Alternative Fuels and Potential Material Compatibility Issues

NEIWPCC
20th Annual National Tanks Conference and Expo
Sheraton Atlanta Hotel, March 17-19, 2008
OVERVIEW

- Background
- Material Compatibility
- System Materials
- Risk Factors Metals and Non-metals
- Fuel Chemistry
- Biodiesel
- E10 and E85
- Conclusion
Background

- Industrialized countries are the largest consumers of oil but until 1998 had not been the most important growth market,

= Industrialized and Newly Industrialized Countries

Newly industrialized countries since 2007

<table>
<thead>
<tr>
<th>Andorra</th>
<th>Czech Rep.</th>
<th>Hong Kong</th>
<th>Japan</th>
<th>New Zealand</th>
<th>Slovenia</th>
<th>Turkey</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>Denmark</td>
<td>Hungary</td>
<td>Latvia</td>
<td>Norway</td>
<td>South Africa</td>
<td>UK</td>
</tr>
<tr>
<td>Austria</td>
<td>Estonia</td>
<td>Iceland</td>
<td>Lithuania</td>
<td>Philippines</td>
<td>South Korea</td>
<td>USA</td>
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<td>Belgium</td>
<td>Finland</td>
<td>India</td>
<td>Luxembourg</td>
<td>Poland</td>
<td>Spain</td>
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</tr>
<tr>
<td>Brazil</td>
<td>France</td>
<td>Ireland</td>
<td>Malaysia</td>
<td>Portugal</td>
<td>Sweden</td>
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</tr>
<tr>
<td>Canada</td>
<td>Germany</td>
<td>Israel</td>
<td>Mexico</td>
<td>San Marino</td>
<td>Switzerland</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>Greece</td>
<td>Italy</td>
<td>Netherlands</td>
<td>Slovakia</td>
<td>Thailand</td>
<td></td>
</tr>
</tbody>
</table>
Background

- OECD countries account for 2/3 of the daily global oil consumption,
- From 1991-1997, demand in the OECD only grew by 11% whereas demand outside the OECD grew by 35%

OECD – Organization for Economic Cooperation and Development

<table>
<thead>
<tr>
<th>Australia</th>
<th>Finland</th>
<th>Ireland</th>
<th>New Zealand</th>
<th>Spain</th>
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<tr>
<td>Austria</td>
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</table>
Background

- Developed economies use crude more intensively than developing economies,
- For example:
  - U.S & Canada ~3 gal. per day per capita
  - OECD* Countries ~1.4 gal per day per capita
  - Outside OECD ~0.2 gal per day per capita

* OECD – Organization for Economic Cooperation and Development
Background

- The United States and Canada use crude oil more for transportation than for heat and power,
- For the rest of the world, the emphasis is reversed, crude is used for power and heat and much less on transportation,
Background

• In the United States, ~2/3 of all crude oil is used for transportation fuels:
• On average, for every 2 gallons of crude per day per capita:
  – Gasoline accounts for 1.28 gal of crude,
  – Diesel accounts for 0.68 gal of crude,
  – Jet fuel accounts for 0.18 gal of crude.
Background

• Therefore, the current solution is to offset the demand on petroleum based transportation fuels through the use of alternative or biomass fuels:

• Current solutions:
  – Fuels replacements such as B100 and E85
  – Non- petroleum additives / fuel extenders such as B20/E10.
Background

Key Cost Drivers to Justify Manufacturing Biofuels:

• Price of crude oil >$60.00 per barrel
• Desire for energy and power self sufficiency
• Access to land
• Cost effective labor
• Access to capital
• Infrastructure and technology
• Domestic & export markets
• Availability and cost of feedstock
Background

• Spark Ignition Engines:
  – Alcohol Fuels
    • Methanol (Aggressive to metal and non-metals)
    • E85 (Fuel Replacement or blend stock)
    • E10 (Fuel Extender)
    • Butanol (Currently under R&D)

• Compression Ignition Engines:
  – Biodiesel & Blends
    • SVO (Leaves residue in engine cylinder)
    • FAEE (Belgium patent in 1937 no further development)
    • B100 (FAME-current common blend stock)
    • B5, B20 (FAME used as a fuel extender)
Fuel System Materials

- A variety of metals used in fuel systems such as:
  - aluminum, brass, copper, steel, zinc
- Non-metals may include:
  - Elastomers
  - Thermoplastics
  - Thermosets
  - Ceramics, pipe dope, and organic coatings
Material Compatibility

In general, when evaluating material compatibility, several perspectives must be considered:

1. Those changes in the physical, chemical or mechanical properties of a material resulting from product exposure,

2. Exposure or contact of a fuel to a metal or non-metal should not alter the performance of the material, induce new or enhance existing failure mechanisms.

3. Conversely, metals or non-metals in contact with a fuel should not corrode thus contaminating the fuel and impairing engine performance.
Risk Factors for Metal Corrosion

- Fluids with conductive properties (polar characteristics,)
- Presence of chemical contaminants which include chlorides and acids that can facilitate corrosion,
- Macro/micro environments with an acidic pH,
- The presence of microorganisms that facilitate/accelerate known corrosion mechanisms,
- Dissimilar metals (anodic / cathodic) present in the same system joined electrically by a conductive fluid separated widely on the galvanic series.
Conductivities of Various Fuels

Electrical Conductivity

<table>
<thead>
<tr>
<th>Product</th>
<th>Conductivity (Siemen per Centimeter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td>1.00E-14</td>
</tr>
<tr>
<td>Diesel</td>
<td>1.00E-13</td>
</tr>
<tr>
<td>B100</td>
<td>1.00E-12</td>
</tr>
<tr>
<td>E100</td>
<td>1.00E-11</td>
</tr>
<tr>
<td>M100</td>
<td>1.00E-10</td>
</tr>
<tr>
<td>Pure Water</td>
<td>1.00E-09</td>
</tr>
</tbody>
</table>
Risk Factor - Metals

Galvanic Series

Most Noble Cathodic

Least Noble Anodic

Graphite
Titanium
Type 316 Stainless (passive)
Type 304 Stainless (passive)
Monel Alloy 400 (65%Ni, 30%Cu)
Silver
Nickel 200
Silver-Brazing Alloys
Inconel Alloy 600 (passive)
70-30 Copper-Nickel
Lead
90-10 Copper-Nickel
Manganese "Bronze" (58%Cu, 39%Zn)
Silicon Bronze (96%Cu)
Tin
Lead - Tin Solder (50%, 50%)
Copper
Red Brass (85%Cu, 15%Zn)
Yellow Brass (65% Cu, 35% Zn)
Naval Brass; Tobin "Bronze" (60%Cu, 39%Zn)
Aluminum Bronze (91%Cu, 7%Al, 2%Fe)
Inconel Alloy 600 (active)
Type 316 Stainless (active)
Type 304 Stainless (active)
HSLA Steel; CorTen
Mild Steel; Cast Iron; Wrought Iron
Cadmium
Aluminum Alloys
Zinc
Galvanized Steel
Magnesium
## Risk Factors for Degradation of Non-metals

<table>
<thead>
<tr>
<th><strong>PERMEATION:</strong></th>
<th>Solvent ingress is related to a system potential driven by a chemical or activity gradient,</th>
<th>$\mu = \mu_0 + RT \ln a/a_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SWELLING:</strong></td>
<td>The result of interaction between the solvent molecule and the polymer matrix (domain),</td>
<td><img src="image" alt="OH R-C-O-CH3" /></td>
</tr>
<tr>
<td><strong>LEACHING:</strong></td>
<td>Loss of antioxidants, fillers, heat stabilizers, plasticizers during solvent permeation and extraction,</td>
<td></td>
</tr>
<tr>
<td><strong>PLASTICIZATION:</strong></td>
<td>Degradation in the performance of the non-metal as a result of solvent diffusion, potentially affecting strength and integrity of the non-metal matrix</td>
<td></td>
</tr>
</tbody>
</table>
# Fuel Chemistry Comparison

<table>
<thead>
<tr>
<th>Petroleum Base Fuels:</th>
<th>Biomass fuels:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Have low conductivities</td>
<td>Are more conductive</td>
</tr>
<tr>
<td>• Gasoline $1 \times 10^{-14}$ mho/cm</td>
<td>• $E_{d95}$ $10^{-9}$ S/cm,</td>
</tr>
<tr>
<td>• Diesel $1 \times 10^{-12}$ mho/cm</td>
<td>• B100 $10^{-12}$ S/cm (Anhydrous)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hold very little water dissolved water</th>
<th>Hold much more water dissolved water</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 60-100 ppm</td>
<td>• E10 3000-5000 ppm (~0.3 - 0.5%)</td>
</tr>
<tr>
<td></td>
<td>• E85 ~100,000 ppm (~10%)</td>
</tr>
<tr>
<td></td>
<td>• B100 1200-2500 ppm</td>
</tr>
</tbody>
</table>

- Do not absorb or permeate through metals,
- Potential compatibility issues have been noted with elastomeric and thermoplastic materials
- Functional groups can increase chemical activity, reactivity, and bioavailability
Biodiesel

• Composition/Feedstock
  – Feedstock vegetable oils, used grease, or animal fats.
  – Different feed stocks for FAME will influence some properties of the fuel (i.e., saturated vs. unsaturated)
Biodiesel

Potential Issues and Concerns (B100):
- Material compatibility issues vary with BXX blends,
- B100 and BXX blends can act as solvents that can release varnish, gums as well as degrade, soften, seep through certain hoses, gaskets, seals with prolonged exposure
- Biodiesel material compatibility issues decline with the concentration of biodiesel,
- Biodiesel has a greater propensity to support microbial growth,
Biodiesel – B100

A sampling of Generally Compatible Materials

• Metals
  – Aluminum
  – Steels

• Elastomers
  – Fluorocarbon
  – PTFE

• Polymers
  – Fluorinated polyethylene
  – Fluorinated polypropylene
  – Polyamide
  – Fiberglass Reinforces Polymers.
Biodiesel – B100

A sampling of materials with vulnerability issues

- Metals
  - brass, bronze, copper, lead, tin, and zinc which may act as catalysts leading to oxidative degradation,

- Elastomer swell:
  - Buna-N
  - Nitrile Rubber
  - Natural rubber
  - Polyvinyl chloride

- Polymers
  - Polyethylene
  - Polypropylene
  - Polyvinyl chloride
Biodiesel – BXX

A sampling of generally compatible materials

- Metals
  - stainless steel,
  - carbon steel, or
  - Aluminum

- Elastomers
  - Fluorocarbon
  - PTFE

- Polymers
  - Fluorinated Plastics
  - Polyamide
  - Thermoplastics
  - Thermoset
Biodiesel – BXX

A sampling of materials with vulnerability issues

- Metals
  - brass, bronze, copper, lead, tin, and zinc which may act as catalysts leading to oxidative degradation

- Elastomer swell
  - Problems tend to diminish as biodiesel concentration decreases

- Polymers
  - Problems tend to diminish as biodiesel concentration decreases
## Biodiesel

<table>
<thead>
<tr>
<th>Elastomers</th>
<th>Blend</th>
<th>Compared to Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>B100</td>
<td>Little Change</td>
</tr>
<tr>
<td>Polyamide</td>
<td>B100</td>
<td>Little Change</td>
</tr>
<tr>
<td>Fluorocarbon</td>
<td>B100</td>
<td>Little Change</td>
</tr>
<tr>
<td>Nitrile</td>
<td>B100</td>
<td>Hardness ↓ - 20% : Swell ↑ - 18%</td>
</tr>
<tr>
<td>Fluorosilicone</td>
<td>B100</td>
<td>Hardness Neg. : Swell ↑ - 7%</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>B100</td>
<td>Hardness Neg. : Swell ↑ - 6%</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>B100</td>
<td>Hardness ↓ - 10% : Swell ↑ - 8-15%</td>
</tr>
<tr>
<td>Polyvinyl</td>
<td>B100-B30</td>
<td>Worse</td>
</tr>
<tr>
<td>Polyvinyl</td>
<td>B20 – B10</td>
<td>Comparable</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>B100</td>
<td>Worse</td>
</tr>
</tbody>
</table>
# Biodiesel

## Biodiesel Metabolism  EPA Standard 560/6-82-003

<table>
<thead>
<tr>
<th>Days</th>
<th>Rape Ethyl Ester</th>
<th>Rape Methyl Ester</th>
<th>Soy Ethyl Ester</th>
<th>Soy Methyl Ester</th>
<th>Neat Rape</th>
<th>Neat Soy</th>
<th>#2 Diesel</th>
<th>Dextrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>69.01</td>
<td>66.32</td>
<td>67.68</td>
<td>68.4</td>
<td>58.39</td>
<td>60.57</td>
<td>13.20</td>
<td>59.84</td>
</tr>
<tr>
<td>14</td>
<td>79.15</td>
<td>80.72</td>
<td>78.40</td>
<td>77.83</td>
<td>70.47</td>
<td>70.12</td>
<td>21.04</td>
<td>80.19</td>
</tr>
<tr>
<td>28</td>
<td>86.92</td>
<td><strong>88.49</strong></td>
<td>86.40</td>
<td><strong>85.54</strong></td>
<td>78.45</td>
<td>75.95</td>
<td><strong>26.24</strong></td>
<td>87.79</td>
</tr>
</tbody>
</table>
E10 Fuel

- Composition & Feedstock
  - 10% Ethanol (EtOH) &
    90% Unleaded gasoline
- Sources of ethanol are:
  - Fermentation from corn at 2.5 gal/bushel (primary source)
  - Chemically from ethylene,
  - Cellulose agricultural waste, starch, or sugar,
Potential Issues and Concerns E10

• Phase separation is the most critical concern,
• Increased fuel conductivity may lead to system corrosion,
• May experience some solvent action,
• May experience some compatibility or permeability issues
• E10 fuels have been on the market since late 1970’s and most metal and nonmetal compatibility issue should be identified and resolved.
Ethanol Fuels $E_d^{85}$

- **Compositions & Feedstocks:**
  - 75% - 85% Ethanol (EtOH) & 15% - 25% Unleaded gasoline
  - Formulation seasonally adjusted

- **Sources Benefits / Comments:**
  - Fermentation from corn at 2.5 gal/bushel (primary source)
  - Chemically from ethylene,
  - Cellulose agricultural waste, starch, or sugar,
Potential Issues and Concerns $E_{d,85}$

- Potential Issues and Concerns
  - Increased Conductivity
  - Solvent Action
  - Compatibility / Permeability
  - Phase Separation
Solvent Action

- As the EtOH concentration increases, hydrogen bonding increases between the EtOH molecules that can form unique molecules that can make fuel behave like a polar and non-polar liquid,
Ethanol Fuels E_{d}85

A sampling of generally compatible materials

- ** Metals**
  - Black Iron
  - Bronze
  - Mild steel
  - Stainless steel
  - Unplated steel
  - Nickel Plating for soft metals (i.e., aluminum)

- **Elastomers**
  - Buna-N (hose & gaskets)
  - Fluorocarbons
  - Nitrile Rubbers
  - Polychloroprene (hose & gaskets)
  - PTFE

- **Polymers**
  - Polypropylene
  - Thermoplastic piping*
  - Thermoset reinforced fiberglass tanks*

*In the fuel path
Ethanol Fuels E\textsubscript{d}85

A sampling of materials with vulnerability issues

- **Metals**
  - Aluminum
  - Brass
  - Copper Alloys
  - Lead
  - Lead Solder
  - Tern-plated steel (Fuel Tanks)
  - Zinc

- **Elastomers**
  - Buna-N (seals only)
  - Polychloroprene (seals only)
  - Natural rubber
  - Cork gasket material, *
  - Leather, *

  *Natural material not elastomer

- **Polymers**
  - Certain polyamides
  - Polyurethane,
  - Polyvinyl chloride,
  - Methylmethacrylate,
  - Certain polymer liners*

*Epoxy and polyester resins manufactured between 1970’s and 1980’s
$E_d^{85}$ - Example of Corrosion

- Same facility
- Same install date
- Top is E85 STP
- Bottom is standard petroleum fuel STP

Photograph Courtesy of Rounds and Associates (Public Domain Information)
$E_{d85} - \text{ Vent Pipe Deterioration}$

Photograph Courtesy of Rounds and Associates (Public Domain Information)
$E_d^{85} - $ Seals and Gasket Leak

Photograph Courtesy of Rounds and Associates (Public Domain Information)
E_{d}85 - Catastrophic Failure

Photograph Courtesy of Rounds and Associates (Public Domain Information)
Conclusion
So…What’s the take home message

• The United States consumer has an infinite appetite for transportation fuels,

• Crude oil and other petroleum resources are not only in limited supply but also affect the environment and the health of the nation,

• It is reasonable to expect that the chemistry of future fuels will change,
So…What’s the take home message

• We need to understand the potential impact of these proposed future fuels on a fuel network that was originally designed safeguard the transportation, storage and distribution of petroleum product,

• However, this has to be done in manner that ensures the transition of these future fuels into the existing fuel network both economically and seamlessly,
Thank You