Recent progress in the synthesis of oxygenate fuels from renewable resources

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Content

1. Overview on oxygenate fuels
2. Dimethyl ether (DME) as a diesel fuel
3. Oxymethylene dimethyl ethers (OMEs) as diesel fuel additives
4. Strategies for OME production
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Oxygenate fuels and additives: An overview

**Short-chain alcohols**

<table>
<thead>
<tr>
<th></th>
<th>Methanol</th>
<th>Ethanol</th>
<th>i-Propanol</th>
<th>i-Butanol</th>
<th>t-Butanol</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 °C (g/ml)</td>
<td>0.796</td>
<td>0.793</td>
<td>0.790</td>
<td>0.803</td>
<td>0.792</td>
<td>0.715-0.780</td>
</tr>
<tr>
<td>LHV (kJ/g)</td>
<td>21.5</td>
<td>28.8</td>
<td>32.4</td>
<td>35.5</td>
<td>35.0</td>
<td>44.1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>65</td>
<td>78</td>
<td>82</td>
<td>108</td>
<td>82</td>
<td>30-190</td>
</tr>
<tr>
<td>Octane number (RON)</td>
<td>116</td>
<td>113</td>
<td>109</td>
<td>102</td>
<td>100</td>
<td>90-98</td>
</tr>
<tr>
<td>Oxygen content (wt.%)</td>
<td>50.0</td>
<td>34.8</td>
<td>26.7</td>
<td>21.6</td>
<td>21.6</td>
<td>–</td>
</tr>
</tbody>
</table>

# Oxygenate fuels and additives: An overview

## Ethers

<table>
<thead>
<tr>
<th></th>
<th>Methyl-\textit{tert}-butyl-ether (MTBE)</th>
<th>Ethyl-\textit{tert}-butyl-ether (ETBE)</th>
<th>\textit{tert}-Amyl-methyl-ether (TAME)</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 °C (g/ml)</td>
<td>0.745</td>
<td>0.756</td>
<td>0.774</td>
<td>0.715-0.780</td>
</tr>
<tr>
<td>LHV (kJ/g)</td>
<td>38.3</td>
<td>39.4</td>
<td>39.4</td>
<td>44.1</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>55</td>
<td>73</td>
<td>86</td>
<td>30-190</td>
</tr>
<tr>
<td>Octane number (RON)</td>
<td>109</td>
<td>110</td>
<td>103</td>
<td>90-98</td>
</tr>
<tr>
<td>Oxygen content (wt.%)</td>
<td>18.2</td>
<td>15.7</td>
<td>15.7</td>
<td>–</td>
</tr>
</tbody>
</table>

**Typical fuel applications:**
Octane enhancers, emissions reduction, anti-icing agents etc.
Use of oxygenate fuels: General aspects

**Advantages and potentials:**
- Clean combustion (soot-free, reduced NO\textsubscript{x}/SO\textsubscript{x} emissions)
- Simplification of exhaust gas treatment
- No sophisticated engine modification necessary
- No elaborate modification of fuel supply infrastructure
- Compatibility with conventional fuels $\Rightarrow$ Blending possible
- Synthesis from renewable resources $\Rightarrow$ Reduction of overall CO\textsubscript{2} emissions
- Production with high atom economy and energy efficiency (oxygen from biomass remains partially in the product!)

**Challenges:**
- Lower heating values compared to hydrocarbons
- Modifications, e.g. adaption of sealing materials and lubricants
- Cost reduction (new technologies desirable, economy of scale)
- Huge market potential, market development necessary
Common pathways for oxygenates production

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Global DME production capacity

Properties and applications of DME

Properties
- Colorless, flammable gas
- Readily liquefiable
- Non-toxic, non-carcinogenic and non-mutagenic

Applications
- Liquefied Petrol Gas (LPG) substitute
- Propellant, refrigerant
- Chemical feedstock, e.g. for dimethyl sulfate production
- Diesel fuel substitute (cetane no. of 55)

T.A. Semelsberger et al., J. Power Sources 2006, 156, 497–511.
Synthesis of DME from synthesis gas (CO/H₂)

- Coal
- Natural gas
- Oil
- Biomass
- CO₂/H₂

→ Synthesis gas

→ Methanol

→ DME

→ Hydrocarbons

→ Hydrogen

→ Methane
DME synthesis

Two-step synthesis

Syngas → Methanol → DME

Single-step synthesis

\[
\begin{align*}
4 \text{H}_2 & + 2 \text{CO} \rightarrow 2 \text{CH}_3\text{OH} \\
2 \text{CH}_3\text{OH} & \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \\
\text{CO} & + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \\
3 \text{H}_2 & + 3 \text{CO} \rightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2
\end{align*}
\]
Two-step synthesis vs. single-step synthesis

Thermodynamics: Calculated CO conversions

Catalyst systems for single-step synthesis

Syngas → Hydrogenation → Methanol → Dehydration → DME

Catalyst: Cu/ZnO/Al₂O₃, γ-Aluminium oxide or zeolite

Admixed systems or Bifunctional catalysts

Zeolite-based bifunctional catalysts

Results of catalyst screening
New methanol catalysts via flame-spray-synthesis

Long-term performance of mixed catalyst systems and passivation-reactivation experiments

1st passivation/reactivation

2nd passivation/reactivation
Up-scaling of DME synthesis

MOSYS (MOBILE SYngas SYNthesis plant)               Synthesis unit of bioliq® plant
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Oxymethylene dimethyl ethers (OMEs) as fuels and fuel additives

Why oxymethylene ethers?
- Absence of carbon-carbon bonds => Soot-free combustion
- Similar properties as conventional diesel => unlimited miscibility with diesel
- Non-toxic, non-corrosive

Combustion of OMEs and combustion of diesel
From DME to POMs – which chain length is appropriate?

- The most suitable OMEs for fuel applications are OME-3, OME-4 and OME-5
- The polymers are commercially available plastics (POMs)
World-wide activities in the field of OMEs

Activities in China are rapidly increasing
Pathway 1 is the most desirable, since it starts directly from the low-cost educts methanol and formaldehyde

But: a series of byproducts is also formed

Synthesis strategies for OMEs

- Methanol → Formaldehyde
- Trioxane
- DME
- Methylal

Chemical structures:
- or
- \[ \text{OME} \]

Institute of Catalysis Research and Technology (IKFT)
Product mixtures in the synthesis of OMEs from methylal and trioxane

Catalysts:

Amberlite powder (< 100 μm)  Zeolite powder (< 100 μm)

Optimized reaction conditions:
38 g methylal (0.5 mol), 15 g trioxane (TRI, 0.5 mol CH₂O), 0.15 g catalyst (1 wt.% with respect to TRI), T = 30 °C
Experimental and calculated product distribution

Schulz-Flory distribution

Synthesis strategies for OMEs

CH₃OH

or

\[ \overset{\text{O}}{\text{O}} \]

+ \[ \overset{\text{H}}{\text{O}} \overset{\text{O}}{\text{O}} \] \[ n \]

\[ \overset{\text{O}}{\text{O}} \overset{\text{O}}{\text{O}} \] \[ n \] + H₂O

Methanol → Formaldehyde → Methylal → Trioxane → OME

DME

1

2

3
OME separation from aqueous reaction solutions by extraction with diesel

⇒ Direct additivation of diesel possible
Product separation by extraction with diesel

![Bar graph showing the distribution of products in diesel and aqueous phases. The graph compares FA, MeOH, Water, Trioxane, OME-1, OME-2, OME-3, OME-4, OME-5, OME-5+, OME-OH-1, OME-OH-2, and OME-OH-3. The x-axis represents the products, and the y-axis represents the wt-% in both phases.]
OME synthesis from methanol and formaldehyde: Process development

**Challenges:**
- Separation of water
- Recycling of educts and byproducts
- Optimization of extraction step
Conclusions

**Gasoline:**
- Oxygenates can contribute significantly to emissions reduction, which is proven by dozens of studies
- Oxygenates are state-of-the-art components of gasoline

**Diesel:**
- The single-step process for DME manufacturing is on an advanced stage of development and can compete with common 2-step processes
- Availability of OMEs is limited and thus, detailed engine tests are still missing; Only basic tests were done, which proved efficiency of this concept
- Efficient OME synthesis is currently subject of intensive R&D and we think that our extraction process is a good option
- Best technologies are currently identified, to create a sound base for evaluation, scale-up and commercialization
- In view of tremendous Chinese activities, market introduction could be realized in China first
Financial support from
• Helmholtz Association
• Helmholtz Research School *Energy-Related Catalysis*

Thank you!

KIT Campus North