

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

4 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 rout only carbon convertible to sugar can yield fuel

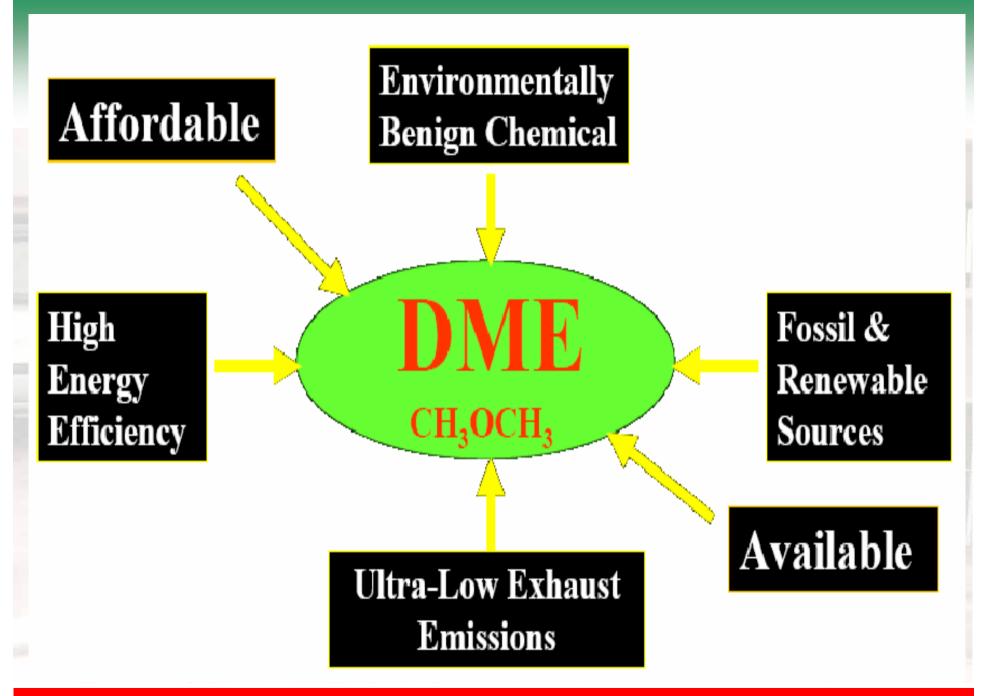
Ethers in Fuel Industry

| Dimethyl Ether (DME) | Alternative Fuel for CI engines |
|---|---|
| Diethyl Ether (DEE) | Used as a ignition Improver Possible Alternative Fuel For CI engines |
| Methyl Tertiary-Butyl Ether (MTBE) | ✓ Additive for gasoline |
| Ethyl <i>ter</i> -butyl ether (ETBE) | ✓ Additive for gasoline |
| Ter-amyl methyl ether (TAME) | Additive for gasoline |
| Ter-amyl ethyl Ether (TAEE) | Additive for gasoline Increases the solubility of ethanol in diesel |

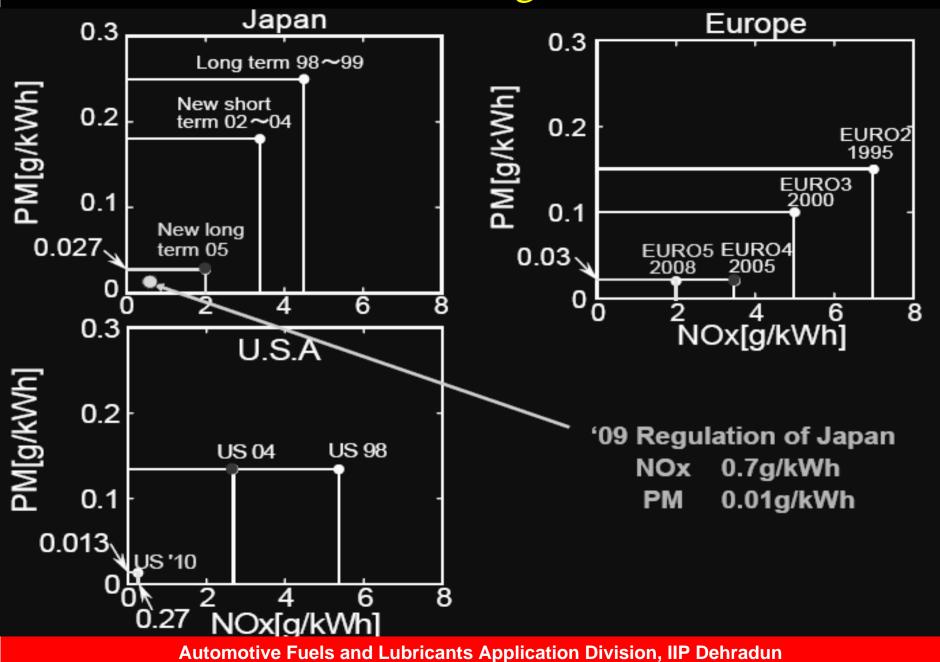
Comparison of Properties of Potential Fuel Components*

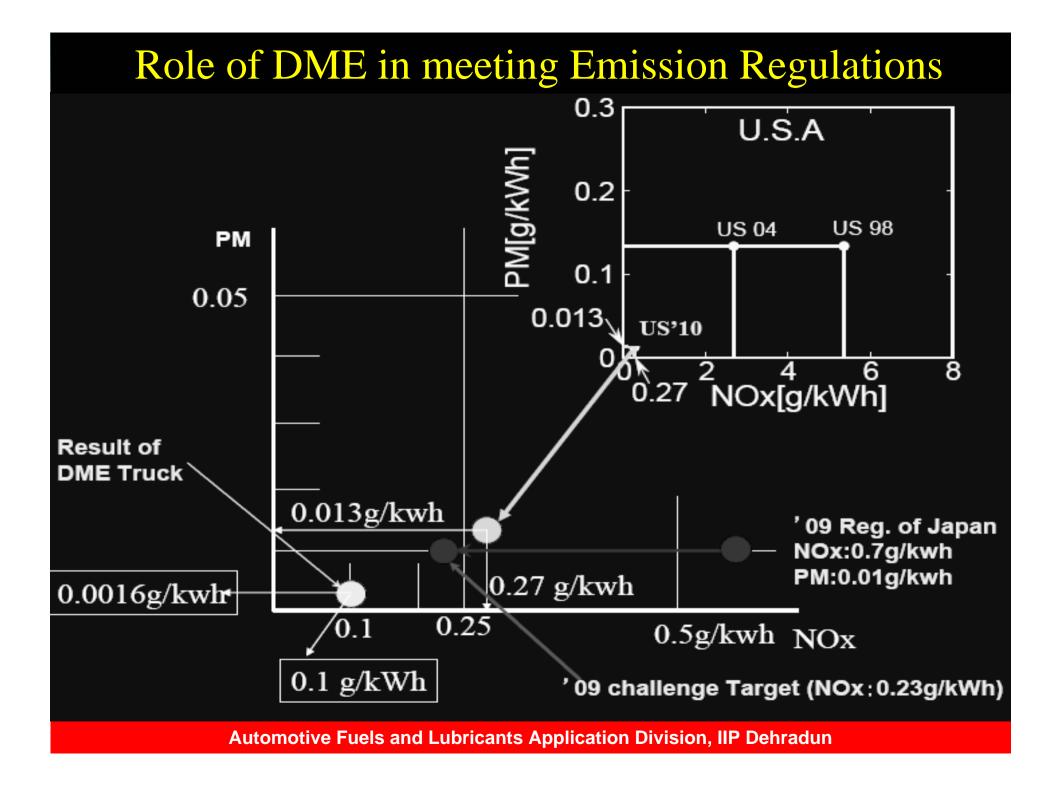
| Property | DF-2 Diesel | FT Diesel | Bio- diesel | Gasoline | CNG | Methanol | Ethanol | DME | DEE |
|---|----------------|--------------|----------------|-------------|------------|-------------------|--------------|--------|--------------|
| Boiling Point, °F | 370 - 650 | 350 - 670 | 36 - 640 | 80 - 437 | n.a. | 149 | 172 | -13 | 94 |
| RVP, psi @ 100 °F | < 0.2 | n.a. | n.a. | 8 – 15 | n.a. | <mark>4.</mark> 6 | 2.3 | 116 | 16.0 |
| Cetane Number | 40 - 55 | >74 | >48 | 13 – 17 | Low | Low | <5 | >55 | >125 |
| Auto ignition Temperature, °F | ~600 | ~600 | | 495 | 990 | 867 | 793 | 662 | 320 |
| Stoichimetric Air/ Fuel Ratio, Wt/Wt. | 15.0 | 15.2 | 13.8 | 14.5 | 16.4 | 6.45 | 9.0 | 8.9 | 11.1 |
| Flammability Limits, Vol. %: Rich | 7.6 | | - | 6.0 | 13.9 | 36.9 | 19.0 | 27.0 | 9.5 36.0 |
| Flammability Limits, Vol. %: Lean | 1.4 | | - | 1.0 | 5.0 | 7.3 | 4.3 | 3.4 | 1.9 |
| Lower Heating Value, Btu/lb | 18,500 | 18,600 | 16,500 | 18,500 | 20,75 0 | 8,570 | 11,500 | 12,120 | 14,571 |
| Viscosity, centipoises at ()°F | 40 (68) | 2.1 100) | 3.5 (100) | 3.4 (68) | 5-1 | 3.5 (100) | 1.19 (68) | - | 0.23 (68) |
| Density, lb/gal | 7.079 | 6.520 | 7.328 | 6.246 | N - 1 | 7.328 | 6.612 | 5.50 | 5.946 |

* Table compiled by N.R. Serer, Southwest Research Institute. SAE paper No : 972978



Emission Regulations





Engine Studies

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 cm³/cylinder

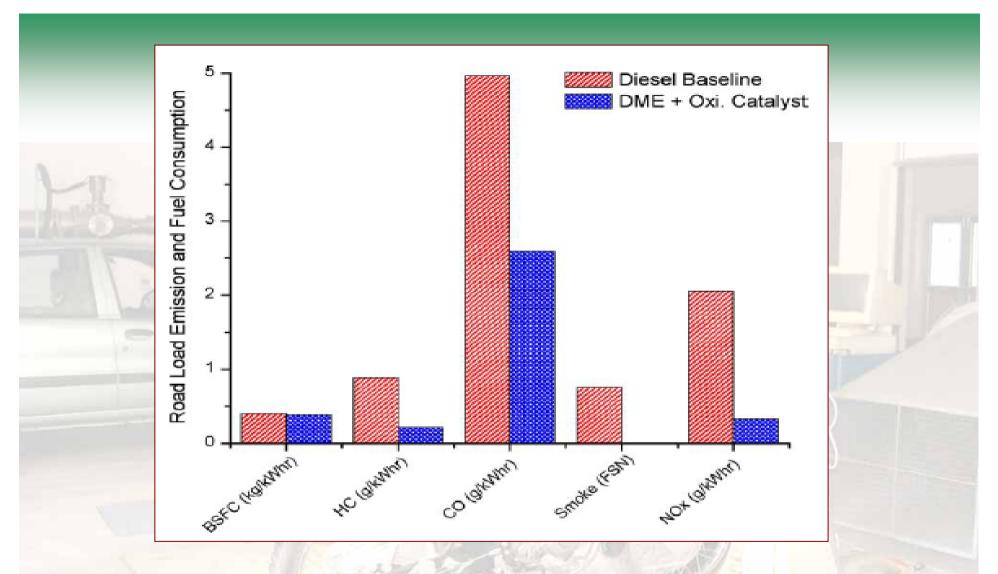
- In all of these studies, soot-free operation has been observed
- NOx emission is found to be generally lower with DME,
 however some studies have reported equal or even higher
 NOx emission as compared to diesel

Benefits of DME

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

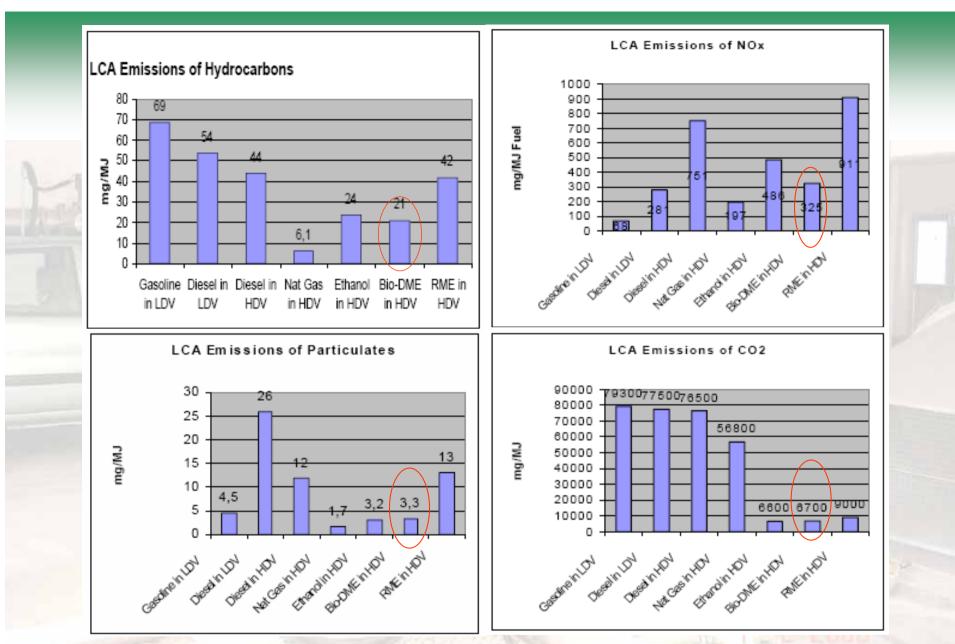
Challenges with DME

- Low Viscosity
- Low Lubricity
- Storage System
- Seal Compatibility



Road load test data comparing engine emissions using diesel and neat DME

J. McCandless, DME as an Automotive Fuel: Technical, Economic and Social Perspectives Energy Frontiers Conference, 2001



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

Data obtained from the Swedish Petroleum Institutes 1999









Estimated Costs of Meeting US 2007 HDD Emissions

| | Cost for | Cost for | |
|-----------------------------|----------|----------|-------------|
| Emissions Control Device | Diesel | DME | Source |
| Base Engine | \$18,000 | \$18,000 | est. |
| Injection System | \$1,800 | \$1,000 | est./Quotes |
| | | | |
| Fuel Storage & Conditioning | \$500 | \$1,000 | est./Quotes |
| Cooled EGR System | \$439 | \$439 | EPA |
| VG Turbo | \$373 | \$373 | EPA |
| Electronics | \$500 | \$500 | est. |
| Catalyzed Particulate Trap | \$1,103 | 0 | EPA |
| NOx Adsorber | \$1,456 | 0 | EPA |
| Oxidation Catalyst | \$338 | \$338 | EPA |
| Total Cost | \$24,509 | \$21,650 | |
| Cost Savings | • | \$2,859 | |

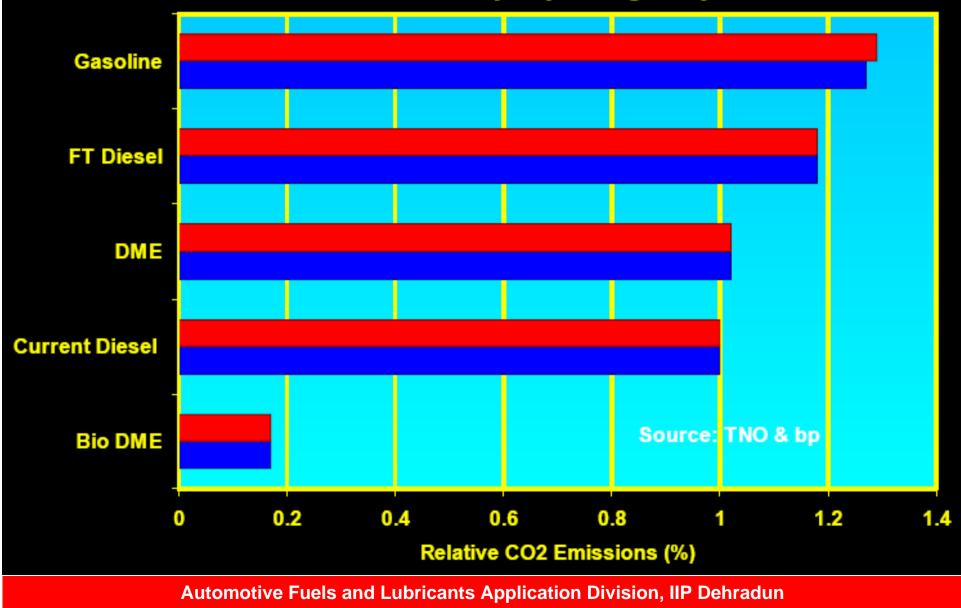
Source: AVL Power train Technologies, Inc

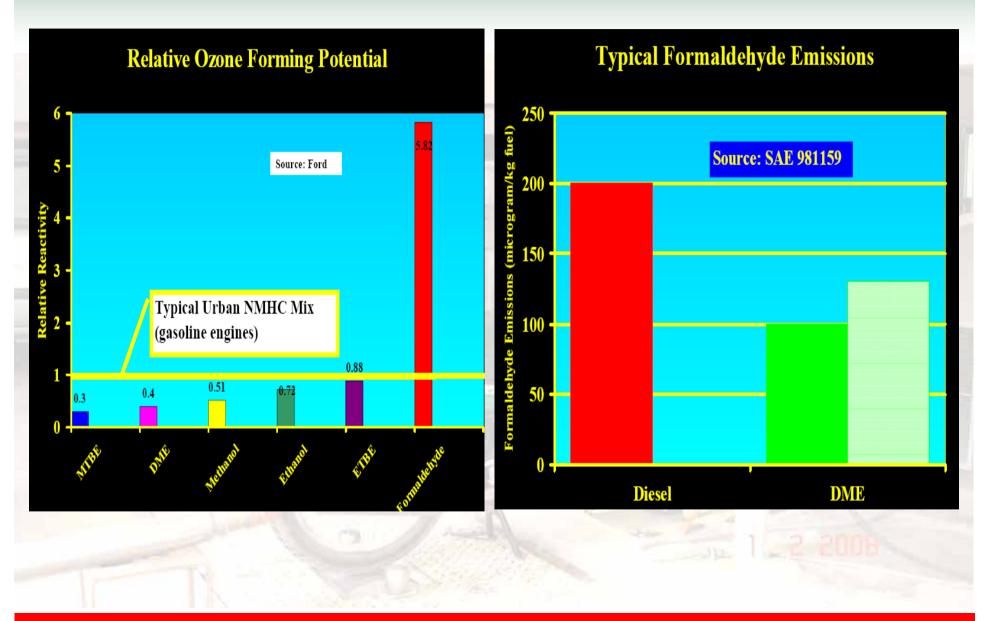
Environmental Concerns

- 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

% Heavy Duty % Light Duty





Economics of Production

The investment cost for a commercial scale *Bio-DME plant producing 200,000 tons of DME per year* has been estimated at approximately \in 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

The Bio-DME Project Report to Swedish National Energy Administration, 23April 2002

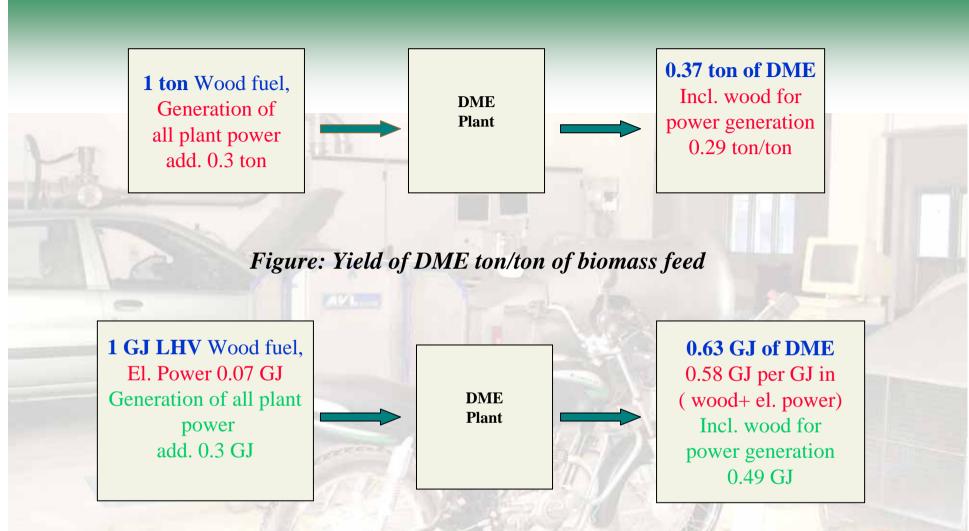
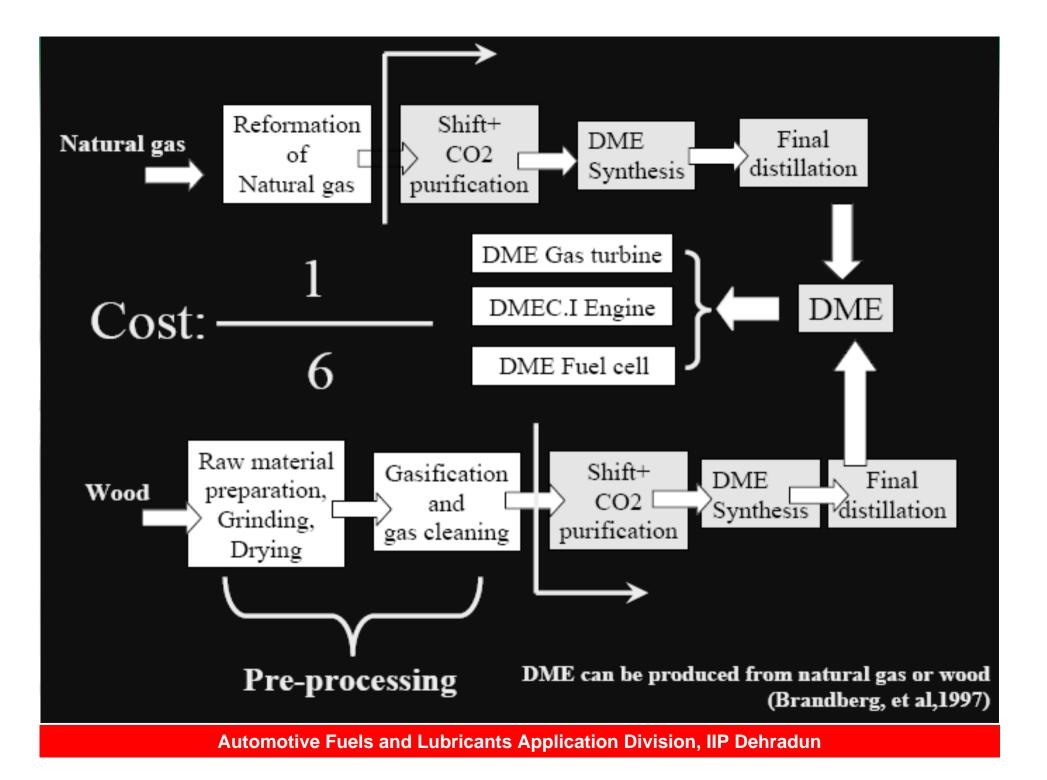


Figure: Energy efficiency for production of DME from biomass

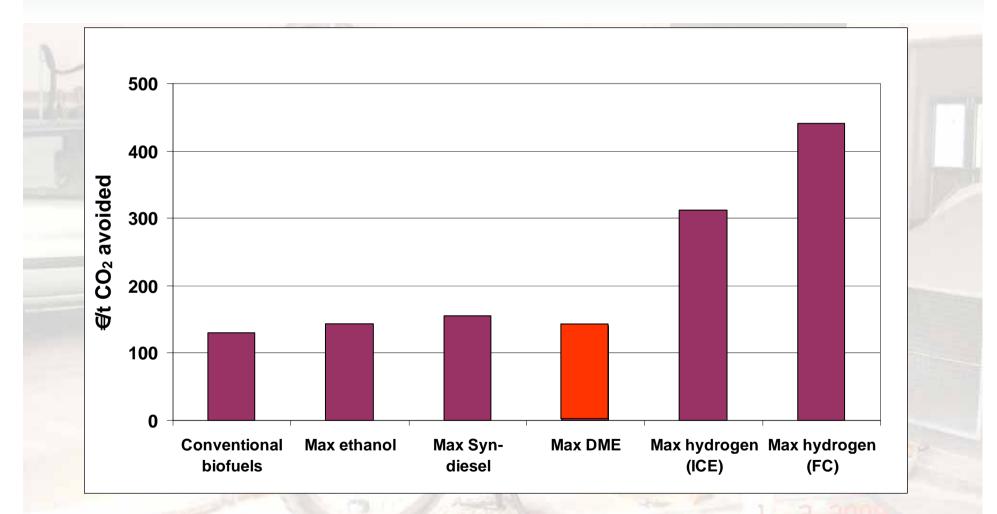
The Bio-DME Project Report to Swedish National Energy Administration, 23April 2002



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

Diethyl Ether

Background

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 CetaneNumber
- Reasonable Energy Density
- Liquid at room temperature

Challenges with DEE

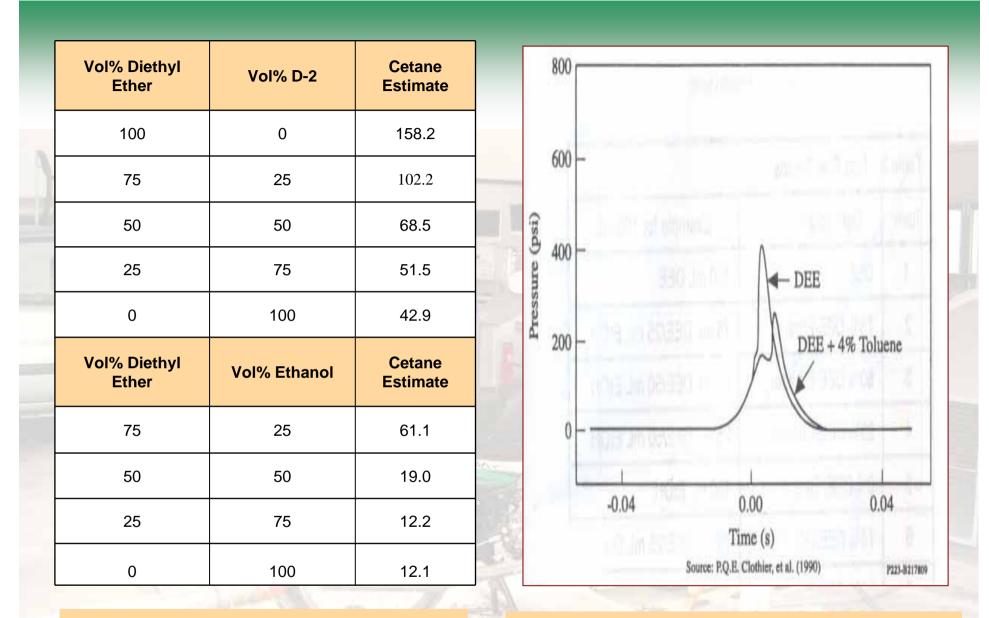
- Stability in Storage
- Lower Lubricity
- Seal Compatibility

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



Cetane Number Determination [J. Erwin.1997]

Ignition Delay Impact from Toluene Blended with DEE. [Clotheir ,1990]

| Diesel (ml) | DEE (ml) | Cetane Number | | |
|-------------|----------|---------------|--|--|
| 1000 | 0 | 49.2 | | |
| 950 | 50 | 53.2 | | |
| 924 | 76 | 52.8 | | |
| 900 | 100 | 50.8 | | |

| Fuel | Cetane Number |
|---------------------------|------------------|
| Diesel | 53.2 |
| Diesel+10 %Ethanol | 52.8 |
| Diesel+10%Ethanol +10%DEE | 50.8 |

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 green house gas emissions and tailpipe aldehyde emissions from DEE are required

Economics of Production

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

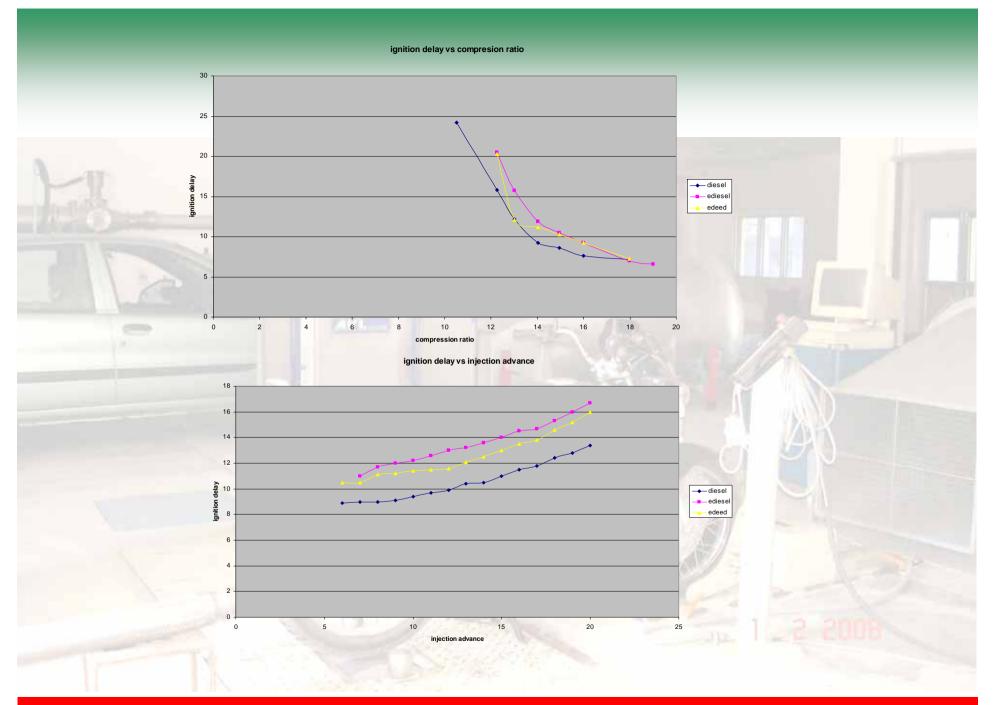
Benefits of Bio-ethers

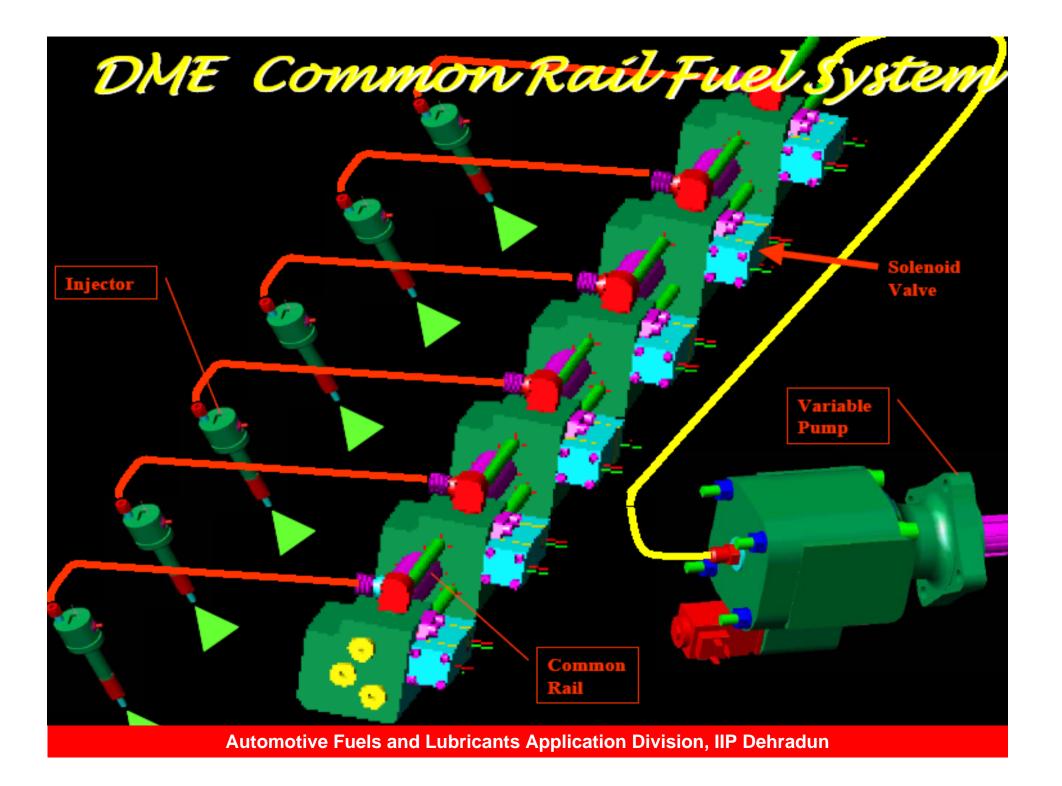
- Bio-ethers have a potential to substantially cut down GHG emissions
- Bio-ethers considerably reduces smoke and PM. This enables use of very high EGR rates for NO_X reduction without jeopardizing the life of engine due to excessive wear.
- Emissions of VOC and CO are of the same magnitude as diesel.
- 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.

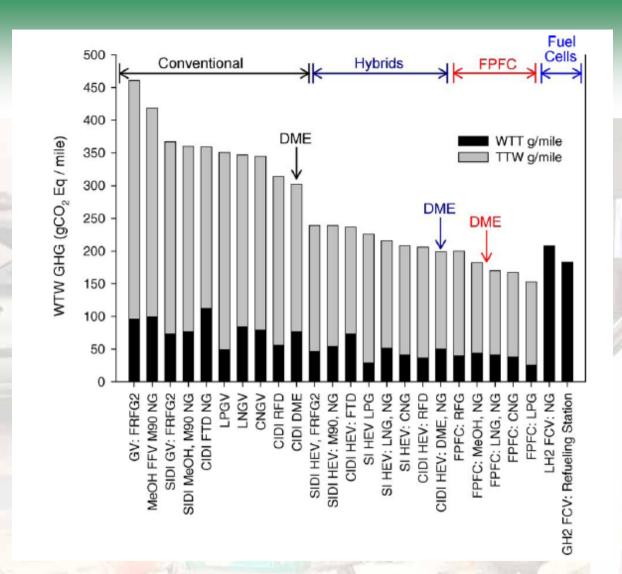
Conclusion

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.

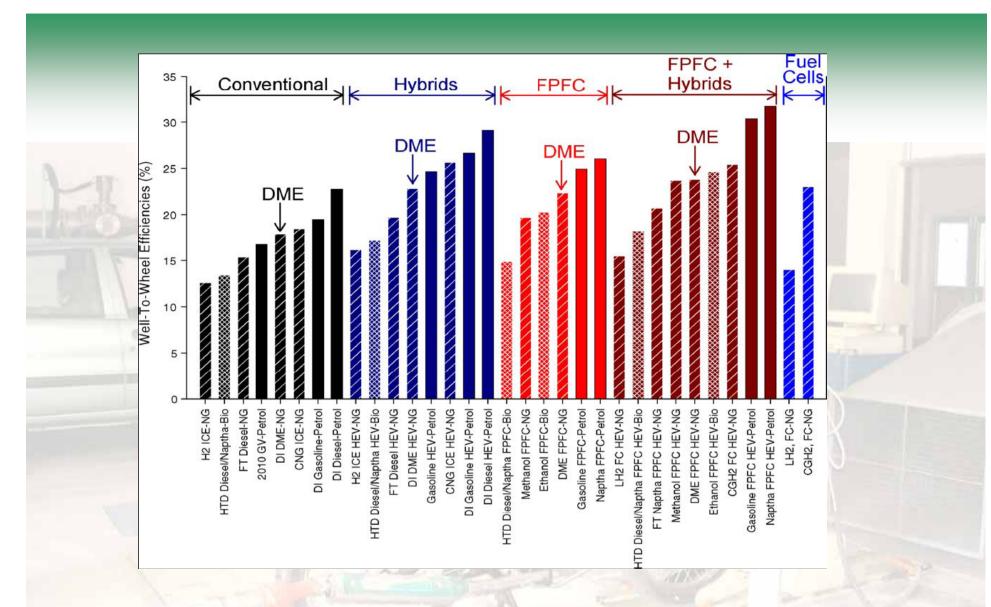








Well-to-wheels greenhouse gas emissions divided into the well-to-tank and tank-to-wheels contributions for various fuels, feedstock's, and vehicle technologies



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

