Conversion of CO$_2$ to Alkyl Carbonates Using Ethylene Oxide as Feedstock (DE-SC0013233)

Integrated Process of CO$_2$ Capture and Conversion to Chemicals: Technology Challenges & Opportunities

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E3Tec Service LLC

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings August 2 through August 31, 2021
Project Overview

➢ Project Started in 2014 with ERA, Alberta Round 1 Grant

➢ SBIR Funding: $2,140,781: total Phase I, II and IIb

➢ Overall Project Performance Dates:
  - SBIR Phase I: 02/17/2015 - 11/16/2015
  - SBIR Phase II: 06/10/2016 - 06/10/2018
  - SBIR Phase IIb: 05/27/2019 - 08/27/2021

➢ Project Participants:
  - Michigan State University (MSU)
  - Illinois Sustainability Technology Center (UIUC/ISTC)
  - Gas Technology Institute (GTI)
  - Air Liquide Advanced Separation (ALAS)
  - Unitel Technologies, Inc.
Project Overview

Overall Project Objectives

**SBIR Phase I and Phase II**: Development of heat-integrated reactive distillation (HIRD) for conversion of captured CO$_2$ to Dimethyl Carbonate (DMC)

**SBIR Phase IIb**: Advancing Phase II process development to an integrated process of capture and conversion of CO$_2$ to alkyl carbonates.
Technology Background

Challenges for Carbon-to-Chemical (C2C)

Technical

➢ Unsuitable process technologies developed for petrochemicals
➢ Lack of credible techno-economic merits of C2C technology
➢ Uncertain market analysis for long-term demands of C2C chemicals
➢ Nascent stage of technologies for conversion of CO₂ to Chemicals

Economic

➢ Uncertainty of imminent regulatory policy for carbon management
➢ Accounting costs associated with CO₂ capture, transportation, sequestration and monitoring
➢ Competitiveness of Green Chemicals versus petroleum derived chemicals
➢ Large investment in R&D leading to Demonstration for innovative C2C processes
**Technology Background**

**Essential 1st Step:** C2C Opportunity Based on Supply Chain and Product Margin to Offset the Cost of CO$_2$ Capture and Sequestration
Technology Background

Solution: Integrated Process of CO₂ Capture and Conversion to DMC

Conversion of Captured CO₂ to DMC using Trickle-Bed Reactor

CO₂ Capture from Primary Sources and Conversion to DMC using Adsorbent Catalytic Reactor

Method of direct conversion of CO₂ to alkyl carbonates using ethylene oxide as feedstock

US Patent, 2021
Technology Background

- Lithium-Ion Batteries
- Polycarbonate Products
- Green Solvent Replacing Ketones
- DMC as Oxygenated Fuel Additive (Diesel)
- Carbon Dioxide
- Dimethyl Carbonate
- Higher Alkyl Carbonates
- Polyurethane Products

Diagram:

1. CO₂
2. DMC & MEG
3. Alkyl Carbonates & Derived Chemicals
Ethylene & Propylene Oxide Based DMC Process

Direct Conversion by Eliminating Ethylene Carbonate Process

SBIR Phase I and SBIR Phase II

\[
\text{Ethylene Carbonate} + 2 \text{ Methanol} \leftrightarrow \text{Dimethyl Carbonate} + \text{Mono-Ethylene Glycol}
\]

SBIR Phase IIb Sequential

\[
\text{Ethylene Oxide} + \text{CO}_2 + 2 \text{ Methanol} \leftrightarrow \text{Dimethyl Carbonate} + \text{Mono-Ethylene Glycol}
\]

\[
\text{Propylene Oxide} + \text{CO}_2 + 2 \text{ Methanol} \leftrightarrow \text{Dimethyl Carbonate} + \text{Propylene Glycol}
\]
## Technology Background

### Green Technology Merits

*High-Purity Products and 9x Reduction in carbon-footprint compared to commercial DMC processes*

<table>
<thead>
<tr>
<th>C-footprint Analysis*[^], kg CO₂ / kg DMC</th>
<th>E3Tec Process</th>
<th>Syngas-Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Consumption[^]</td>
<td>-0.51</td>
<td>NA</td>
</tr>
<tr>
<td>CO₂ Emission Inside Battery Limits (ISBL)</td>
<td>0.58</td>
<td>1.29</td>
</tr>
<tr>
<td>Methanol from Commercial Process</td>
<td>0.39</td>
<td>0.47</td>
</tr>
<tr>
<td>Ethylene Oxide from Commercial Process</td>
<td>0.31</td>
<td>NA</td>
</tr>
<tr>
<td>Total CO₂ Emissions</td>
<td>1.28</td>
<td>1.76</td>
</tr>
<tr>
<td>Offsetting CO₂ Emissions of Coproduction of MEG</td>
<td>-0.58</td>
<td>NA</td>
</tr>
<tr>
<td><strong>Net CO₂ Emissions</strong></td>
<td><strong>0.19</strong></td>
<td><strong>1.76</strong></td>
</tr>
</tbody>
</table>

* Ethylene-oxide based DMC process;  
  ^Captured CO₂ with 90%+ purity
## Technology Background

### Techno-Economic Analysis

*Commerically profitable to syngas-based DMC process*

<table>
<thead>
<tr>
<th>Economic Parameters</th>
<th>E³Tec Process</th>
<th>Syngas-Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC Capacity, kTA</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>MEG Capacity, kTA</td>
<td>40</td>
<td>NA</td>
</tr>
<tr>
<td>Capital Cost (CAPEX), $MM</td>
<td>$198</td>
<td>$219</td>
</tr>
<tr>
<td>Cost of Production, $/tonne DMC*</td>
<td>$488</td>
<td>$685</td>
</tr>
<tr>
<td>Levelized Cost of DMC, %</td>
<td>15% lower</td>
<td>90% to 95%</td>
</tr>
<tr>
<td>DMC Quality</td>
<td>99.9%</td>
<td>90% to 95%</td>
</tr>
</tbody>
</table>

*Includes cost of 60 $/Tonne CO₂ @ 90%+ purity; MEG @ market cost*
Technical Approach/Project Scope

Project Success Criteria

➢ Development of validated design methodology for scale-up from prototype lab testing to commercial-scale plant
➢ Advancing conversion of CO₂ to DMC from TRL-5 of *Laboratory Testing of Semi-Integrated System* to TRL-7 of *Integrated Pilot System Demonstration*
➢ Justification of techno-economic merits of conversion of CO₂ to DMC

Project Risks and Mitigation Strategy

➢ Project Risks: Key technical challenge is to demonstrate synthesis of high-purity (99.9%) DMC by utilization of CO₂ from primary sources
➢ Mitigation Strategy: Reduce technical uncertainty by integrated technology demonstration unit for industry acceptance
Technical Approach/Project Scope

Work Plan

1. Prototype tests for validation of the ASPEN Plus® process scale-up methodology
2. Qualification of catalysts for direct conversion of CO₂ from primary sources to chemical intermediate for further conversion to dimethyl carbonate with HIRD process
3. Comparative analysis of C-footprint based LCA and TEA for a) Captured CO₂; b) Integrated CO₂ Capture and Conversion and c) syngas based DMC
4. Design of Technology Demonstration Unit
Progress and Current Status of Project

Test Units in Phase I, II and II-Sequential

Adsorbent Catalytic Reactor (ACR) Test Unit

Patented Differential Kinetic Test Unit (DKTU)

10-meter Reactive Distillation Columns Integrated with Side Reactors
Progress and Current Status of Project

Aspen Plus® Scale Up Design Methodology

Scale Up to Scale Down

Integrated ASPEN Plus® Process Model

Differential Kinetic Test Unit

Integrated Pilot-Scale Test Unit

Scale Down to Scale Up

Validated ASPEN Plus® Process Model

Commercial Unit

Progress and Current Status of Project
Accomplishment of Milestones

1. Developed validated ASPEN Plus® scale-up model based on prototype test data
2. Developed adsorbent catalytic reactor for direct conversion of CO$_2$ from primary sources
3. Demonstrated favorable economics based on a detailed market analysis
4. C-footprint model interlinked with ASPEN Plus® exemplified that CO$_2$ emissions would be significantly lower compared to commercial syngas DMC process
5. Designed a demo unit and developed industry contacts for the next phase of the project
Progress and Current Status of Project

Synergistic efforts

a. CO₂ capture technology: E3Tec evaluated 2nd generation CO₂ capture technologies for synergistic efforts for implementing C2C technology in the near term

a. Co-product formations: DMC and Glycol are platform chemicals for production of valuable higher alkyl carbonates and consumer products. This multi-faceted technology would be adopted by large chemical manufactures with green agenda of C2C.
Plans for future testing/development/commercialization

Plans for Next Phase

Technology Demonstration Unit Leading to Commercialization

➢ Integration of 1 tonne/day technology demonstration unit with to validate techno-economic merits
➢ Strategic alliance with industry partners for commercial-scale pilot plant with 10 to 20 tonne/day or pre-commercial DMC plant

R&D Efforts

➢ Development of the adsorbent catalytic reactor with improved catalysts and CO$_2$ adsorbents
➢ Application of the HIRD equipped with side reactors and membrane separations to CO$_2$ conversion to other specialty chemicals
Key Findings, Lessons Learned, and Future Plans

➢ Important to evaluate the thermodynamics of conversion of CO$_2$ to specialty chemicals before pursuing significant process development.

➢ SBIR project will be completed in August 2021 and the future-plan focuses on **Technology Demonstration Unit** for validation of the techno-economic merits leading to commercialization.

➢ E3Tec is seeking industry participation for Technology Demonstration Unit.

“Take-Away” Message

*DMC is an ideal platform chemical for CO$_2$ utilization based on expanding market demands of alkyl carbonates for lithium-ion batteries, expanding use of polycarbonates and its use in consumer products such as polyurethane*
Acknowledgements

Financial and Technical Supports

Ethylene-Oxide Based Process Development of DMC Synthesis
Supported by the DOE SBIR Phase I, Phase II and Phase IIb Grants under DOE Contract No. DE-SC0013233.

Ammonia-Based Process Development of DMC Synthesis
Supported by the CCEMC-Alberta (now ERA) Round-1 Grand Challenge.

DOE NETL

Andy Aurelio, DOE Program Manager
Appendix

- Organization Chart
- Gantt Chart
Organization Chart

E3Tec Service, LLC
Project Manager (PM) and PI
C.B. Panchal

Project Team
PM, PI, Co-Investigators

Advisory Panel
Dr. Carl Lira
Dr. Arun Muley

E3Tec
Co-Investigator
C.B. Panchal

Technical Staff
CB Panchal
Richard Doctor
Dennis Miller
Kruti Goyal
Consultant

GTI
Co-Investigator
Shiguang Li

Technical Staff
Shiguang Li
Travis Pyrzynski
Howard Meyer

ISTC
Co-Investigator
B.K. Sharma

Technical Staff
B. K. Sharma
Kevin O’Brien
Vinod Patel
Post Doc

Unitel
Co-Investigator
Ravi Randhava
Gantt Chart – SBIR Phase IIb

Milestones
- Budget Period 1
- Performance model of the reactor
- ASPEN Plus process analysis of the integrated process
- Budget Period 2
- TEA of the integrated process
- LCA of the integrated process
- Design of Technology Demonstration Unit

Process Analysis
- ASPEN Plus analysis of EtO and ammonia based processes
- Documentation of PFD and equipment list
- Comparative process analysis
- Validation of the ASPEN Plus design model
- Qualification of Catalysts for Direct Conversion of CO2
  - Characterization of catalyst effectiveness
  - Merit Analysis to qualify catalyst(s)
  - Determination of kinetic parameters of qualified catalyst(s)
- Performance of Adsorbent Catalytic Reactor (ACR)
  - Performance tests of membrane reactor
  - Performance tests of adsorbent catalytic reactor
  - Development of performance model for the adsorbent catalytic reactor
  - Incorporation of the performance model in to ASPEN Plus process model

TEA of the Integrated Process
- Estimation of CAPEX and OPEX
- ProForma analysis to estimate IRR and NPV
- TEA merit analysis of the integrated process vs. separate CO2 capture and conversion processes
- Risk Register Management (RRM) matrix analysis

LCA of the Integrated Process
- C-footprint analysis and comparison with separate CO2 capture and conversion processes
- Update of the global market demands of DMC and its derived products
- Global CO2 abatement potentials with timeline

Design of Integrated Pilot Plant Test Unit
- ASPEN Plus process design
- Estimation of capital and operating costs

Implementation Plan for Integrated Test Unit
- Development of business plan
- Implementation schedule

Project Management and Reporting