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Aerosols Emitted in Underground Mine Air by Diesel Engine Fueled with Biodiesel

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ABSTRACT

Using biodiesel in place of petroleum diesel is considered by several underground metal and nonmetal mine operators to be a viable strategy for reducing the exposure of miners to diesel particulate matter. This study was conducted in an underground experimental mine to evaluate the effects of soy methyl ester biodiesel on the concentrations and size distributions of diesel aerosols and nitric oxides in mine air. The objective was to compare the effects of neat and blended biodiesel fuels with those of ultralow sulfur petroleum diesel. The evaluation was performed using a mechanically controlled, naturally aspirated diesel engine equipped with a muffler and a diesel oxidation catalyst. The effects of biodiesel fuels on size distributions and number and total aerosol mass concentrations were found to be strongly dependent on engine operating conditions. When fueled with biodiesel fuels, the engine contributed less to elemental carbon concentrations for all engine operating modes and exhaust configurations. The substantial increases in number concentrations and fraction of organic carbon (OC) in total carbon over the baseline were observed when the engine was fueled with biodiesel fuels and operated at light-load operating conditions. Size distributions for all test conditions were found to be single modal and strongly affected by engine operating conditions, fuel type, and exhaust configuration. The peak and total number concentrations as well as median diameter decreased with an increase in

the fraction of biodiesel in the fuels, particularly for high-load operating conditions. The effects of the diesel oxidation catalyst, commonly deployed to counteract the potential increase in OC emissions due to use of biodiesel, were found to vary depending upon fuel formulation and engine operating conditions. The catalyst was relatively effective in reducing aerosol number and mass concentrations, particularly at light-load conditions, but also showed the potential for an increase in nitrogen dioxide concentrations at high-load modes.

INTRODUCTION

As of May 20, 2008, the U.S. Mine Safety and Health Administration (MSHA) regulation¹ limits exposures of underground metal and nonmetal miners to diesel particulate matter (DPM) to 160 $\mu\text{g}/\text{m}^3$ of total carbon (TC). Improvements in mine ventilation and the curtailment of DPM and toxic gaseous emissions from existing and new diesel-powered equipment are commonly perceived as the most promising tools to meet MSHA technology forcing regulations. Although diesel particulate filter (DPF) systems are gradually becoming more utilized for controlling DPM emissions from underground mining vehicles,^{2,3} their acceptance has been hindered by their relative complexity, implementation issues, and expense. Changing fuel supply from petroleum diesel to higher-concentration biodiesel blends is considered by several underground mine operators to be a viable alternative for controlling DPM emissions. The major advantages of biodiesel over petroleum-based diesel fuels with respect to DPM emissions are due to greater cetane number, absence of aromatics, and high oxygen content. In addition, biodiesel was shown to lower the balance point temperature of passively regenerated DPFs and therefore could potentially facilitate regeneration and the implementation of DPF systems in underground mines.^{4,5}

The effects of biodiesel and biodiesel blends on regulated and nonregulated emissions were compared with those of petroleum diesel for various on- and off-road diesel-powered applications. Biodiesel blends were found to reduce emissions of nonvolatile fractions of DPM^{4,6} and to increase the particle-bound volatile organic fraction of DPM.^{6,7} Additionally, biodiesel was found to reduce total polycyclic aromatic hydrocarbons and benzo(a)pyrene equivalent emissions⁸ and to increase carbonyl emissions.⁹ The effects of biodiesel on emissions were

IMPLICATIONS

Changing fuel supply from petroleum diesel to biodiesel fuels has been adopted by several underground mines as a method of choice for controlling the exposure to diesel aerosols. The results of this study provide more insight into potential advantages and disadvantages of using biodiesel fuels for controlling emissions of aerosols and gases. The role of diesel oxidation catalysts in controlling biodiesel emissions has also been re-examined. Substantial changes in physical and chemical properties of aerosols, observed when diesel was replaced with biodiesel, warrant further research on establishing the potential health risks associated with exposure to those aerosols.

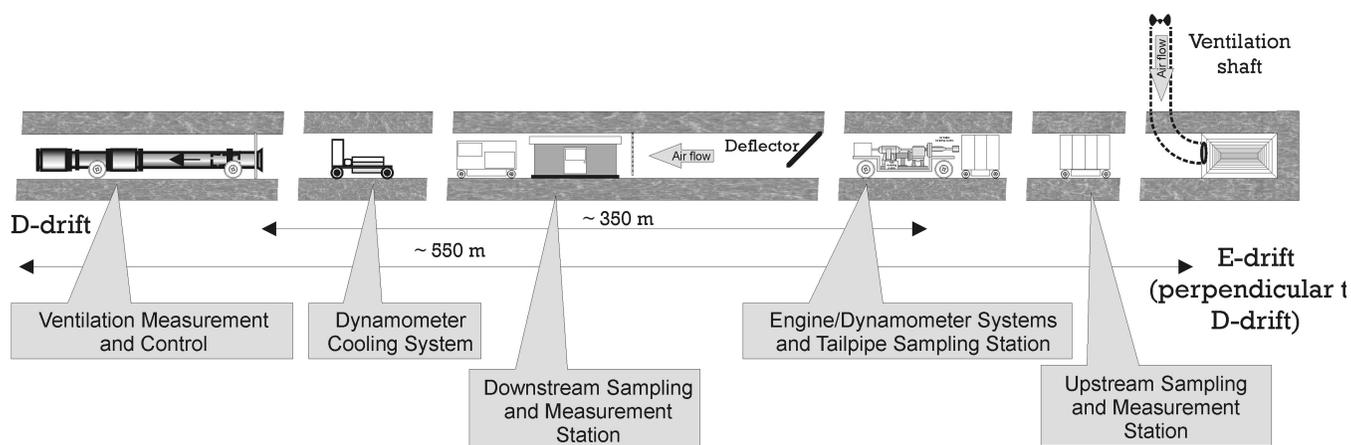


Figure 1. NIOSH Diesel Laboratory in D-drift of LLEM.

found to vary widely with usage conditions, engine type, and age.^{10–12} Mine studies showed the potential of neat biodiesel¹³ and biodiesel blends^{2,3,14} to reduce exposure of underground miners to elemental carbon (EC) and DPM. The biodiesels were shown to increase oxides of nitrogen (NO_x) emissions.^{11,15}

Several researchers have studied the impact of rapeseed and soy methyl ester (SME) biodiesel on size distribution of aerosols emitted by diesel engines in laboratory conditions.^{15–17} An increase in concentrations of smaller particles¹⁵ and nucleation aerosols^{16,17} and a reduction in concentrations of accumulation-mode aerosols^{16,17} were reported. Research on the impact of biodiesel on particle size has not produced consistent results¹⁸ and additional research in this area is needed. Swanson and coauthors¹⁹ concluded that the speculative nature of a reduction in health effects based on chemical composition of biodiesel exhaust needs to be followed up with investigation in biologic systems.

EXPERIMENTAL METHODOLOGY

The objective of this study was to evaluate the effects of SME biodiesel fuels on the concentrations, size distribution, and carbon composition of nano- and ultrafine aerosols in mine air downwind of the exhaust discharge. The effects of neat biodiesel (B100) and a 50/50% blend (B50) of biodiesel and ultralow sulfur diesel (ULSD) were compared with those established for ULSD. The effects were evaluated for the cases when a test engine was fitted with a muffler (Muffler) only or with a diesel oxidation catalyst (DOC) and muffler combination (DOC + Muffler).

The goal was to study the aforementioned effects directly in an occupational setting by using the National Institute for Occupational Safety and Health (NIOSH) Diesel Laboratory. This laboratory, developed in the D-drift of the NIOSH Lake Lynn Experimental Mine (LLEM), is designed to allow evaluation of control technologies in an underground environment.²⁰ The major components of the laboratory (Figure 1) are an engine/dynamometer system, three sampling and measurement stations, and a ventilation measurement and control system.

The fuels were evaluated using a mechanically controlled, naturally aspirated, directly injected Isuzu C240 engine rated at 41 kW (56 hp). The engine was not altered

to accommodate for differences in fuels.⁷ To eliminate the contribution of crankcase emissions, the engine was retrofitted with a closed-loop crankcase filtration system. A DOC with Cordierite substrate and a proprietary catalyst formulation (Engine Control Systems Ltd., model A16-0130) was used in this study.

The engine was operated over four steady-state modes (Table 1) using the water-cooled eddy current dynamometer. The power levels were selected by mapping the engine using all three fuels. One of the selected modes at each of the engine speeds represented full engine load, whereas the other was more representative of intermediate engine load. In the case of M1 and M2 modes, the tests were done for two exhaust configurations: Muffler and DOC + Muffler. In the case of M3 and M4 modes, the tests were done for the Muffler configuration.

Fresh unconditioned and unfiltered air was supplied to the underground facility via a ventilation shaft located in E-drift (Figure 1). An auxiliary fan and a subsonic Venturi meter were used to maintain and measure the constant flow of fresh air through the drift throughout the tests. The measurements showed an average volumetric flow rate of $5.81 \pm 0.05 \text{ m}^3/\text{sec}$ ($12,319 \pm 106 \text{ ft}^3/\text{min}$). The very low test-to-test variability in flow rate eliminated the need for normalization of the data with respect to it. The average exhaust dilution ratios for M1, M2, M3, and M4 engine operating modes were calculated to be 141, 139, 174, and 176, respectively. The average ambient temperatures upstream of the engine were between 7.5 and 17.6 °C. The corresponding average ambient temperatures at the downstream measurement station ranged between 10 and 18.3 °C.

Table 1. Engine operating conditions.

Mode	Engine Speed (rpm)	Torque (Nm)	Power (kW)
M1	2950	63.7	17.2
M2	2950	108.4	34.3
M3	2100	73.2	14.9
M4	2100	138.3	30.6

Table 2. Properties of the B100 and ULSD fuels.

Test	Method	Unit	B100	ULSD
Energy, net	ASTM D-240	kJ/kg (BTU/lb)	39,975 (17,198)	46,486 (19,999)
Density	ASTM D-4052	g/mL	0.8835	0.8050
Oxygen content	ASTM D-5291M	wt %	10.54	0.51
Flash point, PMCC	ASTM D-93A	°C (F)	138 (280)	61 (142)
Sulfur content	ASTM D-5453	mg/kg	5.1	10.0

Notes: PMCC = Pensky–Martens Closed Cup test.

Because quality has been an ongoing issue with biodiesel fuels,²¹ special care was taken to secure SME biodiesel fuel that met all of the specifications for ASTM D6751. B100, produced by the transesterification of soybean oil,²² was supplied by Stepan Company as Stepanol SB-W. The ULSD supplied by Guttman Oil was used as a baseline fuel. The results of the analysis performed on B100 and ULSD fuels by Core Laboratories, Houston, TX, are given in Table 2.

The B50 blend was prepared at the site. The fractions of biodiesel and ULSD were determined volumetrically.

Measurements

The effects of biodiesel fuels were determined from the results of measurements of aerosol size distributions and concentration at the downstream and upstream measurement stations. The downstream ambient monitoring station was located approximately 60 m (197 ft) downwind of the dynamometer, and the upstream ambient monitoring station was located approximately 60 m (197 ft) upwind of the dynamometer. The measurements were taken for each fuel for the aforementioned four steady-state engine speed and load conditions. The tests were between 4 and 9 hr long. The initial hour of each test was dedicated to achieving concentration equilibrium. The measurements were initiated at the beginning of the second hour. The background corrections were made by subtracting the results of measurements performed at the upstream station from the corresponding results obtained at the downstream station.

A custom sampling method was used to collect integrated DPM samples for carbon analysis. Three samples were collected at the downstream and two samples were collected at the upstream sampling stations. Each DPM sample was collected on a stacked primary and secondary filter by merging flows from five inlets distributed on the three levels at a sampling grid. A 10-mm Dorr-Oliver cyclone followed by a single-stage diesel impactor, with removed filters, was used at each inlet as preclassifiers. A flow rate of approximately 2 L/min was maintained through each cyclone and impactor pair. At this sampling flow rate, only particles with geometric mean diameter ($_{50}D_{ae}$) smaller than 0.78 μm were deposited on the filters. All five preclassifiers were attached to a symmetrical plenum, which uniformly distributed a total flow rate of approximately 10 L/min among the five streams. Each of the preclassifier assemblies was connected to the plenum chamber by a 3-ft long section of conductive tubing. The outlet of the plenum was directly connected to a cassette containing two stacked 37-mm tissue quartz fiber filters

(Tissuequartz 2500QAT, Pall Corporation). The total sampling mass flow rates were maintained using an orifice in each of the three sampling lines from the 37-mm cassettes. The total volumetric flow rates through each of the sampling streams were verified periodically by inserting a Gilibrator II bubble flow meter inline, between cassettes and orifices. The volumetric flow rates measured during this study were all corrected to ambient conditions. A model SV25 rotary vane pump from Oerlikon Leybold Vacuum was used to draw the sample through the sampling system. The samples were analyzed for EC and organic carbon (OC) content using the NIOSH analytical method 5040.²³

The aerosol mass and number concentrations and size distributions were measured at a single point at the sampling grids located 60 m downstream and 60 m upstream of the exhaust discharge. A tapered element oscillating microbalance (TEOM) series 1400a ambient particulate monitor from Thermo Scientific was used at the downstream station to measure total particulate matter mass concentrations of particles with mean aerodynamic diameter ($_{50}d_{ae}$) less than 0.82 μm . A second identical instrument was used at the upstream station for the same purpose. Two scanning mobility particle sizers (SMPS; model 3936, TSI)²⁴ were used to measure size distribution and number concentrations of aerosols. One was located at the upstream station and the other at the downstream station. A model CLD 700 AL chemiluminescence analyzer (Eco Physics) was used to measure concentrations of nitric oxide (NO) and nitrogen dioxide (NO₂) at the downstream station.

The exhaust temperatures at the inlet to the muffler or DOC averaged over the measurement periods are summarized in Table 3. The temperatures were affected primarily by engine operating conditions, but also by fuel type. The slightly lower temperatures observed for B100 are consistent with lower energy content of biodiesel.⁷ The higher exhaust temperatures observed during B50 tests were probably an aberration and they can be potentially explained by higher temperature ($\sim 5\text{--}7^\circ\text{C}$ warmer) and higher relative humidity ($\sim 20\%$) of the intake air (mine air) observed for B50 tests than for corresponding ULSD and B100 tests.

RESULTS AND DISCUSSION

Carbon Concentrations

The results of the carbon analysis performed on the samples collected at the downstream sampling station are summarized in Figure 2. The presented EC values are average concentrations for the sampling periods at the

Table 3. Average exhaust gas temperatures (°C).

Exhaust Configuration	Mode	ULSD	B50	B100
Muffler	M1	304.4 ± 0.8	318.1 ± 0.9	307.3 ± 0.5
	M2	461.1 ± 2.0	481.6 ± 1.0	454.1 ± 0.9
	M3	237.2 ± 0.8	253.3 ± 0.9	234.8 ± 0.5
	M4	470.5 ± 3.5	485.3 ± 1.4	452.7 ± 1.3
DOC + Muffler	M1	317.0 ± 0.7	NA	304.3 ± 0.8
	M2	476.1 ± 4.0	NA	453.6 ± 2.0

Notes: NA = not applicable.

prevailing ventilation. The analysis of the upstream samples showed an undetectable level of EC in the background air and therefore background correction of EC data was not necessary. The results of carbon analysis performed on the primary filters were used to examine the relation between OC and TC.

The analysis showed that the use of biodiesel fuels substantially reduced concentrations of EC for all test modes (Figure 2a). The highest reductions (~60%) were observed for B100 when the engine was operated at M2 and M4 modes. The observations on reductions in EC concentrations are corroborated with observations on the decrease in median diameter of accumulation-mode aerosols discussed in the section on size distribution.

The effects of the DOC on concentrations of EC varied depending upon engine operating conditions and fuel type. When the engine was operated at M1, the DOC reduced the EC mass concentrations by 31.6, 20.8, and 16% for ULSD, B50, and B100, respectively. A DOC associated reduction of 26.1% in concentrations of EC was also found for ULSD when the engine was operated at M2. The DOC was found to increase concentrations of EC by 23.8% when the engine was operated at M2 using B50. The change in EC concentrations for B100 when the engine was operated at M2 was not significant.

The carbon analysis of the primary filters showed a positive correlation between the fraction of OC in TC and the fraction of biodiesel in the fuel (Figure 2b). These results are in agreement with previous findings^{6,7} on increase in the particle-bound volatile organic fraction of

DPM with the use of biodiesel blends. When the DOC was incorporated in the exhaust, the fractions of OC in TC on the primary filter were substantially lower for all tested fuels and for both modes (M1 and M2).

Mass and Number Concentrations

Table 4 summarizes the results of measurements made with the TEOM and SMPS for ULSD, B50, and B100. All concentrations are reported as the averages of values measured during the second hour of measurement at prevailing ventilation conditions. The corresponding standard deviations were reported next to the averages. The concentrations were not corrected for the differences in dilutions between test modes.

The upstream aerosol mass and number concentrations in unfiltered dilution air were found to be less than 16 and 1.7%, respectively, of the corresponding downstream concentrations. The changes in mass and number concentrations resulting from the use of B50 and B100 in place of ULSD are reported in Figure 3. The reduction was regarded as a positive change.

Biodiesel fuels reduced total mass concentrations for all modes and both exhaust configurations. With a few exceptions, reductions in total mass concentrations rose with an increase in the biodiesel fraction. When the engine was operated at M1, the DOC reduced total mass concentrations by 33.3, 49.5, and 31.4% for ULSD, B50, and B100, respectively. For M2, the effects of the DOC on mass concentrations were found to be dependent on fuel formulation: the DOC reduced concentrations by 26.3%

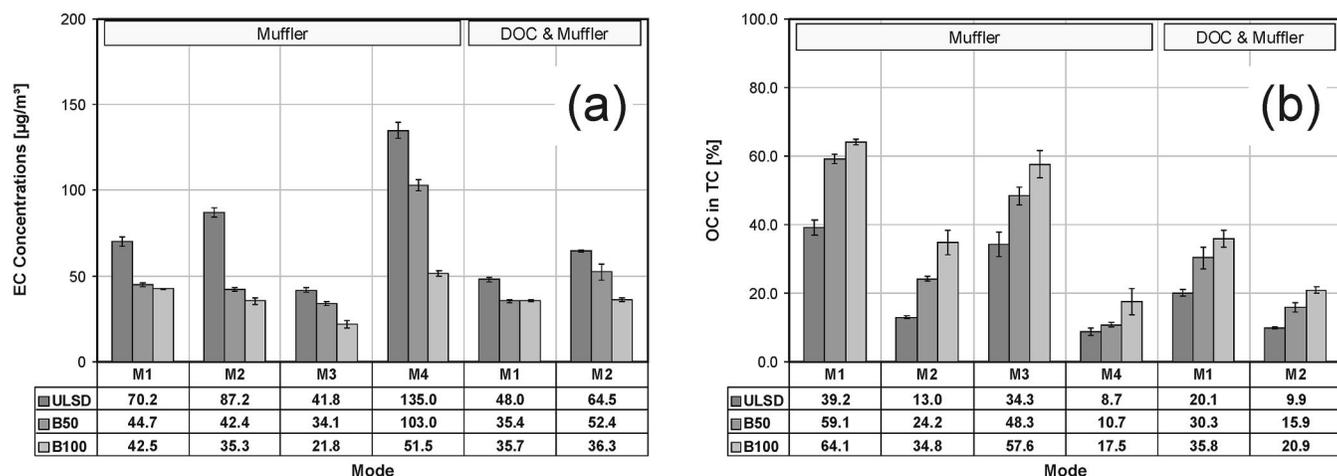


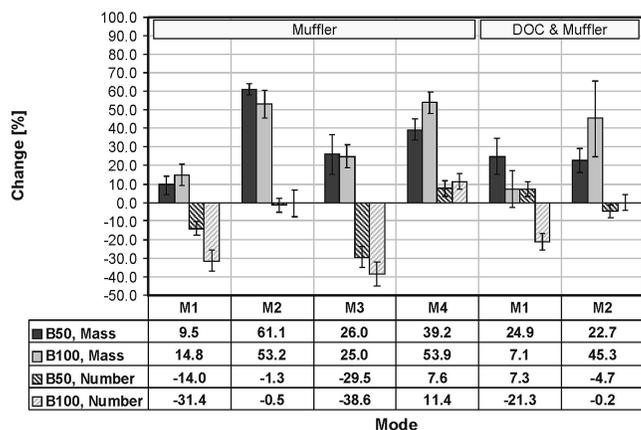
Figure 2. Carbon analysis: (a) EC concentrations and (b) percentage of OC in TC for the primary filters.

Table 4. Total aerosol mass (TEOM) and number concentrations (SMPS) at downstream and upstream stations.

Fuel	Exhaust Configuration	Mode	Mass (TEOM; $\mu\text{g}/\text{m}^3$)	Mass Background (TEOM; $\mu\text{g}/\text{m}^3$)	Number (SMPS; particles/ cm^3 [10^4])	Number Background (SMPS; particles/ cm^3 [10^4])	
ULSD	Muffler	M1	136.2 \pm 5.9	3.6 \pm 1.2	87.28 \pm 1.91	32.0 \pm 3.7	
		M2	154.1 \pm 2.6	0.0 \pm 2.0	64.96 \pm 1.83	88.0 \pm 1.9	
		M3	84.7 \pm 4.1	0.0 \pm 1.4	34.75 \pm 1.25	35.0 \pm 1.0	
		M4	220.2 \pm 10.3	3.8 \pm 1.9	67.73 \pm 2.50	37.0 \pm 9.3	
B50	DOC + Muffler	M1	90.9 \pm 7.3	9.6 \pm 1.2	66.43 \pm 1.77	110.0 \pm 22.0	
		M2	113.5 \pm 6.0	0.0 \pm 1.5	57.15 \pm 1.54	28.0 \pm 6.4	
		Muffler	M1	123.9 \pm 2.2	3.9 \pm 1.4	100.80 \pm 2.66	170.0 \pm 12.0
			M2	65.3 \pm 2.6	5.4 \pm 1.5	65.91 \pm 1.55	100.0 \pm 6.4
B100	Muffler	M3	69.3 \pm 7.8	6.5 \pm 1.3	45.05 \pm 1.48	51.0 \pm 9.1	
		M4	144.2 \pm 4.3	12.7 \pm 1.7	63.20 \pm 1.55	94.0 \pm 13.0	
		DOC + Muffler	M1	62.5 \pm 1.2	1.5 \pm 1.6	61.01 \pm 1.77	45.0 \pm 6.4
			M2	92.3 \pm 2.8	4.5 \pm 2.5	59.90 \pm 1.37	34.0 \pm 1.9
	Muffler	M1	112.9 \pm 4.1	0.0 \pm 2.5	114.40 \pm 4.60	13.0 \pm 5.1	
		M2	74.8 \pm 10.7	2.7 \pm 2.4	64.72 \pm 4.38	33.0 \pm 1.9	
		M3	63.6 \pm 2.0	0.0 \pm 2.0	48.35 \pm 1.84	67.0 \pm 6.5	
		M4	101.0 \pm 2.8	1.2 \pm 1.6	60.21 \pm 1.40	53.0 \pm 11.0	
DOC + Muffler	M1	77.4 \pm 2.1	1.9 \pm 2.1	79.41 \pm 2.27	18.0 \pm 7.1		
	M2	74.0 \pm 3.1	11.9 \pm 21.9	57.41 \pm 1.81	45.0 \pm 24.0		

in the case of ULSD, increased concentrations by 41.2% for B50, and did not change concentrations for B100. These results corroborate with the results of carbon analysis.

Biodiesel fuels increased total number concentrations of aerosols between 15 and 39% for M1 and M3, but total number concentrations of aerosols remained virtually unchanged for M2 and decreased 6–11% for M4. Increases in total number concentrations for M1 and M3 rose with an increase in fraction of biodiesel in the fuels. Reductions in total number concentrations for M4 increased with a greater fraction of biodiesel in the fuels. For all tested fuels the effects of the DOC on number concentrations were more pronounced for M1 mode than for the M2 mode. The most significant reductions of 39% in number concentrations were attributed to the DOC when the engine was operated at light-load M1 using B50 fuel.

**Figure 3.** Change in mass (TEOM) and number (SMPS) concentrations with use of B50 and B100 (reduction is positive).

Size Distributions

The average number size distributions of aerosols measured by the SMPS at the downstream sampling station are shown for each of the four modes in Figure 4. The scales on the x- and y-axes were kept equal on all four graphs to allow for easier comparison. In the case of M1 and M2 modes, the aerosol distributions were measured for two exhaust configurations: Muffler and DOC + Muffler. In the case of M3 and M4 modes, the effects on aerosol distributions were examined only for the cases when the engine was fitted with the muffler. The markers show the average values measured during the third hour of each test, whereas the corresponding error bars represent single positive and negative standard deviations. The presented distributions were not corrected for background concentrations and/or adjusted for prevailing dilution ratios. The average distributions were fitted with lognormal curves using DistFit software from Chimera Technologies. The count median electrical mobility diameters ($s_{0d_{em}}$), standard deviation of means (SDOM), and total number concentrations for the lognormal distributions are summarized in Table 5. The total concentrations for fitted and average measured distributions were given for comparison purposes.

In general, aerosol size distributions were strongly affected by engine operating conditions, fuel type, and exhaust configuration. The size distributions (Figure 4 and Table 5) were found to have a single accumulation mode for all studied conditions. The peak and total concentrations were highest when the engine was outfitted with a muffler and was operated at M1 (Figure 4a and Table 5). For the same conditions, peak concentrations increased (Figure 4a) and the median diameter ($s_{0d_{em}}$) slightly decreased (Table 5) with an increase in the fraction of biodiesel in the fuel. These changes in aerosol concentrations and properties can be related to observed increases in total number and decreases in total mass of aerosols (Figure 3) with the use of

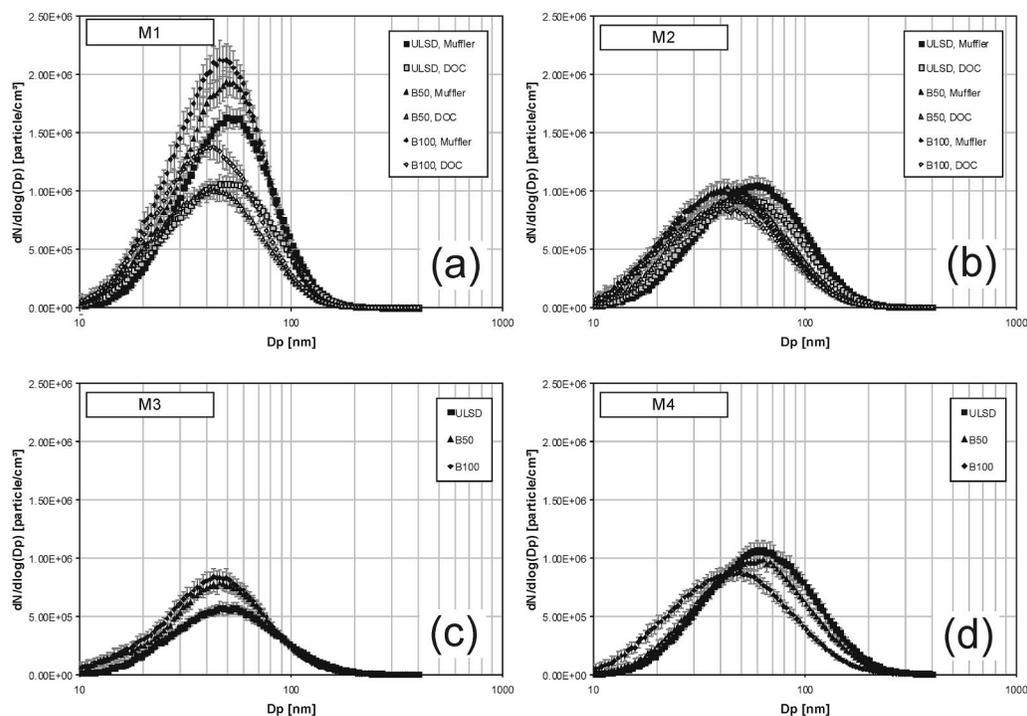


Figure 4. Size distributions measured with SMPS for (a) M1 (Muffler and DOC + Muffler), (b) M2 (Muffler and DOC + Muffler), (c) M3 (Muffler), and (d) M4 (Muffler) tests.

biodiesel. At the exhaust temperatures observed for M1 (Table 3), the DOC was found to be effective in oxidizing the organic aerosols. Consequently, the peak (Figure 4a) and total number concentrations (Table 5) were substantially lower than those observed for the muffler only. The median diameters of the aerosols recorded in the mine air during M1 tests for the engine equipped with a DOC and muffler were slightly lower than those observed during the corresponding tests when the engine was only fitted with a muffler.

In the case of M2, B50 and B100 did not substantially change the peak (Figure 4b) and total number (Table 5) concentrations. The median diameter was found to slightly decrease with a greater fraction of biodiesel in the fuel (Figure 4b and Table 5). Despite higher exhaust temperatures (Table 3), the DOC had less pronounced effects on peak (Figure 4b) and total number concentrations (Table 5) for M2 than for M1.

Table 5. Statistical parameters for lognormal size distributions.

Fuel	Exhaust Configuration	Test Mode	Accumulation-Mode Parameters			Measured
			$50d_{em}$ (nm)	SDOM (nm)	Total Concentration (particles/cm ³ [10 ⁴])	Total Concentration (particles/cm ³ [10 ⁴])
ULSD	Muffler	M1	48.3	1.62	86.75	87.28
		M2	53.5	1.72	64.32	64.96
		M3	48.5	1.74	34.76	34.75
		M4	60.1	1.76	67.55	67.73
B50	Muffler	M1	44.8	1.71	65.77	66.43
		M2	49.9	1.75	60.23	57.15
		M3	43.8	1.73	44.44	45.05
		M4	55.3	1.78	63.03	63.20
B100	Muffler	M1	39.5	1.70	60.72	61.01
		M2	44.2	1.76	59.67	59.90
		M3	42.8	1.61	112.60	114.40
		M4	43.8	1.85	60.45	60.21
B100	DOC	M1	39.1	1.68	79.29	79.41
		M2	39.7	1.81	57.58	57.41
		M3	42.0	1.72	47.90	48.35
		M4	43.8	1.85	60.45	60.21

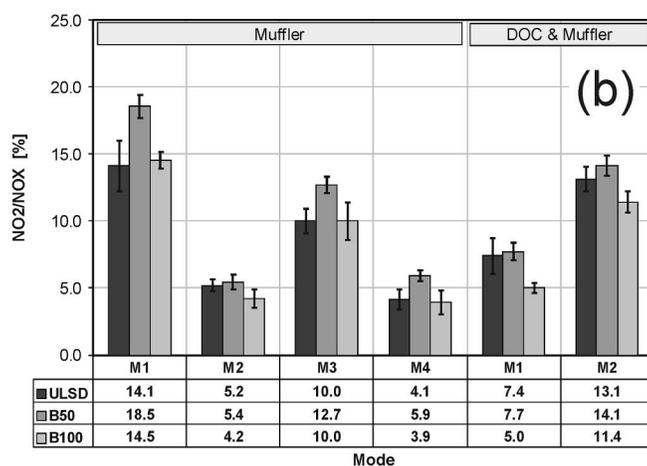
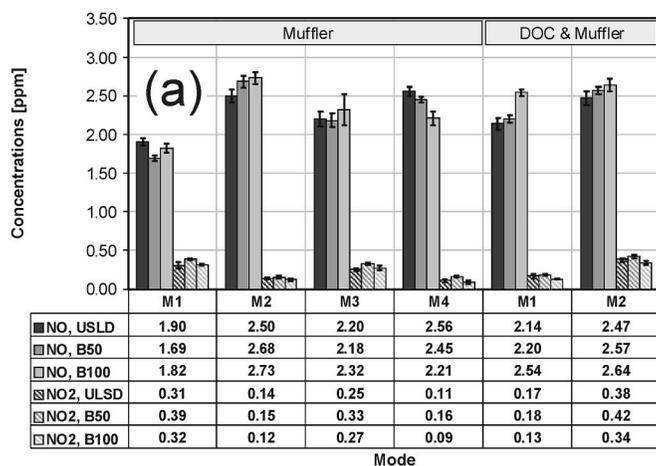


Figure 5. Effects of fuels and DOC on (a) concentrations of NO and NO₂ and (b) NO₂/NO_x ratio.

In the case of M3, peak (Figure 4c) and total concentrations (Table 5) increased whereas median diameters decreased (Table 5) with a greater fraction of biodiesel in the fuels. The peak (Figure 4d) and total concentrations (Table 5) as well as median diameter (Table 5) decreased with an increase in the fraction of biodiesel in the fuels for M4.

It is important to note that the pronounced nucleation mode previously observed during some laboratory studies involving biodiesel^{16,17} was not observed in this study. It appears that, under prevailing conditions and in the presence of high concentrations of accumulation-mode aerosols, most semivolatile aerosols condensed and adsorbed on accumulation-mode aerosols.

NO_x

The effects of all fuels on concentrations of NO_x were dependent on the engine operating condition (Figure 5). The biodiesel fuels produced minor effects on NO concentrations for all operating conditions. B50 increased NO₂ concentrations by 24, 14, 32, and 46% for M1, M2, M3, and M4, respectively. The effects of B100 for all of the modes were found to be minor and within measurement accuracy. The NO₂/NO_x ratio was found to be 2–3 times higher for light than for heavy engine loads (Figure 5b).

The effects of the DOC on concentrations of NO_x were strongly affected by engine operating conditions (Figure 6). When the engine was operated at M1, the DOC increased concentrations of NO and reduced the concentrations of NO₂. For M2 conditions, the DOC increased approximately 3-fold the concentrations of NO₂, but the changes in NO concentrations were found to be within measurement accuracy. It is important to note that despite those 3-fold increases, the absolute NO₂ concentrations did not exceed NO₂ concentrations observed during the corresponding tests conducted at M1 with the engine fitted only with the muffler (Figure 5a).

These results corroborate the findings of Katare and coauthors,²⁵ who found that aged DOCs are net consumers of NO₂ when exhaust temperature is relatively low and high concentrations of hydrocarbons and carbon monoxide are present in the exhaust, conditions similar to those observed for mode M1. The NO₂ was formed in DOCs at the higher exhaust temperatures under conditions similar

to those observed for M2, at which hydrocarbons and carbon monoxide are oxidized.

CONCLUSIONS

The evaluated SME biodiesel fuels demonstrated the potential to substantially reduce the mine air concentrations of EC and total DPM mass generated by a naturally aspirated, mechanically controlled engine. The rate of reductions varied depending on engine operating conditions, but, in general, they were higher for B100 than for the B50 blend. The downside of using biodiesel fuels was an increase in the fraction of particle-bound volatile organics and number concentrations of aerosols, particularly for light-load engine operating conditions.

These results showed that a DOC (which is similar to those that are commonly used on underground mining engines to control carbon monoxide and hydrocarbon emissions) can be used to control the potential increase in emissions of OC aerosols resulting from the use of biodiesel. The effects of the DOC on the concentrations of EC were found to be dependent on fuel type and engine operation conditions. Generally, these were less pronounced than the effects on the concentrations of OC. The biggest downside of using this type of DOC was a substantial increase in NO₂ concentrations observed

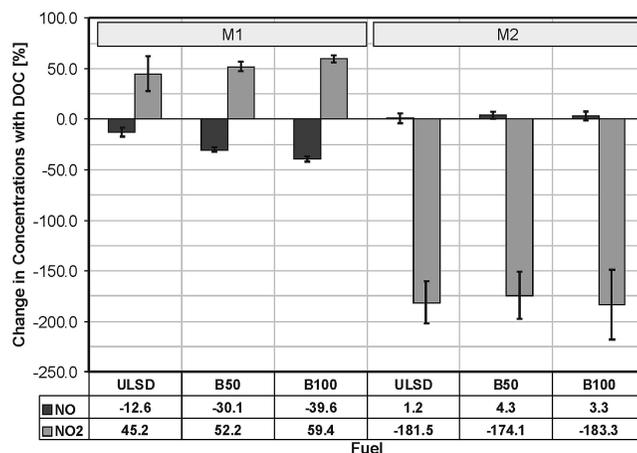


Figure 6. Effects of DOC on NO and NO₂ concentrations.

when the engine was operated at high-load modes. Therefore, DOCs for underground mining applications should be optimized to provide substantial reductions in concentrations of hydrocarbons and OC without increasing NO₂ concentrations.

Although the findings of this study should contribute to a better understanding of the effects that biodiesel has on diesel aerosols, additional work is needed to establish a relationship between substantial changes in physical and chemical properties of diesel and biodiesel aerosols and the potential health risks associated with worker exposure to these aerosols.

REFERENCES

1. Diesel Particulate Matter Exposure of Underground Metal and Non-metal Miners. Limit on Concentration of Diesel Particulate Matter; 30 CFR 57.5060; *Fed. Regist.* **2006**, *71*, 28924.
2. Bugarski, A.D.; Schnakenberg, G.H.; Noll, J.D.; Mischler, S.E.; Patts, L.D.; Hummer, J.A.; Vanderslice, S.E. *Effectiveness of Selected Diesel Particulate Matter Control Technologies for Underground Mining Applications: Isolated Zone Study, 2003*; Publication No. 2006-126; Report of Investigations 9667; U.S. Department of Health and Human Services: Washington, DC, 2006.
3. Bugarski, A.D.; Schnakenberg, G.H.; Mischler, S.E.; Noll, J.D.; Patts, L.D.; Hummer, J.A. *Effectiveness of Selected Diesel Particulate Matter Control Technologies for Underground Mining Applications: Isolated Zone Study, 2004*; Publication No. 2006-138; Report of Investigations 9668; U.S. Department of Health and Human Services: Washington, DC, 2006.
4. Williams, A.; McCormick, R.L.; Hayes, R.; Ireland, J. *Biodiesel Effects on Diesel Particle Filter Performance*; Milestone Report NREL/TP-540-39606; National Renewable Energy Laboratory: Golden, CO, 2006.
5. Boehman, A.L.; Song, J.; Alam, M. Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters; *Energy Fuels* **2005**, *19*, 1857-1864.
6. Purcell, D.J.; McClure, B.T.; McDonald, J.; Basu, H.N. Transient Testing of Soy Methyl Ester Fuels in an Indirect Injection, Compression Ignition Engine; *J. Am. Oil Chem. Soc.* **1996**, *73*, 381-388.
7. McDonald, J.F.; Purcell, D.L.; McClure, B.T.; Kittelson, D.B. Emissions Characteristics of Soy Methyl Ester Fuels in an IDI Compressions Ignition Engine; Society of Automotive Engineers (SAE) Technical Paper 950400; SAE: Warrendale, PA, 1995.
8. Yuan, C.-S.; Lin, H.-Y.; Lee, W.-J.; Lin, Y.-C.; Wu, T.-S.; Chen, K.-F. A New Alternative Fuel for Reduction of Polycyclic Aromatic Hydrocarbon and Particulate Matter Emissions from Diesel Engines; *J. Air & Waste Manage. Assoc.* **2007**, *57*, 465-471; doi: 10.3155/1047-3289.57.4.465.
9. Liu, Y.-Y.; Lin, T.-C.; Wang, Y.-J.; Ho, W.-L. Carbonyl Compounds and Toxicity Assessments of Emissions from a Diesel Engine Running on Biodiesels; *J. Air & Waste Manage. Assoc.* **2009**, *59*, 163-171 doi: 10.3155/1047-3289.59.2.163.
10. Chen, Y.C.; Wu, C.H. Emissions of Submicron Particles from a Direct Injection Diesel Engine by Using Biodiesel; *J. Environ. Sci. Health* **2002**, *A37*, 829-843.
11. McCormick, R.L. Effects of Biodiesel on NO_x Emissions. Presented at Air Resources Board Biodiesel Workshop. National Renewable Energy Laboratory: Golden, CO, 2005; available at <http://www.nrel.gov/vehiclesandfuels/nppbf/pdfs/38296.pdf> (accessed 2009).
12. Durbin, D.T.; Cocker, D.R., III; Sawant, A.A.; Johnson, K.; Miller, J.W.; Holden, B.B.; Helgeson, N.L.; Jack, J.A. Regulated Emissions from Biodiesel Fuels from On/Off-Road Applications; *Atmos. Environ.* **2007**, *41*, 5647-5658.
13. McDonald, J.F.; Cantrell, B.K.; Watts, W. F.; Bickel, K.L. Evaluation of a Soybean Oil Based Diesel Fuel in an Underground Gold Mine; *CIM Bull.* **1997**, *91*, 91-95.
14. Watts, W.F.; Spears, M.; Johnson, J. *Evaluation of Biodiesel Fuel and Oxidation Catalyst in an Underground Mine*; Report to the Diesel Emissions Evaluation Program Technical Committee; 1998; available at http://www.deep.org/reports/inco_bio.pdf (accessed 2009).
15. Tsolakis, A. Effects on Particles Size Distribution from the Diesel Engine Operating on RME-Biodiesel with EGR; *Energy Fuels* **2006**, *20*, 1418-1424.
16. Jung, H.; Kittelson, D.B.; Zachariah, M.R. Characteristics of SME Biodiesel-Fueled Diesel Particle Emissions and the Kinetics of Oxidation; *Environ. Sci. Technol.* **2006**, *40*, 4949-4955.
17. Chung, A.; Lall, A.A.; Paulson, S.E. Particulate Emissions by a Small Non-Road Diesel Engine: Biodiesel and Diesel Characterization and Mass Measurements Using the Extended Idealized Aggregates Theory; *Atmos. Environ.* **2008**, *42*, 2129-2140.
18. McCormick, R.L. The Impact of Biodiesel on Pollutant Emissions and Public Health; *Inhalation Toxicol.* **2007**, *19*, 1033-1039.
19. Swanson, K.J.; Madden, M.C.; Ghio, A.J. Biodiesel Exhaust: the Need for Health Effects Research; *Environ. Health Perspect.* **2007**, *115*, 496-499.
20. Bugarski, A.D.; Schnakenberg, G.H.; Hummer, J.A.; Cauda E.; Janisko, S.J.; Patts, L.D. Effects of Diesel Exhaust Aftertreatment Devices on Concentrations and Size Distribution of Aerosols in Underground Mine Air; *Environ. Sci. Technol.* **2009**, *43*, 6737-6743.
21. Alleman, T.L.; McCormick, R.L.; Deutch, S. *2006 B100 Quality Survey Results*; Milestone Report NREL/TP-540-41549; U.S. Department of Energy, National Renewable Energy Laboratory: Golden, CO, 2007.
22. Graboski, M.S.; McCormick, R.L. Combustion of Fat and Vegetable Oils Derived Fuels in Diesel Engines; *Prog. Energy Combust. Sci.* **1998**, *24*, 125-164.
23. Elemental Carbon (Diesel Particulate): Method 5040, Issue 3 (Interim). In *NIOSH Manual of Analytical Methods*, 4th rev. ed.; National Institute for Safety and Health: Cincinnati, OH, 1999; available at <http://www.cdc.gov/niosh/nmam/pdfs/5040f3.pdf> (accessed 2009).
24. Wang, S.C.; Flagan, R.C. Scanning Electrical Mobility Spectrometer; *Aerosol Sci. Technol.* **1990**, *13*, 230-240.
25. Katare, S. Aged DOC is a Net Consumer of NO₂: Analysis of Vehicle, Engine Dynamometer and Reactor Data; Society of Automotive Engineers (SAE) Technical Paper 2007-01-3984; SAE: Warrendale, PA, 2007.

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