Alternative Fuels as a Diesel Emissions Control Strategy

By Aleksandar Bugarski, Ph.D.

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Diesel Fuels

• Diesel fuels
  – Petroleum based
  – Biodiesel
  – Synthetic diesel

• Properties and quality of diesel fuels and lubricants play major role in efforts of underground mining industry to control emissions from diesel powered equipment.

• Reformulated conventional petroleum diesel and alternative fuels such as biodiesel and synthetic diesel can be used to reduce emissions from existing and new design diesel engines.
Regulations Pertinent to Use of Diesel Fuel in Underground Metal/nonmetal (MNM) Mines in the U.S.

  - LSD - 500 ppm sulfur

  - ULSD - 15 ppm sulfur

Petroleum Diesel

- The quality of the diesel fuels in the U.S. is specified by ASTM International standard ASTM D 975

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Test Method</th>
<th>Limits for various grades</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. 1- D S15</td>
<td>No. 1- D S500</td>
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<tr>
<td>Flash Point, °C, min.</td>
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<td>Distillation Temperature, °T₉₀ %, % vol recovered, min</td>
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<td>Distillation Temperature, °T₉₀ %, % vol Max</td>
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<tr>
<td>Kinematic Viscosity, mm²/S at 40°C Max</td>
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<tr>
<td>Ash % mass, max</td>
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<tr>
<td>Sulfur, ppm (µg/g)Æ max % mass, max</td>
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<td>...</td>
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<td>Copper strip corrosion rating, max</td>
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<td>No. 3</td>
</tr>
<tr>
<td>Copper strip corrosion rating, max</td>
<td>D 130</td>
<td>...</td>
</tr>
<tr>
<td>Cetane number, min</td>
<td>D 613</td>
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</tr>
<tr>
<td>Cetane index, min</td>
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<tr>
<td>Aromaticity, % vol, max</td>
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<tr>
<td>Lubricity, HFRR @ 60°C, micron, max</td>
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<td>520</td>
</tr>
<tr>
<td>Units (C.U.), min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

One of the following properties must be met:

(1) Cetane index, min
(2) Aromaticity, % vol, max
Petroleum Diesel

• Hydrocarbons
  – Saturated acyclic (aliphatic) hydrocarbons (parafins or alkanes), $C_nH_{2n+2}$;
  – Unsaturated hydrocarbons with double bonds (olefins and alkenes) or triple bonds (acetylene or alkynes), $C_nH_{2n}$ (double bonds) and $C_nH_{2n-2}$ (triple bonds);
  – Cyclic (aliphatic) hydrocarbons, either saturated (cycloalkanes or naphtenes) or unsaturated (cycloalkenes or cycloalkynes), $C_nH_n$;
  – Aromatic hydrocarbons (arenes).

• Trace elements
  – Sulfur and sulfur compounds,
  – Water and sediments,
  – Ash etc.
Effects of Diesel Fuel Properties on Emissions

- **Sulfur content:**
  - Higher sulfur content results in higher emissions of SO$_2$ and sulfate particulates;
  - Minor effects on NO$_X$, CO and HC.
- **Cetane number:**
  - Slight reductions in NO$_X$, CO and HC emissions;
  - Minor effect on PM emissions.
- **Density:**
  - Fuels with lower density tend to benefit PM emissions;
  - But those can possibly increase HC emissions.
- **Aromatics**
  - Fuels with lower content of aromatics benefit PM and HC emissions
- **Oxygen content (e.g. biodiesel):**
  - Lower PM emissions;
  - Increase in HC emissions.
Identifying contributions from individual properties to the overall effects presents challenge

- Changes in some fuel properties generally result in concurrent changes in other fuel properties, e.g.:
  - Increase in specific gravity reduces Cetane number.
  - Specific gravity increases with total aromatic content.
  - Increase in total aromatic content reduces Cetane number.

  - Literature review (~33 studies);
  - Multi-parameter regression analysis;
  - Engines built between 1979 and 2002 with different engine designs:
    - Type of injection;
    - Rated speed;
    - Injection control.
EPA (2001), Results

The effects of fuel on emissions in general depend on engine design and engine operating conditions.

- The engines equipped with EGR exhibit no benefits in NO$_X$ emissions from higher Cetane (EPA 2003).
- PM emissions from DI engines are more sensitive to fuel changes than those from IDI engines.
- Increase in Cetane number reduced NO$_X$ emissions from DI and increased NO$_X$ emissions from IDI engines.

The effects of fuel properties on emissions are much smaller than the differences in emissions from engine to engine.
Biodiesel

• Biofuels:
  – long chain fatty acid methyl esters (FAME) – oxygenated biodiesel;

• Biodiesel fuels are appealing because of:
  – renewable, nontoxic, and biodegradable nature;
  – significance to the efforts to reduce dependence on imported petroleum;
  – potential to reduce DPM emissions.

• Most common sources of biomass for FAME:
  – virgin vegetable oil:
    • Soy, rapeseed (canola), corn, cottonseed, sunflower, palm oil.
  – animal fats:
    • Beef tallow, pork lard
  – waste cooking oil.
Regulations Pertinent to Use of Biodiesel in Underground Mines in the U.S.

- The neat biodiesel fuels must meet the specifications of ASTM D6751 standard.

- The blends with 6 to 20 percent of biodiesel must meet ASTM D7467 standards.

- The blends below B5 typically meets the ASTM D975 diesel fuel specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Test Method</th>
<th>B100 (ASTM D 6751)</th>
<th>B6 to B20 (ASTM D7467)</th>
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<tr>
<td>Property</td>
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<td>S500</td>
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<td>Flash Point, °C, min.</td>
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<td>Methanol Content, % vol., max</td>
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<td>Sulfur, ppm (µg/g)</td>
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<td>Sulfated Ash, mass %</td>
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<td>Cetane Number, min</td>
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<td>Cloud Point, °C,</td>
<td>D 2500</td>
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<td>Report to customer</td>
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<td>Ramsbottom Carbon Residue on 10% bottoms, % mass, max</td>
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<td>Free Glycerin, % mass</td>
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<td>Total Glycerin, % mass</td>
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<td>Phosphorus Content, % mass</td>
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<td>Calcium and Magnesium, combined, ppm (µg/g) max</td>
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<td>Cold Soak Filtration, for use in temperatures below -12 °C, seconds, max</td>
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<td>Oxidation Stability, hours</td>
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<tr>
<td>Biodiesel Content, % (vol/vol)</td>
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<td>100</td>
<td>100</td>
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## FAME Biodiesel vs. ULSPD Properties

<table>
<thead>
<tr>
<th>Fuel Property</th>
<th>Test Method</th>
<th>ULSPD</th>
<th>B20</th>
<th>B50</th>
<th>B57</th>
<th>B100</th>
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<tbody>
<tr>
<td>Fatty Acid Methyl Ester Content [%]</td>
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<td>48.56</td>
<td>56.5</td>
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<td>Heat of Combustion [BTU/gal]</td>
<td>ASTM D240</td>
<td>133194</td>
<td>135286</td>
<td>131184</td>
<td>128118</td>
<td>126089</td>
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<td>API Gravity @ 15.6 °C [°API]</td>
<td>ASTM D1298</td>
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<td>34.6</td>
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<td>-10</td>
<td>-8</td>
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<td>10</td>
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<td>Pour Point [°C]</td>
<td>ASTM D97</td>
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<td>-14</td>
<td>-13</td>
<td>-2</td>
<td>1</td>
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<td>Flash Point, Closed Cup [°C]</td>
<td>ASTM D93</td>
<td>67</td>
<td>68</td>
<td>74</td>
<td>80</td>
<td>173</td>
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<tr>
<td>Lubricity, HFRR, Wear Scar Diameter [µm]</td>
<td>ASTM D6079</td>
<td>640</td>
<td>190</td>
<td>170</td>
<td>230</td>
<td>240</td>
</tr>
</tbody>
</table>

- Biodiesel is oxygenated fuel (~10-11%)
- Biodiesel has:
  - Lower energy content
  - Lower density
  - Similar or lower Cetane number
  - Sulfur content similar to the one of ULSPD
  - No aromatics
  - Higher lubricity
Effects of FAME Biodiesel on DPM Emissions
Underground Experimental Mine Evaluation

- Experimental work done at NIOSH Mobile Engine Emissions Laboratory (MEEL) at Lake Lynn Experimental Mine (LLEM)
Effects of FAME Fuels and DOC on Average Aerosol Mass Concentrations [µg/m³]

- Biodiesel fuels increased total mass concentrations for M1 (muffler only) and M3, but
- Total mass concentrations decreased for M2 (muffler and DOC) and M4.
Effects of Fuel and DOC on Total Number Concentrations with $d_{50} \text{ em}$ between 10 and 400 nm

- Biodiesel fuels increased total number concentrations of aerosols for M1 and M3, but

- Total number concentrations of aerosols remained unchanged for M2 and decreased slightly for M4.
Effects of FAME Biodiesel on Emissions

- Effects of biodiesel fuels on size distribution, number and mass concentrations, and EC concentrations strongly dependent on engine operating mode.

- Reductions in EC were observed for all engine operating modes and exhaust configurations when biodiesel fuels were used.

- The increase in number and mass concentrations are observed for the light-load engine operating conditions. Those can be attributed to increase in semi-volatile organic compounds.

- The advantage of using DOC are particularly evident in the case of light-load engine operating conditions.

- The downside of using the DOC might be increase in NO₂ concentrations at high-load engine operating conditions.

Effects of FAME Biodiesel on DPM Emissions
Underground Production Mine Evaluation

- The evaluation was conducted in an active underground mine using a production vehicle using isolated zone methodology.
- The vehicle/engine was operated for extended period of time in the 600 feet long section of main drift of the isolated zone.
- The vehicle/engine duty cycle consisted of several repetitions of a 300-second long simulated haulage-truck duty cycle.
Biodiesel fuels reduced EC, OC, and TC concentrations of aerosols in mine air.

The reductions in EC and TC (dominated by EC) concentrations were directly related to biodiesel content in the blends.
Effects of FAME Fuels on Number Size Distributions

- In general, the size distributions of aerosols observed for the biodiesel blends were found to be characterized by smaller median diameter ($D_{50}$) and lower peak concentrations than the corresponding size distributions observed for the ULSD.
Biodiesel in Underground Mining

• Relatively simple to implement.
  – B5 to B20 - quite straightforward
  – B20 to B100 – number of uncertainties

• The major issues preventing a wider use of biodiesel in the U.S. underground mines:
  – availability;
  – quality;
  – low-temperature operability;
  – engine compatibility;
  – compatibility with exhaust aftertreatment technologies;
  – cost;
  – safety.
Low Temperature Operability

• At cold temperatures FAME fuels crystallize, clog the fuel filters and eventually gel so they cannot be pumped from the fuel tank to the engine.

• The cold flow properties of FAME fuels depend strongly on feedstock: e.g. soy methyl ester has cloud point of 0 °C (32 °F) and edible tallow methyl ester has cloud point of 19 °C (66 °F) [NREL 2009].

• Since FAME fuel gels at temperatures 11 °C to 17 °C (20 °F to 30 °F) higher than petroleum diesel, the handling of neat and blended FAME fuels during cold temperatures is a major issue.
Low Temperature Operability

• The critical properties for identifying the low-temperature operability of FAME fuels are cloud point, pour point, cold filter plugging point and low-temperature flow test. Cloud point is the most widely used and provides the most conservative estimate of the cold weather operability.

• The typical diesel cold flow additives have a limited effectiveness on B100, but work with varying degrees of effectiveness with B20 [NREL 2009].

• Storing biodiesel in the underground or heated fuel tanks can help mitigate issues with operability during periods of cold weather
Engine Compatibility

• Engine manufacturers approve use of biodiesel blends with up to 5 and 20% biodiesel
  – cold flow properties;
  – material compatibility;
  – maintenance intervals;
  – fuel stability;
  – biological growth;
  – energy content;
  – emissions;
  – overall handling
• Warranty issues.
Compatibility with Exhaust Aftertreatment Technologies

• Theoretically, biodiesel fuels that are found to reduce total PM emissions, increase NO\textsubscript{X} emissions, and produce DPM with higher soluble organic fraction should have positive effect on performance of DPF systems.

• Due to reductions in DPM emissions and slight increase in NO\textsubscript{X} emissions, the NO\textsubscript{X}/DPM ratio in the exhaust of an engine fueled by biodiesel should be higher than the same engine fueled with petroleum diesel. Higher NO\textsubscript{X}/DPM ratio is desirable for the DPF systems that are designed to regenerate passively by NO\textsubscript{2} oxidation.

• B20 and neat SME biodiesel were shown to lower balance point temperature of catalyzed diesel particulate filter by 45 °C and 112 °C, respectively [Williams et al. 2006].
Compatibility with Exhaust Aftertreatment Technologies

• Increase in levels of SME and RME biodiesel in the fuel results in increase in the rate of DPF regeneration at any given engine operating conditions [Williams et al. 2006, Fukuda et al. 2008].

• The fuels with high content of biodiesel were found to hinder regeneration of the CRT and CCRT systems that are regenerated with help of after- and post-injection of fuel [Fukuda et al. 2008]. Lower heating value of biodiesel and changes in fuel injection characteristics are potential culprits.
Synthetic Diesel Fuels

• The following fuels fall in this category:
  – gas-to-liquid (GTL),
  – coal-to-liquid (CTL), and
  – biomass-to-liquid (BTL) fuels.

• The most widely used process to produce synthetic fuels is the one patented by Fischer and Tropsch in 1930.

• Synthetic diesel
  – near-zero sulfur content,
  – near 100% paraffinic, near-zero aromatic content, and
  – high Cetane number, typically in excess of 70
Effects of Synthetic Diesel Fuels on Emissions

  - PM between 22 and 35%,
  - NO\textsubscript{X} between 7 and 35%,
  - HC between 5 and 46%, and
  - CO between 11 and 38%.

- Decrease number concentrations of nucleation mode particles in diesel engine exhaust is observed when GTL fuel is used [Li and Zen 2009].
Effects of Synthetic Diesel Fuels on Engine Performance

• Synthetic diesel fuels have poor lubricity and cold weather flow properties when compared with petroleum diesel fuel:
  – Lubricity additives are used to prevent fuel-injection system wear.
  – Additives and/or appropriate handling practices need to be followed to prevent gelling in cold environments.

• Synthetic diesel fuels do not require
  – modifications on the engine;
  – new or modified pipelines, storage tanks, or pumps.

• Fuel consumption might go up 3-5%.
Other Issues with Using Alternative Diesel Fuels

• Blending: The cost effectiveness diminishes for both biodiesel and synthetic diesel fuels when percentage of blended alternative fuel exceed approximately 50.

• Optimization: The effects of alternative fuels on the emissions could be further reduced through optimization of engine design to account for differences in fuel properties.

• Compatibility with engine components:
  – Engines with high pressure fuel injection systems are more sensitive to fuel quality issues
  – High levels of biodiesel present in the engine oil may result in polymerization and cause serious engine oil sludge problems. Therefore, when high blends of biodiesel are used, the engine oil change intervals should be significantly shortened.
Other Issues with Using Alternative Diesel Fuels

• Compatibility with aftertreatment: The reformulated fuels might aide or diminish performance of exhaust aftertreatment technologies:
  – different composition of DPM;
  – different exhaust temperatures.
Fuel Additives

• Fuel additives are added to diesel fuel for a wide variety of purposes:
  – Improvement in the fuel delivery system performance (injector cleaners, lubricity additives);
  – Improvement in the combustion process (cetane number improvers, smoke suppressants);
  – Fuel handling (antifoam, de-icing, low-temperature operability additives);
  – Fuel stability (antioxidants, stabilizers, metal deactivators, dispersant);
  – Contaminant control (biocides, deemulsifiers, corrosion inhibitors)
  – Emissions control (oxygenated compounds, biodiesel, diesel/water emulsions)
  – Enhancing the regeneration of DPF systems.
Fuel Additives

• Multifunctional packages added at the refinery or at the terminal;
  – Organosilicone compounds - to suppress foaming;
  – Alcohols/glycols - to prevent turning free water in diesel fuel in ice crystals;
  – Various polymers - to improve cold flow properties of diesel fuel
  – Mono acids, amides, and esters - to improve lubricity of hydrotreated diesel fuels;
  – Alkyl nitrates, nitrates, peroxides - to improve cetane number;
  – Ashless polymeric detergents - to clean fuel injector deposits;
  – Hindered phenols and certain amines - to suppress oxidation of diesel fuel;
  – Alcohols, glycol ethers and esters, and methyl esters (biodiesel)-to reduce diesel emissions.

• With some exception, the concentration of these additives in the diesel fuel is typically low, on the order of a couple ppm to a couple ppt.
Fuel Additives

• Aftermarket additives:
  – Water/diesel emulsions;
  – Fuel borne catalyst (FBC):
    • bulk fuel supply dedicated to the vehicles equipped with DPFs;
    • via onboard dosing systems.
  – Biodiesel.
Regulations Pertinent to Use of Fuel Additives in the U.S. Underground Mines

• Only fuel additives registered with the EPA are able to be used in underground mines in the U.S. [66 Fed. Reg. 27864 (2001), 71 Fed. Reg. 28924 (2006)].

  – survey existing scientific information on each product, and analyze the combustion and evaporative emissions generated by fuels and additives (Tier 1),
  – conduct testing to determine the potential adverse effects of inhalation of fuels and fuel additive emissions (Tier 2), and if adequate information is not available,
  – conduct additional testing focusing on areas of concern (Tier 3).
The FBC Additives Containing Transition Metals

- The FBC additives containing transitional metals are of major concern.

- The use of small concentrations of FBC in engines equipped with DPF systems has not been shown to substantially increase the risk associated with exposure to aerosols and gases emitted by diesel-powered equipment.

- In the case of DPF equipped engines, the concentrations of metals, from FBC dosing, emitted into the environment have been shown to be minimal.

- Metallic materials in these additives will add to the amount of ash captured in the DPF and thus, even at low dosages, shorten the ash removal servicing intervals.
The FBC Additives Containing Transition Metals

• It is absolutely critical that FBC-treated fuels not be used in engines not fitted with DPF systems. This precaution should also be taken to prevent the use of FBC-treated fuels in engines equipped with compromised DPF systems.

• A potential engineering solution, for this problem, would involve the deployment of onboard dosing systems, with closed feedback loops, monitoring the exhaust backpressure and shutting off the dosing system in the case of a DPF failure [Lemaire 1999, Seguelong and Quigley 2002, D’Urbano and Mayer 2007].
Lubricating Oil

• The performance of contemporary diesel engines and advanced exhaust aftertreatment systems is highly sensitive to properties and quality of lubricants.


• Removal of sulfur from the fuel and lubricating oil minimized sulfate production and poisoning of the catalyst.

• Minimizing ash content in lubricating oil helps minimizing ash accumulation and extending periods between DPF cleaning.
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