Conversion of CO$_2$ to Alkyl Carbonates Using Ethylene Oxide as Feedstock

C.B. Panchal, Richard Doctor, Rachel Sturtz and John Prindle

E3Tec Service, LLC
2815 Forbs Avenue, Suite 107
Hoffman Estates, Illinois 60192

cpanchal@e3-tec.com
www.e3-tec.com
SBIR Phase II Project Status

➢ **Technical**: Developed validated ASPEN Plus® design based on pilot-scale tests at Michigan State University

➢ **Economic Analysis**: CAPEX for a 50 kTA DMC plant, competitive selling price of DMC compared to syngas-based DMC production, *ProForma* based NPV & IRR

➢ **Intellectual Property**: Two patents on DMC process plus one patent on Differential Kinetic Test Unit (DKTU)

➢ **Industry Interactions**: Interactions with potential industrial organizations for feedback on TRL status and economic analysis

➢ **Path Forward**: Commercial demonstration (build and operate) to validate techno-economic merits
Alkyl Carbonates - Ideal Candidates for Conversion of CO₂ to Value-Added Products

Expanding Market Demands

➢ High market growth considering replacement of phosgene based process and to meet expanding demands for polycarbonates and surging demand for Li-ion batteries

➢ E3Tec focus on high-purity 99.9%+ CO₂ based DMC

➢ MEG is one of the top 50 chemicals

<table>
<thead>
<tr>
<th>Application</th>
<th>Global DMC Market Potential - kTA*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2017</td>
</tr>
<tr>
<td>DMC in Polycarbonate Production</td>
<td>2,440</td>
</tr>
<tr>
<td>Li-Ion Battery Electrolyte</td>
<td>45</td>
</tr>
<tr>
<td>Solvents (replacing ketones)</td>
<td>1,430</td>
</tr>
<tr>
<td>Chemical Intermediate, e.g. Polyurethane</td>
<td>11,350</td>
</tr>
<tr>
<td>Potential diesel oxygenate additive**</td>
<td></td>
</tr>
</tbody>
</table>

* kTA - Thousand Tonnes Per Year  ** Based on government approval for pollution control
**Alkyl Carbonate Supply Chain**

### Present Supply Chain

**E3Tec Process**

- Alkyl Carbonates (DMC)

**Chemical Manufacturing**

- Mono-Ethylene Glycol (MEG)
- Polyethylene Terephthalate (PET)
- Polycarbonate Plastics
- Intermediate, e.g. isocyanate
- Lithium-Ion Batteries
- Fuel Additives
- Solvents
- Paints

**Consumer Products**

- Fiber, Film, Bottles
- Plastic Products
- Commodity Chemicals
- Energy Storage
- Diesel
- Low VOC Paints

### Alternate Supply Chain

- Methanol
- Captured CO2
- Ethylene Oxide

**E3Tec Process**

- Alkyl Carbonates (DMC)

**Chemical Manufacturing**

- Mono-Ethylene Glycol (MEG)
- Polyethylene Terephthalate (PET)
- Polycarbonate Plastics
- Intermediate, e.g. isocyanate
- Lithium-Ion Batteries
- Fuel Additives
- Solvents
- Paints

**Consumer Products**

- Fiber, Film, Bottles
- Plastic Products
- Commodity Chemicals
- Energy Storage
- Diesel
- Low VOC Paints

**SynGas Process**

- NG
- NG and Methanol

**Phosgene Process**
E3Tec’s Process Based on Two Chemical Pathways

Ethylene-Oxide-Based Process with Selective Co-Production of Mono-Ethylene Glycol (MEG)

\[
\text{Ethylene Oxide} + \text{CO}_2 \rightarrow \text{Ethylene Carbonate}
\]

\[
\text{Ethylene Carbonate} + 2 \text{CH}_3\text{OH} \leftrightarrow \text{H}_3\text{C}O\text{O}O\cdot\text{CH}_3 + \text{HOC}--\text{COH}
\]

Di-Methyl Carbonate (DMC)  Mono-Ethylene Glycol
E3Tec’s Process Based on Two Chemical Pathways

Urea-based Process with Ammonia Acting as a Chemical Carrier and for Breaking DMC/Methanol Azeotrope

\[ \text{NH}_3 + \text{CO}_2 \xleftrightarrow{\text{CH}_3\text{OH}} \text{H}_2\text{N} \overset{\text{O}}{\text{O}^-\text{NH}_4^+} \xleftrightarrow{\text{NH}_3} \text{H}_2\text{N} \overset{\text{NH}_2}{\text{O}} + \text{H}_2\text{O} \]

Ammonia  Carbon Dioxide  Ammonium Carbamate  Urea  Water

\[ \text{H}_2\text{N} \overset{\text{NH}_2}{\text{O}} \xrightarrow{\text{CH}_3\text{OH}} \text{H}_2\text{N} \overset{\text{O}}{\text{O}^-\text{NH}_4^+} + \text{NH}_3 \xleftrightarrow{\text{CH}_3\text{OH}} \text{H}_3\text{C} \overset{\text{O}}{\text{O}} \xrightarrow{\text{NH}_3} \text{H}_2\text{N} \overset{\text{NH}_2}{\text{O}} \]

Urea  Methyl Carbamate  Ammonia  DMC  Ammonia
Heat Integrated Reactive Distillation (HIRD) Process
Equipped with Side Reactors & PerVap Membrane

DMC  51.7 kTA  MEG  35.8 kTA  CO₂ Consumption  25.6 kTA

Purity of Products:  DMC  99.99% wt  MEG  98.9% wt

US Patent 9,518,003 B1 December 2016 and 9,796,656 B1 October 2017
Integrated CO₂ Source DMC Process

CO₂ Capture

CO₂ Source

2 to 3 Stage Compressor

P ~ 3.5 bar

P ~ 35 bar

DMC Process

Methanol

Ethylene Oxide

Cooling Water

Electric Power

Steam

Combined Heat & Power

DMC

MEG

Natural Gas

Captured CO₂ Ethylene Oxide High-Purity DMC High-Purity MEG
### Economic Analysis of Integrated Process

**Case Study: 15 MWe Coal Plant**

<table>
<thead>
<tr>
<th>Baseline Case</th>
<th>UIUC 15 MW Coal Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power Generation</strong></td>
<td>15 MWe</td>
</tr>
<tr>
<td><strong>CO₂ Emission</strong></td>
<td>300 Tonnes / day</td>
</tr>
<tr>
<td><strong>CO₂ Capture &amp; Sequestration Costs</strong></td>
<td>$56.2 $ / Tonne CO₂</td>
</tr>
<tr>
<td><strong>CO₂ Capture Costs</strong></td>
<td>$16,860 $ / day</td>
</tr>
<tr>
<td><strong>Sequestration Costs</strong></td>
<td>$44.8 $ / Tonne CO₂</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$10,080 $ / day</td>
</tr>
<tr>
<td><strong>COE Impact (assuming 90% availability)</strong></td>
<td></td>
</tr>
<tr>
<td><strong>CO₂ Capture</strong></td>
<td>$52 $ / MWe</td>
</tr>
<tr>
<td><strong>CO₂ Sequestration</strong></td>
<td>$31 $ / MWe</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>$83 $ / MWe</td>
</tr>
<tr>
<td><strong>DMC/MEG Production</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Fraction of CO₂ Emission Consumed in DMC</strong></td>
<td>25%</td>
</tr>
<tr>
<td><strong>CO₂ Consumption</strong></td>
<td>75 Tonnes / day</td>
</tr>
<tr>
<td><strong>DMC Production</strong></td>
<td>150 kTA</td>
</tr>
<tr>
<td><strong>MEG Production</strong></td>
<td>105</td>
</tr>
<tr>
<td><strong>Annual DMC Production</strong></td>
<td>50.0</td>
</tr>
<tr>
<td><strong>Annual MEG Production</strong></td>
<td>35.0</td>
</tr>
<tr>
<td><strong>Product Margin Required for Offsetting CO₂ Costs</strong></td>
<td>$180</td>
</tr>
<tr>
<td><strong>CO₂ Capture &amp; Sequestration</strong></td>
<td>$1,789 $ / Tonne DMC</td>
</tr>
<tr>
<td><strong>Commercial Price of 99.99 wt % Purity DMC</strong></td>
<td>$1,285 $ / Tonne DMC</td>
</tr>
<tr>
<td><strong>Production Costs of CO₂-Based DMC</strong></td>
<td>$504</td>
</tr>
</tbody>
</table>
Dimethyl Carbonate (DMC) / Ethylene Glycol (EG) Process Block Diagram

C-footprint Analysis

ASPEN Plus® based process block diagram
# C-footprint Analysis

## Offsetting CO\textsubscript{2} Emissions

<table>
<thead>
<tr>
<th></th>
<th>CO\textsubscript{2}-Based Process</th>
<th>Syngas-Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2} Consumption, tonne CO\textsubscript{2}/tonne DMC</td>
<td>-0.51</td>
<td>0</td>
</tr>
<tr>
<td>CO\textsubscript{2} Emission Inside Battery Limits (ISBL)</td>
<td>0.58</td>
<td>1.29</td>
</tr>
<tr>
<td>Energy Consumption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal, MWh/Tonne DMC</td>
<td>2.87</td>
<td>4.41</td>
</tr>
<tr>
<td>Electric, MWh/tonne DMC</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Cooling water, tonnes/tonne DMC</td>
<td>108.0</td>
<td>206.5</td>
</tr>
<tr>
<td>CO\textsub{2} emission Outside Battery Limits (OSBL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol, tonne CO\textsub{2}/tonne DMC</td>
<td>0.39</td>
<td>0.47</td>
</tr>
<tr>
<td>Ethylene oxide, tonne CO\textsub{2}/tonne DMC</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Total CO\textsub{2} Emission, tonnes CO\textsub{2}/tonne DMC</td>
<td>1.28</td>
<td>1.76</td>
</tr>
<tr>
<td>Offsetting CO\textsub{2} Emission of MEG Production</td>
<td>-0.58</td>
<td>0</td>
</tr>
<tr>
<td>Net Emission tonne CO\textsub{2}/tonne DMC</td>
<td>0.19</td>
<td>1.76</td>
</tr>
</tbody>
</table>
## Potential Abatement of CO$_2$ Emissions

<table>
<thead>
<tr>
<th>Application</th>
<th>Global CO$_2$ Abatement Potentials* kTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2018</td>
</tr>
<tr>
<td>DMC in Polycarbonate Production</td>
<td>3,831</td>
</tr>
<tr>
<td>Li-Ion Battery Electrolyte</td>
<td>71</td>
</tr>
<tr>
<td>Solvents (replacing ketones)</td>
<td>2,245</td>
</tr>
<tr>
<td>Chemical Intermediate, e.g. Polyurethane</td>
<td>17,820</td>
</tr>
<tr>
<td>Potential diesel oxygenate additive**</td>
<td></td>
</tr>
</tbody>
</table>

*Based on offsetting CO$_2$ emissions by commercial production of DMC by syngas and MEG by hydration of ethylene oxide processes

** Based on government approval for pollution control
## Economic Analysis

### Competitive Product Margin

<table>
<thead>
<tr>
<th>Plant Capacity, kTA</th>
<th>E3Tec Process</th>
<th>Syngas Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMC</td>
<td>51.7</td>
<td>50.0</td>
</tr>
<tr>
<td>MEG</td>
<td>35.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Capital Costs (CAPEX), $ Million</th>
<th>E3Tec Process</th>
<th>Syngas Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ 164</td>
<td>$ 223</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Costs $/tonne DMC</th>
<th>E3Tec Process</th>
<th>Syngas Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Variable</td>
<td>$ 291</td>
<td>$ 431</td>
</tr>
<tr>
<td>Total Fixed</td>
<td>$ 196</td>
<td>$ 254</td>
</tr>
<tr>
<td>Cash Cost of Production</td>
<td>$ 487</td>
<td>$ 685</td>
</tr>
<tr>
<td>Capital Charge</td>
<td>$ 798</td>
<td>$ 1,104</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Selling Price</th>
<th>E3Tec Process</th>
<th>Syngas Based Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ 1,285 *</td>
<td>$ 1,789</td>
<td></td>
</tr>
</tbody>
</table>

**Product Margin**  
$ 504

*Taking into credit for MEG as co-product*
<table>
<thead>
<tr>
<th>Economic Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant Service Life</td>
<td>30 Years</td>
</tr>
<tr>
<td>Normal Discount Rate</td>
<td>9%</td>
</tr>
<tr>
<td>Corporate Income Tax</td>
<td>34%</td>
</tr>
<tr>
<td>Inflation Rate</td>
<td>Between 2.2% &amp; 3.0%</td>
</tr>
<tr>
<td>Net Present Value (NPV)</td>
<td>$249 million</td>
</tr>
<tr>
<td>Internal Rate of Return (IRR)</td>
<td>21%</td>
</tr>
</tbody>
</table>
Technology Demo Unit as Next Step

Design Criteria

➢ Skid-mounted unit with DMC capacity of one tonne per day
➢ Total Installed Cost (TIC) within $10 million
➢ Continuous operation of fully integrated process, including recycle streams
➢ Catalyst activities for an extended period (12 months or more)
➢ Demonstrate product yield and purity – DMC and MEG
➢ Scale-up from MSU test unit ➔ Demo Unit ➔ Commercial plant
➢ Validation of the ASPEN Plus® design model as well as reactor models
MSU Test Unit

Feed: Ethylene carbonate dissolved in methanol

M: Methanol
D: DMC
EG: Ethylene Glycol
EC: Ethylene Carbonate
H: HEMC

Experimental Data
ASPEN Plus Prediction

E: Ethylene
P: Propylene

Methanol
DMC
EG
EC
HEMC

Side Draw for EG

Bottom Product

HE-10
HE-11
HE-12
HE-13
HE-14
SR-3

SR-1
SR-2
HE-1
HE-2
HE-3
HE-4
HE-5
HE-6
HE-7
HE-8
HE-9

MeOH
MeOH/
DMC/
HEMC

HE-7
Technology Demo Unit Scaled up from MSU Test Unit

- **Recycle MeOH to Side Reactors**
- **Recycled MeOH**
- **Side Reactor**
- **Reaction Column**
- **Methanol Recovery Column**
- **Product Recovery Column**
- **High-Purity EG**
- **High-Purity DMC**
- **MeOH Storage**
- **Recycle MeOH with EC Feed**
- **Recycle from Reaction Column**
- **Mixing Tank**
- **Ethylene Carbonate**
- **To MeOH Recovery Column**
- **Side Reactor**
- **Recycled MeOH**
- **Fresh MeOH**
Path Forward

Partnership Opportunities

- **Funding and Investment**: Pilot plant demonstration of the technology at a cost of $10 million with a possibility of SBIR Phase III CRADA funding

- **Licensing Partners**: Licensing the patented technologies and/or strategic alliances for advancing TRL to commercialization stage

- **Facilities**: Industrial site for pilot plant demonstration

- **Collaboration for Marketing**: DMC Offtakes

- **Path Forward**: Commercial demonstration (build and operate) to validate techno-economic merits