Beyond GTL-FT: Large-scale gas conversion through oxygenates

by
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Presented at
7th Natural Gas Conversion Symposium
June 9, 2004
Dalian, China
Market Led GTL: The Oxygenate Strategy

Paper presented at 6th NGCS in 2001

- Oxygenates (Methanol, DME) have huge market potential
- Oxygenates are clean, high performing products and chemical feedstocks

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>LPG</td>
<td>❌</td>
<td>✓</td>
</tr>
<tr>
<td>Diesel Engines</td>
<td>❌</td>
<td>✓</td>
</tr>
<tr>
<td>Fuel Cells</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>MTO, MTP and MTG</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

- Cost reductions are important (technologies, economy of scale)
- Market development is required
Focus: Significant progress since 2001 to commercialize GTL technologies for producing oxygenates

- About Methanol: Trends, Supply, New Markets
- About DME: Global Commercialization Activities
- “Poly-DMM” and DMC – Promising Fuels for Blending
- Beyond Methanol
- Key Messages
Methanol Plant Costs are Decreasing

BP and Methanex announced that the industry pacesetter 5,000 TPD Atlas plant started-up on June 2, 2004.
The changing methanol business

Today: Methanol

- 31 Million MT/yr commodity chemical business
- Derivative Slate: Formaldehyde, Acetic Acid, MTBE, DME.
- Industry rationalizing
- New Markets: DME, Olefins and Power.

Methanol Production

New Markets

Methanol Derivatives

- Formaldehyde
- Acetic Acid
- MTBE
- DME
- Olefins (MTO/MTP)
- Power, Fuel Cells
- New Products

Plastics, Polymers, Paints, Consumer products, Fuels
Transition: Chemical to New Markets

Methanol (DME) Price/Cost, $/ton

Today

Future

Conventional Fuels at $20/B crude oil

Industry Trend

Today

Future

Methanol (DME) Price/Cost, $/ton

8
7
6
5
4
3
2
1
0

$/MMBTU

8
7
6
5
4
3
2
1
0

$/MMBTU

50 (70)

100 (140)

150 (210)
Large Methanol/MTO/DME plants (built, proposed)

Trinidad – (2) 5,000 TPD
Atlas Methanol
Methanol Holdings

NPC/Iran Methanol
5,000 TPD

Oman Methanol
5,000 TPD

Methanol Australia
5,000 TPD

Memo: Not including <5,000 MTPD methanol plants
Large Methanol/MTO/DME plants (built, proposed)

- **Trinidad** – (2) 5,000 TPD Atlas Methanol Methanol Holdings
- **NPC/Iran** Methanol 5,000 TPD
- **Oman Methanol** 5,000 TPD
- **Qatar/PetroWorld** >12,000 TPD
- **Nigeria/Eurochem** 7,500 TPD MTO
- **PetroWorld/Starchem** >12,000 TPD
- **Methanol Australia** 5,000 TPD

Memo: Not including <5,000 MTPD methanol plants
Proposed Supply for New Methanol/DME Markets: 23 MMTPA methanol

(Equivalent to 200,000 B/D GTL-FT)

Memo: Not including <5,000 MTPD methanol plants
Low-cost methanol production and technology developments create opportunities for large ethylene and propylene markets.

Technology Developers
- **MTO**
  - UOP/Norsk Hydro
  - ExxonMobil
- **MTP**
  - Lurgi/Statoil

Eurochem/Nigeria Gas to Polymers
7,500 tpd methanol, MTO
Methanol and DME for Power Generation

- Methanol/DME are excellent gas turbine fuels
- GE, Siemens Westinghouse provide commercial offerings of Methanol/DME-fired E class and F class gas turbines
- GE, SW guarantee power output, heat rate and performance
- Methanol/DME exhibit record efficiencies and low emissions

Fuel Grade Methanol for Power Generation - PetroWorld:

- Africa West Coast: 12,000-15,000 T/D, StarChem, July 2003

Picture Courtesy of GE
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Methanol and DME: Twin Pillars

- DME Today: 0.15 million tpa specialty product business (aerosol propellant)
- Potential for very large fuel markets
- Manufacturing plants are very similar
- Capital cost differential small
- Co-production feasible
- Both can be versatile chemical feedstocks

DME can be manufactured from multi-feedstocks similar to methanol production ...

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
<th>Propane (Butane)</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (deg C)</td>
<td>-25</td>
<td>-42 (-0.5)</td>
<td>65</td>
</tr>
<tr>
<td>Vapor Pressure @ 20 deg C (bar)</td>
<td>5.1</td>
<td>8.4 (2.1)</td>
<td>0.3</td>
</tr>
<tr>
<td>Liquid Density (kg/m³)</td>
<td>670</td>
<td>500 (610)</td>
<td>790</td>
</tr>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>28</td>
<td>46 (46)</td>
<td>20</td>
</tr>
<tr>
<td>Auto Ignition Temp @ 1 atm (deg C)</td>
<td>235-350</td>
<td>470 (365)</td>
<td>465</td>
</tr>
<tr>
<td>Explosion/Flammability Limit in air (vol %)</td>
<td>3.4-17</td>
<td>2.1-9.4 (1.9-8.4)</td>
<td>7.3-36</td>
</tr>
<tr>
<td>Octane, (R+M)/2</td>
<td>low</td>
<td>104</td>
<td>100</td>
</tr>
<tr>
<td>Cetane</td>
<td>55-60</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

- Today: Current suppliers for propellant market include Akzo Nobel, DuPont, and Mitsubishi Gas Chemicals.
- Tomorrow: Future mega-plant technology providers include Haldor Topsoe, Lurgi, Toyo Engineering, Mitsubishi Gas Chemicals and JFE Holdings.
Over the past 3 years, global recognition of DME’s potential manifested by the formation of three associations representing about 160 companies, technical institutes, universities and individuals

- To promote public awareness and DME application.
- www.aboutdme.org

- To coordinate Japanese National DME Initiative - $200 million over 2002-2005
- To develop DME manufacturing technology, shipping/distribution and marketing for multiple end-use applications

- To advance understanding and use in Korea.

Your are cordially invited to attend the First International DME Conference, October 12-14, 2004
Potential DME Demand in Asia

2010

Total = 105 Million T/yr

Source: JFE, “Feasibility Study of DME from Brown Coal in Australia, 2001
**DME in China**

**Shandong Jiutai Chemical Industry, Linyl, Shandong**
- 30,000 T/yr. December 2003 start-up.
- 60,000 T/yr. Construction started January 2004
- Plans to increase production capacity to 300,000 T/yr by end of 2005; then to 1 million T/yr by 2009.

**Luthianhua Group Inc, Luzhou, Sichuan**
- 10,000 T/y – Commercial DME plant for fuel use - August 2003 start-up. Toyo Engineering methanol dehydration technology.
- 110,000 T/y – with 2005 start-up

• In the next 5 - 10 years, China will construct a group of large dimethyl ether units.
• Besides the units in Shandong and Sichuan, dimethyl ether units with different capacities will also be put up in Ningxia, Shanghai, Xinjiang and Shaanxi.

So: China Chemical Reporter, May 26, 2004
DME in Japan

Japan DME Forum coordinates multiple programs.....

• Utilization
  • Power generation systems
  • Household/industry fuel
  • Diesel related technologies
  • Emission tests from diesel engine
  • Marketing study
  • Road test of DME vehicles

• Production
  • Production technologies
  • Ocean transportation

• Codes & Standards
  • Studies for standardization of DME fuel

DME Commercial Projects - Studies
• Japan DME Ltd: 5,000 t/d, Western Australia
• DME International Inc, 2,500-4,000 t/d, Qatar/Indonesia/Australia
• Mitsui & Co, TEC: 7,000 t/d, Iran, Indonesia

Direct process (JFE)
100t/d demonstration plant (2003-)
DME in Korea

- Conducting engine research, elaster testing
- DME Pilot Plant (100 kg/d), KOGAS R&D Center
DME in Iran

Commercial Methanol-DME Plant (proposed)
- South Pars Field
- 1.7 million tpa methanol equivalent
- 50% methanol converted to DME
- DME for domestic LPG market as 20% blend

DME R&D Project
- Technology Assessment
- Economic Studies
- Study of application as fuel

Source: K. Sadaghiani, RIPI, Iran, CWC GTL Summit, May 19, 2004
Other DME Activities Around the World *

Sweden
- DME from Biomass Gasification Project
- Fossil Fuel Free Växjö

Russia
- Moscow program: "Alternative fuels use in city’s motor transport for 2002-2004”
- VNIIGAZ (GAZPROM Research Institute) developing technology to manufacture DME

USA
- DME-Fueled Shuttle Bus Demonstration, Penn State University

Italy
- Snamprogetti Program: DME as LPG substitute, and LPG/DME interchangeability in diesel engines (with SwRI)

Brazil
A network, headed by the Petrobras Research Centre, was established including one Research Institute and three University Laboratories.

Europe/USA
- AFFORHD. Alternative Fuel for Heavy Duty Engines
- Volvo, AVP/PTI, DTU, BP, TNO, Växjö
- 2002-2004, 4 million euro

Ocean Transport
- DME has been accepted in the IMO Gas Carrier Code, according to Norske Veritas, DNV. DNV can issue safety certificates for gas carriers to transport DME (September 2003)

* Only a partial list of the extensive global efforts
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“Poly-DMM” – Diesel Blending Stock

Dimethoxymethane (DMM)

Dimethyldioxymethylene (DMM$_2$)

Poly-Dimethoxymethane (DMM$_x$)

DMM$_{3-8}$

- Most suitable DME analog
- Can be blended with diesel without engine modifications
- Low emissions in engine testing
- Made from methanol, DME and formaldehyde via low temperature catalytic distillation reactor with acidic catalyst

<table>
<thead>
<tr>
<th></th>
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<th>DMM$_2$</th>
<th>DMM$_{3-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP, °F</td>
<td>107</td>
<td>221</td>
<td>306-599</td>
</tr>
<tr>
<td>Flash Pt., °F</td>
<td>0</td>
<td>&lt;75</td>
<td>150</td>
</tr>
<tr>
<td>Cetane No.</td>
<td>28</td>
<td>41</td>
<td>76</td>
</tr>
</tbody>
</table>

PM and NOx Emissions of 7 test fuels

Source: DOE/SWRL
Dimethylcarbonate (DMC) for Gasoline Blending

- High octane and oxygen content
- Non-toxic and biodegradable
- High oxygen content leads to lower emissions
- Manufacturing:
  - Oxidative Carbonylation of methanol
    \[2 \text{CH}_3\text{OH} + \text{CO} + 0.5 \text{O}_2 \rightarrow \text{CH}_3\text{O}\text{COOCH}_3 + \text{H}_2\text{O}\]
  - Needs to be improved

It’s time to take another look at DMC
Beyond Methanol: Looking to the Future

- BP working with Berkeley, CalTech and the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences
- Over 50 researchers and faculty focus on creating breakthrough – eg. Direct conversion routes
**Key Messages**

Dramatic progress has been made in the past 3 years in cost reduction and market development.

- Lower-cost methanol is creating new market opportunities
- DME is the most promising methanol derivative
- A global DME effort has evolved - led by Asia. IDA, JDF and KDF have been formed.
- Poly-DMM for and DMC represent research opportunities as fuel additives

*The Future is Now*