Alternative Fuels as a Diesel Emissions Control Strategy

By Aleksandar Bugarski, Ph.D.

Diesel Aerosols and Gases in Underground
Metal and Nonmetal Mines,
14th U.S. / North American Mine Ventilation Symposium
Salt Lake City, Utah, June 17th, 2012

CDC Workplace Safety and Health
National Institute for Occupational Safety and Health NIOSH

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.

- 71 Fed. Reg. 28924 [2006]. **Mine Safety and Health Administration**: 30 CFR 57.5060, Diesel particulate matter exposure of underground metal and nonmetal miners. Limit on concentration of diesel particulate matter. Final rule. Code of Federal Regulations, Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
  - LSD - 500 ppm sulfur

- 66 Fed. Reg. 5001 [2001]. **Environmental Protection Agency**: 40 CFR Parts 69, 80, and 86. Clean Diesel Trucks, Buses, and Fuel: Heavy-duty Diesel Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements. Final Rule. U.S. Code of Federal Regulations, Washington, DC: U.S. Government Printing Office, Office of the Federal Register.
  - ULSD - 15 ppm sulfur

- 69 Fed. Reg. 38957 [2004]. **Environmental Protection Agency**: 40 CFR Parts 9, 69, 80, 86, 89, 94, 1039, 1048, 1051, 1065, and 1068. Control of Emissions of Air Pollution from Nonroad Diesel Engines and Fuel. Final rule. U.S. Code of Federal Regulations, Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Petroleum Diesel

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

Property	ASTM Test Method	Limits for various grades						
		No. 1-D S15	No. 1-D S500	No. 1-D S5000	No. 2-D S15	No. 2-D S500	No. 2-D S5000	No. 4-D
Flash Point, °C, min.	D 93	38	38	38	52	52	52	55
Water and Sediment, % vol, max	D 2709 D 1796	0.05 …	0.05 …	0.05 …	0.05 …	0.05 …	0.05 …	… 0.50
Distillation Temperature, °T_{90} %, % vol recovered, min Max	D 86	... 288	… 288	… 288	282 338	282 338	282 338	… …
Kinematic Viscosity, mm^2/S at 40°C min Max	D 445	1.3 2.4	1.3 2.4	1.3 2.4	1.9 4.1	1.9 4.1	1.9 4.1	5.5 24.0
Ash % mass, max	D 482	0.01	0.01	0.01	0.01	0.01	0.01	0.10
Sulfur, ppm (µg/g)*F* max % mass, max % mass, max	D 5453 D 2622 D 129	15 … …	… 0.05 …	… … 0.50	15 … …	… 0.05 …	… … 0.50	… … 2.00
Copper strip corrosion rating, max (3 h at a minimum control temperature of 50°C)	D 130	No. 3	No. 3	No. 3	No. 3	No. 3	No. 3	…
Cetane number, min One of the following properties must be met: (1) Cetane index, min. (2) Aromaticity, % vol, max	D 613 D 976–80 D 1319	40 40 35	40 40 35	40 … …	40 40 35	40 40 35	40 … …	30 … …
Lubricity, HFRR @ 60°C, micron, max	D 6079	520	520	520	520	520	520	
Conductivity, pS/m or Conductivity Units (C.U.), min	D 2624/D 4308	25	25	25	25	25	25	

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.

- EPA 2001. Strategies and Issues in Correlating Diesel Fuel Properties with Emissions. Staff Discussion Document. EPA420-P-01-001.
  - 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;
  - biomass-to-liquid (BTL) – non-oxygenated.
- 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.

Property	ASTM Test Method	B100 (ASTM D 6751)		B6 to B20 (ASTM D7467)	
		S15	S500	S15	S500
Flash Point, °C, min.	D 93	93	93	52	52
Alcohol Control – One of the following must be met Methanol Content, % vol., max Flash Point °C, min	EN 14110 D 93	0.2 130	0.2 130	0.2 130	0.2 130
Water and Sediment, % vol., max	D 2709	0.05	0.05	0.05	0.05
Distillation Temperature, T_{90}, °C, max	D 1160	360	360	-	-
Distillation Temperature, T_{90}, °C, max	D 86	-	-	343	343
Kinematic Viscosity, mm^2/S at 40°C	D 445	1.9-6.0	1.9-6.0	1.9-4.1	1.9-4.1
Sulfur, ppm (μg/g)	D 5453	15	500	15	500
Sulfated Ash, mass %	D 874	0.02	0.02		
Copper Strip Corrosion Rating, max	D 130	No. 3	No. 3	No. 3	No. 3
Cetane Number, min	D 613	47	47	40	40
Cloud Point, °C,	D2500	Report to customer	Report to customer	Report to customer	Report to customer
Carbon Residue, % mass, max	D4530	0.05	0.05	-	-
Ramsbottom Carbon Residue on 10% bottoms, % mass, max	D524	-	-	0.35	0.35
Acid Number, mg KOH/g	D664	0.50	0.50	0.30	0.30
Ash Content, mass%, max	D482	-	-	0.01	0.01
Free Glycerin, % mass	D6584	0.02	0.02	-	-
Total Glycerin, % mass	D6584	0.24	0.24	-	-
Phosphorus Content, % mass	D4951	0.001	0.001	0.001	0.001
Sodium and Potassium, combined, ppm	EN 14538	5	5	5	5
Calcium and Magnesium, combined, ppm (μg/g) max	EN 14538	5	5	5	5
Cold Soak Filtration, seconds, max	Annex to D 6751	360	360	-	-
Cold Soak Filtration, for use in temperatures below -12 °C, seconds, max	Annex to D 6751	200	200	-	-
Lubricity, HFRR @ 60 °C, micron, max	D6079	-	-	520	520
Oxidation Stability, hours	EN14112	3	3	6	6
Biodiesel Content, %, (vol/vol)	-	100	100	6-20	6-20

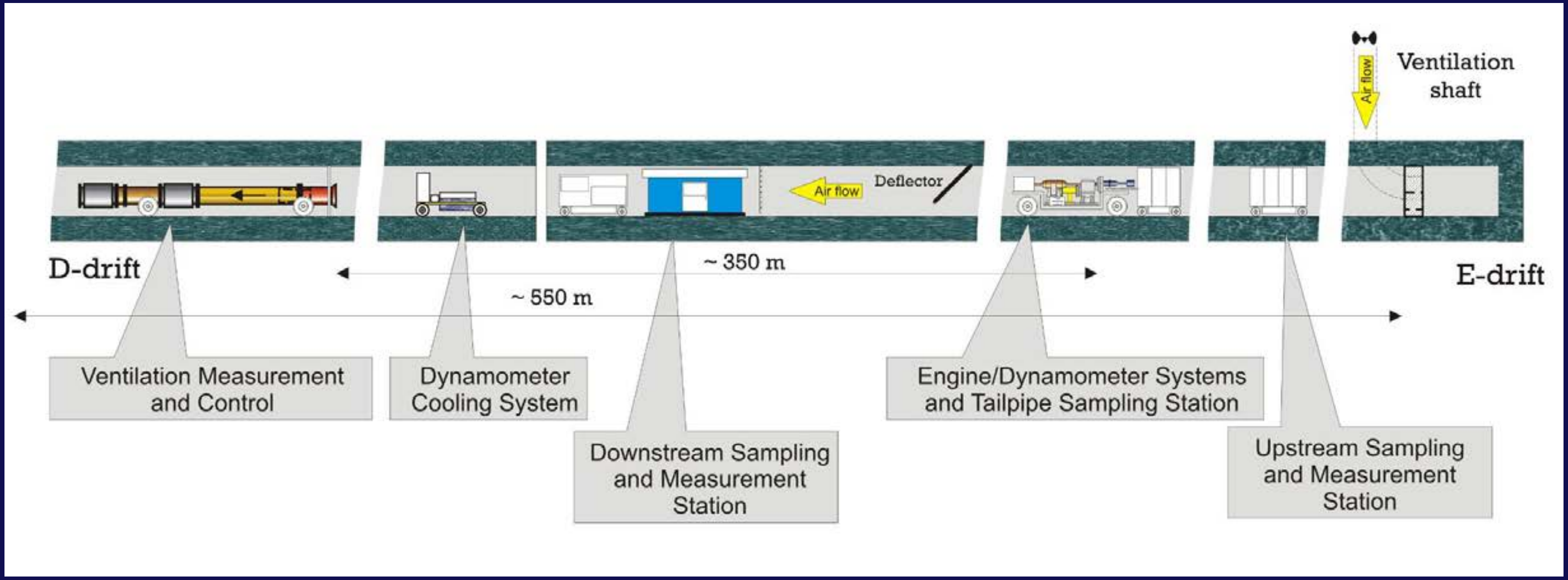
FAME Biodiesel vs. ULSPD Properties

Fuel Property	Test Method	ULSPD	B20	B50	B57	B100
Fatty Acid Methyl Ester Content [%]	ASTM 7371	N/A	22.76	48.56	56.5	100
Heat of Combustion [BTU/gal]	ASTM D240	133194	135286	131184	128118	126089
API Gravity @ 15.6 °C [°API]	ASTM D1298	38.1	35.8	34.6	32.2	29.8
Cetane Number	ASTM D613	60	50	50	53	52
Sulfur by UV [ppm]	ASTM D5453	11.07	2.74	5.06	6.04	8.36
Cloud Point [°C]	ASTM D2500	-9	-10	-8	1	10
Pour Point [°C]	ASTM D97	-24	-14	-13	-2	1
Flash Point, Closed Cup [°C]	ASTM D93	67	68	74	80	173
Lubricity, HFRR, Wear Scar Diameter [µm]	ASTM D6079	640	190	170	230	240

- 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

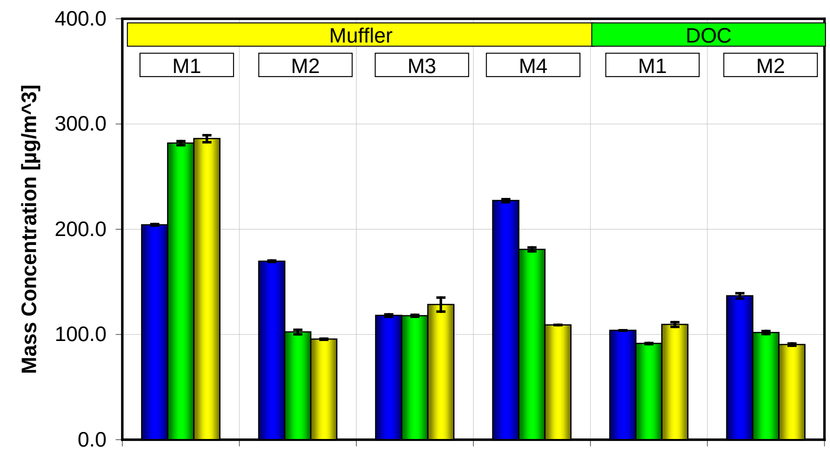
Effects of FAME Biodiesel on DPM Emissions
Underground Experimental Mine Evaluation

- 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/m^3]

- Biodiesel fuels increased total mass concentrations for M1 (muffler only) and M3, but
- Total mass concentrations decreased for M2 (muffler and DOC) and M4.

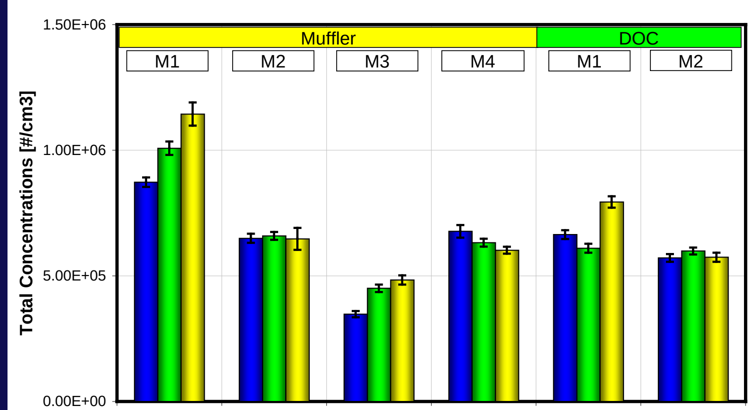


	M1	M2	M3	M4	M1	M2
ULSD	204.2	169.6	118.0	227.2	103.8	136.7
B50	281.8	102.4	117.8	180.8	91.4	101.8
B100	286.0	95.5	128.4	109.0	109.5	90.4

Exhaust/Mode

Effects of Fuel and DOC on Total Number Concentrations with $_{50}d_{em}$ 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.



	M1	M2	M3	M4	M1	M2
ULSD	872800	649600	347500	677300	664300	571500
B50	1008000	659100	450500	632000	610100	599000
B100	1144000	647200	483500	602100	794100	574100

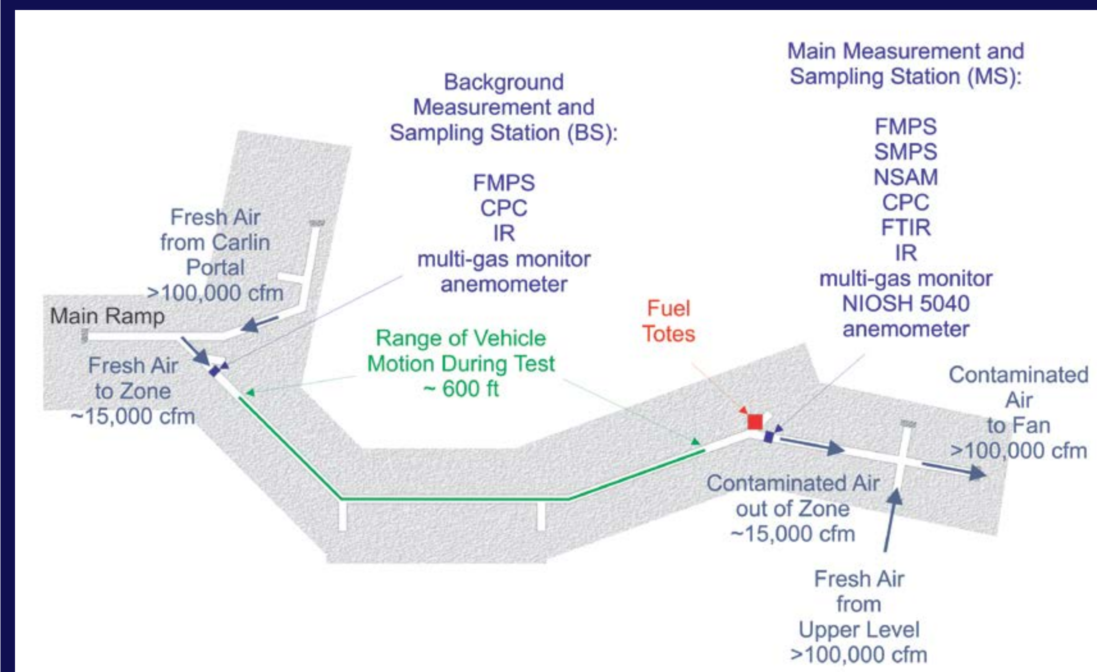
Mode/Exhaust System

Effects of FAME Biodiesel on Emissions

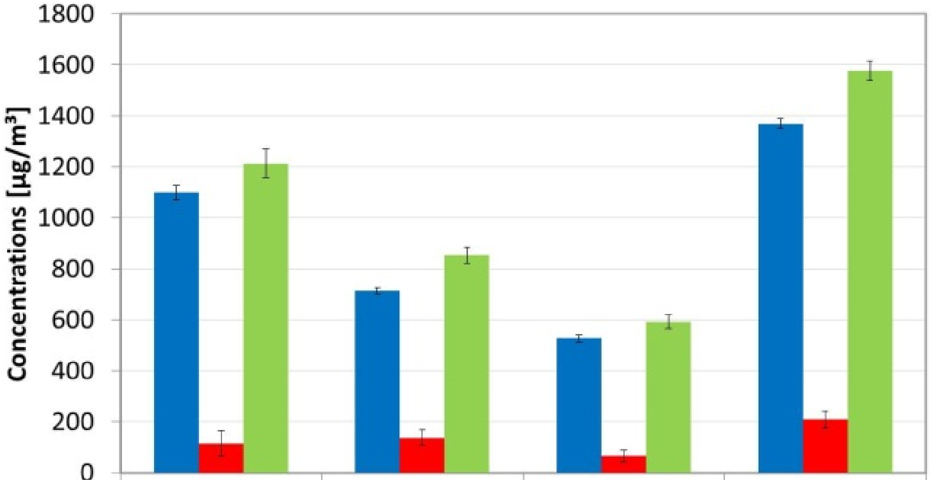
- Effects of biodiesel fuels on size distribution, number and mass concentrations, and EC concentrations strongly dependent on engine operating mode.
- Reductions in EC were observed for all engine operating modes and exhaust configurations when biodiesel fuels were used.
- The increase in number and 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 NO_2 concentrations at high-load engine operating conditions.
- Results are published in: Bugarski, A.D., Cauda E., Janisko, S.J., Hummer, J.A., Patts, L.D. [2010]. Aerosols Emitted in Underground Mine Air by Diesel Engine Fueled with Biodiesel. Journal of Air and Waste Management Association. 60, 237-244.

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.

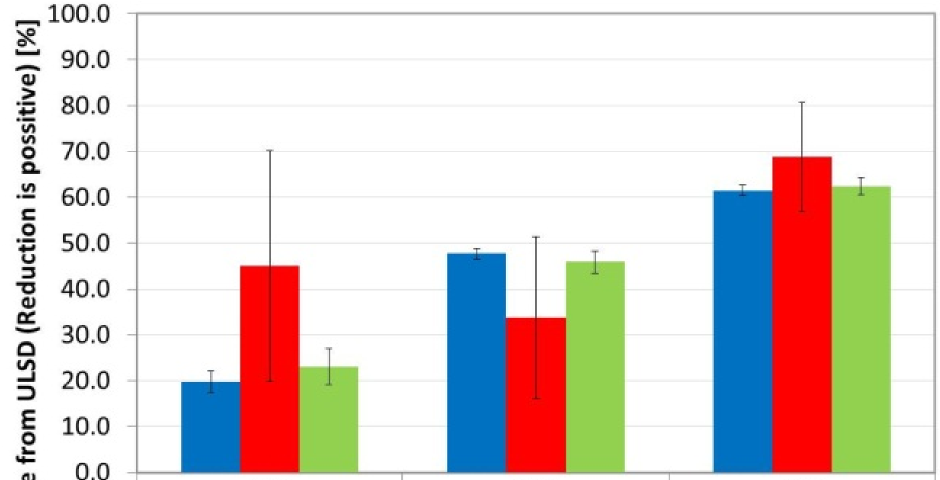


Effects of FAME Fuels on Average EC, OC, and TC Concentrations [μg/m³] Emitted by the Haulage Truck Powered by Tier 3 Engine



Fuel	B20	B50	B57	ULSD
EC	1098	715	527	1368
OC	115	138	65	208
TC	1213	853	592	1576

Fuel



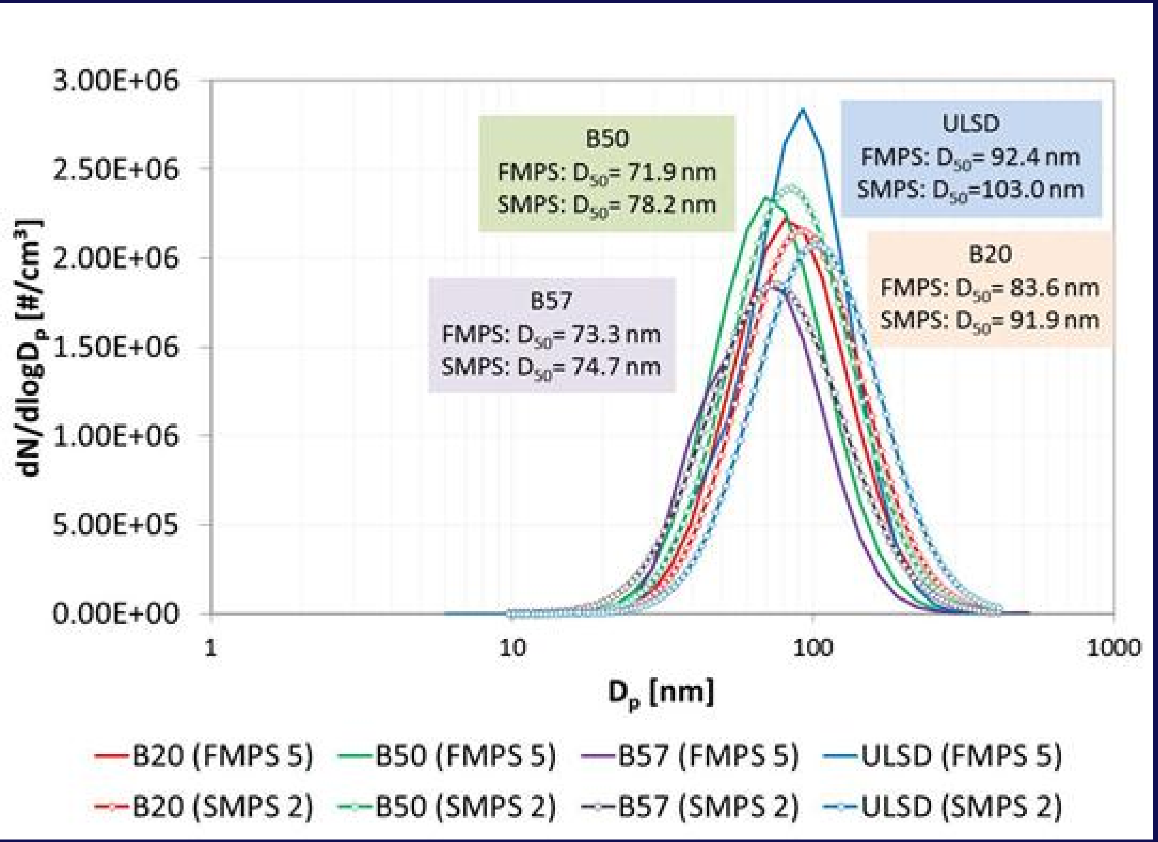
Fuel	B20	B50	B57
EC	19.7	47.7	61.4
OC	45.0	33.8	68.8
TC	23.1	45.9	62.4

Fuel

- 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 strait forward
  - 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 ºC (32 ºF) and edible tallow methyl ester has cloud point of 19 ºC (66 ºF) [NREL 2009].

- Since FAME fuel gels at temperatures 11 ºC to 17 ºC (20 ºF to 30 ºF) 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_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_X emissions, the NO_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_X/DPM ratio is desirable for the DPF systems that are designed to regenerate passively by NO_2 oxidation.

- B20 and neat SME biodiesel were shown to lower balance point temperature of catalyzed diesel particulate filter by 45 ºC and 112 ºC, 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

- Substantial reductions in regulated emissions when neat GTL fuels are used in place of petroleum based diesel fuels even in unmodified engines [Schaberg et al. 1997, Norton et al. 1998, Maly 2004, Alleman et al. 2005, CEC 2006, Maly et al. 2007, Li and Zhen 2009]:
  - PM between 22 and 35%,
  - NO_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)].

- 66 Fed. Reg. 5001 [2001] and 69 Fed. Reg. 38957 [2004] require registration of additives with EPA . The manufacturers need to prove, through a three-tier process, that the fuel additives are safe and do not change or create new/harmful emission species.
  - 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.

- Improvements in quality of diesel fuels and lubricants brought by EPA regulations [66 Fed. Reg. 5001 (2001), 69 Fed. Reg. 38957 (2004)], particularly reduction in sulfur content to less than 15 ppm, and introduction of low-ash lubricating oil (API CJ4), played important role in enabling development and implementation of catalyzed DPF technology across wide spectrum of applications.

- 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.

Thank you for your attention!

Aleksandar Bugarski
abugarski @cdc.gov
412.386.5912