Synthesis of DME and Gasoline from Biomass-Derived Synthesis Gas

7th ASIAN DME CONFERENCE
November 16-18, 2011
Niigata, Japan

Ulrich Arnold, Miriam Stiefel, Ruaa Ahmad, Herbert Lam, Manfred Döring
Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen
Biofuels: An overview

Biodiesel
- Transesterification of rapeseed oil with methanol

Pure vegetable oil
- Squeezing or extraction

**HydroThermal Upgrading (HTU) + HydroDeOxygenation (HDO)**

**Biomass Wastes etc.**
- Fermentation of sugars and starch
- Degradation of (ligno)cellulose + fermentation
- Anaerobic digestion
- Hydrothermal gasification
- Fermentation

Pyrolysis
- Pyrolyzate

Gasification
- Hydrogen
- Methane

**Syngas**
- Water gas shift reaction
- Methanization

**Fischer-Tropsch-Synthesis (FT-Synthesis)**

Conversion of Olefins to Distillate
COD

Diesel
- Gasoline
- Olefins
- Dimethylether
- Methanol

Butanol
- ABE-Fermentation

**Methanol To-Olefins (MTO)**

**Methanol To-Gasoline (MTG)**

**Methanol To-Synfuel (MTS)**

Direct synthesis
- Low temperature synthesis
- Direct synthesis

**COD**

**Direct gasification**
- CO, H₂, CO₂, H₂S, COS, NH₃ etc.

**Fermentation**

**Reforming**

**Hydrogen**
- MTBE
- Isobutylene
- ETBE

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Related activities:

GTL-, CTL- and BTL-processes for fuel production

**GTL = Gas-To-Liquid (Syngas from natural gas)**
- Motunui, New Zealand (Mobil)
- Topsøe Integrated Gasoline Synthesis (TIGAS process), Texas, USA (Haldor Topsøe)
- Mobil Olefin-To-Gasoline/Distillate process (MOGD)
- Lurgi's Methanol-To-Synfuel process (MTS)
- CAC plant, Freiberg, Germany

**CTL = Coal-To-Liquid (Syngas from coal)**
- Medicine Bow, Wyoming, USA (ExxonMobil)
- Jincheng, Shanxi Province, China (JAM + Uhde)
- Adams Fork Energy, Mingo County, West Virginia, USA (Uhde)

**BTL = Biomass-To-Liquid (Syngas from biomass)**
- CHEMREC process (production of dimethyl ether, DME): Chemrec, ETC, Volvo, Delphi, Haldor Topsøe, Preem, Total, SEA
- Choren process (Fischer-Tropsch-Technology, FT)
- French CEA project in Bure Saudron: CNIM group, Air Liquide, Choren, SNC Lavalin, Foster Wheeler-France, MSW Energy (FT)
- BioTfueL project: Uhde Prenflo-PDQ-process, Total, IFP, French Atomic Energy Board, Sofiproteol (FT)
- Güssing gasifier (woodchips), Oxford Catalysts (Velocys Inc., now part of the Oxford Catalysts Group), SGC Energia (Portugal), microreactor technology (FT)
The bioliq® process at KIT

Biodiesel
Transesterification of rapeseed oil with methanol

Pure vegetable oil
Squeezing or extraction

HydroThermal Upgrading (HTU) + HydroDeOxygenation (HDO)

Fischer-Tropsch-Synthesis (FT-Synthesis)

COD

Diesel
Gasoline
Olefins
Dimethylether

Methanol-To-Olefins (MTO)
Methanol-To-Gasoline (MTG)
Methanol-To-Synfuel (MTS)

Direct synthesis
Low temperature synthesis

Direct synthesis

Biomass Wastes etc.

Pyrolysis
Pyrolyzate

Gasification
Syngas

Fermentation of sugars and starch
Degradation of (ligno)cellulose + fermentation

Anaerobic digestion
Hydrothermal gasification
Fermentation

Water gas shift reaction
Methanization

Hydrogen
Methane

Fermentation

ABE-Fermentation

Butanol

CO, H₂, CO₂, H₂S, COS, NH₃ etc.

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3rd Asian DME Conference, November 16-18, 2011
Dr. Ulrich Arnold, IKFT
Investigated processes at KIT-IKFT

Syngas ($H_2/CO \leq 1$)

**Direct Synthesis of DME**

$$3 \text{ CO} + 3 \text{ H}_2 \rightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2$$

**Direct Synthesis of Ethanol**

$$3 \text{ CO} + 3 \text{ H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CO}_2$$

**Synthesis of Olefins from DME**

$$\text{CH}_3\text{OCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$$

**Synthesis of Gasoline from DME**

$$n \text{ CH}_3\text{OCH}_3 \rightarrow "(\text{CH}_2)_2n" + n \text{ H}_2\text{O}$$
Focus on direct conversion of SYNGAS-TO-DME (STD)

Syngas (H₂/CO ≤ 1)

Direct Synthesis of DME

3 CO + 3 H₂ → CH₃OCH₃ + CO₂

Direct Synthesis of Ethanol

3 CO + 3 H₂ → C₂H₅OH + CO₂

Synthesis of Olefins from DME

CH₃OCH₃ → C₂H₄ + H₂O

Synthesis of Gasoline from DME

n CH₃OCH₃ → “(CH₂)₂n“ + n H₂O
Direct conversion of carbon monoxide-rich syngas to DME

Three reactions take place simultaneously:

● **Synthesis of methanol:**
  \[2 \text{ CO} + 4 \text{ H}_2 \rightleftharpoons 2 \text{ CH}_3\text{OH}\]
  \(\Delta H^\circ = -182.2 \text{ kJ/mol}\)

● **Dehydration of methanol:**
  \[2 \text{ CH}_3\text{OH} \rightleftharpoons \text{ H}_3\text{COCH}_3 + \text{ H}_2\text{O}\]
  \(\Delta H^\circ = -23.5 \text{ kJ/mol}\)

● **Water-gas shift reaction:**
  \[\text{CO} + \text{ H}_2\text{O} \rightleftharpoons \text{ H}_2 + \text{ CO}_2\]
  \(\Delta H^\circ = -41.2 \text{ kJ/mol}\)

● **Total reaction:**
  \[3 \text{ CO} + 3 \text{ H}_2 \rightleftharpoons \text{ H}_3\text{COCH}_3 + \text{ CO}_2\]
  \(\Delta H^\circ = -246.9 \text{ kJ/mol}\)
Laboratory plant for the STD process

- **Fixed bed reactor:**
  - \( D_i = 1.6 \text{ cm} \)
  - \( L = 30 \text{ cm} \)
  - \( V = 60.3 \text{ cm}^3 \)

- **Catalyst:**
  Bifunctional catalyst system comprising a methanol- and a dehydration-catalyst

- **Reaction conditions:**
  - \( p = 51 \text{ bar} \)
  - \( T = 200 - 250 \text{ °C} \)
  - \( \text{GHSV} = 20 - 150 \text{ Nml/(min·g}_{\text{Cat}}) \)
  - Dilution: 70% inert gas
Typical results from the STD reaction

<table>
<thead>
<tr>
<th>$\text{H}_2/\text{CO}$</th>
<th>$\text{CO}$ conversion (%)</th>
<th>DME selectivity (%)</th>
<th>$\text{CO}_2$ selectivity (%)</th>
<th>MeOH selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>61</td>
<td>67</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>45</td>
<td>66</td>
<td>33</td>
<td>1</td>
</tr>
<tr>
<td>0.67</td>
<td>34</td>
<td>65</td>
<td>34</td>
<td>1</td>
</tr>
</tbody>
</table>

**Reaction conditions:**
- Pressure: 51 bar
- Temperature: 250 °C
- Space velocity: 20 - 150 Nml/(min·g$_{\text{Cat}}$)
- Dilution: 70% inert gas

Influence of temperature and $\text{H}_2/\text{CO}$ ratio on DME synthesis

- Large influence of temperature on CO conversion; Optimum range: 250 - 260 °C
- CO conversion increases with increasing $\text{H}_2$ content in the synthesis gas; Temperature dependence decreases with decreasing $\text{H}_2$ content
Almost maximum CO conversion at a flow rate of 50 ml/min at 250 °C
Increase of CO conversion by increase of residence time is independent of \( \text{H}_2/\text{CO} \) ratio
The lower dilution the higher CO conversion
The H₂/CO ratio influences CO conversion:
Maximum increase was observed at H₂/CO = 1

p = 51 bar, T = 250 °C, V_{total} = 100 Nml/min
Influence of catalyst poisons on DME synthesis

- Strong deactivation by acidic catalyst poisons within 24 h
- CO conversion decreases but DME selectivity remains constant
- Influence of NH$_3$ is negligible within 24 h

T = 250 °C, p = 51 bar, H$_2$/CO = 1, V$_{total}$ = 167 Nml/min
Long-term performance of the catalyst system in the absence and presence of CO$_2$

- Typical loss of activity within the first days but CO conversion remains in an acceptable range
- DME selectivity remains constant and high during three weeks

Gas composition:
- H$_2$ = 35 mlN/min, CO = 35 mlN/min, N$_2$ = 20 mlN/min, Ar = 27 mlN/min
- H$_2$ = 35 mlN/min, CO = 35 mlN/min, N$_2$ = 10 mlN/min, Ar = 27.5 mlN/min, CO$_2$ = 9.5 mlN/min

p = 51 bar, T = 250 °C, V$_{\text{total}}$ = 117 Nml/min
The bioliq® process chain

Gasification (bioliq® II) → Syngas

Fast pyrolysis (bioliq® I) → Pyrolyzate

HTHP gas cleaning + SYNGAS-TO-DME, STD (bioliq® III) → Methanol

DME-TO-GASOLINE, DTG (bioliq® IV) → Olefins

DME → Gasoline

Biomass
# Dimensioning of the bioliq® process

<table>
<thead>
<tr>
<th>Technology</th>
<th>bioliq® I</th>
<th>bioliq® II</th>
<th>bioliq® IIIa+b</th>
<th>bioliq® IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fast pyrolysis</td>
<td>Entrained flow gasification</td>
<td>bioliq® IIIa: High Temperature, High Pressure (HTHP), Syngas Cleaning</td>
<td>DME-To-Gasoline (DTG)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>bioliq® IIIb: Syngas-To-DME (STD)</td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>Bio-slurry</td>
<td>Synthesis gas</td>
<td>DME</td>
<td>Gasoline</td>
</tr>
<tr>
<td>Dimensioning</td>
<td>0.5 t/h dry biomass (2 MW)</td>
<td>~ 1 t/h bio-slurry (5 MW)</td>
<td>~ 150 kg/h DME</td>
<td>~ 80 kg/h gasoline</td>
</tr>
</tbody>
</table>
Fuel production within the bioliq® process

Flow chart for DME and gasoline production (bioliq® IIIb and IV)
bioliq® plant: View from southeast

Financial support from
bioliq® plant: View from northeast

Cooperation between: C·A·C® and KIT
# Product options within the bioliq® process

<table>
<thead>
<tr>
<th>Feed</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Reactor 3</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water-gas</td>
<td>MeOH/DME</td>
<td>Gasoline</td>
<td></td>
</tr>
<tr>
<td></td>
<td>shift reaction</td>
<td>production</td>
<td>synthesis</td>
<td></td>
</tr>
<tr>
<td>Syngas</td>
<td>+</td>
<td>+</td>
<td>+ (Modified catalyst)</td>
<td></td>
</tr>
<tr>
<td>H₂:CO = 1:1</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+/-</td>
<td>+</td>
<td>+</td>
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<tr>
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<td>+/-</td>
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</tr>
<tr>
<td></td>
<td>+/-</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

- **H₂**
- **MeOH**
- **DME**
- **Gasoline**
- **Kerosene**
Why the methanol/DME pathway instead of a Fischer-Tropsch process?

- High flexibility: Production of various fuels and chemicals is possible
- High selectivity: No elaborate product separation technologies
- Processes are tunable to a large extent (catalysts, conditions, reactors etc.)
- Large optimization potential

<table>
<thead>
<tr>
<th>Comparison of Fischer-Tropsch with MTG</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Methane</td>
</tr>
<tr>
<td>Ethylene</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Propylene</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Butylene</td>
</tr>
<tr>
<td>Butane</td>
</tr>
<tr>
<td>C5+ Gasoline</td>
</tr>
<tr>
<td>Gasoil/Distillate</td>
</tr>
<tr>
<td>Heavy Oil/Wax</td>
</tr>
<tr>
<td>Oxygenates</td>
</tr>
<tr>
<td><strong>Σ</strong></td>
</tr>
</tbody>
</table>

Sources:
Conclusions

- Catalyst systems for the direct synthesis of DME in fixed bed reactors are mature
- Optimum reaction parameters are identified
- Higher H\textsubscript{2} content in syngas increases CO conversion
- High DME selectivity (60 - 68\%) even at H\textsubscript{2}/CO ≤ 1
- Main byproduct: CO\textsubscript{2} from the water-gas shift reaction
- Low amounts of methanol (< 2\%) in the product mixture; Fast and almost complete dehydration of methanol
- Almost no further byproducts (< 0.1\%); Traces of methane, propane, propene, butane
- CO\textsubscript{2} concentration should be low (< 5\%); Otherwise significant decrease of CO conversion
- Major challenge: Up-scaling and reactor technology
Thank you!