Alternative Routes to MEG
The Many “Colors” of Technology

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Technology and Analytics Group
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Monoethylene Glycol (MEG): The 3rd Largest Volume Ethylene Derivative

- First commercialized in 1925 by what became UCC, now Dow
- End-uses: PET (fiber and bottle resin), antifreeze & specialty chemicals
- Demand: 23 million tons (2013 global)
- 30 million tons by 2018

Conventional and High Efficiency Routes

NGLs (Ethane) → Ethylene

O₂ → Ethylene Oxide

Water → MEG

CH₂=CH₂ + O₂ → CH₂-CH₂ + H₂O → HOCH₂CH₂OH

DEG/TEG → MEG
Technology Innovation: A Key Factor as Global MEG Capacity Changes

Million Metric Tons


North America
Middle East
Hypo NAM
South America
Indian Subc.
Hypo ISC
Europe
Asia
Hypo Asia

IHS Chemical
World Petrochemical Conference
MEG Technology is Very Diverse

- Biomass
- NGLs (Ethane)
- Naphtha
- Coal
- Natural Gas

- Ethylene
- Ethylene Oxide
- Synthesis Gas
- Cellulosic Sugars
- Hemicellulosic Sugars
- Diester Oxalate
- DEG/TEG
- Ethylene Carbonate
- MEG
- Xylitol
- Bio-Ethanol

- O₂
- H₂O
- CO₂
- H₂
- CO
- O₂
- NO/ROH

IHS Chemical
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Direct Oxidation to Ethylene Oxide

- **Ethylene** + Oxygen $\xrightarrow{\text{Ag Catalyst}}$ Ethylene Oxide (EO)

- State-of-art – 90% selectivity
- Heterogeneous silver catalyst
- EO is very reactive
- EO is a gas at ambient conditions
- EO expensive to ship

Source: Shell
Leading EO Technology Providers

- Dow Chemical (original Union Carbide Technology) – METEOR Process (Most Effective Technology for Ethylene Oxide Reactions)

- Scientific Design (SD) – owned 50/50 by SABIC/Sud Chemie

- Shell Chemical – MASTER Process (Most Advanced and Sustainable Technology for the EO Reaction) (Shell’s EG Technology is known as the OMEGA (Only MEG Advantage)}
Conventional Conversion of EO to EG is Based on Simple Chemistry

Ethylene Oxide (EO) \[ + \text{H}_2\text{O} \rightarrow \text{Mono Ethylene Glycol (MEG)} \]

\[ \sim 9\% \text{ DEG} \quad \& \quad \sim 1\% \text{ TEG} \]

Dow’s METEOR Process is an example of EO/EG improvements:

- The 2008 version of Dow’s technology is a more simplified process design (including large single EO reactor)
- Has \( \sim 98\% \) selectivity to MEG
- There are 6 METEOR-based process operation globally
Selectivity to MEG has Driven Innovation

- Shell’s OMEGA Process (commercialized in 2003) has:
  - Significantly lower capital cost
  - Good environmental position
  - 4 operating plants globally

- Using MCC’s catalyst gives a 99.8% selectivity to MEG
- CO2 is stoichiometrically neutral
Coal Chemistry: Synthesis Gas-to-MEG

Syngas (CO) + Alkyl Nitrate → Dimethyl Oxalate + MonoEthylene Glycol (MEG)

COAL Gasification to syngas: CO/H₂

RECYCLE

O₂ + H₂O → Nitric Oxide + Alcohol
“Black” MEG

Coal → Gasification → Purified Syngas → Hydrogenation Reactor → MEG

Make-up NO
Make-up ROH

O₂

CO

NO

ROH

H₂

Oxalate Ester
Coal-to-Syngas-to-Oxalate Ester-to-MEG

- Developed in China with low cost/abundant coal
- Palladium catalyst for oxidative coupling
- Copper zinc catalyst for hydrogenation

- 6 coal-MEG plants in China; 13 by 2018
- By 2018 such capacity is expect to reach 2.3 MMTPA
Developments are continuing

Eastman and Johnson Matthey are developing a process for the direct conversion of syngas to MEG

Eliminating the oxalate ester, but it is in early stages
“Green” MEG: Developing Routes

Ethanol → Conventional Ethylene → Conventional EO MEG →

70% 30%

Ethanol → Conventional Ethylene → Conventional EO MEG →

70% 30%

AN INNOVATION

Xylose - Hemicellulose

H₂ → Ni Cat

Xylitol

H₂ → Cat

Ethylene Glycol + Propylene Glycol
Bio Ethanol and Bio Glycols Co-Production

- The literature (1) suggests selective hydrogenolysis of biomass-derived xylitol to EG and PG on an oxide-promoted Ni/C catalysts in the presence of solid bases, e.g. Ca(OH)$_2$ and CeO$_2$
- Xylitol conversions of 100% were reported; selectivities of ~70% to EG/PG at 203°C and 40 bar
- Xylitol can be produced from hydrogenation of xylose
- This process will require significant purification of the EG and PG

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Sugar to bio-ethanol and dehydration to ethylene are well known.

- M&G has 2\textsuperscript{nd} generation biomass-ethanol in Italy.
- Has small pilot plant (2012) in Italy to co-product bio-MEG.
- M&G announced in Nov 2013, with the Guozhen Group, a 2\textsuperscript{nd} generation bio-refinery in China:
  - Conversion of 1 million metric tons of biomass into 220 KTPA bio-ethanol and 220 KTPA bio-glycols.
  - Will have a 45 MW cogeneration plant.

Expected to start-up in 2015, at a cost of USD 500 million.
## Economic Comparison: MEG @ 400KTPA 2013

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Shell OMEGA</th>
<th>Dow METEOR</th>
<th>Coal SCGP/Fujian</th>
<th>Coal SCGP/Fujian</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>ETHYLENE AND O2 VIA EO</td>
<td>SHELL HIGH EFFICIENCY</td>
<td>DOW HIGH EFFICIENCY</td>
<td>SCGP/FUJIAN PROCESS</td>
<td>SCGP/FUJIAN PROCESS</td>
</tr>
<tr>
<td>Location</td>
<td>USGC</td>
<td>USGC</td>
<td>USGC</td>
<td>USGC</td>
<td>China</td>
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<tr>
<td>Feedstock Type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Capital MM US$</td>
<td>598</td>
<td>494</td>
<td>516</td>
<td>2,057</td>
<td>1,543</td>
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<tr>
<td>Ethylene Price, $/T</td>
<td>1,221</td>
<td>1,221</td>
<td>1,221</td>
<td>1,221</td>
<td>1,280</td>
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<tr>
<td>Coal Price, $/T</td>
<td></td>
<td></td>
<td></td>
<td>57</td>
<td>60</td>
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<tr>
<td>Variable Cost</td>
<td>827</td>
<td>770</td>
<td>811</td>
<td>312</td>
<td>449</td>
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<tr>
<td>Oper &amp; Maint.</td>
<td>44</td>
<td>38</td>
<td>43</td>
<td>179</td>
<td>121</td>
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<tr>
<td>Plant Cash Costs, $/T</td>
<td>871</td>
<td>807</td>
<td>854</td>
<td>490</td>
<td>570</td>
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<tr>
<td>Overhead &amp; Taxes</td>
<td>48</td>
<td>40</td>
<td>43</td>
<td>177</td>
<td>106</td>
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<tr>
<td>Depreciation</td>
<td>150</td>
<td>123</td>
<td>129</td>
<td>514</td>
<td>386</td>
</tr>
<tr>
<td>G&amp;A, Sales, R&amp;D</td>
<td>68</td>
<td>61</td>
<td>64</td>
<td>217</td>
<td>182</td>
</tr>
<tr>
<td>Production Costs, $/T</td>
<td>1,137</td>
<td>1,032</td>
<td>1,090</td>
<td>1,398</td>
<td>1,244</td>
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<tr>
<td>Less Depreciation</td>
<td>987</td>
<td>909</td>
<td>961</td>
<td>884</td>
<td>858</td>
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<tr>
<td>Pretax 15% Roi</td>
<td>224</td>
<td>185</td>
<td>193</td>
<td>771</td>
<td>579</td>
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<tr>
<td>Product Value, $/T</td>
<td>1,361</td>
<td>1,217</td>
<td>1,283</td>
<td>2,169</td>
<td>1,823</td>
</tr>
</tbody>
</table>

(1) Includes $106/T DEG/TEG Byproduct Credit

**Source:** IHS’ Process Economic Program (PEP)
### Economic Comparison

#### Production Costs, $/t

- **Conventional**
- **Shell OMEGA**
- **Dow METEOR**
- **Coal SCGP/Fujian**

#### Process Steps
- Conventional: 2
- Shell (OMEGA): 3
- Dow (METEOR): 2
- Coal via Syngas: 4

#### Carbon Consumed/Ton EG
- Conventional: 0.513
- Shell (OMEGA): 0.457
- Dow (METEOR): 0.484
- Coal via Syngas: 0.469 on CO

#### Overall Process Yield
- Conventional: 75.5%
- Shell (OMEGA): 84.7%
- Dow (METEOR): 80.1%
- Coal via Syngas: 84.2%

#### Capital Intensity, $/Ton
- Conventional: 1,633
- Shell (OMEGA): 1,235
- Dow (METEOR): 1,290
- Coal via Syngas: 5,143
Conclusions

- Technology Innovations in MEG technology over the past decade are “impressive”
- These new MEG technologies are fully commercialized
- They include technologies that are:
  - High capital efficiency
  - “100%” selective to MEG
  - Coal feedstock-based
  - Bio feedstock-based

- The METEOR and OMEGA processes have a capital cost advantage over conventional technology ~15%; and >5% improved ethylene yields to glycols
Conclusions (continued)

• The coal-based technology is China-centric;
  • Variable cost < 40% of conventional
  • capital intensive @ 4x conventional process

• Nevertheless, the China’s coal-based technology is expected to grow significantly in global capacity share

<table>
<thead>
<tr>
<th>Process Type</th>
<th>2013, KTPA</th>
<th>%</th>
<th>2018, KTPA</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>Conventional</td>
<td>20,429</td>
<td>78</td>
<td>22,534</td>
<td>70</td>
</tr>
<tr>
<td>METEOR (Dow)</td>
<td>2,880</td>
<td>11</td>
<td>3,680</td>
<td>11</td>
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<tr>
<td>OMEGA (Shell)</td>
<td>1.865</td>
<td>7</td>
<td>3.540</td>
<td>11</td>
</tr>
<tr>
<td>Coal (via Oxalate Ester)</td>
<td>850</td>
<td>3</td>
<td>2.300</td>
<td>7</td>
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<tr>
<td>Other</td>
<td>248</td>
<td>1</td>
<td>273</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total Global</strong></td>
<td><strong>26,272</strong></td>
<td><strong>100</strong></td>
<td><strong>32,327</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Final Point: Feedstock Type has Driven MEG Technology Innovation

**Naphtha & Ethane**
1. Conventional EO Hydration
2. Selective EO Hydration
3. Highly selective
4. CO₂/ethylene carbonate route

**Biomass**
1. Ethanol/ethylene
to EG & PG
2. Xylose hydrogenolysis
to EG & PG
3. Sobitol hydrogenolysis
to EG/PG

**Coal**
1. Synthesis gas via oxalate ester
2. Synthesis gas without oxalate ester
MEG-Related IHS Process Economics Program (PEP) Reports

Since its inception in 1962, PEP has covered the technology advancement, process design, and economics:

- PEP 70A - Ethylene Glycols, Glycol Ethers (pub. Oct 1975)
- PEP 70B - Ethylene Glycols, Glycol Ethers (pub. July 1978)
- PEP 9F - Terephthalic Acid (pub. Aug 2005)
- PEP 2I - Ethylene Oxide and Ethylene Glycol (pub. Sept 2009)
- PEP 78-2-1 - Ethylene Glycol via Oxalate Esters (pub. Sept 1979)
- PEP 81-2-1 - Ethylene Glycol via Oxalate Esters (pub. March 1981)
- PEP IX-3-3 - Ethylene Glycol from Synthesis Gas (pub. May 1974)
- PEP X-3-3 - Ethylene Glycol via Glycol Esters (pub. June 1975)
- PEP 79-2-1 - Ethylene Glycol via Ethylene Carbonate (pub. March 1980)
- PEP 92-1-1 - Coproduction of Dimethyl Carbonate and Ethylene Glycol by Transesterification (pub. May 1993)
THANK YOU!