimental results
   - Investigate the effects of the dielectric constant

3) Industrial process modeling
   - Baseline case with SMR process
Thank you!
Appendix
<table>
<thead>
<tr>
<th>Task Description</th>
<th>Quarter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1: Evaluate increase the energy efficiency using a packed bed, plasma with catalysts and nanosecond pulses</td>
<td>1 2 3 4 5 6 7 8</td>
</tr>
<tr>
<td>Task 2: Evaluate extent of coke formation in extended duration tests using our plasma DMR reactor</td>
<td></td>
</tr>
<tr>
<td>Task 3: Perform lab tests and evaluate conversion and selectivity using simulated feedstocks that may contain steam, nitrogen, and/or impurities</td>
<td></td>
</tr>
<tr>
<td>Task 4: Develop a predictive tool for plasma DMR by combining our CH(_4) and CO(_2) plasma chemistry models in one code including coupling reactions</td>
<td>x x x x x</td>
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<tr>
<td>Task 5: Improve scaling analysis and develop a scaled-up reactor design</td>
<td>x x x x x</td>
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<tr>
<td>Task 6: Perform process flow analyses and optimization studies</td>
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<tr>
<td>Reporting</td>
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<tr>
<td>Briefings</td>
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<tr>
<td>Midterm/Continuation Report</td>
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<td>Final Report</td>
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