Wrocław University of Technology

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Fuels and lubricants chemistry

Ecology and Safety as a Driving Force
in the Development of Vehicles
IP Radom, 02 March - 15 March, 2008
Fuels and lubricants chemistry

Billions of light duty vehicles

Source: Sustainable Mobility Project calculations.
Fuels and lubricants chemistry

Conventional Fuels
High in Sulfur
High Aromatics

Clean conventional Fuels
Sulfur-free
Low Aromatics

Synthetic (GTL) Fuels
Low Emissions

Synthetic (BTL) Fuels
Low Emissions + Low in CO₂

Hydrogen
Emission-free + CO₂-free

Based on Crude Oil
Based on Nat. Gas
Based on Biomass
Based on Ren. Energy

Ecology and Safety as a Driving Force in the Development of Vehicles
IP Radom, 02 March - 15 March, 2008
Typical Gasoline Properties

- Gravity
- Aromatics
- Vapor Pressure Distillation
- Octane Number
- Solvent Washed Gum
- Saturates
- Benzene
- Alcohols
- Ethers
- Olefins
- Sulphur
Vehicle Emissions - Gasoline Effects

Changes in gasoline properties and composition can help reduce vehicle emissions. Certain gasoline modifications are very effective in enabling vehicle emissions control systems to perform at their optimum levels. But other gasoline modifications are not nearly as effective at reducing emissions compared to the use of the vehicle emission control systems. The explanations here apply chiefly to vehicles built since 1985.

**Sulphur**
- Sulphur oxides in the exhaust gases, becomes poison the three-way catalyst.
- Reducing sulphur content in gasoline increases converter efficiency and decreases VOC, CO, NOx, and toxics emissions.
- Reducing the sulphur content also reduces the direct emission of sulphur dioxide — a criteria pollutant.
**Vapor Pressure**
Decreasing the vapor pressure of gasoline reduces evaporative VOC emissions and to a lesser extent can reduce exhaust VOC and CO.

**Oxygenates**
- CO is the result of incomplete combustion and its formation is very dependent on the Air/Fuel. In older cars, adding oxygenates to gasoline has the same effect as increasing the amount of combustion air. It adds more oxygen to the combustion chamber, makes combustion more complete, and reduces formation of carbon monoxide.
Oxygenates also tend to reduce exhaust VOC emissions somewhat, but they increase aldehyde emissions and tend to increase NOx emissions in many vehicles.

NOx formation is increased by excess oxygen and higher combustion temperatures. This potential relationship between oxygen and increased NOx caused California to limit the oxygen content of Phase 2 reformulated gasoline to 2.7 mass %.
The emissions benefit of oxygenates was greatest in pre-1990 vehicles with less effective A/F control systems. The closed-loop A/F control systems in newer vehicles have become progressively better and better over time.

By adjusting intake A/F based on the oxygen content of the exhaust, these systems decrease intake air to compensate for oxygen in the fuel, negating most of the emissions benefit associated with having oxygenate in the gasoline. The addition of adaptive learning systems has improved A/F control even more.

Consequently, oxygenates seem to have little effect on exhaust emissions from these newer vehicles, so long as they are operating in closed-loop mode.
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Vehicle Emissions - Gasoline Effects

**Olefins**
- Increasing the olefin content of gasoline tends to reduce exhaust VOC emissions, because olefins burn more easily and more completely than the other classes of hydrocarbons in gasoline. However, *increasing olefin content also tends to increase NOx formation.* And it increases the olefin content of evaporative emissions, which is undesirable because olefins are among the most reactive hydrocarbons for ozone formation. For reformulated gasoline's, the choice is to decrease olefins.

**Aromatics**
- Decreasing the total aromatics content of gasoline may reduce CO and exhaust VOC emissions, but the effects are variable and complex, probably because the aromatic compounds in gasoline are so diverse. *Decreasing aromatics content reduces benzene in vehicle exhaust emissions* because larger aromatic molecules are partly converted to benzene during combustion or in the catalytic converter.
Vehicle Emissions - Gasoline Effects

Benzene
- Decreasing the benzene content of gasoline reduces the amount of benzene in both evaporative and exhaust VOC emissions.

Distillation Profile Temperatures
- Gasoline containing significant amounts of high boiling components tends to give high VOC exhaust emissions. High boiling components are more difficult to vaporize, especially in a cold engine, making complete combustion more difficult. Thus, placing limits on the distillation profile can lower VOC emissions.
Typical Diesel Fuel Properties

- Gravity
- Flash Point
- Colour
- Viscosity
- Cloud Point
- Pour Point
- Sulphur

- Distillation
- Carbon Residue
- Corrosion
- Ash
- Cetane Number
- Aromatics
- Aniline Point
Vehicle Emissions - Diesel Fuel Effects

Advances in engine design have produced very large reductions in NOx and PM emissions since the EPA began setting emission standards for diesel engines in 1971. The composition of diesel fuel has had much less influence on emissions, but reformulated diesel fuels have played a small role in achieving needed emissions reductions. The most important fuel parameters in this regard are:

Sulfur

- The sulphur content of diesel fuel affects PM emissions because some of the sulphur in the fuel is converted to sulphate particles in the exhaust. The fraction converted to PM varies from one engine to another, but reducing sulphur decreases PM linearly in almost all engines. For this reason, the EPA limits the sulphur content of on-road diesel fuel (low sulphur diesel fuel) to 0.05% mass (500 ppm) maximum and CARB applies the same limit to all vehicular diesel fuel (on-road and off-road). As a result, the national average sulphur content for low sulphur diesel fuel is between 300 and 350 ppm. At a sulphur level of 300 ppm, sulphate particles comprise about 10% of total PM emissions for an engine emitting 0.1 g PM/bhp-hr.
Vehicle Emissions - Diesel Fuel Effects

- **Cetane Number**  Increasing the cetane number improves fuel combustion and tends to reduce NOx and PM emissions. NO\textsubscript{x} seems to be reduced in all engines, while PM10 reductions are more engine-dependent. These cetane number effects also tend to be non-linear in the sense that increasing the cetane number does the most good when starting with a relatively low cetane number fuel.

- **Density**  Changes in fuel density affect the energy content of the fuel brought into the engine at a given injector setting. European studies indicate that reducing fuel density tends to decrease NO\textsubscript{x} emissions in older technology engines that cannot compensate for this change. Emissions from modern engines, with electronic injection and computer control, appear to be independent of density.
Vehicle Emissions - Diesel Fuel Effects

- **Aromatics**  Reducing the aromatics content of diesel fuel reduces NO\(_x\) and PM10 in some engines. Recent European studies indicate that polynuclear aromatics content is key to the reduction, and that the concentration of single-ring aromatics is not a factor.

- **Volutility**  T95 is the temperature at which 95% of a particular diesel fuel distils in a standardized distillation test (ASTM D 86). Reducing T95 decreases NO\(_x\) emissions slightly, but increases hydrocarbon and CO emissions. PM10 emissions are unaffected.
Diesel Fuel aromatic content and NO$_x$ emissions relationship

![Graph showing the relationship between aromatic content decrease and NO$_x$ emissions decrease.](image-url)
The effects of changes in Diesel Fuel properties on emissions

Diezel Fuel specific gravity and NO\textsubscript{x} emissions relationship
# Properties of fuels

<table>
<thead>
<tr>
<th>Properties</th>
<th>Gasoline</th>
<th>Diesel fuel</th>
<th>Ethanol</th>
<th>Propane</th>
<th>CNG</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>100~105</td>
<td>105~200</td>
<td>46.07</td>
<td>44.1</td>
<td>16.04</td>
<td>2.02</td>
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<tr>
<td>Specific gravity, 15.5°C</td>
<td>0.72 - 0.78</td>
<td>0.81 - 0.89</td>
<td>0.796</td>
<td>0.508</td>
<td>0.424</td>
<td>0.07</td>
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<tr>
<td>Composition,</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Carbon, wt.%</td>
<td>85-88</td>
<td>84-87</td>
<td>52.2</td>
<td>82</td>
<td>75</td>
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<tr>
<td>Hydrogen, wt.%</td>
<td>12-15</td>
<td>33-16</td>
<td>13.1</td>
<td>18</td>
<td>25</td>
<td>100</td>
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<tr>
<td>Oxygen, wt.%</td>
<td>0</td>
<td>0</td>
<td>34.7</td>
<td>—</td>
<td>—</td>
<td>0</td>
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</table>
Properties of fuels

**EUROPE:**

For passenger cars and light duty vehicles:
Directive 70/220/EEC with review 98/69/EC (Euro 3 i 4)

For heavy duty vehicles and buses:
Directive 88/77/EEC with review 2001/27/EC (Euro 4 i 5)

**USA:**

For passenger cars and light duty vehicles:
EPA Tier 2
California Standards Tier 1/LEV II

For heavy duty vehicles and buses:
EPA Emission Standards for MY 2004 - 06

**Greenhouse gases**

Kyoto Protocol since 16th February 2005
ACEA Declaration, CO₂ emission – 14.0 g/km in 2008 – 2012 period
The Emission Reduction for Passenger Cars and Light Duty Vehicles [g/km]

<table>
<thead>
<tr>
<th>NAME</th>
<th>Date of introduction</th>
<th>CO</th>
<th>HC</th>
<th>NOx</th>
<th>HC + NOx</th>
<th>PM</th>
</tr>
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<tbody>
<tr>
<td><strong>Gasoline</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1</td>
<td>07. 1992</td>
<td>2.72</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2</td>
<td>01. 1996</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>01. 2000</td>
<td>2.30</td>
<td>0.20</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Euro 4</td>
<td>01. 2005</td>
<td>1.0</td>
<td>0.10</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5</td>
<td>2008</td>
<td>1.0</td>
<td></td>
<td></td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td><strong>Diesel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Euro 1</td>
<td>07. 1992</td>
<td>2.72</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
<td>0.14</td>
</tr>
<tr>
<td>Euro 2, IDI</td>
<td>01. 1996</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>0.08</td>
</tr>
<tr>
<td>Euro 2, DI</td>
<td>01. 1996</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.9</td>
<td>0.10</td>
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<tr>
<td>Euro 3</td>
<td>01. 2000</td>
<td>0.64</td>
<td>-</td>
<td>0.50</td>
<td>0.56</td>
<td>0.05</td>
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<td>Euro 4</td>
<td>01. 2005</td>
<td>0.50</td>
<td>-</td>
<td>0.25</td>
<td>0.30</td>
<td>0.025</td>
</tr>
<tr>
<td>Euro 5</td>
<td>2008</td>
<td>0.50</td>
<td></td>
<td></td>
<td>0.08- 0.20</td>
<td>0.005 - 0.015</td>
</tr>
</tbody>
</table>
### The Emission Reduction for Heavy Duty Vehicles [g/kWh]

<table>
<thead>
<tr>
<th>NAME</th>
<th>Date of introduction</th>
<th>CO</th>
<th>HC</th>
<th>NOx</th>
<th>PM</th>
<th>Smoke</th>
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<td>Euro I</td>
<td>&lt;85 kW, 1992</td>
<td>4.5</td>
<td>1.1</td>
<td>8.0</td>
<td>0.612</td>
<td>-</td>
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<tr>
<td></td>
<td>&gt;85 kW, 1992</td>
<td>4.5</td>
<td>1.1</td>
<td>8.0</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>Euro II</td>
<td>10. 1996</td>
<td>4.0</td>
<td>1.1</td>
<td>7.0</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10. 1998</td>
<td>4.0</td>
<td>1.1</td>
<td>7.0</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Euro III</td>
<td>10. 1999 EEVs</td>
<td>1.5</td>
<td>0.25</td>
<td>2.0</td>
<td>0.02</td>
<td>0.15</td>
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<tr>
<td></td>
<td>10.2000</td>
<td>2.1</td>
<td>0.66</td>
<td>5.0</td>
<td>0.10</td>
<td>0.8</td>
</tr>
<tr>
<td>Euro IV</td>
<td>10. 2005</td>
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<td>0.46</td>
<td>3.5</td>
<td>0.02</td>
<td>0.5</td>
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<tr>
<td>Euro V</td>
<td>2008</td>
<td>1.5</td>
<td>0.46</td>
<td>2.0</td>
<td>0.02</td>
<td>0.5</td>
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<tr>
<td>Euro VI</td>
<td>2013</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Directions of Engine Emission Reduction

- Fuels conventional fuels quality improvement:
  - alternative fuels including biofuels,
  - conventional fuels quality improvement.

- Engines:
  - combustion process improvement,
  - fuel consumption reduction.

- Effective exhaust gases reduction systems.
Gasoline Quality Changes

- Pb elimination
- Sulphur reduction \((SO_2, HC, PM)\)
- Benzene reduction
- Total aromatics reduction \((CO, HC, benzene, deposits)\)
- Olefins reduction \((deposits)\)
- Vapour pressure optimization \((HC, CO)\)
- \(T_{90}\) reduction \((HC, deposits)\)

(based on Auto Oil: EPEFE in Europe and AQIRP in USA)
## Improvement of Gasoline Properties in UE - EN 228

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
<td>min</td>
<td>max</td>
<td>min</td>
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<tr>
<td>Vapour press. (summer)</td>
<td>kPa</td>
<td>35</td>
<td>70</td>
<td>35</td>
<td>70</td>
<td>45</td>
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<tr>
<td>Boiling range</td>
<td>%</td>
<td>40</td>
<td>65</td>
<td>40</td>
<td>65</td>
<td>46</td>
</tr>
<tr>
<td>$V_{100}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>$V_{150}$</td>
<td>85</td>
<td>-</td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Olefins cont.</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21,0</td>
<td>18,0</td>
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<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>Benzene content</td>
<td>%</td>
<td>5,0</td>
<td>5,0</td>
<td>1,0</td>
<td>1,0</td>
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<tr>
<td>Oxygen cont.</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td></td>
<td>2,7</td>
<td>2,7</td>
</tr>
<tr>
<td>Methanol</td>
<td>%</td>
<td></td>
<td></td>
<td>3</td>
<td>3</td>
<td></td>
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<tr>
<td>Ethanol</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
<td>5</td>
<td></td>
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<tr>
<td>Isopropanol</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>t-butanol</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>ethers C ≥ 5 others</td>
<td></td>
<td></td>
<td></td>
<td>15</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Sulphur cont.</td>
<td>mg/kg</td>
<td>1000</td>
<td>500</td>
<td>150</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Pb cont.</td>
<td>mg/l</td>
<td>13 000</td>
<td>13 000</td>
<td>50</td>
<td>5</td>
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</table>
When Europe started to phase down lead octane additives in petrol in the 1980s, many refiners usually replaced them with aromatics, which represented the lowest-cost alternative at the time.

Towards the end of the 1990s, new environmental regulations started to limit the aromatic content of gasoline. A convenient replacement for aromatics is MTBE, a high octane, easy-to-blend, reasonable cost oxygenate, which is essentially a drop-in blending component for the refiner.

Potential alternatives to MTBE include oxygenates such as alcohols or other ethers, aromatics and fuel components such as alkylates and isomerates. Oxygenates are produced from a variety of feedstock's. Methanol, derived primarily from natural gas, is one feedstock used in the production of MTBE. Ethanol, another oxygenate, is derived primarily by a fermenting process from corn and other agricultural products and is used directly as an additive or as a feedstock for the production of ETBE.

There are a few other non-aromatic octane options such as alkylates, isomerates and ethanol, but they are very limited in terms of both octane contribution and supply availability. In addition, they provide fewer air quality benefits. Each of the various octane alternatives has advantages and disadvantages in numerous related aspects, which need to be considered in an objective comparison. These include octane contribution, supply availability, cost and environmental impact.
Gasoline Quality

In 2003, the EU adopted directive 2003/30, which aims at promoting the use of biofuels or other renewable fuels to replace diesel or petrol for transport purposes in each Member State, with a view to contributing to objectives such as meeting climate change commitments, environmentally friendly security of supply and promoting renewable energy sources. Allowed biofuels include alcohols such as bio-ethanol and ethers such as bio-ETBE and bio-MTBE. The directive indicates that Members States should set national indicative targets for a minimum proportion of biofuels and other renewable fuels to be placed on their markets, these targets being **2 % in 2005 and 5.75 % in 2010** in terms of energy content.

Today, the high cost of production of biofuels requires that they benefit from fiscal incentives to become economically viable. Directive 2003/30 has therefore been complemented by Directive 2003/96 on the taxation of energy products, which allows Member States to apply a total or partial tax exemption to biofuels.

Of all the options for replacing lead and aromatics in petrol, MTBE is the most effective from both octane supply and air quality perspectives.
Future Changes of Fossil Fuels Properties
Clean Fuels Gasoline’s

- sensitivity LOB - LOM optimization
- optimization of distillation range
- new generation of detergent additives
- olefins content reduction?
- aromatics content reduction?
- metal free fuel (Si, P, Mn, Fe)
## Improvement of Diesel Fuel Properties in UE - EN 590

<table>
<thead>
<tr>
<th></th>
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<tr>
<td></td>
<td></td>
<td>min</td>
<td>max</td>
<td>min</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>49,0</td>
<td>49,0</td>
<td>51,0</td>
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<td>51,0</td>
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<tr>
<td>Density, 15°C</td>
<td>kg/m³</td>
<td>820</td>
<td>860</td>
<td>820</td>
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<td>820</td>
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<tr>
<td>Boiling range, T&lt;sub&gt;95&lt;/sub&gt;</td>
<td>ºC</td>
<td>370</td>
<td>370</td>
<td>360</td>
<td></td>
<td>360</td>
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<td>PAH</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td></td>
<td>11</td>
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<tr>
<td>Sulphur</td>
<td>mg/kg</td>
<td>2000</td>
<td>500</td>
<td>350</td>
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<td>50/10</td>
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Future Changes of Fossil Fuels Properties
Clean Fuels Diesel Fuels

- Sulphur reduction (PM, SO$_2$)
- Density reduction (PM, CO)
- PAH reduction (PM, NO$_x$)
- C Ind. improvement (CO, HC)
- T$_{95}$ reduction (HC, deposits)
Diesel Fuel Quality Changes

- C Ind. improvement (to 55 ?)
- Total aromatics reduction
- PAH reduction
- New generation of additives
- Ash content reduction
- Impurities reduction (< 1µ)
- Lubricity improvement
- Metal free fuel (Zn, Si, Fe, Cu)
Future Changes of Fossil Fuels Properties
Clean Fuels Diesel Fuels

Gasoline's  Diesel Fuels

Next generation: hybrid designed fuels for Homogeneous Charge Compression Ignition (HCCI) engines
Effectiveness of Restrictive Emissions Programs

![Graph showing emissions of various pollutants from 1985 to 2015. The graph indicates a significant decrease in CO₂ emissions due to improvements in conventional vehicles and fuels. The focus is shifting to greenhouse gases (GHG) for global warming. Source: European Commission.]
Alternative Fuels

- Natural gas and liquid fuels domestically produced from natural gas
- Methanol, ethanol, and other alcohols
- Blends of 85% or more of alcohol with gasoline
- Liquefied petroleum gas (propane)
- Coal-derived liquid fuels
- Hydrogen
- Biodiesel
- Fuels (other than alcohol) derived from biological materials
Alternative Fuels

biofuels from biomass
- bioethanol and derivates
- bioester FAME, FAEE
- biogas and derivates
- bioethanol and derivates
- biohydrogen

fuels from natural gas or refinery gases
- LPG
- CNG, LNG
- H₂
- Gas to Liquid
Biofuels - Directive 2003/30/EC

2005

2 % energetic value
2.9 % for bioethanol
2.2 % for FAME

2010

5.75 % energetic value
8.5 % for bioethanol
6.3 % for FAME

2015

7 % energetic value
10.4 % for bioethanol
7.6 % for FAME

Ecology and Safety as a Driving Force in the Development of Vehicles
IP Radom, 02 March - 15 March, 2008
What is "Oxygenated Gasoline"?

"Oxygenated gasoline" is a mixture of gasoline and one or more combustible liquids which contain oxygen.

At present, two different classes of oxygenates are being added to gasoline: alcohols and ethers.

**Alcohols**

- **Ethanol** ("grain alcohol") is the alcohol most commonly added to gasoline. Oxygenated gasoline containing 10% ethanol has been commercially available in the mid-Western states of US since the late '70s.

- **Methanol** ("wood alcohol") also may be added to gasoline. Because methanol is less soluble in gasoline than ethanol, it is used in combination with another oxygenated liquid (a "cosolvent"). A number of manufacturers recommend against using gasoline oxygenated with methanol in their engines.

**Ethers**

- At present, **methyl tertiary-butyl ether (MTBE)** is the principal ether being added to gasoline. Other ethers that may eventually be used in significant amounts include ethyl tertiary-butyl ether (ETBE) and tertiary-amyl methyl ether (TAME).
What is "Oxygenated Gasoline"?

The federal clean air standard limits the concentration of carbon monoxide in ambient air to 9 parts per million. Many metropolitan areas exceed this limit on some days -- primarily during the winter months.

While the exhaust of gasoline vehicles consists mostly of carbon dioxide and water, it contains some carbon monoxide. Most of the carbon monoxide is converted to carbon dioxide by the catalytic converter in the exhaust systems of newer vehicles.

Older vehicles without catalytic converters are the major vehicular source of carbon monoxide. Newer vehicles also emit more carbon monoxide when they are first started -- before the catalytic converter has reached its operating temperature.

Oxygenated gasoline reduces carbon monoxide emissions in both of these cases.

All gasoline during the winter months when the carbon monoxide level is the highest must be oxygenated gasoline with an oxygen content of 2.7%.
Bioethanol

Ethanol is an alcohol-based alternative fuel produced by fermenting and distilling starch crops that have been converted into simple sugars. Feedstock's for this fuel include corn, barley, and wheat. Ethanol can also be produced from "celluloses biomass" such as trees and grasses and is called bio-ethanol. Ethanol is most commonly used to increase octane and improve the emissions quality of gasoline.

Ethanol can be blended with gasoline to create E85, a blend of 85% ethanol and 15% gasoline. E85 and blends with even higher concentrations of ethanol, E95, for example, qualify as alternative fuels under the (Energy Policy Act 1992). Vehicles that run on E85 are called flexible fuel vehicles (FFVs) and are offered by several vehicle manufacturers.

In some areas of the United States, lower concentrations of ethanol are blended with gasoline. The most common low concentration blend is E10 (10% ethanol and 90% gasoline). While it reduces emissions, E10 is not considered an alternative fuel under Energy Policy Act 1992 regulations.
Bioethanol Feedstock's

- sugar derived from: grain starches (wheat and corn):
  - sugar beets
  - sugar crops

- surplus wine ethanol

- non sugar lignocelluloses fractions and crops (grasses and trees)

- waste biomass:
  - crop residue,
  - forestry waste,
  - municipal waste,
  - food processing waste
Bioethanol

- Ethanol (ethyl alcohol, grain alcohol, Et-OH) is a clear, colourless liquid. In dilute aqueous solution, it has a somewhat sweet flavour, but in more concentrated solutions it has a burning taste. Ethanol (CH\textsubscript{3}CH\textsubscript{2}OH) is made up of a group of chemical compounds whose molecules contain a hydroxyl group, -OH, bonded to a carbon atom. Ethanol made from cellulosic biomass materials instead of traditional feedstocks (starch crops) is called bio-ethanol.

- The Clean Air Act Amendments of 1990 mandated the sale of oxygenated fuels in areas with unhealthy levels of carbon monoxide. Since that time, there has been strong demand for ethanol as an oxygenate blended with gasoline. In the United States each year, approximately 2 billion gallons are added to gasoline to increase octane and improve the emissions quality of gasoline.

- In some areas, ethanol is blended with gasoline to form an E10 blend (10% ethanol and 90% gasoline).
Bioethanol
What Types of Vehicles Use Ethanol?

- All gasoline vehicles are capable of operating on gasoline/ethanol blends with up to 10% ethanol. In fact, some lands require the seasonal or year-round use of up to 10% ethanol as an oxygenate additive to gasoline to mitigate ozone formation. These low percentage oxygenate blends are not classified as alternative fuels. We speak of ethanol vehicles as those specifically manufactured to be capable of running on up to 85% denatured ethanol, 15% gasoline (E85), or any mixture of the two up to the 85% ethanol limit. E85 may be seasonally adjusted in colder climates such that the real proportion of E85 is less than 85% ethanol. Vehicles manufactured for E85 use are commonly called flexible fuel vehicles (FFVs).

- Light-duty FFVs include a wide range of vehicles, from compacts to sport utility vehicles to pickup trucks.

Unlike bi-fuel natural gas and propane vehicles that have two unique fuelling systems, FFVs have only one fuelling system.

To qualify as an alternative fuel vehicle (AFV) for tax credits, incentives to meet requirements for mandated fleets (in USA federal, state, and fuel provider fleets) under the Energy Policy Act of 1992 (EPAct), a vehicle must be capable of using fuel blends up to 85% ethanol.
The Bioethanol Utilisation as Motor Fuels

Otto Engines:

- E5 - 5 % bioethanol in gasoline (EU)
- E10 - 10 % bioethanol in gasoline (USA)
- E25 - 25 % bioethanol in gasoline (Brasilia)

FFV (Flexible Fuel Vehicles)*:

- E85 – 85 % bioethanol in gasoline
  (USA, Sweden)

Diesel Engines:

- ED95 – 95 % bioethanol, 5 % additives
- ED15 – ethanol-diesel emulsion

Ecology and Safety as a Driving Force in the Development of Vehicles
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Why use MTBE?

MTBE has many properties that make it a good gasoline component for technical and environmental reasons:

- **MTBE** can be used as fuel that can supplement the supply of gasoline components.

- Its high octane rating makes it an ideal substitute for other octane components, e.g. lead.

- It is an oxygenate, which can be used in the formulation of cleaner-burning gasoline.

Lead has traditionally been added to gasoline due to its high octane rating, which prevents engine "knock". Lead is, however, a toxic compound, and leaded gasoline has been phased out in most areas of the world, including Europe.

**MTBE,** which has a very high octane number but is not toxic, is ideally suited to produce high octane, unleaded gasoline.
Why use MTBE?

Adding oxygen to gasoline allows more complete combustion of the fuel, and this reduces exhaust emissions of CO (carbon monoxide).

Furthermore, when used as part of the gasoline formulation, MTBE leads to a reduction in emissions of exhaust pollutants such as VOCs (volatile organic compounds), NO$_x$ (nitrogen oxides) and PM (particulates). Reducing these pollutants improves air quality.

By reducing the Ozone Forming Potential (OFP) of volatile organic compounds, MTBE performs significantly better than other octane blending components.

It generates about half of the ozone when compared to iso/alkylates and one-tenth that of aromatics.

For all these reasons MTBE has been widely used all over the world for the last 20 years.
Higher blends, even pure biodiesel (100% biodiesel), may be able to be used in some engines (built since 1994) with little or no modification. However, engine manufacturers are concerned about the impact of biodiesel engine durability. Additionally, biodiesel is generally not suitable for use in low temperature conditions. Transportation and storage of biodiesel, however, require special management.

Using biodiesel in a conventional diesel engine substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulphates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. These reductions increase as the amount of biodiesel blended into diesel fuel increases.
FAME Production in Europe

Source: Cargill Refined Oils Europe
The use of biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in biodiesel enables more complete combustion to $\text{CO}_2$) and reduces the sulphate fraction (biodiesel contains less than 15 ppm sulphur, while the soluble, or hydrocarbon, fraction stays the same or increases.

Biodiesel works well with emission control technologies such as diesel oxidation catalysts (which reduce the soluble fraction of diesel particulate but not the solid carbon fraction).

Emissions of nitrogen oxides increase with the concentration of biodiesel in the fuel and the increase is roughly 2% for B 20.

Some biodiesel produces more nitrogen oxides than others, and some additives have shown promise in reducing the increases.
Natural Gas

- Natural gas is a mixture of hydrocarbons (mainly methane — CH₄) and is produced either from gas wells or in conjunction with crude oil production.

- Chemical Properties: The main constituent of natural gas is methane, which is a relatively unreactive hydrocarbon. Natural gas as delivered through the pipeline system also contains hydrocarbons such as ethane and propane; and other gases such as nitrogen, helium, carbon dioxide, hydrogen sulphide and water vapor.
The FAME Utilization as Motor Fuels

- B 100 – 100 % FAME (EN 14214)
- B 5 – 5 % FAME in diesel fuel (EN 590:2004)
- B 20, B 30
  - poor stability
  - filter blocking deposits
  - poor water tolerance
  - microbiological contamination
  - poorer properties in low temperature
## Biofuels - positives and negatives

<table>
<thead>
<tr>
<th>Positives</th>
<th>Negatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>alternative, renewable resources</td>
<td>different chemical structure – compatibility problems</td>
</tr>
<tr>
<td>lower CO$_2$ emission in cycle of live</td>
<td>necessity of engine and cars adaptations for biofuels</td>
</tr>
<tr>
<td>free of S and aromatics</td>
<td>Different performance properties, lack of testing methods</td>
</tr>
<tr>
<td>contain oxygen, lower emission of CO, PM</td>
<td>Higher price, poorer availability</td>
</tr>
<tr>
<td></td>
<td>Necessity of separate distribution systems</td>
</tr>
</tbody>
</table>

**Ecology and Safety as a Driving Force in the Development of Vehicles**  
**IP Radom, 02 March - 15 March, 2008**
Standardization of alternative fuels in EU

Alternative liquid automotive fuels

- Diesel EN-590
  - FAME B 30
  - FAME B 100 EN-14214
  - FAEE 100 and FAEE5
  - Alcohol and alcohol derivatives in diesel fuels
  - Diesel emulsion
  - Synthetic Fischer Tropsch Diesel

- Gasoline EN-228
  - E 10
  - E 15

- Methanol
  - M 85
  - Methanol for blending

- Ethanol
  - Ethanol for blending
  - E 85
  - E 95

Legend:
- Normalized products
- Standard under elaboration
- For normalization during 5 years period
- For normalization during 5-10 years period
- For normalization during 10 - 20 years period
Standardization of alternative fuels in EU

Alternative gaseous automotive fuels

LPG
EN 589

Natural gas

Biogas

Hydrogen

CNG

LNG
EN 1160

Normalized products

For normalization during 5 - 10 years period
Future Fuels Solutions

% of new cars

Diesel (inc Bio-diesel/GTL)

Gasoline (inc Ethanol)

Hydrogen

LPG/CNG

Methanol

Hybrid-Fuels

Compression ignition engines

HCCI

Spark ignition

Fuel cell

2000 2010 2020

Ecology and Safety as a Driving Force in the Development of Vehicles
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Classification of Lubricants

- **Animal**  
  (Animal lubricants may not be used for internal combustion engines because they produce fatty acids)

- **Vegetable**  
  (Animal and vegetable oils have a lower coefficient of friction than most mineral oils but they rapidly wear away steel)

- **Mineral**  
  (These lubricants are used to a large extent in the lubrication of aircraft internal combustion engines)

There are three classifications of mineral lubricants:
- Solid
- Semisolid
- Fluid

- **Synthetic**  
  (Synthetic lubricants do not break down easily and do not produce coke or other deposits)
Lubricating Oil Properties

- Proper understanding of the lubricant chemistry is critical in understanding the long term viability of the product.
- Refining processes can improve the quality of the base stock.
- Additives play an important role in lubricant life.

**Gravity**
**Flash Point**
**Viscosity**
**Cloud Point**
**Pour Point**
**Carbon-Residue Test**
**Ash Test**

**Precipitation Number**
**Corrosion and Neutralization Number**
**Oiliness**
**Extreme-Pressure (Hypoid) Lubricants**
**Chemical and Physical Stability**
Gravity

- The gravity of petroleum oil is a numerical value which serves as an index of the weight of a measured volume of this product.
- There are two scales generally used by petroleum engineers:
  - Specific-gravity scale
  - American Petroleum Institute gravity scale
The flash point of an oil is the temperature to which the oil must be heated in order to give off enough vapor to form a combustible mixture above the surface that will momentarily flash or burn when the vapor is brought into contact with a very small flame.
Viscosity

- Viscosity is technically defined as the fluid friction of an oil.
- To put it more simply, it is the resistance an oil offers to flowing.
- Heavy-bodied oil is high in viscosity and pours or flows slowly.
Cloud Point

- The cloud point is the temperature at which the separation of wax becomes visible in certain oils under prescribed testing conditions.
- When such oils are tested, the cloud point is slightly above the solidification point.
Pour Point

- The pour point of an oil is the temperature at which the oil will just flow without disturbance when chilled.
The purpose of the carbon-residue test is to study the carbon-forming properties of a lubricating oil.
Ash Test

- The ash test is an extension of the carbon-residue test.
- If an unused oil leaves almost no ash, it is regarded as pure.
- The ash content is a percentage (by weight) of the residue after all carbon and all carbonaceous matter have been evaporated and burned.
Precipitation Number

- The precipitation number recommended by the ASTM is the number of milliliters of precipitate formed when 10 ml of lubricating oil is mixed with 90 ml of petroleum naphtha under specific conditions and then centrifuged.
Lubricant Requirements and Functions

- Characteristics of Lubricating Oil
- Functions of Engine Oil
- Straight Mineral Oil
- Ash-less Dispersant Oil
- Multi-viscosity Oil
Characteristics of Lubricating Oil

- It should have the proper body (viscosity)
- High antifriction characteristics
- Maximum fluidity at low temperatures
- Minimum changes in viscosity with changes in temperature
- High anti-wear properties
- Maximum cooling abilities
- Maximum resistance to oxidation
- Non-corrosive
Functions of Engine Oil

- Lubrication, thus reducing friction
- Cools various engine parts
- Seals the combustion chamber
- Cleans the engine
- Aids in preventing corrosion
- Serves as a cushion between impacting parts
In certain circumstances, all single-grade oils have shortcomings.

In cold-weather starts, single grade oil generally flows slowly to the upper reaches and vital parts of the engine.

Multigrade oils have viscosity characteristics that allow for better flow characteristics at engine start.
Important Lubricant Measurements

- Viscosity
- Viscosity Index
- Pour Point
- Flash/Fire Point
- Vapor Pressure
- Aniline Point
- Miscibility
- Solubility
Lubricant Types

- Mineral Oils
  - Naphthenic
  - Paraffinic
  - Hydrocracked
- Alkyl Benzene
- Polyalphaolefin
- Polyol Esters
- Polyalkylene Glycols
Typical Mineral Oil Molecule

Ideal Mineral Oil Molecule

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Typical Polyalkylene Glycol Molecule

Polyol Ester

\[
R\left(\text{C-C-O}_{n}\right)\text{C-C-O}\left(\text{C-C-O}_{m}\right)\text{C-C-OH}
\]

\[
R\text{C-O-C-C-C-O-C-R}
\]
Typical Alkyl Benzene Molecule
How Big is an Oil Molecule?

- Across Head of a Pin
  - 12,000,000

- Fill the Volume of the Head of a Pin
  - 472,900,000,000,000,000

- Fill a Pint
  - 602,200,000,000,000,000,000,000
Crude Oil Breakdown

CRUDE OIL

LPG

GASOLINE

JET FUEL

KEROSENE

STOVE OIL

DIESEL OIL

FURNACE OIL

HEAVY FUEL OIL

LUBRICATING OIL

ASPHALT
Properties of Naphthenic Mineral Oils

- High Aromatic/Unsaturated Content
- High Volatility
- Very Low Viscosity Index
- Low Wax Content
- Naturally Low Pour Point
- High Oxidation Rate
- Higher Solubility in Ammonia
- Must be Changed Frequently
Properties of Paraffinic Mineral Oil

- Reduced Aromatic/Unsaturated Content
- Contain Polar Species
- Poor Low Temperature Properties
- Marginal Oxidation Rate
- Low Volatility
- Extended Change Intervals
Properties of Hydro Cracked Mineral Oil

- Low Volatility
- Oxidatively Stable
- High Pour Point
- Good Additive Response
- Good Shear Stability
- High Viscosity Index
- High Aniline Point
Reaction Chemistry of Mineral Oils
Typical Reaction Mechanism

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Reaction Mechanism

\[ \text{HEAT} \]
\[ \text{C–C–C–C} \quad \rightarrow \quad \text{HEAT} \]
\[ \text{C–C–C–C} \ + \ \text{O}_2 \]

\[ \text{C–C–C–C–C} \quad \rightarrow \quad \text{C–C–C–C–C} \quad \text{Free Radical} \]

\[ \text{C–C–C–C–C–O} \quad \cdot \quad + \quad \text{H–C–C} \]

\[ \text{C–C–C–C–C–O–H} \quad \text{Organic Acid} \]

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Reactive Components of Mineral Oils

- **Unsaturates**
  - Susceptible to reaction with contaminants
  - Thermally unstable

- **Aromatics**
  - Increase solvency
  - Thermally unstable

- **Polar Compounds**
  - Absorb water
  - React with elastomers
Aromatic and unsaturated carbons have reactive bonds that can form free radicals.

Polar atoms are also susceptible to reaction due to the presence of free electrons.

Saturated hydrocarbons have greater chemical stability.
Lubricant Additives

- Antioxidants
- Rust and corrosion inhibitors
- Antiwear additives
- Pour point depressants
- Anti-foam agents
Thank you for attention