The DMC/DPC route to Polycarbonate Feeds: Integrated DMC-DPC Plant for Green Polycarbonate Production

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versalis technology conference: value to compete
November 14, 15 2013

Bangkok, Thailand
Agenda

• Overview
• DMC
• DPC
• Technology Integration
• Summary
Technology Alliance

- Versalis SpA
- CB&I
### Role of Partners

**Technology Licensing**

<table>
<thead>
<tr>
<th>Service</th>
<th>CB&amp;I</th>
<th>Versalis</th>
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<tbody>
<tr>
<td>Marketing and licensing</td>
<td>✔</td>
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<tr>
<td>Process design</td>
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<td>Training</td>
<td>✔</td>
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<td>Start-up assistance</td>
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<td>Catalyst supply</td>
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<td>Follow-up technical service</td>
<td>✔</td>
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**Technology Maintenance**

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<tr>
<th>Service</th>
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<tbody>
<tr>
<td>Process enhancements</td>
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<tr>
<td>Catalyst R&amp;D</td>
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<tr>
<td>Technology Development</td>
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Proven history...

**Licensed 100kTA DPC Plant for Polycarbonate Production in 2010**

- **1983 Ravena Plant**
  5,000 tons/year Prototype DMC Plant

- **1988 Ravena Revamp**
  Production increased to 8,000 tons/year by adding second train

- **2002**
  Spain revamp to 96,600 tons/year

- **2007**
  Versalis/Lummus Partnership

- **2010**
  Licensed 100kTA DPC Plant for Polycarbonate Production in 2010

Licensed to GE for production of polycarbonates
Dimethyl Carbonate (DMC) – a “green” industrial chemical

- Benign solvent with low HSE impact
  - used in Li ion battery production
- Versatile reagent
- Excellent fuel additive properties
- Phosgene substitute in the production of aromatic polycarbonates (PC)
Phosgenation process
- Reaction of methanol with phosgene
- One European plant shut down after accident
- Chinese companies still operating

Carboxylation processes using an organic oxide
- Reaction of organic oxides with carbon dioxide yielding cyclic carbonates followed by trans-esterification with methanol
- Japanese process uses ethylene oxide
- Chinese companies use propylene oxide

Oxidative carbonylation processes using an oxidizing compound
- Reaction of methanol with carbon monoxide and an oxidizing compound
- Japanese process uses nitrous oxide (NO)
- Versalis/Lummus process uses oxygen (O₂)
<table>
<thead>
<tr>
<th>Route</th>
<th>Company</th>
<th>Main By-Product</th>
<th>By-Product Recycle</th>
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<tbody>
<tr>
<td>Phosgenation</td>
<td>Chinese Companies</td>
<td>Hydrochloric Acid</td>
<td>Difficult</td>
</tr>
<tr>
<td>Carboxylation</td>
<td>Japanese</td>
<td>Ethylene Glycol</td>
<td>Difficult</td>
</tr>
<tr>
<td></td>
<td>Chinese Companies</td>
<td>Propylene Glycol</td>
<td>Difficult</td>
</tr>
<tr>
<td>Oxidative Carbonylation</td>
<td>Japanese</td>
<td>HNO$_3$ (Diluted Solution)</td>
<td>Difficult</td>
</tr>
<tr>
<td></td>
<td>Versalis Europa</td>
<td>CO$_2$</td>
<td>Easy</td>
</tr>
</tbody>
</table>
Using O₂ (Versalis/Lummus Process)

$$2\text{CH}_3\text{OH} + \text{CO} + 0.5 \text{O}_2 \rightarrow (\text{CH}_3\text{O})_2\text{C}=\text{O} + \text{H}_2\text{O}$$

Advantages

• 1-step reaction process
• No dangerous intermediates and by-products
• No catalyst make-up in normal operation
• Proven at large, world-scale capacity plants
• Typical plant capacity: 25-75 kta - larger plant capacity also possible
$2\text{CH}_3\text{OH} + \text{CO} + 0.5 \text{O}_2 \rightarrow (\text{CH}_3\text{O})_2\text{C}=\text{O} + \text{H}_2\text{O}$
• Single stage CSTR reactor operating at moderate pressure and temperature
• Employs partially soluble copper based catalyst
• *In situ* continuous catalyst regeneration – no catalyst make-up in normal operation
• Extensive energy integration
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<tbody>
<tr>
<td>Methanol selectivity to DMC</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>Methanol selectivity to by-products</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>Oxygen conversion per pass</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Oxygen selectivity to DMC</td>
<td>&gt;60%</td>
</tr>
<tr>
<td>Oxygen selectivity to CO₂</td>
<td>&lt; 40%</td>
</tr>
</tbody>
</table>
Versalis/Lummus DMC Technology Advantages

• ‘On purpose’ technology
  – No byproducts formation

• Commercially well proven technology
  – Four commercial plants designed and operated
  – Currently three units operating (one in Japan and two in Spain)

• Inherently safe technology
  – Use of phosgene avoided
  – No intermediate chemicals unlike competing technologies
  – Reactor kept well outside of the flammability envelope

• Superior product quality
  – 99.9% purity with less than 5 wppm chlorine

• High purity DMC design option (HDMC)
  – Increase purity to 99.99+% with proprietary design
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Diphenyl Carbonate (DPC) – key intermediate for polycarbonate production

- Phosgene substitute in the production of aromatic polycarbonates (PC)
- White solid powder at room temperature
Two step reaction

- **Step 1** – PMC formation: phenol + DMC $\rightarrow$ PMC + methanol
- **Step 2** – DPC formation: 2 PMC $\rightarrow$ DPC + DMC

Heat integration with DMC unit
Non-phosgene Route to Polycarbonate

- Non-phosgene route – avoids toxicity
- No use of chlorinated solvent – avoids environmental issues
- Improved quality of polycarbonate product suitable for optical grades
- No glycol byproducts
Versalis/Lummus DPC Technology Advantages

• Superior yield
  – 99.3% yield – best in the market

• Commercially well-proven technology
  – Four commercial plants designed and operated
  – Currently two units operating (in Spain)
  – New 100 kta DPC plant starting up in November 2013

• Superior product quality
  – 99.6% purity with less than 0.1 ppm titanium and iron
  – Better polycarbonate purity
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• DMC and DPC technologies can be integrated to achieve the best raw material and energy efficiencies
  – Methanol from DPC unit is recycled back to DMC unit along with some DMC
    • Avoids additional processing in DPC unit
    • Internal recycle of DMC and methanol
  – DPC unit uses high pressure steam and allows low pressure steam production
    • Low pressure steam is then used in DMC unit - overall reduction in energy requirements
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• Unique position to offer full range of phenolic technologies for green polycarbonate production
• State of the art commercially proven technologies
• Only licensor/operator with over 45 years of operating experience
• Commercially well proven DMC-DPC technologies

• DMC technology
  – On-purpose DMC production technology
  – High product purity of 99.9%
  – HDMC (high purity DMC) of 99.99%+ design available

• DPC technology
  – High conversion of phenol per pass
  – Highest selectivity (99.3% yield) of phenol
  – Nearly stoichiometric consumption of DMC and phenol
  – Product purity of > 99.6%

• Integration options
  DMC ↔ DPC ↔ PC