XTL via Methanol and DME

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Former BP Gas Conversion Network Leader

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Outline

This presentation will address the “what, who, where, when and why” of global methanol and methanol derivatives commercialization activities, with focus on new fuel markets particularly for DME.

- About Methanol and DME
  - Properties
  - Fuel markets
  - Production technologies
- Health, Safety and Environmental Aspects
- Economics
- Key Messages
XTL Summit Presentations

Methanol and DME

THE OPPORTUNITIES BEYOND F-T
• What are the prospects for alternative conversion technologies and process options beyond Fischer-Tropsch?

• The future for MTG as an alternative fuel.

• Progress in the commercialisation of methanol and DME.

Speakers
• Mitch L Hindman, Licensing Manager, ExxonMobil R & E
• Ingvar Landälv, Chief Technology Officer, Chemrec
• Gregory Dolan, Vice President, Methanol Institute
About Methanol and DME

• Properties
<table>
<thead>
<tr>
<th>Property</th>
<th>Methanol</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (deg C)</td>
<td>65</td>
<td>-25</td>
</tr>
<tr>
<td>Vapor Pressure @ 20 deg C (bar)</td>
<td>0.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Liquid Density (kg/m³)</td>
<td>790</td>
<td>670</td>
</tr>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>Auto Ignition Temp @1 atm deg C)</td>
<td>465</td>
<td>235-350</td>
</tr>
<tr>
<td>Explosion/Flammability Limit in air (vol %)</td>
<td>7.3-36</td>
<td>3.4-17</td>
</tr>
<tr>
<td>Octane, (R+M)/2</td>
<td>100</td>
<td>low</td>
</tr>
<tr>
<td>Cetane</td>
<td>5</td>
<td>55-60</td>
</tr>
</tbody>
</table>
## Properties of Methanol and Gasoline

<table>
<thead>
<tr>
<th>Property</th>
<th>Methanol</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (deg C)</td>
<td>65</td>
<td>27-225</td>
</tr>
<tr>
<td>Reid Vapor Pressure @100 deg F (psi)</td>
<td>4.6</td>
<td>8-15</td>
</tr>
<tr>
<td>Liquid Density (kg/m³)</td>
<td>790</td>
<td>720-780</td>
</tr>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>Auto Ignition Temp @1 atm deg C)</td>
<td>465</td>
<td>257</td>
</tr>
<tr>
<td>Explosion/Flammability Limit in air (vol %)</td>
<td>7.3-36</td>
<td>1.4-7.6</td>
</tr>
<tr>
<td>Octane, (R+M)/2</td>
<td>100</td>
<td>87-92</td>
</tr>
</tbody>
</table>
DME has similar physical properties as LPG but different thermal properties

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
<th>Propane</th>
<th>N-Butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (deg C)</td>
<td>-25</td>
<td>-42</td>
<td>-1</td>
</tr>
<tr>
<td>Vapor Pressure @ 20 deg C (bar)</td>
<td>5.1</td>
<td>8.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Liquid Density @ 20 deg C (kg/m³)</td>
<td>668</td>
<td>501</td>
<td>610</td>
</tr>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>28.4</td>
<td>46.4</td>
<td>45.7</td>
</tr>
<tr>
<td>Octane, (R+M/2)</td>
<td>10-15</td>
<td>104</td>
<td>94</td>
</tr>
<tr>
<td>Cetane</td>
<td>55-60</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

- Hydrogen
- Carbon
- Oxygen

- 1.6 MT DME equivalent to 1 MT LPG
- 1.2 m³ DME equivalent to 1 m³ LPG
## Properties of DME and Diesel – Relevant to Combustion and Fuel Injection

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (deg C)</td>
<td>-25</td>
<td>180-370</td>
</tr>
<tr>
<td>Liquid Density @ 40°C (kg/m³)</td>
<td>634</td>
<td>840</td>
</tr>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>28</td>
<td>43</td>
</tr>
<tr>
<td>Viscosity (cst)</td>
<td>&lt;0.3</td>
<td>~ 3</td>
</tr>
<tr>
<td>Cetane</td>
<td>~ 65</td>
<td>40-50</td>
</tr>
</tbody>
</table>

About Methanol and DME

- Markets
Methanol Market – Overview

• Methanol market has been primarily for chemicals markets but significant fuels markets are evolving for methanol and DME (dimethyl ether), a derivative.

• Distribution infrastructure modifications varying from minor to major are required for the various fuels markets.

• Major challenges for success are new market development and robust economics, at today’s methanol price, rather than technology/production advances.
Methanol Industry Today

• 40 million MT per year (2009) global industry — energy equivalent to about 400,000 bpd diesel*

70 plants with 100,000 + mtpa capacity

• Is primarily produced from natural gas (except in China from coal)

• Has diversified end uses

Traditional Uses
(Mature Markets)

- Formaldehyde
  Pharmaceuticals, Wood Industry, Automotive

- Acetic Acid
  Fleece, Adhesives, Paints

- Dimethyl Terephthalate
  Recyclable plastic bottles

- Methyl Chloride
  Silicones

Energy Uses
(High Growth Potential Markets)

- DME
  (dimethyl-ether)

- Fuel Blending

- Biodiesel

* equivalency calculated by RSills
About DME

- Colorless gas at normal temperature and pressure, with a slight sweet ether odor
- Burns like natural gas, and handles like LPG
- Environmentally friendly with significant global consumer history as propellant

www.AboutDME.org
DME Markets

Three Major Fuel Applications

Today’s market

LPG Blendstock

Ready

Power Generation

DME

Demonstration Stage

Transportation Fuel

Other markets include petrochemicals feedstock to produce olefins
DME / LPG Blending – Factors Driving Growth

More than 80% of DME currently produced is blended with LPG

- Blending ~20% DME/ 80% LPG
- Market development best in countries that:
  - Import LPG
  - Have local feed stocks to produce DME
- Largest market is China (5+MMTPY installed capacity)
- Major companies in Japan, Egypt, Indonesia, Korea and India preparing to enter this market
The best markets are in those countries that import LPG and/or have domestic feedstock to make DME.
Diesel Substitution - Factors Driving Growth

Opportunities
- Can be used in conventional diesel engines with a modified fuel injection system
- High cetane, and quiet combustion
- Clean burning: sootless – no smoke or particulates, 100% SOx reduction
- Market potential is very large

Challenges
- Technical and regulatory hurdles remain
- Lower lubricity requires lubricating agent
- Lower viscosity can cause leakage
- Large volume vehicle production
- LPG-like distribution infrastructure

So: International DME Association, 9/2009
Global Demand Growth

- Demand into energy applications expected to drive higher industry growth

(000s tonnes)

1995 - 2008 CAGR: 4.5%

2009 - 2014 CAGR: 8%

≈13 million mtpa

Source: Chemical Market Associates Inc. (CMAI) World Methanol Analysis, September 2009
- Excludes 4.4 million tonnes of forecasted methanol demand for methanol to olefins and propylines (captive demand) in 2010-2014
Other Fuel Markets

Gasoline Blending
• Significant quantities of methanol are blended into gasoline in China: about 3 million tpa (est. 2007)
• Most current blends envisioned for vehicle fuel range from 5-15% up to 70-85% methanol content,

MTBE/TAME
• Very high octane gasoline blendstocks that contain oxygen for reducing emissions
  • MTBE (methyl tertiary butyl ether) is produced by reacting methanol with isobutene (C4 olefin) -- Octane = 107
  • TAME (tertiary amyl methyl ether) is produced by reacting methanol with isoamylenes (C5 olefin) -- Octane = 105

Methanol-to-Gasoline (MTG)
• Presentation by ExxonMobil
BioDiesel

- Biodiesel is diesel fuel that has been sourced from biodegradable materials, specifically vegetable, waste, or rendered oils, rather than from petroleum distillate.

- Biodiesel is made by reacting vegetable oils and animal fats with pure methanol in the presence of sodium or potassium hydroxide catalyst. The chemical process is called transesterification. The objective is to convert fat molecules in the oils into an ester (biodiesel), and the remainder into glycerol, a byproduct that can be processed to make soap.
About XTL via Methanol

• Production Technologies
Production Technologies - Overview

• Technologies have been applied for many years primarily for conversion of natural gas-derived synthesis gas.

• Significant advances in reactor technology and catalyst development over the past 50 years primarily in scale of operation.
  • BASF introduced the first large-scale commercial methanol in 1923, using a zinc chromite catalyst at 300-400 C and 250-350 atm, from coal-derived syngas.
  • ICI began making methanol using new lower pressure (50-100 atm), lower temperature (200-280 C) technology in 1966, using copper zinc catalyst, from natural gas-derived syngas.
  • Today, numerous technology providers Lurgi, ICI, Haldor Topsoe, Mitsubishi Gas Chemical, and Toyo Engineering, using a copper-based synthesis catalyst.
Methanol is the **Heart** of non-FT XTL technologies.

### Fuel Uses
- Gasoline Blending
- DME (Dimethyl Ether)
- Gasoline (MTG)
- MTBE/TAME
- BioDiesel
- Other – power generation and fuel cells

Future demand for methanol and methanol derivatives as fuel primarily depends on market developments.

10th XTL Summit Presentations will include Gasoline Blending, MTG and DME.
Atlas Methanol Plant in Trinidad

- 5,000 mtpd methanol plant, LHV equivalent to 18,000 bpd diesel
- Start-up in June 2004
- Operated by Methanex
How is methanol produced

An Example

Source: Marathon Presentation
Methanol Synthesis - Process

• Reactions – limited by thermodynamic equilibrium
  (1) \( \text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta H = -91 \text{ kJ/mol} \)
  (2) \( \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H = -41 \text{ kJ/mol} \)

Stoichiometric Ratio = \((\text{H}_2-\text{CO}_2)/(\text{CO} + \text{CO}_2)\) ratio of 2.0

• Operating Conditions
  • Temperature: 200-280 C
  • Pressure: 50-100 atm

• Catalyst:
  • Composition: Copper oxide, 60-70%; Zinc oxide, 20-30%, alumina, 5-15%
  • Poisons: sulfur and chlorine
  • Life: 2-4 years

• Methanol Yields generally over 99.5%
  • Generally over 99.5% methanol,
Reactor Design

• Several converter designs are commercially available.
  • Single or Multi-fixed bed adiabatic reactors, with inter-bed cooling via heat exchange or inter-bed gas quench.
  • Tubular, isothermal reactors, primarily with boiling to remove heat.

• Recirculation required to achieve reasonable yields.

• Conversion increases with increasing pressure and lower temperature.
Distillation and Methanol Purification

- Crude methanol from synthesis section contains water and impurities.
  - Impurities include higher alcohols, dimethyl ether, methyl formate, ketones, aldehydes and paraffinic hydrocarbons.

- U.S. Grade AA Methanol (>99.85% methanol; <0.1% water; <10 mg/kg ethanol) for chemical applications, requires 2 or 3 column system.

- Fuel grade methanol could be produced from single column.
Conversion of Synthesis Gas

• Higher thermal efficiency, less exothermic
• Greater selectivity (99.9% achievable) to desired product with minimal byproducts
• Requires distillation rather than hydrocracking to make finished product.
About XTL via DME

• Production Technologies
DME Reactor in NZ MTG Facility

New Zealand MTG Facility: New Plymouth NZ

SynGas and MeOH Generation

MTG

14,500 BPD plant in New Plymouth New Zealand. Plant ownership 75% NZ Government and 25% ExxonMobil.
Methanol to DME to Gasoline

Reaction Path

Figure 14 - Product time plot of products in w/w% against space time in hours
How is DME produced

• Reaction: methanol dehydration

\[ 2 \text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{-O-CH}_3 + \text{H}_2\text{O} \quad \Delta H = -23.4 \text{ kJ/mol} \]

1.4 MT methanol → 1 MT DME

• moderately exothermic
• limited by equilibrium
• highly selective

Source of process diagram: “Cost Effective Topsoe DME Production Technology, 2007”
How is DME produced

- **Reaction:** methanol dehydration
  \[ 2 \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O-CH}_3 + \text{H}_2\text{O} \quad \Delta H = -23.4 \text{ kJ/mol} \]

- **Reactor:** Adiabatic bed
- **Feed:** High purity methanol or crude methanol
- **Catalyst:** alumina (with acidic sites)
- **Temperature (inlet):** 220-250 C (inlet); 300-350 C (outlet)
- **Pressure:** 10 – 20 atm
- **Methanol Conversion:** 75-80%
  Unconverted methanol is recycled or is a co-product
- **Selectivity:** >99.9%

Source of process diagram: “Cost Effective Topsoe DME Production Technology, 2007”
How is DME produced

- Reaction: methanol dehydration

$$2 \text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{-O-CH}_3 + \text{H}_2\text{O} \quad \Delta H = -23.4 \text{ kJ/mol}$$

- Technology Providers include: Haldor Topsoe, Lurgi, Mitsubishi Gas Chemicals, Toyo Engineering

Source of process diagram: “Cost Effective Topsoe DME Production Technology, 2007"
About Methanol and DME

- Health, Safety and Environment
- Economics
Methanol is a hazardous chemical with significant toxic, flammable, and reactive properties that can also produce deleterious impacts to human health and the environment when not properly handled.

Humans are exposed to methanol from many sources. Not only does methanol occur naturally in the human body, but humans are exposed routinely to methanol through air (e.g. cigarette smoke), water, and food (e.g. aspartame).

The Methanol Institute's Product Stewardship Committee is responsible for methanol health and safety initiatives, including product risk evaluation, exposure risks throughout the supply chain, education, and training on proper methanol handling.

Visit Methanol Institute Website: [www.methanol.org](http://www.methanol.org) for copy of Methanol Safe Handling Manual.
Environment, Health, and Safety

DME

• HEALTH:
  • Approved as consumer product propellant
  • No human hazard relative to toxicity or carcinogenicity within exposure limits

• SAFETY
  • Flammable liquid like LPG
  • Thermally stable
  • No tendency to peroxide formation found
  • Visible flame

• ENVIRONMENT
  • Low emission fuel (LPG, Power, Diesel)
  • Does not deplete ozone
  • Minimal impact on water due to volatility

Visit International DME Association website: www.aboutdme.org

Photos Courtesy of Akzo Nobel and DuPont
Delivered Cost of Methanol and DME

• Methanol and DME produced in large-scale plants in Middle East from natural gas and delivered to Far East

Illustrative economics indicate that methanol and DME from large-scale plants using low-cost natural gas can be competitive with crude oil-derived gasoline/diesel.

Bases
• Natural Gas @ $1.25/MMBtu
• 5,000 mtpd Methanol Plant @ $500/tpa
• 3,500 mtpa DME Plant @ 8% more than methanol plant
• 70% LHV thermal efficiency, both plants
• Capital Costs @ 20% capital recovery factor
Key Messages
Key Messages

• The worldwide methanol market is changing due to its use in new fuel markets including conversion to DME.

• XTL via methanol and DME is a viable alternative to FT-XTL

• Production technologies are commercially proven, with numerous technology providers

• The primary new fuel markets today are gasoline blending for methanol and LPG blending for DME, particularly in Asia.
  • Diesel substitution is the most significant potential market for DME.

• The major challenge is the on-going development of new fuel markets.
Acknowledgments and Disclaimer

**Acknowledgments**

Ronald A. Sills LLC gratefully acknowledges the significant information provided by others used in this presentation, particularly Methanex and the International DME Association and its members.

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Questions

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