XTL via Methanol and DME

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Executive Briefing- 10th World XTL Summit

London, May 10, 2010

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.

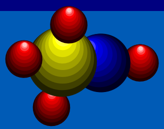
Speakers

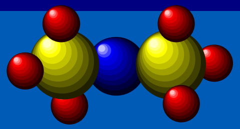
- Mitch L Hindman, Licensing Manager, ExxonMobil R & E
- Ingvar Landälv, Chief Technology Officer, Chemrec
- Gregory Dolan, Vice President, Methanol Institute

About Methanol and DME

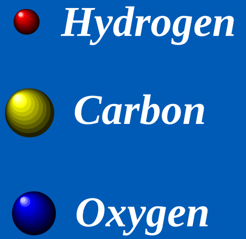
- Properties

Properties of Methanol and DME





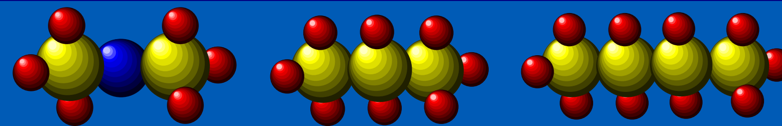
Property	Methanol	DME
Boiling Point (deg C)	65	-25
Vapor Pressure @ 20 deg C (bar)	0.3	5.1
Liquid Density (kg/m^3)	790	670
Lower Heating Value (MJ/kg)	20	28
Auto Ignition Temp @1 atm deg C)	465	235-350
Explosion/Flammability Limit in air (vol %)	7.3-36	3.4-17
Octane, (R+M)/2	100	low
Cetane	5	55-60



Properties of Methanol and Gasoline

Property	Methanol	Gasoline
Boiling Point (deg C)	65	27-225
Reid Vapor Pressure @100 deg F (psi)	4.6	8-15
Liquid Density (kg/m^3)	790	720-780
Lower Heating Value (MJ/kg)	20	43
Auto Ignition Temp @1 atm deg C)	465	257
Explosion/Flammability Limit in air (vol %)	7.3-36	1.4-7.6
Octane, (R+M)/2	100	87-92

DME has similar physical properties as LPG but different thermal properties



Property	DME	Propane	N-Butane
Boiling Point (deg C)	-25	-42	-1
Vapor Pressure @ 20 deg C (bar)	5.1	8.4	2.1
Liquid Density @ 20 deg C (kg/m^3)	668	501	610
Lower Heating Value (MJ/kg)	28.4	46.4	45.7
Octane, (R+M/2)	10-15	104	94
Cetane	55-60	5	10

Hydrogen *Carbon* *Oxygen*

- 1.6 MT DME equivalent to 1 MT LPG
- 1.2 m^3 DME equivalent to 1 m^3 LPG

Properties of DME and Diesel – Relevant to Combustion and Fuel Injection

Property	DME	Diesel
Boiling Point (deg C)	-25	180-370
Liquid Density @ 40°C (kg/m^3)	634	840
Lower Heating Value (MJ/kg)	28	43
Viscosity (cst)	<0.3	~ 3
Cetane	~ 65	40-50

Presented by D. W. Gill, AVL, at DME 2 Conference, London, 2006

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.

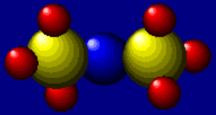
Methanol Industry Today

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

70 plants with 100,000 + mtpa capacity

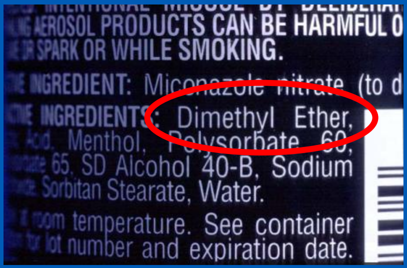
- Is primarily produced from natural gas (except in China from coal)
- Has diversified end uses

* 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

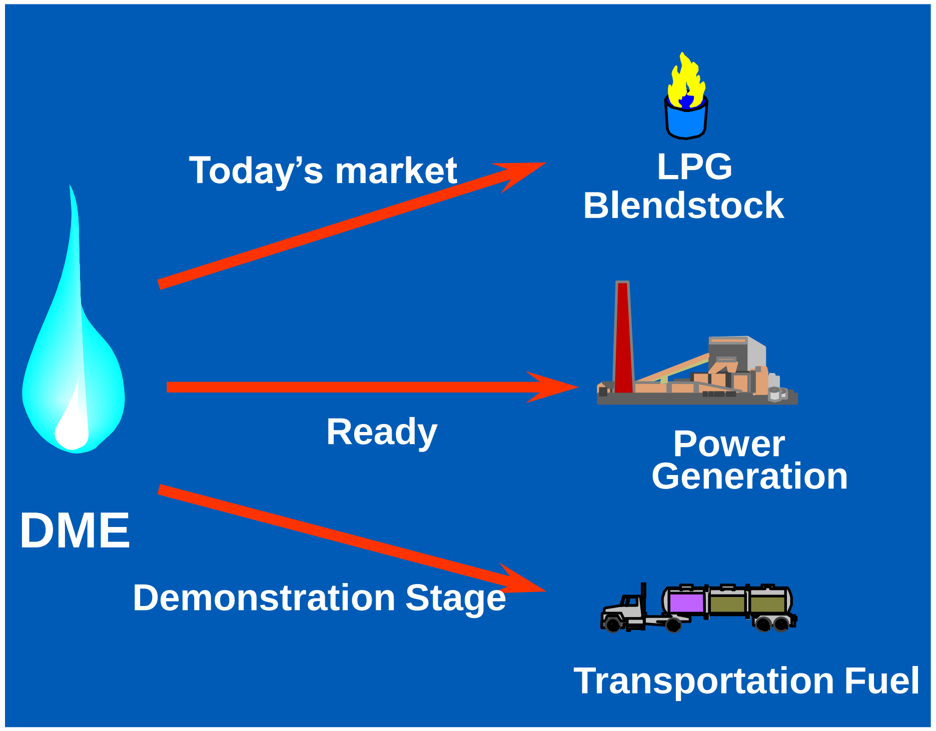


www.AboutDME.org

DME Markets

CFC Replacement

Three Major Fuel Applications

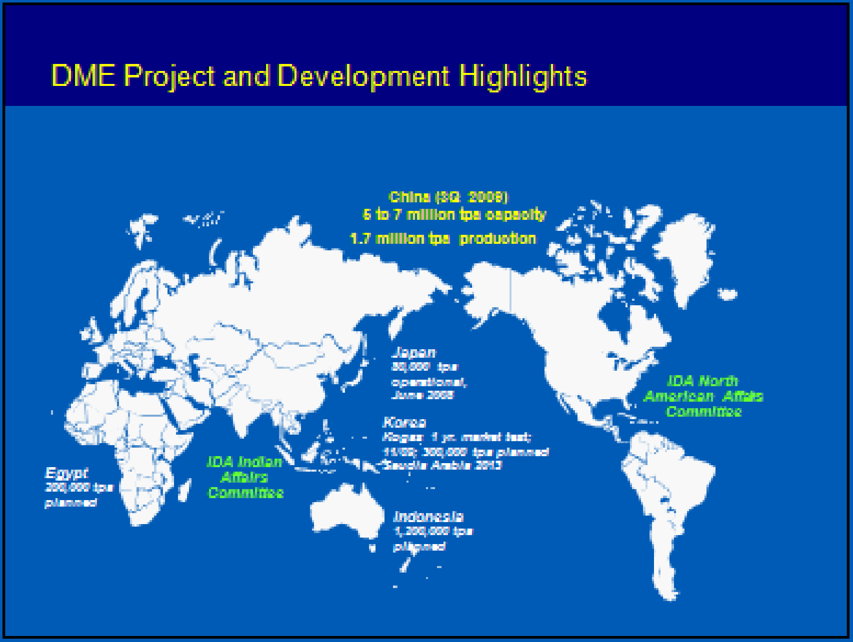


Other markets include petrochemicals feedstock to produce olefins

DME / LPG Blending – Factors Driving Growth

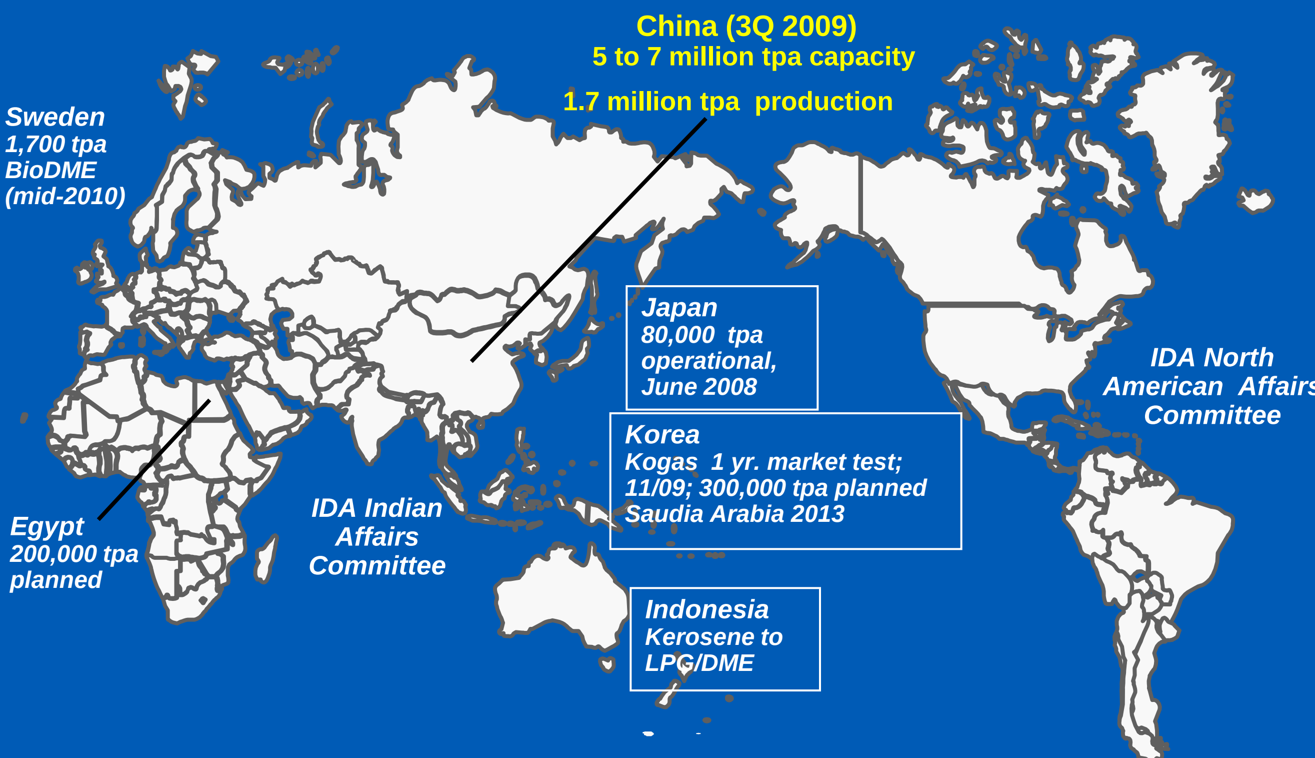
More than 80% of DME currently produced is blended with LPG

- 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



DME Project and Development Highlights

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

Much Work Underway

Volvo DME Truck

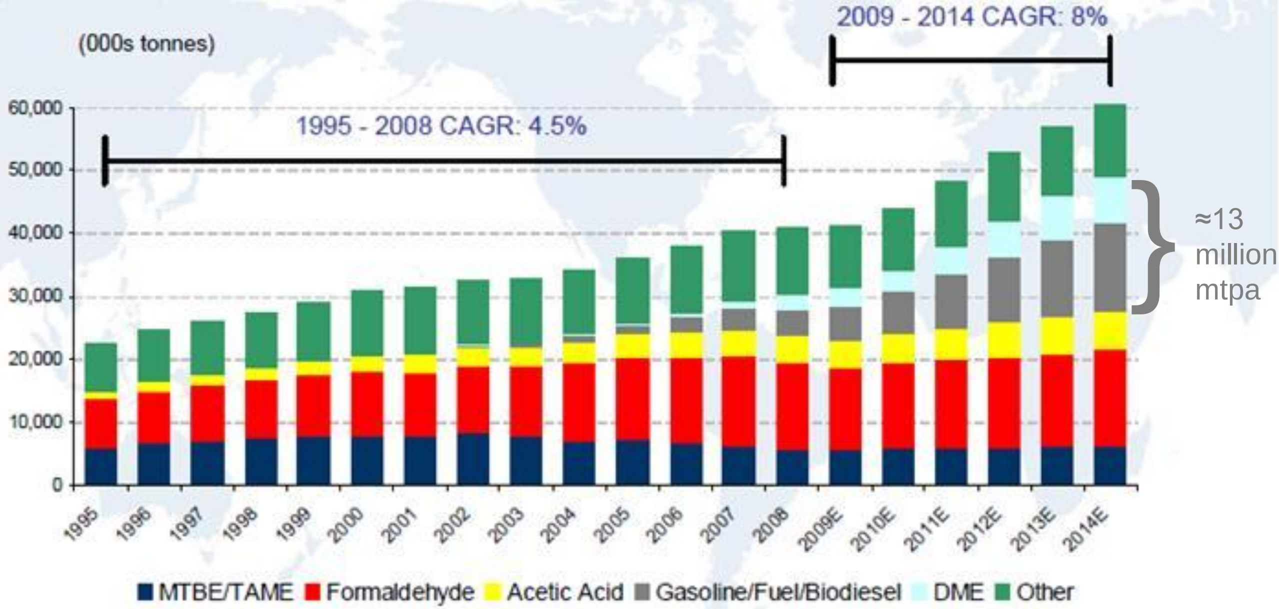
Nissan NTSL DME Diesel Truck

SJTU DME Diesel Bus (China)

So: International DME Association, 9/2009

Global Demand Growth

- Demand into energy applications expected to drive higher industry growth



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 propylenes (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

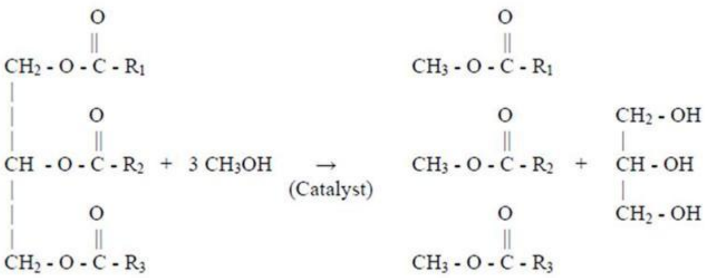
Other Fuel Markets (2)

BioDiesel

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

100 lbs of oil + 10 lbs of methanol → 100 lbs of biodiesel + 10 lbs of glycerol

This equation is a simplified form of the following ***transesterfication*** reaction.



triglyceride methanol mixture of fatty esters glycerol

Figure 1. Transesterification Reaction

where R_1, R_2, and R_3 are long chains of carbons and hydrogen atoms, sometimes called fatty acid chains.

- 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

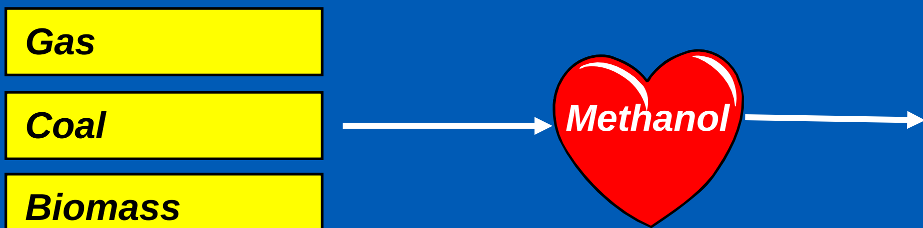
- Production Technologies

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

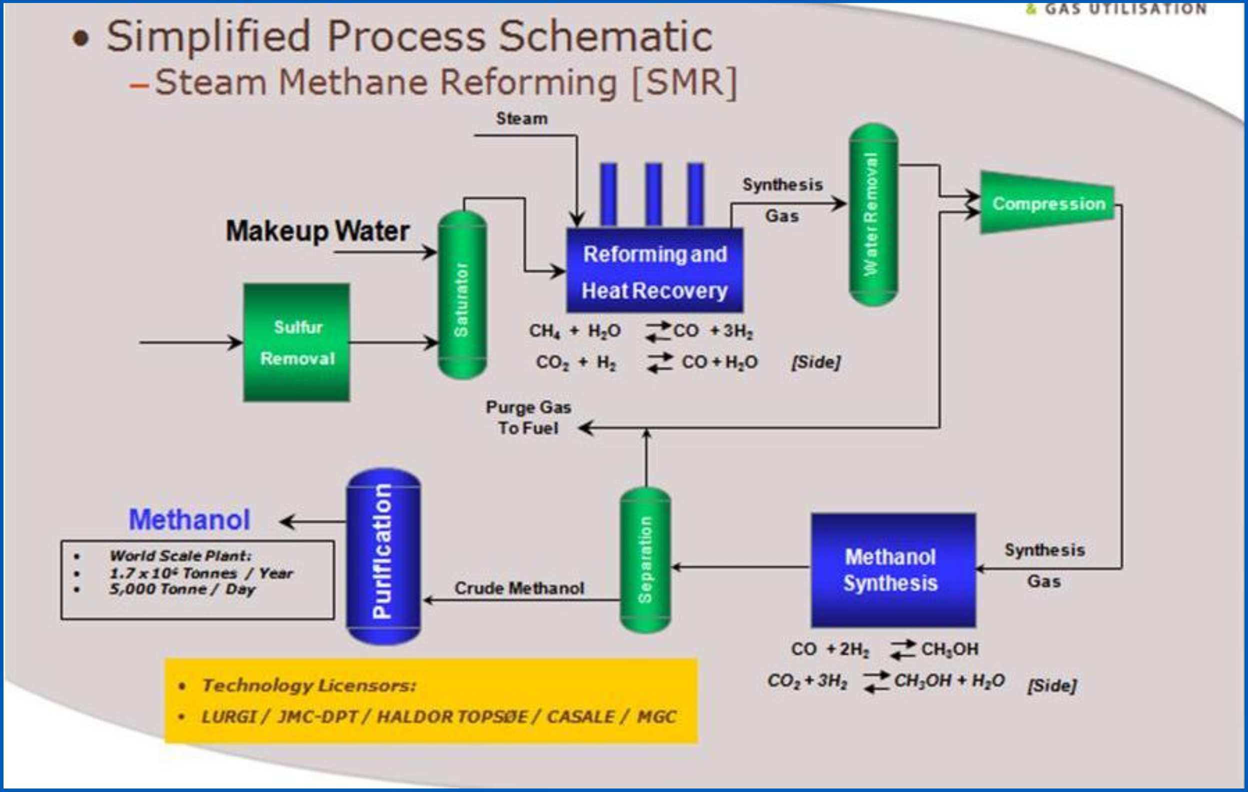
•5,000 mtpd methanol plant , LHV equivalent to 18,000 bpd diesel

•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) $CO + 2H_2 \Leftrightarrow CH_3OH$ $\Delta H = -91$ kJ/mol

(2) $CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$ $\Delta H = -41$ kJ/mol

Stoichiometric Ratio = $(H_2-CO_2)/(CO + CO_2)$ 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.

Methanol XTL Comparison with FT-XTL

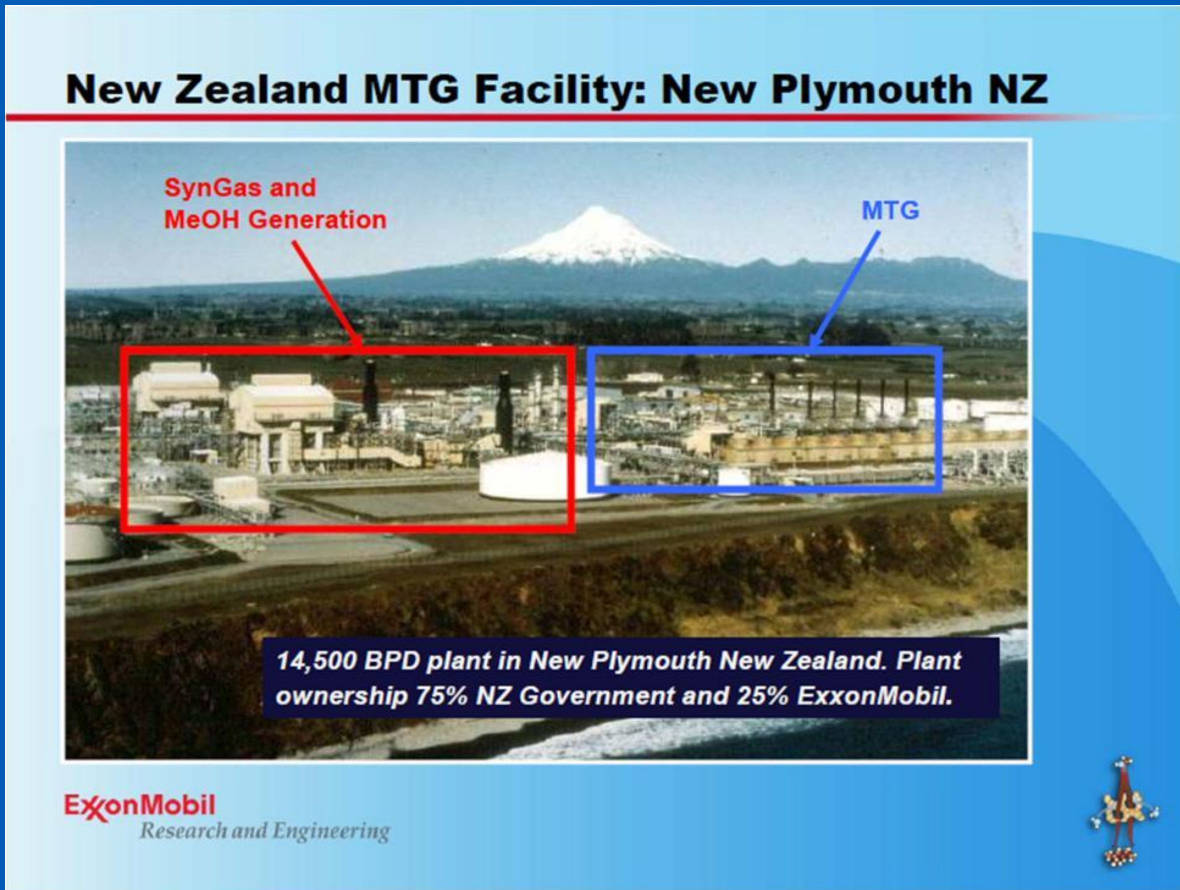
Conversion of Synthesis Gas

- 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



Methanol to DME to Gasoline

Reaction Path

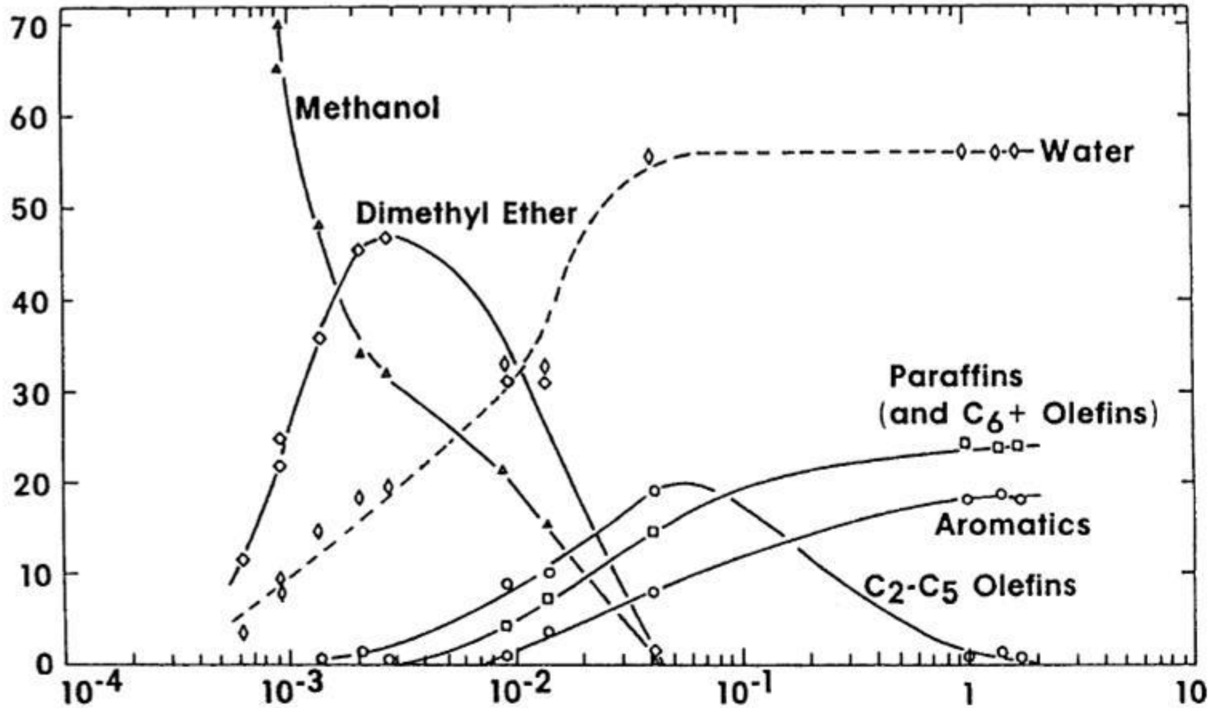


Figure 14 - Product time plot of products in *w/w*% against space time in hours

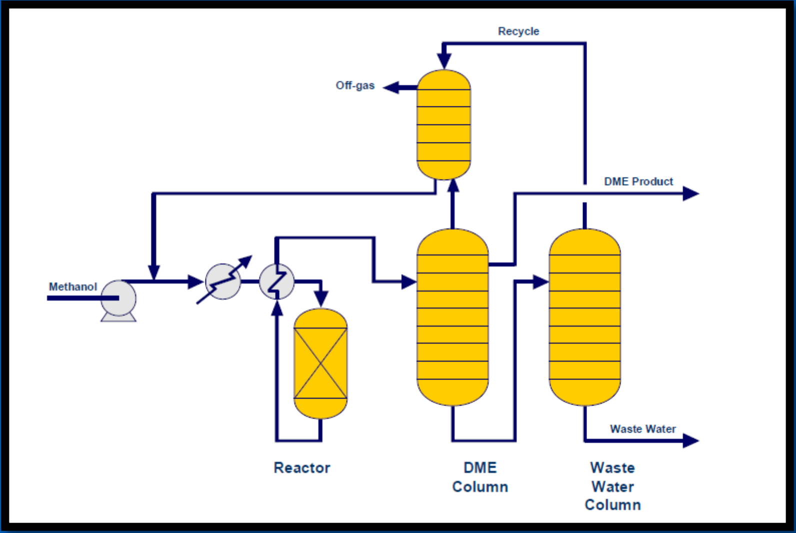
How is DME produced

- Reaction: methanol dehydration

  2 $CH3OH \Leftrightarrow CH3\text{-}O\text{-}CH3 + H2O$ $\Delta H = -23.4$ 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

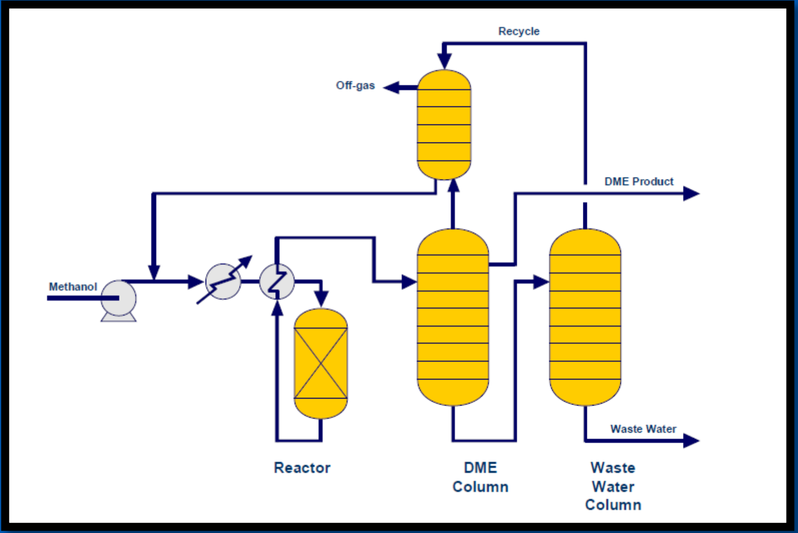
- Reaction: methanol dehydration

  $2\ CH_3OH \Leftrightarrow CH_3\text{-}O\text{-}CH_3 + H_2O \quad \Delta H = -\ 23.4\ kJ/mol$

- 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%



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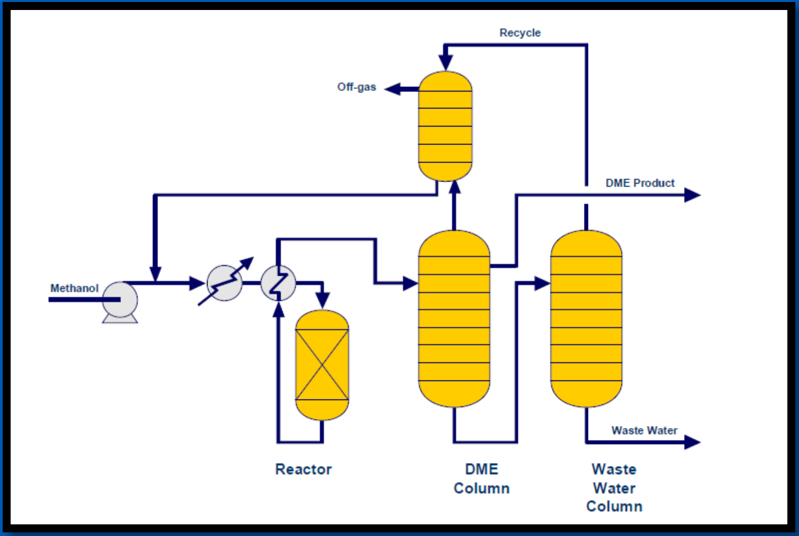
- Technology Providers include: Haldor Topsoe, Lurgi, Mitsubishi Gas Chemicals, Toyo Engineering



Source of process diagram : "Cost Effective Topsoe DME Production Technology, 2007

About Methanol and DME

- Health, Safety and Environment
- Economics

Environment, Health, and Safety

Methanol

- **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

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

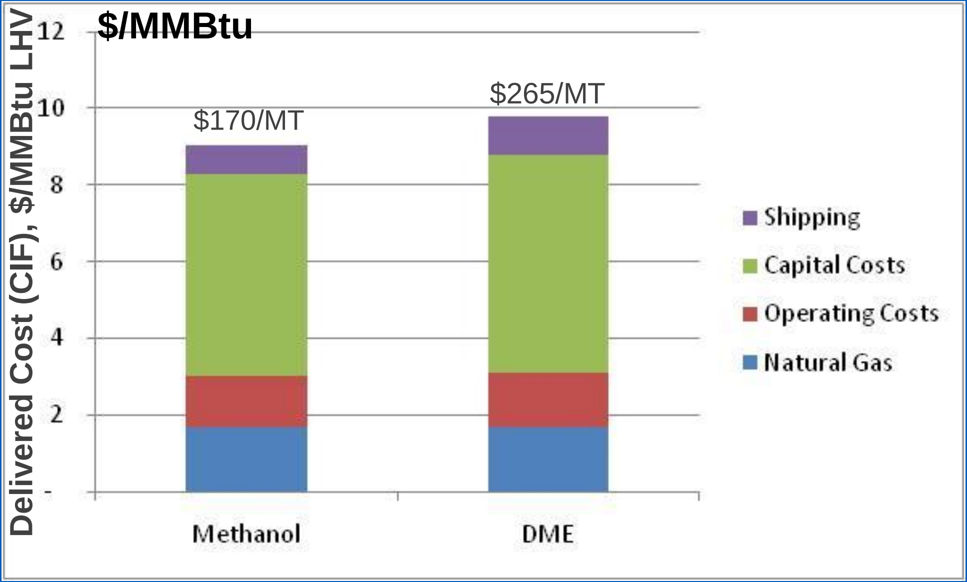
Photos Courtesy of Akzo Nobel and DuPont

Visit International DME Association website:
www.aboutdme.org

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.

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



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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Ronald A. Sills, LLC has prepared this presentation utilizing reasonable care and skill in applying methods of analysis consistent with normal industry practice.

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Questions

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