Separation Enhanced Dimethyl Ether (DME) Synthesis
Dr. Ir. Jurriaan Boon
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Separation enhanced DME synthesis

- DME: promising fuel for compression ignition vehicles
- Production of DME from biomass
- Conventional production of DME
- Separation enhanced DME synthesis
- Fledged: DME from biomass, renewable electricity
Dimethyl ether (DME)
DME: Fuel of choice
DME: Fuel of choice

• Promising in terms of GHG emissions, efficiency, economy

• Can be handled like LPG

• Behaves like diesel in a compression ignition engine
  *without soot formation!*
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SPECIAL FOCUS: CLEAN FUELS

DME as a diesel alternative in North America

Major trends in the global hydrocarbon processing industry include the regulatory-driven demand for clean, low-emissions fuels. Two decades of global efforts have shown that dimethyl ether (DME) can satisfy these drivers.

Sills, R. A., XTL & DME Institute

Major trends in the global hydrocarbon processing industry include the regulatory-driven demand for clean, low-emissions fuels. Two decades of global efforts have shown that dimethyl ether (DME) can satisfy these drivers. 1 DME has been used for many years as an aerosol propellant in cosmetic and other personal and household products, but this represents a small market. DME was first commercialized as a fuel in China as a liquefied petroleum gas (LPG) blendstock for the domestic home cooking/heating market. As a result, it now represents about 5% of global methanol demand. 2 This article focuses on the challenges and the significant progress that has been made of commercializing DME as a diesel alternative.
Fledged: DME from biomass and hydrogen

\[ M = \frac{[H_2]}{[CO] + [CO_2]} = 2 \]
Production of DME

Methanol synthesis

\[ \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \]

Water-gas shift (WGS)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \]

Methanol dehydration

\[ 2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \]
Conventional production of DME

Synthesis gas → Methanol synthesis → Methanol separation → H₂/CO/CO₂ recycle
Conventional production of DME

Synthesis gas → Methanol synthesis → Methanol separation → DME synthesis → DME separation → DME

H₂/CO/CO₂ recycle → Methanol recycle
Production of DME from biomass

Biomass

Steam

Air (if ind. gas)

Gasification process

Tar/PM removal

WGS unit

CO₂ separation

H₂S separation

ASU

O₂

H₂/CO/CO₂ recycle

MeOH synthesis

MeOH separation

MeOH synthesis

DME synthesis

DME separation

DME

MeOH recycle
Conventional versus direct synthesis

Conventional DME production

- Synthesis gas
- Methanol synthesis
- Methanol separation
- DME synthesis
- DME separation
- DME
- H₂/CO/CO₂ recycle
- Methanol recycle

Direct DME production

- Synthesis gas
- Direct DME synthesis
- DME separation
- DME
- CO/CO₂ recycle
- Optional CO recycle
Steam separation enhanced DME synthesis

Methanol synthesis

\[ \text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \]

Water-gas shift (WGS)

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \]

Methanol dehydration

\[ 2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \]
Thermodynamic equilibrium

\[ M = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} = 2 \]

25 bar(a)
54 mol% H₂
15 mol% CO
7.7 mol% CO₂
Equilibrium with in situ water removal

275 °C
25 bar(a)

54 mol% H₂
15 mol% CO
7.7 mol% CO₂

Composition / mol%
Steam slip / mol%

Composition
DME
CH₃OH
CO
CO₂

0.001 0.01 0.1 1
0 5 10 15 20 25 30 35 40

Experimental: sorption enhanced DME synthesis

[Diagram showing the process of sorption enhanced DME synthesis with Zeolite 3A, Cu/ZnO/Al₂O₃ catalyst, syngas, effluent, 275 °C, 25 bar(a) and 400 °C, 2 bar(a)].
Experimental: sorption enhanced DME synthesis
Experimental: breakthrough test

- **MS signal / A**
- **NDIR concentration / mol%**
- **Time / min**

**Composition 3**

- 275 °C
- 25 bar(a)
- 54 mol% H₂
- 15 mol% CO
- 7.7 mol% CO₂

**Proof of concept**
Separation enhanced DME synthesis

- Increased CO/CO$_2$ flexibility
- Increased DME yield
- Decreased CO$_2$ content

$M = 2$

Conventional direct DME synthesis
(thermodynamic calculation)

Sorption enhanced DME synthesis
(experimental observation)

275°C, 25 bar

- MethOH
- CO
- CO$_2$
- DME

Product C-distribution [mol%]
Conventional, direct, sorption-enhanced synthesis

Conventional DME production

- Synthesis gas → Methanol synthesis → Methanol separation → DME synthesis → DME separation → DME
  - H$_2$/CO/CO$_2$ recycle → Methanol recycle

Direct DME production

- Synthesis gas → Direct DME synthesis → DME separation → DME
  - CO/CO$_2$ recycle

Sorption-enhanced DME production (SEDMES)

- Synthesis gas → SEDMES → DME separation → DME
  - Optional CO recycle
Production of DME from biomass

Biomass
Steam
Air (if ind. gas)

Gasification process
Tar/PM removal
WGS unit
CO₂ separation
H₂S separation

O₂

ASU

MeOH synthesis
MeOH separation

H₂/CO/CO₂ recycle

MeOH recycle

MeOH

DME synthesis

DME separation

DME
Production of DME from biomass

The **FLEDGED** project will deliver a process for *bio-based dimethyl ether (DME)* production from *biomass* gasification, validated in *industrially relevant* environment (TRL5).
Separation enhanced DME synthesis

• DME: promising fuel for compression ignition vehicles
• Production of DME from biomass
• Conventional production of DME
  – Low DME yield
  – CO$_2$ production
  – Complex separation
• Sorption enhanced DME synthesis
  – Increased CO/CO$_2$ flexibility
  – Increased DME yield
  – Decreased CO$_2$ content
• Fledged: DME from biomass, renewable electricity
Gas separation, treatment & conversion

- Development of sorption technology to reduce industrial CO₂ emissions
- Development of membrane reactors for hydrogen production
- Conversion of industrial waste streams into chemicals and transport fuels
Industrial integration of renewable electricity

• Development of processes to produce chemicals and fuels with the help of electricity, e.g. hydrogen
• Development of technology to flexibly convert renewable electricity into heat
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