Effects of corn-based FAME biodiesels on particulate and gaseous emissions from a naturally aspirated diesel engine

By
Aleksandar D. Bugarski, Jon A. Hummer, and Shawn Vanderslice
National Institute for Occupational Safety and Health (NIOSH)
Office of Mine Safety and Health Research (OMSHR)

Department of Health and Human Services
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
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CDC Workplace NIOSH

Introduction

- Fuels derived from biomass, commonly known as a biodiesel, are considered as viable alternatives to petroleum derived diesel fuels.
- Biodiesel fuels most widely used in the U.S. are made of long-chain, fatty acid methyl esters (FAME) obtained from vegetable oils and animal fats.
- FAME biodiesel based fuels are currently used as alternative to petroleum based diesel fuels by several underground mining operations in the U.S. to control exposures of miners to total and elemental carbon emitted by diesel-powered equipment.

Petroleum based diesel and FAME biodiesel fuels differ substantially in chemical and physical properties.

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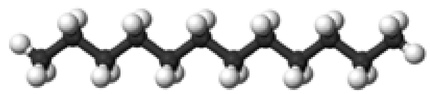
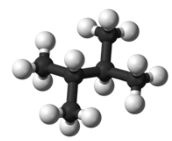
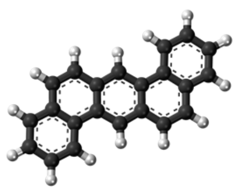
- Petroleum based diesel is made of alkanes (paraffins, C_nH_{2n+2}), alkenes (olefins, C_nH_{2n}), and arenes (aromatic hydrocarbons).
- The general formula would be $C_{12}H_{23}$ ($C_{10}H_{20}$-$C_{15}H_{28}$).



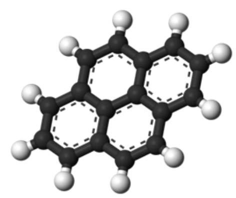
Dodecane



2,3-Dimethylbutane



Dibenz(a,h)anthracene



Pyrene

Biodiesel fuels used in the States are made primarily of fatty acids methyl esters.

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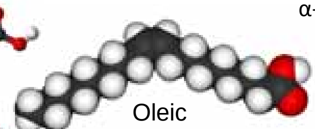
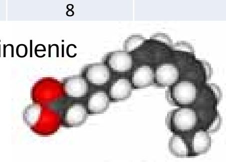
Content of Fatty Acids in FAME Biodiesels	Myristic Acid	Palmitic Acid	Stearic Acid	Oleic Acid	Linoleic Acid	Linolenic Acids
Source	14:0	16:0	18:0	18:1	18:2	18:3
Soybean Oil		6-10	2-5	20-30	50-60	5-11
Corn Oil	**1-2**	**8-12**	**2-5**	**19-49**	**34-62**	
Canola Oil		4	1	60	20	13
Palm Oil		44	5	39	10	
Tallow	3-6	24-32	20-25	37-43	2-3	
Yellow Grease	1-2	17	13	55	8	

Palmitic



Oleic

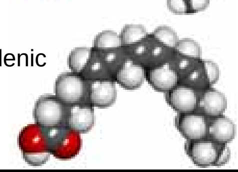
α-Linolenic



Stearic

Linoleic

ϒ-Linolenic



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Objective

- Previous field and laboratory studies showed that FAME biodiesel fuels have potential to reduce concentrations of diesel particulate matter (DPM), particularly elemental carbon (EC) in underground mines.
  - Bugarski, A.D., Cauda E., Janisko, S.J., Hummer, J.A., Patts, L.D. [2010]. Journal of Air and Waste Management Association, 60, 237-244.
  - Bugarski, A.D., Janisko S.J., Cauda E.G., Patts L.D., Hummer J.A., Westover C., Terrillion T. (2014). Annals of Occupational Hygiene 2014; doi: 10.1093/annhyg/meu049.

- The National Institute for Occupational Safety and Health (NIOSH) conducted a laboratory study in order to quantify and characterize the effects of corn derived FAME biodiesel fuels on physical, chemical and toxicological properties of aerosols emitted by diesel engines equipped with diesel oxidation catalytic converter (DOC),

- The effects of two blended (B20, B50) and neat biodiesel (B100) corn FAME fuels were compared with the corresponding effects of petroleum based ultralow sulfur diesel (ULSD) fuel.

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Methodology

The corn-based FAME biodiesel was supplied by Peter Cremer NA (Cincinnati, OH).

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- ULSD supplied by Gutman Oil was used as a baseline fuel.
- The results of analysis performed on the fuels by Bentley Tribology Services, Minden, NV are given in the following table:

Fuel Property	Test Method	ULSD	B100
Fatty Acid Methyl Ester Content [%]	ASTM 7371	N/A	100
Heat of Combustion [BTU/gal]	ASTM D240	138422.0	125846.0
API Gravity @ 15.6 °C [°API]	ASTM D1298	35.0	28.8
Cetane Number	ASTM D613	45.3	51.2
Sulfur by UV [ppm]	ASTM D5453	4.9	0.1
Cold Filter Plug Point [°C]	ASTM D6371	-15.0	-6.0
Flash Point, Closed Cup [°C]	ASTM D93	60.5	180.0

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The experimental part of the study took place at the diesel laboratory at NIOSH OMSHR.

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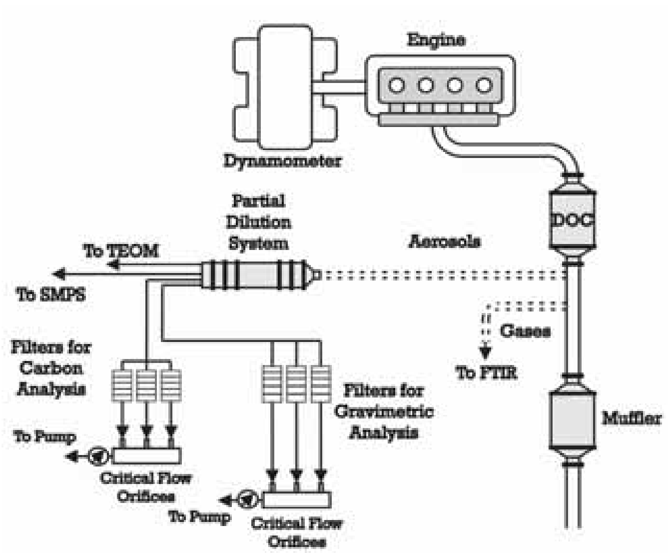

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Dynamometer , Engine, and Exhaust Aftertreatment

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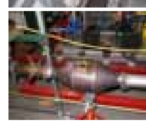
Test Vehicle	Specifications
Dynamometer Manufacturer	SAJ, Pune, India
Dynamometer Model	SE150
Engine Manufacturer	Isuzu
Engine Model	C240
Number of Cylinders	4 (inline)
Engine Displacement	2.4 l
Engine Type	liquid cooled, naturally aspirated
Engine Output	41.8 KW (56 hp)
Exhaust Aftertreatment Supplier	Lubrizol, New Market, ON
Exhaust Aftertreatment Type	**diesel oxidation catalytic converter (DOC)**



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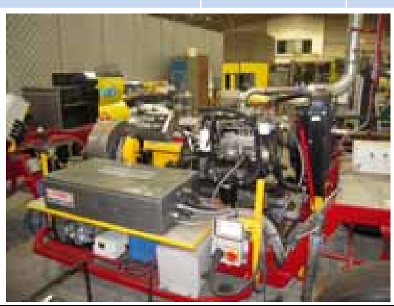
The effects of fuels were evaluated for four steady-state operating conditions.

Conditions	Description	Engine Speed	Torque	Power
		rpm	Nm	kW
R50	Rated speed and 50% load	2950	55.6	17.2
R100	Rated speed and 100% load	2950	111.2	34.3
I50	Intermediate speed and 50% load	2100	69.1	14.9
I100	Intermediate speed and 100% load	2100	136.9	30.6



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The aerosol sampling and measurements were conducted in the exhaust diluted approximately 30 times using a partial dilution system.

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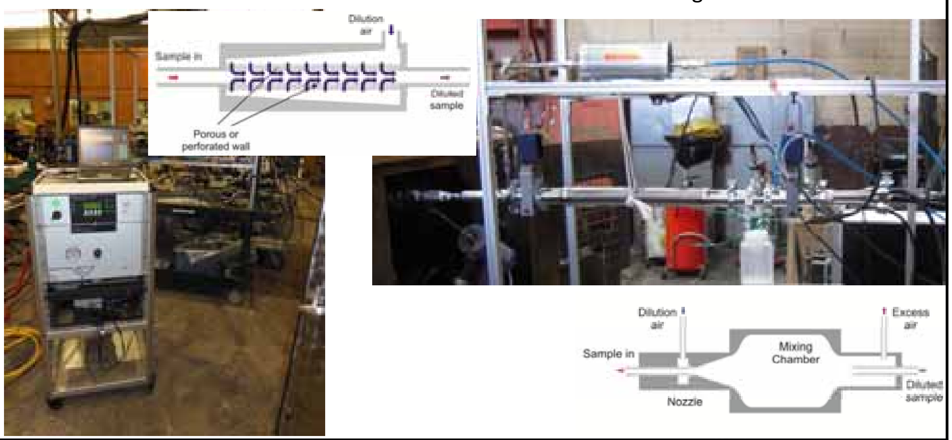
- Dekati FPS4000 is designed to dilute exhaust in two stages.
- Primary dilution occurred in perforated disk diluter;
- Secondary dilution was provided by ejector diluter;
- The residence chamber was inserted between those two stages.



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Aerosols Sampling and Measurements

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- Total mass concentrations of aerosols were determined using:
  - Results of measurements performed in diluted exhaust using Tapered Element Oscillating Microbalance (Thermo, TEOM 1405). Only data collected during the last hour of the tests were used in the analysis.
  - Results of gravimetric analysis performed on the filter samples collected from the diluted exhaust. The samples were collected over 2-hour periods on 2-µm Teflo membrane disc filters (Pall Corporation). The gravimetric analysis was done using Mettler Toledo UMX2 balance.

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Aerosols Sampling and Measurements

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- The effects on mass concentrations of elemental carbon (EC) and total carbon (TC) were determined using the results of thermal optical transmittance-evolve gas analysis (TOT-EGA) performed on the filter samples collected on quartz fiber filters drawn from the diluted exhaust. The Sunset Laboratory OC-EC Aerosol Analyzer and NIOSH 5040 Method were used to carry out carbon analysis.

- Number concentrations and size distributions of aerosols were measured in diluted exhaust using Scanning Mobility Particle Sizer (TSI, Model 3936 SMPS). The data collected during the second hour of the two-hour tests were used to access average concentrations. The effects of the fuels on size and distribution of aerosols were studied on the measurements performed for the selected events.

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Measurements of Gaseous Emissions

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- The effects on concentrations of criteria (CO, CO_2, NO, and NO_2) and other gases (N_2O, 1,3 Butadiene, HCOH, CH_3COH), were determined using results of measurements made in undiluted exhaust using the Fourier Transform Infrared (FTIR) analyzer (Gasmet, Model 4000).

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Results

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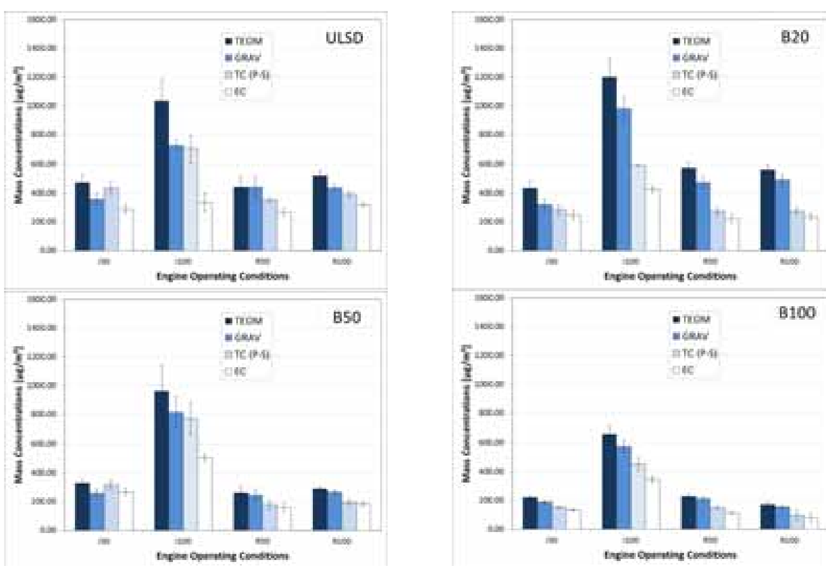
The effects on mass concentrations of aerosols were examined
on the results of TEOM measurements, gravimetric analysis, and carbon analysis.



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Results of Measurements with TEOM 1405

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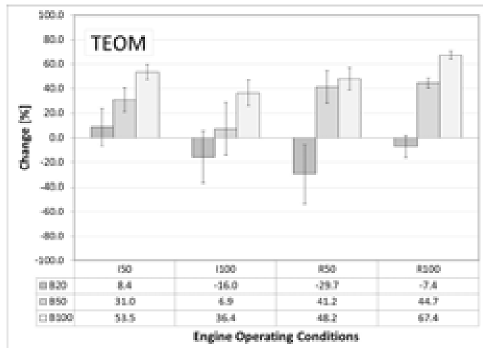
- In all test cases, the test engine emitted less total DPM when fueled with B50, and B100 than with ULSD.
- On contrary, in the majority of test cases (I100, R50, R100), B20 had an adverse effect on DPM mass concentrations.
- The effects on total DPM mass concentrations were found to be directly proportional to the biodiesel content in the fuel.



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Results of the Gravimetric Analysis.

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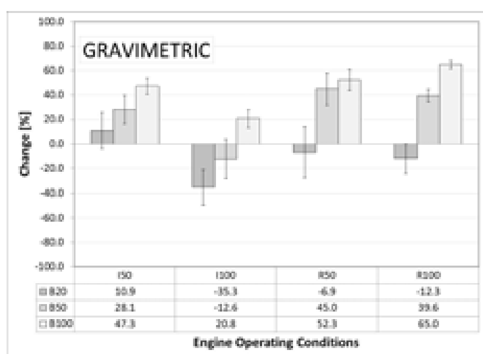
- The conclusions derived from the results of gravimetric analysis are in general agreement with those derived from the results of TEOM measurements.
- For the majority of the test cases, the test engine emitted less total DPM when fueled with B50, and B100 than with ULSD.
- The results of gravimetric analysis confirmed that in the majority of test cases (I100, R50, R100), B20 had adverse effect on DPM mass concentrations.
- It is important to note that the TEOM results obtained for the last hour of the tests were consistently higher than the corresponding two-hour averages obtained using the gravimetric analysis.



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Effects on mass concentrations of total carbon (TC) were assessed using results of the TOT-EG analysis.

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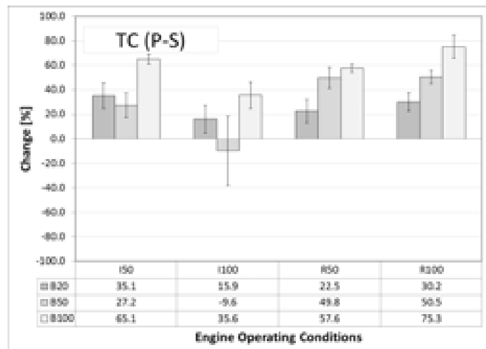
- With exception for one of the test cases (B50, I100), the test engine emitted on average less TC mass when fueled with B20, B50, and B100 than with ULSD.
- For the R50 and R100 engine operating conditions, the effects on TC mass were found to be directly proportional to the biodiesel content in the fuel.
- The same relationship was not observed for I50 and I100 conditions.



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Effects on mass concentrations of elemental carbon (EC) were also assessed using results of the TOT-EG analysis.

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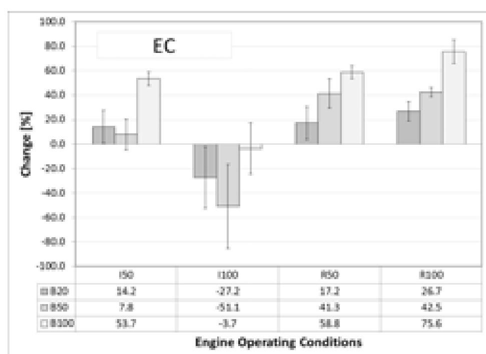
- With the exception of the I100 test cases, the test engine emitted less EC mass when fueled with B20, B50, and B100 than with ULSD.
- For R50 and R100 conditions, the effects on TC mass were found to be directly proportional to the biodiesel content in the fuel. The same relationship was not observed for I50 and I100 conditions.
- It appears that for I100 condition, using fuels of different physical and chemical properties presented a challenge to either the fueling system and/or combustion process.



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The effects on total number concentrations (TNC) of diesel aerosols were assessed using the results of measurements with SMPS 3936.

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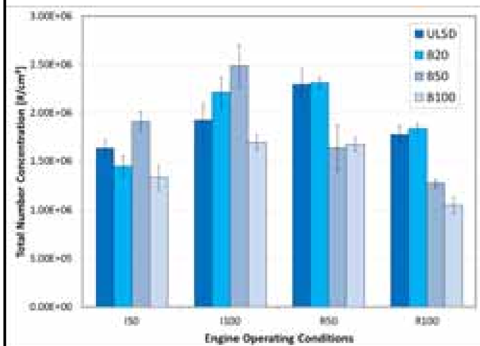
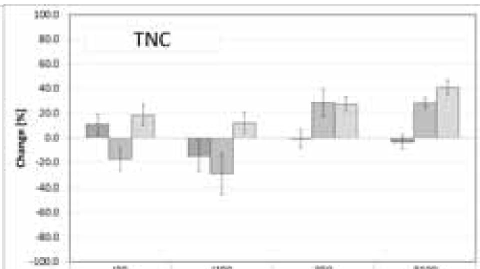
- TNC of aerosols were strongly dependent on the engine operating conditions.
- In the case of R50 and R100 conditions, the engine emitted equivalent or lower TNC of aerosols when fueled with B20, B50, and B100 than with ULSD.
- In the case of I50 and I100 conditions, the use of B100 resulted in lower TNC of aerosols, while B20 and B50 fuels resulted in equivalent or higher number concentrations of aerosols.





	I50	I100	R50	R100
B20	11.1	-14.8	-0.7	-3.3
B50	-17.2	-29.0	28.7	28.4
B100	18.5	12.1	27.2	40.8

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The effects on size distribution of aerosols were assessed using the results of measurements with SMPS 3936 for selected instances for selected tests.

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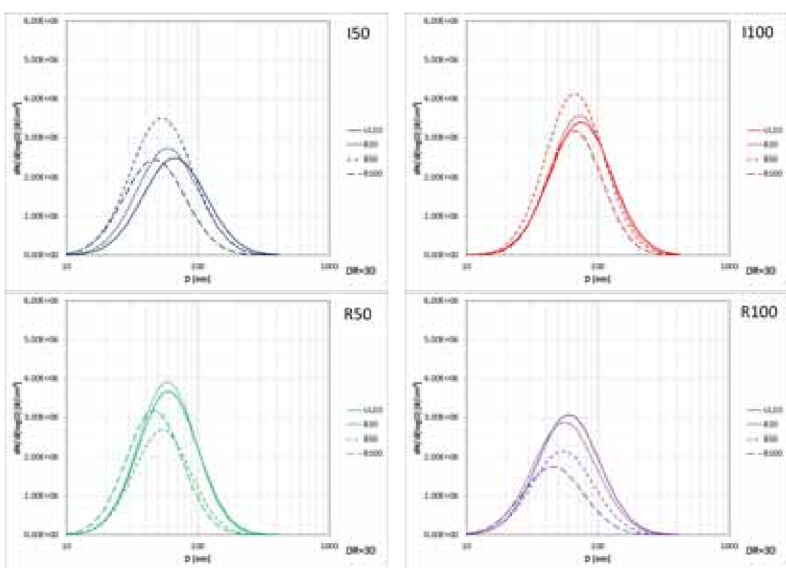

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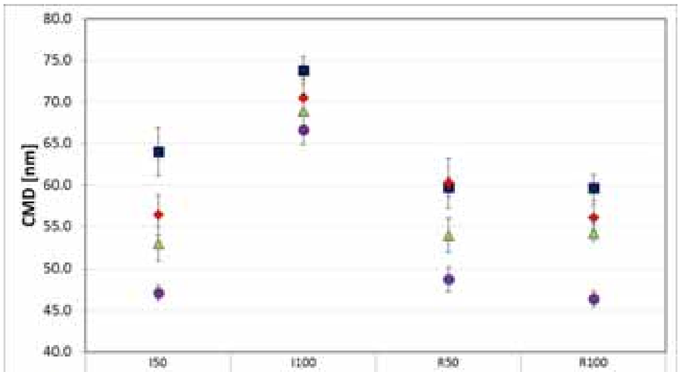
For all test conditions, the distributions were single modal. In general, the count median diameters (CMDs) of aerosols decreased with increase in biodiesel content in the fuels.



	I50	I100	R50	R100
ULSD	64.0	73.8	59.7	59.7
B20	56.4	70.5	60.3	56.1
B50	53.0	68.9	54.0	54.3
B100	47.1	66.7	48.8	46.4

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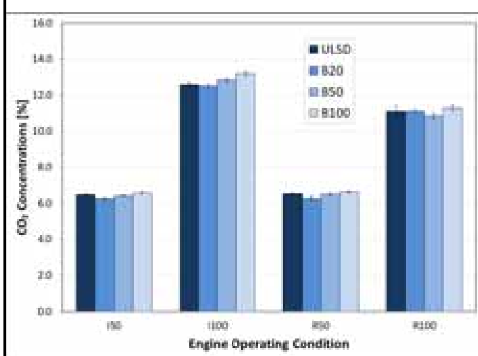
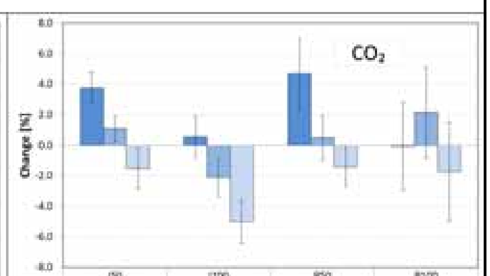
The effect of fuels on CO_2 emissions were found to be minor.

- The test-to-test differences in CO_2 emissions were within ± 5 percent.
- In the majority of the cases, the CO_2 emissions tended to increase with increase in biodiesel content in the fuels.





	I50	I100	R50	R100
B20	3.8	0.6	4.7	-0.1
B50	1.1	-2.1	0.5	2.2
B100	-1.5	-5.0	-1.4	-1.7

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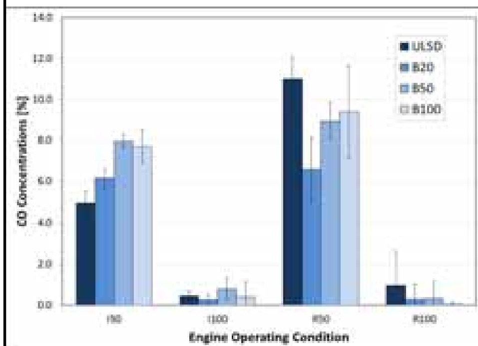
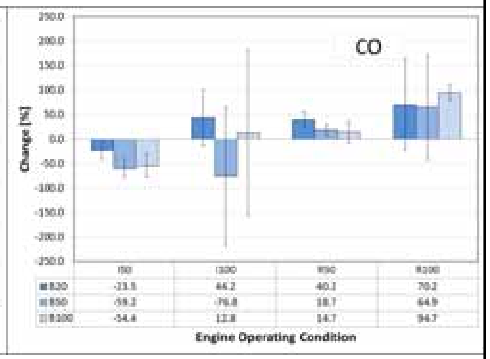
The CO concentrations in the exhaust of the test engine equipped with DOC were quite low, not exceeding 12 ppm for any of the test conditions.

- In the case for I50 and R50 conditions, the CO emissions increased with increase in biodiesel content in the biofuels.
- In the case of I100 and R100 conditions, the uncertainties in the CO measurements at the observed low levels preclude drawing conclusions on the effects of the fuels on CO emissions.





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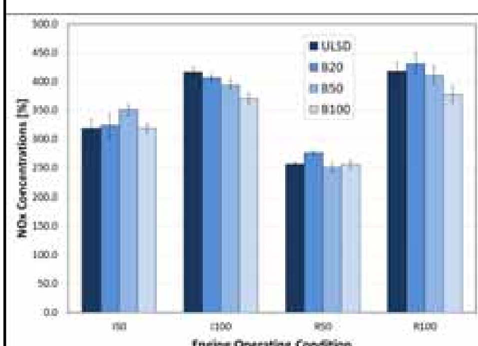
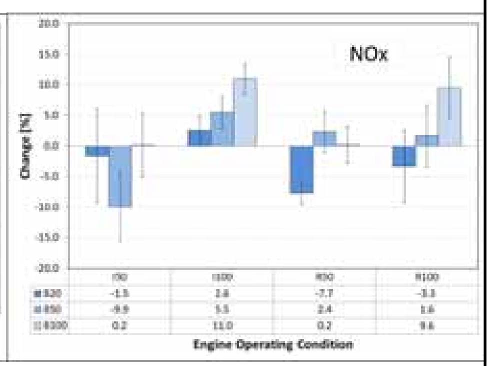
The effects of biodiesel fuels on NOx emissions were relatively minor and varied widely with engine operating conditions.

- At I50 and R50 conditions, the concentrations of NOx were adversely affected by some of the biodiesel containing fuels.
- At I100 and R100 conditions, the concentrations of NOx in the exhaust decreased when the engine was fueled with B50 or B100.





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The NO_2 emissions from the DOC equipped engine were relatively low for light load conditions (I50 and R50, 0.8 to 6.5 percent of NOx) and relatively high for high load conditions (I100 and R100, 6 to 13.5 percent of NOx).

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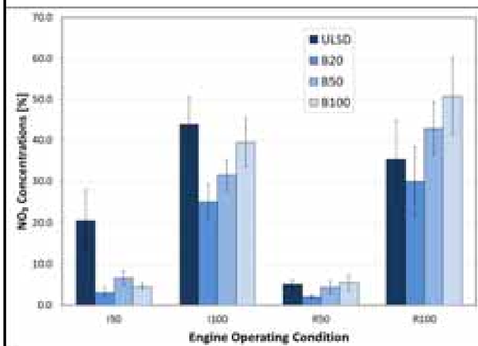
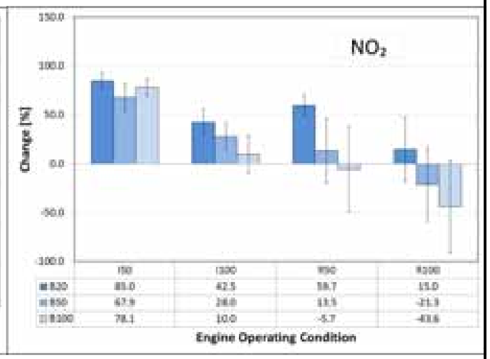
- For I100, R50, and R100 conditions, the NO_2 emissions increased with increase in biodiesel content in the biofuels.
- For R100 conditions and B50 and B100 fuels, the NO_2 concentrations exceeded the baseline (ULSD) concentrations.





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The N_2O emissions were relatively high for light load conditions (I50 and R50, 0.24 to 0.61 percent of NOx) and relatively low for high load conditions (I100 and R100, 0.01 to 0.04 percent of NOx).

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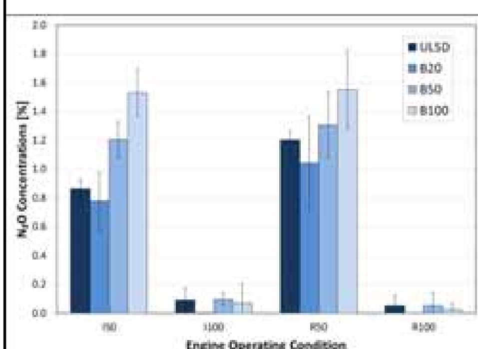
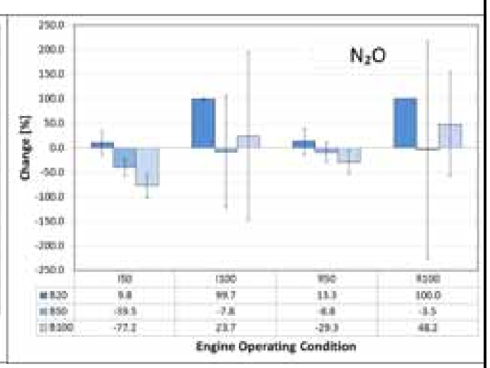
- In the case of I50 and R50 conditions, the N_2O emissions increased with increase in biodiesel content in biofuels.
- The uncertainties of the results for I100 and R100 conditions precluded drawing any conclusions on the effects of the fuels on N_2O emissions for those conditions.





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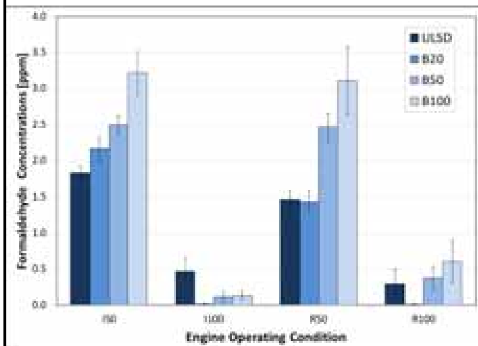
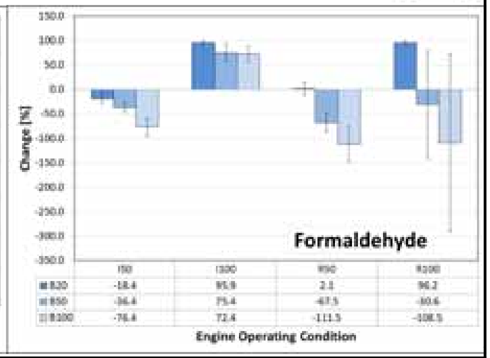
The formaldehyde (HCOH) emissions were substantially higher for light load conditions (I50 and R50) than for high load conditions (I100 and R100).

- For all conditions but I100, the B50 and B100 adversely affected formaldehyde emissions.
- In general, the formaldehyde emissions increased with increase of biodiesel content in biofuels.
- Formaldehyde is recognized by NIOSH as a potential human carcinogen.
- NIOSH REL: TWA 0.016 ppm, C 0.1 ppm (15-minute).





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Summary

- Therefore, this study confirmed that biodiesel fuels with higher biodiesel content (B50, B100) as a control strategy have potential to reduce DPM, TC, and EC mass concentrations. The effects for B20 were less clear.
- The study also showed that under certain conditions FAME biodiesel fuels can increase TNCs of aerosols and concentrations of NO_2, N_2O, and formaldehyde emitted by a naturally aspirated engine equipped with DOC.
- The other important aspect to consider is effects of FAME biodiesel fuels on toxicity of aerosols emitted by diesel engines:
  - Yanamala, N., Hatfield, M.K., Farcas, M.T., Schwegler-Berry, D., Hummer, J.A., Shurin, M.R., Birch M.E., Gutkin, D.W., Kisin, E., Kagan, V.E., Bugarski, A.D., Shvedova, A.A. (2013). Toxicology and Applied Pharmacology 272 (2013) 373–383.

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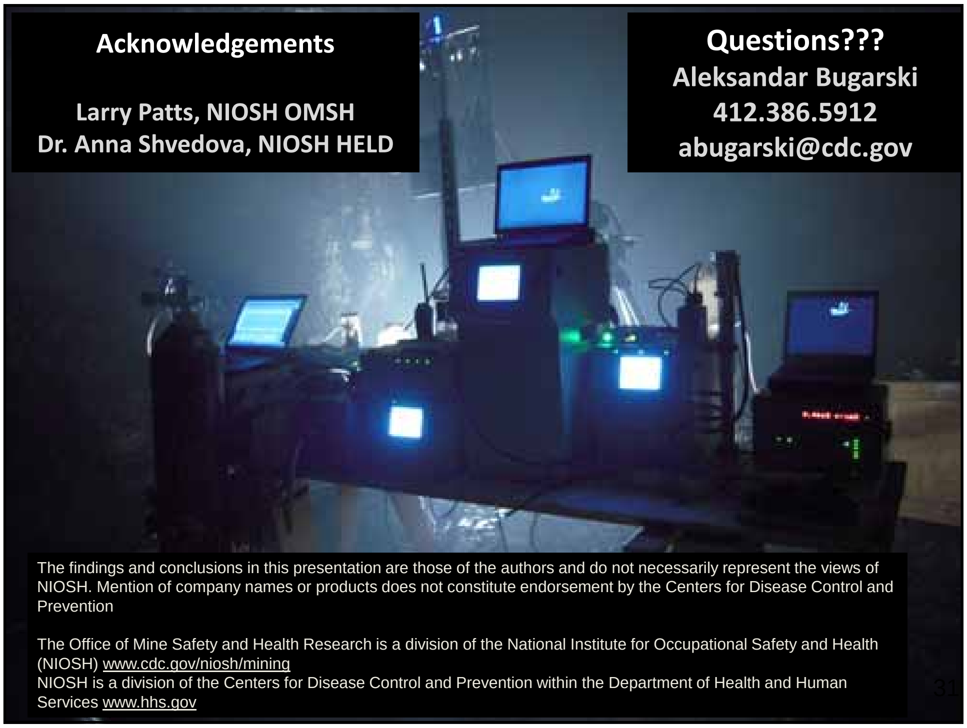
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Questions???
Aleksandar Bugarski
412.386.5912
abugarski@cdc.gov
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