Novel Catalytic Process Technology for Utilization of CO$_2$ for Acrylonitrile Production

DE-FE0030678

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RTI International

Andrew Jones
US Department of Energy
National Energy Technology Lab
Objective: Develop and optimize novel catalytic process for utilization of CO\(_2\) as a feedstock and oxidant to produce valuable chemicals

Key Metrics
- Demonstration of CO\(_2\)-ACN catalyst reactivity showing percent-level production ACN
- Data from lab-scale testing showing 50% yield CO

Specific Challenges
- Development of catalyst with required selectivity
- Cost competitiveness with commercial ACN

Timeframe: 10/01/2017 to 06/30/2020
Total Funding: $1,000,000
BP2 Tasks

Task 6.0 Evaluation and Optimization of the CO$_2$-Reducing Catalysts for Propylene Ammoxidation

Task 7.0 Build Aspen Process Model for ACN Process

Task 8.0 ACN Process TEA and LCA

Task 9.0 Technology gap analysis
# BP2 Tasks and Milestones

<table>
<thead>
<tr>
<th>BP</th>
<th>ID</th>
<th>Task #</th>
<th>Description</th>
<th>Planned Completion</th>
<th>Actual Completion</th>
<th>Verificatio n Method</th>
<th>Comments</th>
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<tbody>
<tr>
<td>2</td>
<td>F</td>
<td>6</td>
<td>Demonstration of CO$_2$-ACN catalyst reactivity in fixed-bed microreactor showing percent-level production of acrylonitrile (5% based on propylene) and CO (50% based on CO$_2$).</td>
<td>12/31/19</td>
<td>12/09/2019</td>
<td>Quarterly Report</td>
<td>Adjusted to reflect revised topic and schedule after contract modification.</td>
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<tr>
<td>2</td>
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<td>Completion of Aspen process model build for CO$_2$-ACN process.</td>
<td>03/31/20</td>
<td>03/31/2020</td>
<td>Quarterly Report</td>
<td>Changed focus of scope but maintained planned completion</td>
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<tr>
<td>2</td>
<td>H</td>
<td>8</td>
<td>Update of Aspen process model for CO$_2$-ACN process with heat and material balances from Task 6.</td>
<td>06/30/20</td>
<td>07/31/2020</td>
<td>Quarterly Report</td>
<td>Model updated after review of data from Q2 lab testing</td>
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<tr>
<td>2</td>
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<td>8</td>
<td>Data from lab-scale testing of CO$_2$-ACN showing at least 50% yield CO based on CO$_2$ and 5% yield ACN based on propylene.</td>
<td>06/30/20</td>
<td>07/31/2020</td>
<td>Quarterly Report</td>
<td>Achieved in BP2</td>
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<td>2</td>
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<td>Preliminary TEA and GHG LCA of CO$_2$-ACN process using process model</td>
<td>03/31/20</td>
<td>04/30/2020</td>
<td>Topical Report</td>
<td>Completed</td>
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<tr>
<td>2</td>
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<td>Completion of CO$_2$-ACN Technology Gap Analysis</td>
<td>06/30/20</td>
<td>07/31/2020</td>
<td>Quarterly Report</td>
<td>Analysis changed to reflect topic change and completed.</td>
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### Updated Schedule and Budget Projection

#### Task: Project Management and Planning
- **Evaluation and Optimization of the CO₂-Reducing Catalysts for Propylene Ammoxidation**
- **Evaluate and Optimize the Catalysts for Propylene Ammoxidation**
- **Parametric Testing of Optimized Catalysts**

#### Task: Build Aspen Process Model for ACN Process
- **Process Modeling, Techno-econmic, and GHG Analyses of CO₂-ACN Process**
- **Update ASPEN Process Model**
- **Perform CO₂-ACNTEA and GHG LCA**

#### Task: Technology Gap Analysis

#### Budget Period 2

<table>
<thead>
<tr>
<th>Months following contract award</th>
<th>Budget Period 2 (BP2)</th>
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#### Budget Planning

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<tr>
<td>1.0</td>
<td>Project Management and Planning</td>
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<tr>
<td>6.0</td>
<td>Evaluation and Optimization of the CO₂-Reducing Catalysts for Propylene Ammoxidation</td>
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<tr>
<td>6.1</td>
<td>Evaluate and Optimize the Catalysts for Propylene Ammoxidation</td>
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<td>6.2</td>
<td>Parametric Testing of Optimized Catalysts</td>
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<td>Build Aspen Process Model for ACN Process</td>
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<tr>
<td>8.0</td>
<td>Process Modeling, Techno-economic, and GHG Analyses of CO₂-ACN Process</td>
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<tr>
<td>8.1</td>
<td>Update ASPEN Process Model</td>
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<tr>
<td>8.2</td>
<td>Perform CO₂-ACNTEA and GHG LCA</td>
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<td>9.0</td>
<td>Technology Gap Analysis</td>
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#### Reporting / Deliverables

<table>
<thead>
<tr>
<th>Milestone Log</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>K</th>
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<tbody>
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<td>Q5 Total Project</td>
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<td>$536,991</td>
<td>$87,670</td>
<td>$624,661</td>
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#### Project Meeting

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#### Budget Plan

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<th>Non-Federal Share</th>
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#### Phase 1
- 4/1/19-6/30/19
- 7/1/19-9/30/19

#### Budget Period 2
- 10/1/18-12/31/18
- 1/1/19-3/31/19
CO$_2$ Utilization in Acrylonitrile (ACN) Process Overview
Material Background

**Previous Work (NETL, DE-FE00004329)**

- Required high temperature for removal of oxygen from CO\(_2\) (~800° C)
- High temperature difficult for selective oxidations
- Needed to develop new material

- Mixed metal oxide (MMO) developed
- \((\text{Fe}_2\text{O}_3)(\text{SnO}_2)_{1.41}(\text{Al}_2\text{O}_3)_{1.82}\)
- Utilization of CO\(_2\) for char gasification


Market Potential: Carbon Monoxide

- CO produced has numerous applications
- More than 59 MT of CO are used annually
- Large and growing market for CO globally ($23 billion, 5.7% expected annual growth)
- Industrial CO source could drive new economic activity
- Significant CO stream
Characterizing the MMO using pulsed CO$_2$-Chemisorption

Experimental demonstration of CO$_2$ reduction

- **Supported metals with higher oxidation forms**
- **Metal reduction by $\text{H}_2$**
- **CO$_2$ dissociation on $M_A$ accompanied by O spill-over to $M_B$ species**
- **Metal reduction accompanied by re-dispersion**
- **CO$_2$ absorption on metal sites**

Micromeritics Autochem

**Test conditions:**
- 400-600° C
- 5% $\text{H}_2$ at 400° C reduction step
- 1 atm CO$_2$ pulses
CO₂ Conversion 400 - 600°C

- Confirms CO₂ reduction
- 400°C low level of activity
- 500-600°C higher activity
- ~2 wt% CO₂ reduction capacity shown in these experiments (gravimetric capacity)
- CAT B type catalysts were the focus of further study due to ammoxidation performance
CAT B Hydrothermally Synthesized Catalysts

- TEM images of catalysts synthesized
- 20-50 nm sized crystals
- XRD confirms crystallinity
- Mixtures of 2-6 MO phases from ACN literature
Opportunity

- $1500-$1700/ton
- ~10MT/year demand
- ~3.5% anticipated growth
  - PAN
  - ABS
  - SAN
  - Nylon 6,6

Long history of production starting with the SOHIO process using a fluidizable catalyst, propylene, ammonia, and oxygen.

$\text{CO}_2$ utilizing route would consume $\text{CO}_2$ as a feedstock and produce CO as a second product.

\[ \Delta G_{700} = -2.731 \]
Favorable Gibb’s energy calculations for utilization of CO$_2$ with propylene to make acrylonitrile (blue circles) or syn gas (red circles)
Equilibrium composition calculations for carbon dioxide, ammonia, and propene over the temperature range 0-1000°C. Left shows full scale, right is magnification of relevant area.

Thermodynamic control of reaction products compared to kinetic control.
Reactor Testing

- Reaction Conditions:
- Feed Composition: Stoichiometric
- Reaction T: 500-800° C
- Reaction P: 1 atm
- Catalyst Loading: 0.5 grams
Developed online analysis for CO, acrylonitrile, and acrolein

PID reactor in RTI Johnson Lab 288
Reactor Results

CAT B-1

CO₂ reduction @ 600°C, CO₂ = 50 sccm, (P = 0 bar)
Ammonoxidation @ 500°C, C₃H₆ = 2 sccm, NH₃ = 2 sccm

CAT B-2

CO₂ reduction @ 650°C, CO₂ = 50 sccm, (P = 0 bar)
Ammonoxidation @ 550°C, C₃H₆ = 2 sccm, NH₃ = 2 sccm

CAT B-3

CO₂ reduction @ 700°C, CO₂ = 50 sccm, (P = 0 bar)
Ammonoxidation @ 500°C, C₃H₆ = 2 sccm, NH₃ = 2 sccm

CAT B-4

CO₂ reduction @ 650°C, CO₂ = 50 sccm, (P = 0 bar)
Ammonoxidation @ 500°C, C₃H₆ = 2.3 sccm, NH₃ = 1.7 sccm

CAT B-5

CO₂ reduction @ 650°C, CO₂ = 50 sccm, (P = 0 bar)
Ammonoxidation @ 500°C, C₃H₆ = 1.6 sccm, NH₃ = 2.4 sccm

CAT B-6

CO₂ reduction @ 650°C, CO₂ = 50 sccm, (P = 3 bar)
Ammonoxidation @ 500°C, C₃H₆ = 1.6 sccm, NH₃ = 2.4 sccm
Highest ACN Production

CO₂ reduction@650 C, CO₂ = 50 sccm. (w 5 g)
Ammoxidation@500 C, C₃H₆ = 2 sccm, NH₃ = 2 sccm
TEA Assessment

CO$_2$ Capture Plant

Power Plant

NH$_3$ Plant

NG Processing Plant

> 95% CO$_2$

CO$_2$-reduction

Catalyst

Ammoxidation

Methanol Synthesis

C$_3$H$_6$

C$_3$H$_3$N

CH$_3$OH

NH$_3$

Research Scope

TEA & LCA Scope
### TEA Summary

<table>
<thead>
<tr>
<th>Case</th>
<th>Case 1A: Reference Plant</th>
<th>Case 1B: RTI Process</th>
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<tbody>
<tr>
<td><strong>CAPEX, MM</strong></td>
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<td></td>
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<tr>
<td>Total Installed Cost (TIC)</td>
<td>$637</td>
<td>$587</td>
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<td>Total Plant Cost (TPC)</td>
<td>$824</td>
<td>$773</td>
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<tr>
<td>Total Overnight Cost (TOC)</td>
<td>$1,003</td>
<td>$952</td>
</tr>
<tr>
<td><strong>OPEX, MM/yr (100% Capacity Factor Basis)</strong></td>
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<td></td>
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<tr>
<td>Total OPEX</td>
<td>$334.3</td>
<td>$319.5</td>
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<tr>
<td><strong>Plant Output</strong></td>
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<td></td>
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<tr>
<td>Acrylonitrile Product, tonnes per year</td>
<td>280,000</td>
<td>279.853</td>
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<tr>
<td>CO₂ Emissions, tonnes per year</td>
<td>277,303</td>
<td>(218,277)</td>
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<tr>
<td><strong>RSP</strong></td>
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<td>Required Selling Price, $/MT</td>
<td>2168.38</td>
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• Developed two types of catalysts which are both effective at CO\textsubscript{2} reduction at 500-600° C

• Showed both catalysts can reduce CO\textsubscript{2} to CO with 50% yield meeting milestone

• Down-selected hydrothermally synthesized catalysts for further development for ACN production

• Showed 8-9% single pass yield ACN based on propylene meeting milestone

• Reproduced literature models in Aspen Plus for three types of ACN reactors satisfying milestone

• Performed TEA of RTI CO\textsubscript{2} Utilizing process and compared to SOHIO process and showed a lower required selling price compared to acrylonitrile and methanol produced by conventional methods

• LCA analysis showed the RTI CO\textsubscript{2} utilizing route consumes a comparable amount of CO\textsubscript{2} to the amount which is actually emitted by the conventional ACN process producing the same output of acrylonitrile per year.