Sustainable Conversion of Carbon Dioxide and Shale Gas to Green Acetic Acid via a Thermochemical Cyclic Redox Scheme

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Cost share partner: Praxair Inc.
Project Overview

Project Funding: DOE - $797,244; Cost share - $199,606

Performance Period: 02/01/2019 – 01/31/2022

Project Participants: North Carolina State University, Susteon Inc., Praxair Inc. (cost share partner); Project Manager: Andy O’Palko

Project Objective: To develop a process for sustainable and cost-effective production of acetic acid from carbon dioxide, domestic shale gas, and waste heat.

Proposed Strategy: To perform CO2-splitting and methane partial oxidation (POx) in a synergistic two-step, thermochemical redox scheme via a hybrid redox process (HRP).

Waste Heat (and/or concentrated solar energy)

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{POx} \rightarrow \text{CO} + 2\text{H}_2 \\
\text{CO}_2 & \rightarrow \text{SPLITTING} \rightarrow \text{CO}
\end{align*}
\]

\[
\text{CH}_3\text{COOH} \rightarrow \text{Acetic Acid}
\]

<table>
<thead>
<tr>
<th>Industry/Furnace Type</th>
<th>Waste Heat @700° C (GJ)</th>
<th>CO₂ Converted (tonne/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel/EAF</td>
<td>36,547,000</td>
<td>6,180,000</td>
</tr>
<tr>
<td>Steel/BOP</td>
<td>14,300,000</td>
<td>2,260,000</td>
</tr>
<tr>
<td>Glass/Oxy-fuel</td>
<td>4,033,000</td>
<td>683,000</td>
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</tbody>
</table>
>98% $\text{CO}_2$ conversion and >95% syngas selectivity, but requires >930 °C

Zhang, Haribal, and Li., Science Advances, 2017 , 3 (8), e1701184
“Low Temperature” HRP Redox Catalyst

Oxygen Vacancy Formation Energy ($\Delta E_v$)

- CeO$_2$ bulk
- CeO$_2$ (111)
- LaCeO$_{3.5}$ bulk
- LaCeO$_{3.5}$ (111)

Syngas yield (mmol/g redox catalyst)

Satisfactory performance at 650 °C
Project Plan

Research Plan:
Year I. Redox catalyst synthesis, screening and characterization; Preliminary TEA and LCA.
Year II. Stability validation of redox catalysts; Refined TEA and LCA models.
Year III. Redox catalyst demonstration and reactor design; Process scale-up and high fidelity techno-economics.

Key Milestones/Successful Criteria and Timeline:

Q3  Title: Milestone 2.2: Redox material down selection Select at least 4 redox catalyst with >20% \( \text{CO}_2/\text{PO}_x \) kinetics improvements and/or >40% per cycle CO yield increase vs the CaO-SrFeO\(_3\) reference material.

Q4  Title: Milestone 3.2 Redox performance & stability (decision point): Show \( \text{CO}_2 \) and methane conversions of >85% at temperatures \( \leq 700 \, ^\circ\text{C} \) after 50 cycles.

Q8  Title: Milestone 5.2 Large lab-scale performance verification (decision point): Show methane and \( \text{CO}_2 \) conversions of >85% at temperatures \( \leq 700 \, ^\circ\text{C} \) after 500 cycles in a .75” I.D. packed bed.

Q10 Title: Milestone 7.1 Optimized reactor Sizing: Report modified reactor sizing based upon TEA optimized catalyst.

Q12 Title: Milestone 7.2 Scalable up material validation: Report \( \text{CO}_2 \) and methane conversions of >85% at process optimized temperature and cycle timing for redox material over 500 Cycles for a one pot synthesize catalyst.
Thank you