Bio-Ethers as Transportation Fuel: A Review

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What Are Bio-Ethers

- Bio-Ethers are produced by dehydration of bio-based alcohols
- Bio-Ethers have superior combustion and emission characteristics as compared to other bio-fuels
What Are Bio-Ethers

Can Be Produced by:

- Partial oxidation of biomass to synthesis gas and then to alcohols and then dehydrating them to Ethers using suitable catalysts.

- The achievable yield of bio-ether from biomass via the gasification/synthesis gas route is higher than via the hydrolysis/fermentation route.

- In gasification/synthesis gas route all carbon can be converted to fuel while in fermentation route only carbon convertible to sugar can yield fuel.
# Ethers in Fuel Industry

<table>
<thead>
<tr>
<th>Ethers</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Ether (DME)</td>
<td>✓ Alternative Fuel for CI engines</td>
</tr>
<tr>
<td>Diethyl Ether (DEE)</td>
<td>✓ Used as a ignition Improver ✓ Possible Alternative Fuel For CI engines</td>
</tr>
<tr>
<td>Methyl Tertiary-Butyl Ether (MTBE)</td>
<td>✓ Additive for gasoline</td>
</tr>
<tr>
<td>Ethyl ter-butyl ether (ETBE)</td>
<td>✓ Additive for gasoline</td>
</tr>
<tr>
<td>Ter-amyl methyl ether (TAME)</td>
<td>✓ Additive for gasoline</td>
</tr>
<tr>
<td>Ter-amyl ethyl Ether (TAEE)</td>
<td>✓ Additive for gasoline ✓ Increases the solubility of ethanol in diesel</td>
</tr>
</tbody>
</table>
## Comparison of Properties of Potential Fuel Components*

<table>
<thead>
<tr>
<th>Property</th>
<th>DF-2 Diesel</th>
<th>FT Diesel</th>
<th>Bio-diesel</th>
<th>Gasoline</th>
<th>CNG</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>DME</th>
<th>DEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVP, psi @ 100 °F</td>
<td>&lt;0.2</td>
<td>n.a.</td>
<td>n.a.</td>
<td>8 – 15</td>
<td>n.a.</td>
<td>4.6</td>
<td>2.3</td>
<td>116</td>
<td>16.0</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40 – 55</td>
<td>&gt;74</td>
<td>&gt;48</td>
<td>13 – 17</td>
<td>Low</td>
<td>Low</td>
<td>&lt;5</td>
<td>&gt;55</td>
<td>&gt;125</td>
</tr>
<tr>
<td>Auto ignition Temperature, °F</td>
<td>~600</td>
<td>~600</td>
<td>-</td>
<td>495</td>
<td>990</td>
<td>867</td>
<td>793</td>
<td>662</td>
<td>320</td>
</tr>
<tr>
<td>Stoichimetric Air/Fuel Ratio, Wt/Wt.</td>
<td>15.0</td>
<td>15.2</td>
<td>13.8</td>
<td>14.5</td>
<td>16.4</td>
<td>6.45</td>
<td>9.0</td>
<td>8.9</td>
<td>11.1</td>
</tr>
<tr>
<td>Flammability Limits, Vol. %: Rich</td>
<td>7.6</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>13.9</td>
<td>36.9</td>
<td>19.0</td>
<td>27.0</td>
<td>9.5</td>
</tr>
<tr>
<td>Flammability Limits, Vol. %: Lean</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>5.0</td>
<td>7.3</td>
<td>4.3</td>
<td>3.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Lower Heating Value, Btu/lb</td>
<td>18,500</td>
<td>18,600</td>
<td>16,500</td>
<td>18,500</td>
<td>20,750</td>
<td>8,570</td>
<td>11,500</td>
<td>12,120</td>
<td>14,571</td>
</tr>
<tr>
<td>Viscosity, centipoises at (°F)</td>
<td>40 (68)</td>
<td>2.1 (100)</td>
<td>3.5 (100)</td>
<td>3.4 (68)</td>
<td>-</td>
<td>3.5 (100)</td>
<td>1.19 (68)</td>
<td>-</td>
<td>0.23 (68)</td>
</tr>
<tr>
<td>Density, lb/gal</td>
<td>7.079</td>
<td>6.520</td>
<td>7.328</td>
<td>6.246</td>
<td>-</td>
<td>7.328</td>
<td>6.612</td>
<td>5.50</td>
<td>5.946</td>
</tr>
</tbody>
</table>

* Table compiled by N.R. Serer, Southwest Research Institute. SAE paper No : 972978
Automotive Fuels and Lubricants Application Division, IIP Dehradun

- Affordable
- Environmentally Benign Chemical
- High Energy Efficiency
- Fossil & Renewable Sources
- Available

DME
\(\text{CH}_3\text{OCH}_3\)

Ultra-Low Exhaust Emissions
Emission Regulations

Japan
- Long term 98～99
- New short term 02～04
- New long term 05

Europe
- EURO2 1995
- EURO3 2000
- EURO4 2005
- EURO5 2008

U.S.A
- US 04
- US 98
- US ‘04

‘09 Regulation of Japan
- NOx 0.7g/kWh
- PM 0.01g/kWh
Role of DME in meeting Emission Regulations

Result of DME Truck:
- PM: 0.0016 g/kWh
- NOx: 0.27 g/kWh

'09 Reg. of Japan:
- NOx: 0.7 g/kWh
- PM: 0.01 g/kWh

'09 challenge Target (NOx: 0.23 g/kWh)

U.S.A:
- NOx: 0.27 g/kWh
- PM: 0.013 g/kWh
- US 04
- US 98
- US'10

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Due to expensive production initially DME was considered as ignition improver for other fuels, mainly methanol.

DME has been tested in a number of direct injection diesel engines, ranging in size from 273 to 1220 cm$^3$/cylinder.

In all of these studies, soot-free operation has been observed.

NOx emission is found to be generally lower with DME, however some studies have reported equal or even higher NOx emission as compared to diesel.
**Benefits of DME**

- High Cetane Number
- Smokeless combustion
- High Volatility
- LPG Infrastructure can be used for transportation and Storage.

**Challenges with DME**

- Low Viscosity
- Low Lubricity
- Storage System
- Seal Compatibility
Road load test data comparing engine emissions using diesel and neat DME

Combined Emissions from Production, Distribution and Use in vehicles from various Fuels

Data obtained from the Swedish Petroleum Institutes 1999

Automotive Fuels and Lubricants Application Division, IIP Dehradun
DME Vehicles

- DME at Volvo initiated Q1, 1995
- DME, the long term future fuel for VTC, Q3, 1996
- 1st generation HD DME prototype vehicle 1999

The Finished Product (Volvo 9L)

- Common Rail Ass’y
- Control Module
- ECM
- Fuel Filter
- H.P. Pump

2003 China DME forum (Shanghai)
(LPG+DME)
Spark ignition Engine
## Estimated Costs of Meeting US 2007 HDD Emissions

<table>
<thead>
<tr>
<th>Emissions Control Device</th>
<th>Cost for Diesel</th>
<th>Cost for DME</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Engine</td>
<td>$18,000</td>
<td>$18,000</td>
<td>est.</td>
</tr>
<tr>
<td>Injection System</td>
<td>$1,800</td>
<td>$1,000</td>
<td>est./Quotes</td>
</tr>
<tr>
<td>Fuel Storage &amp; Conditioning</td>
<td>$500</td>
<td>$1,000</td>
<td>est./Quotes</td>
</tr>
<tr>
<td>Cooled EGR System</td>
<td>$439</td>
<td>$439</td>
<td>EPA</td>
</tr>
<tr>
<td>VG Turbo</td>
<td>$373</td>
<td>$373</td>
<td>EPA</td>
</tr>
<tr>
<td>Electronics</td>
<td>$500</td>
<td>$500</td>
<td>est.</td>
</tr>
<tr>
<td>Catalyzed Particulate Trap</td>
<td>$1,103</td>
<td>0</td>
<td>EPA</td>
</tr>
<tr>
<td>NOx Adsorber</td>
<td>$1,456</td>
<td>0</td>
<td>EPA</td>
</tr>
<tr>
<td>Oxidation Catalyst</td>
<td>$338</td>
<td>$338</td>
<td>EPA</td>
</tr>
<tr>
<td>Total Cost</td>
<td>$24,509</td>
<td>$21,650</td>
<td></td>
</tr>
<tr>
<td><strong>Cost Savings</strong></td>
<td></td>
<td><strong>$2,859</strong></td>
<td></td>
</tr>
</tbody>
</table>

Source: AVL Power train Technologies, Inc
Environmental Concerns

- Non-Toxic to Humans
- Not Carcinogenic and Non Mutagenic
- Very Low Reactivity
- Short Half-Life in Troposphere
- Long, Positive Experience
Relative Well to Wheel CO₂ Emissions

- Gasoline
- FT Diesel
- DME
- Current Diesel
- Bio DME

% Heavy Duty vs % Light Duty

Relative CO₂ Emissions (%)

Source: TNO & bp

Automotive Fuels and Lubricants Application Division, IIP Dehradun
Automotive Fuels and Lubricants Application Division, IIP Dehradun
The investment cost for a commercial scale **Bio-DME plant producing 200,000 tons of DME per year** has been estimated at approximately **€390 Millions** at a green field location.

However, if oxygen and utilities can be purchased “over the fence” at an industrial site the total investment may be reduced by about **€ 100 Millions**.

For these two location alternatives, the production cost of Bio-DME has been estimated at **€393 - €438 per ton of DME or about €0.49 - €0.55 per litre of diesel equivalent**.
1 ton Wood fuel, Generation of all plant power add. 0.3 ton

0.37 ton of DME Incl. wood for power generation 0.29 ton/ton

Figure: Yield of DME ton/ton of biomass feed

1 GJ LHV Wood fuel, El. Power 0.07 GJ Generation of all plant power add. 0.3 GJ

0.63 GJ of DME 0.58 GJ per GJ in (wood+ el. power) Incl. wood for power generation 0.49 GJ

Figure: Energy efficiency for production of DME from biomass

The Bio-DME Project Report to Swedish National Energy Administration, 23 April 2002
Automotive Fuels and Lubricants Application Division, IIP Dehradun

Natural gas → Reformation of Natural gas → Shift+ CO2 purification → DME Synthesis → Final distillation

Cost: \[
\frac{1}{6}
\]

DME Gas turbine, DMEC.I Engine, DME Fuel cell

Wood → Raw material preparation, Grinding, Drying → Gasification and gas cleaning → Shift+ CO2 purification → DME Synthesis → Final distillation

Pre-processing

DME can be produced from natural gas or wood (Brandberg, et al, 1997)
Ahlvik, P. and Brandberg, (2001) showed that bio-DME is the most energy efficient bio-fuel to produce both in terms of fuel production and well-to-wheel efficiency (total system efficiency)

The EUCAR/CONCAWE/JRC well-to-wheel project reached the conclusion that net emission of CO2 from a diesel engine running on bio based DME are very low
Cost of CO₂ Avoidance with Biomass

Well to Wheel analysis of future automotive fuels and powertrains in the European context
Jean-François Larivé, CONCAWE, June 2006
First ether engine was a combined water-ether steam engine. It was built in Marseilles in 1850 for marine application.

From 1919-1923 in British Guiana an alcohol based motor fuel named Alcolene was produced from sugarcane molasses which consisted of 63% ethanol, 35% DEE, and 1% gas oil and pyridine.

Near the end of World War II, blending DEE to ethanol was adopted as an acceptable method to improve performance of ethanol in Japan.

Antonini (1981) reported DEE as a option for diesel engine fuels by mixing it with vegetable oil and/or diesel fuel.
Benefits of DEE

- Very High Cetane Number
- Reasonable Energy Density
- Liquid at room temperature

Challenges with DEE

- Stability in Storage
- Lower Lubricity
- Seal Compatibility
Information available on engine testing on DEE is limited

Particulate emission from a DICI Engine running on DEE were found very low relative to the diesel fuel

It has been shown that 5% DEE/Diesel blend gives better performance and low emissions compared to other blends of DEE and diesel fuel

Tests on Volvo AH10A245 diesel engine using ethanol DEE blends indicate that it is necessary to mix in at least 50% DEE in order to run the engine over the whole range of operation and 60% is recommended
<table>
<thead>
<tr>
<th>Vol% Diethyl Ether</th>
<th>Vol% D-2</th>
<th>Cetane Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>158.2</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
<td>102.2</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>68.5</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>51.5</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>42.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vol% Diethyl Ether</th>
<th>Vol% Ethanol</th>
<th>Cetane Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>25</td>
<td>61.1</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>19.0</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>12.2</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>12.1</td>
</tr>
</tbody>
</table>

**Cetane Number Determination**  
[J. Erwin, 1997]

**Ignition Delay Impact from Toluene Blended with DEE.**  
[Clothere, 1990]
<table>
<thead>
<tr>
<th>Diesel (ml)</th>
<th>DEE (ml)</th>
<th>Cetane Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0</td>
<td>49.2</td>
</tr>
<tr>
<td>950</td>
<td>50</td>
<td>53.2</td>
</tr>
<tr>
<td>924</td>
<td>76</td>
<td>52.8</td>
</tr>
<tr>
<td>900</td>
<td>100</td>
<td>50.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Cetane Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel</td>
<td>53.2</td>
</tr>
<tr>
<td>Diesel+10%Ethanol</td>
<td>52.8</td>
</tr>
<tr>
<td>Diesel+10%Ethanol +10%DEE</td>
<td>50.8</td>
</tr>
</tbody>
</table>
Environmental Concerns

- Non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic

- Reactivity of DEE is 5 times higher than MTBE. DEE is estimated to be stable for approximately nineteen hours.

- Studies about well-to-wheel greenhouse gas emissions and tailpipe aldehyde emissions from DEE are required.
DEE can be manufactured by dehydration of bio-ethanol using an acid clay catalyst with 90% conversion.

NREL conducted a process simulation exercise which showed that hydrous ethanol could be converted to DEE.

The analysis shows that the cost of fuel grade DEE would be only slightly higher than that of anhydrous ethanol.
Benefits of Bio-ethers

- Bio-ethers have a potential to substantially cut down GHG emissions.

- Bio-ethers considerably reduce smoke and PM. This enables the use of very high EGR rates for NO\textsubscript{X} reduction without jeopardizing the life of the engine due to excessive wear.

- Emissions of VOC and CO are of the same magnitude as diesel.

- Bio-ethers are non-corrosive to metals and do not require special materials for structural components of fuel systems.

- Bio-ethers are sulphur free; this facilitates the use of effective after treatment devices.

- Bio-ethers can be used in DI diesel Engines without major modifications. Therefore field retrofit is possible.
Conclusion

Among all the biofuels, bio-ethers seem to be very attractive as Alternative transportation fuel due to their energy efficient production, higher well-to-wheel efficiency and substantially low GHG emissions.
Thank You
Ignition delay vs compression ratio

Ignition delay vs injection advance
DME Common Rail Fuel System

Injector
Solenoid Valve
Variable Pump
Common Rail

Automotive Fuels and Lubricants Application Division, IIP Dehradun
Well-to-wheels greenhouse gas emissions divided into the well-to-tank and tank-to-wheels contributions for various fuels, feedstock’s, and vehicle technologies.
Well-to-wheel efficiencies for various fuels, feedstocks, and vehicle technologies. Solid bars are petroleum-based fuels, diagonal hatched bars are natural gas-based fuels, and the cross hatched bars are biomass-based fuels.
Comparison Of Performance for DME and Diesel fuel at 2000rpm
System efficiency (well-to-wheel) for various fuels and powertrains
Best fuel/powertrain combination for each fuel – fuels from biomass

- DME diesel-hyb: 11.4%
- GH2 FC-hyb: 11.2%
- MeOH diesel-hyb: 10.8%
- LH2 FC-hyb: 9.7%
- EtOH diesel-hyb: 9.4%
- Syn diesel-hyb: 9.1%
- CBG FC-hyb: 8.9%
- SNG FC-hyb: 8.4%
- Ei-GH2 FC-hyb: 7.2%