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Effects of an Oxidation Catalytic Converter and a Biodiesel Fuel on the Chemical, Mutagenic, and Particle Size Characteristics of Emissions from a Diesel Engine

SUSAN T. BAGLEY

Department of Biological Sciences, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931-1295

LINDA D. GRATZ AND JOHN H. JOHNSON

Department of Mechanical Engineering–Engineering Mechanics, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931-1295

JOSEPH F. MCDONALD*

Center for Diesel Research, Department of Mechanical Engineering, University of Minnesota, 111 Church Street SE, Minneapolis, Minnesota 55455-0111

This study was conducted to obtain additional information on exhaust emissions with potential health importance from an indirect injection diesel engine, typical of those in use in underground mines, when operated using a soy-derived, fatty-acid mono-ester (or biodiesel) fuel and an oxidation catalytic converter (OCC). Compared to emissions with the diesel fuel without the OCC, use of the diesel (D2) and biodiesel fuel with the OCC had similar reductions (50–80%) in total particulate matter (TPM). The solid portion of the TPM was lowered with the biodiesel fuel. Particle-associated polynuclear aromatic hydrocarbon and 1-nitropyrene emissions were lower with use of the biodiesel fuel as compared to the D2 fuel, with or without the OCC. Vapor-phase PAH emissions were reduced (up to 90%) when the OCC was used with either fuel. Use of the OCC resulted in over 50% reductions in both particle and vapor-phase-associated mutagenic activity with both fuels. No vapor-phase-associated mutagenic activity was detected with the biodiesel fuel; only very low levels were detected with the D2 fuel and the OCC. Use of the OCC caused a moderate shift in the particle size/volume distribution of the accumulation mode particles to smaller particles for the diesel fuel and a reduction of particle volume concentrations at some of the tested conditions for both fuels. The nuclei mode did not contribute significantly to total particle volume concentrations within the measured particle size range (~ 0.01 – $1.0 \mu\text{m}$). The biodiesel fuel reduced total particle volume concentrations. Overall, use of this OCC for the engine conditions tested with the biodiesel fuel, in particular, resulted in generally similar or greater reductions in emissions than for use of the D2 fuel. Use of the biodiesel fuel should not increase any of the potentially toxic, health-related emissions that were monitored as part of this study.

Introduction

Mono-ester diesel fuels, collectively referred to as “biodiesel”, have shown considerable promise for use as passive control strategies for particulate matter emissions from diesel equipment operated in confined spaces such as underground mines (1, 2). Biodiesel fuels, such as those derived from soybean and rapeseed oils, have advantages over petroleum-based fuels in being renewable sources of energy, virtually free of sulfur and aromatic compounds, producing lower particulate matter emissions due to reduced particle formation (1, 2), and being nontoxic and biodegradable (3). Biodiesel fuels have demonstrated decreased total hydrocarbons emissions, but the levels of particle-phase volatile organic compounds (also termed soluble organic fraction or SOF) associated with the diesel total particulate matter (TPM) have been shown to increase (1, 2, 4–6). An increase in the fraction of fine particles present in the nuclei mode size range (0.01 – $0.05 \mu\text{m}$ volume mean diameter) in diluted exhaust has been demonstrated using biodiesel fuel (2). Only limited and somewhat contradictory information has been available concerning the mutagenic activity of emissions or the effects on emissions with potential health effects, such as polynuclear aromatic hydrocarbons (PAH), for diesel engines using biodiesel fuels (7–9).

When combined with a modern, platinum–palladium oxidation catalytic converter (OCC) to reduce hydrocarbon and SOF emissions, biodiesel fuels have been found to have good potential for reducing particulate matter as compared to using petroleum-based, no. 2 diesel (D2) fuel for underground mines using similar OCC devices (1, 2). Analysis of a limited number of SOF samples at Michigan Technological University (MTU) indicated that decreases occurred in both PAH levels and mutagenic activity while using biodiesel fuels as compared to using D2 fuel (2). Concerns about the increase in SOF levels were raised by the Mine Safety and Health Administration (MSHA) during its 1994 review of U.S. Bureau of Mines (USBM) Health Research Division activities related to control of particle concentrations in underground mines. The purpose of this study was to provide some of the detailed information necessary to evaluate the impact of using a biodiesel fuel on potentially health-related emissions from a diesel engine typical of those used in many underground mining operations. This additional information was considered necessary to evaluate whether the possible health risks typically associated with increased SOF levels would be offset by the observed reductions in TPM. This study began as collaborative effort between researchers at MTU and the USBM Diesel Technology Group. The personnel, research facilities, and responsibility for participation in this study with MTU were transferred to the University of Minnesota—Center for Diesel Research (UM-CDR) April 1, 1996, as part of the closure of the USBM. The primary objectives of the study were to

(a) Obtain samples of particulate and vapor phase organic material from a typical mining diesel engine operating on D2 fuel and biodiesel fuel with and without an OCC control device.

(b) Measure the potentially health-related emissions, particularly PAH, nitro-PAH, and mutagenic activity.

(c) Determine the effects of the fuels and OCC on the size distribution of the diesel particulate matter.

(d) Analyze all of the data obtained as part of this project in order to evaluate the effectiveness of the biodiesel fuels

* Corresponding author present address: 812 Pauline Blvd., Ann Arbor, MI 48103; e-mail address: shane-mcdonald@worldnet.att.net.

and control devices for potential use in the underground mine environment as a method for controlling TPM emissions.

Experimental Methods

Engine/Dynamometer Test Cell. Engine testing and exhaust emissions sampling were performed at the former USBM Diesel Emissions Research Laboratory facilities in Minneapolis, MN. Tests were conducted using a 1983 Caterpillar 3304 PCNA, 7 L, indirect injection, naturally aspirated engine. A detailed description of the engine is located in Table S-1 of the Supporting Information. The engine is typical of engines used with underground coal mine haulage vehicles and some underground metal mine applications. This particular engine has been used in previous USBM-MTU collaborative studies on effects of control devices and fuels on emissions (10, 11). Load was provided to the engine using an eddy-current engine dynamometer. Descriptions of the engine and test cell, experimental apparatus, and test procedures are presented elsewhere (1, 2, 12).

Test Cycles. To generate exhaust samples for the chemical and biological characterization, the engine was tested using light-duty and heavy-duty transient speed/load test cycles developed by the USBM for laboratory exhaust emissions evaluations. These test cycles consist of 16 continuously repeated speed/load segments, each of approximately 10 s duration. The light-duty transient cycle is designed to replicate operating conditions that may lead to high SOF emissions. The high speed, light load conditions of this cycle tend to increase engine lubricating oil consumption and lubricant-associated SOF (11). The oxidation efficiency of the OCC is often lower at these conditions due to the lighter loads and subsequent lower exhaust temperatures of this cycle. The heavy-duty transient test cycle utilizes more severe load and acceleration cycles in order to replicate operating conditions that produce high TPM and visible smoke emissions, such as mucking operations by load-haul-dump (LHD) equipment. Due to the general similarities in the test results, only data from the light-duty cycle are included in this paper; similar data obtained from engine operation during the heavy-duty cycle are included in the Supporting Information.

Particle size measurements were conducted primarily at three steady-state speed load conditions: 100% load at 2200 rpm ($=0.67$), 100% load at 1500 rpm ($=0.64$), and 50% load at 1500 rpm ($=0.33$). Steady-state operation was necessary in order to stabilize particle concentrations and size distributions sufficiently for the instrumentation to complete sequential measurement of the particle size data for each size interval.

Test Fuels. Two fuels were tested: a single batch of a commercially available, low sulfur D2 fuel; and a vacuum distilled, 100% soy methyl ester biodiesel fuel. Fuel properties are summarized in Table 1. The distribution of fatty acid methyl esters of the biodiesel fuel used for this experiment was presented previously (2) and is also included in Table S-2 in the Supporting Information. Approximately 80% of the fatty acids in the soy methyl ester biodiesel fuel were unsaturated. Methyl linoleate was the largest fatty acid mono-ester component in the biodiesel fuel ($>52\%$ by mass). Linoleic acid, other highly unsaturated fatty acids, and their methyl ester derivatives are relatively unstable during long-term storage (13). To retard oxidation during storage, 200 ppm of *tert*-butylhydroquinone (TBHQ) antioxidant was added to the biodiesel, as per recommendations of Du Plessis et al. (13).

Oxidation Catalytic Converter. The OCC utilized a combination of platinum and palladium catalysts with a proprietary wash coating on a ceramic, honeycomb-shaped

TABLE 1. Fuel Properties^a

properties	D2	biodiesel
cetane no. (ASTM D613)	43.2	54.7
lower heating value, MJ/kg (ASTM D240)	42.8	37.1
C:H:O molar ratio	16:30:0	19:34:2
sulfur, mass % (ASTM D129)	0.01	<0.005
oxygen, mass %	0	11.0
aromatics, mass % (ASTM D1319)	39.0	0.0
kinematic viscosity, cSt at 40 °C (ASTM D445)	2.37	3.05
density, g/cm ³ at 15 °C (ASTM D1298)	0.8515	0.8859
cloud point, °C (ASTM D2500)	-21	-2
flashpoint, °C (ASTM D93)	68	160

^a D2, U.S. low-sulfur no. 2 petroleum diesel fuel. Biodiesel, fatty acid methyl esters of soy oil.

monolith. The monolith had a diameter of 24.1 cm, was 7.6 cm long, and had a cell density of 46.5 cells/cm².

TPM, SOF, and XOC Determinations. The engine, OCC, and dilution tunnel sampling system were conditioned for 16 h at high exhaust temperature conditions (rated speed and load) before testing each fuel and exhaust aftertreatment combination. Conditioning was necessary in order to volatilize adsorbed organic and sulfate material from the exhaust sampling system.

Approximately 5% of the engine exhaust was diverted into a mini-dilution tunnel for dilution with clean air at a dilution ratio of approximately 14 (± 2):1 (air:exhaust gases). The mini-dilution tunnel and sample collection procedures are described in detail in McClure et al. (11). The TPM and vapor phase samples were collected from the diluted exhaust using 508 \times 508 mm Teflon-coated glass fiber filters and XAD-2 polymer adsorbent. The filters were equilibrated and weighed in a class 300 clean room (14) before and after exposure. The TPM mass on the filter was determined from the difference in mass before and after exposure to the dilute exhaust. After the second mass determination, the exposed filters and XAD-2 samples were shipped on dry ice to MTU and were stored at -18 ± 4 °C until they were extracted. The exposed filter and XAD-2 samples were extracted (separately) for 24 h with dichloromethane in a Soxhlet apparatus to obtain the particle-associated SOF and the extractable organic component from the XAD-2 adsorbent (XOC), respectively. Blank filters and XAD-2 resin were also extracted for analysis. The mass of SOF or XOC was determined gravimetrically on a small (100 L) aliquot of the total extract, which was brought to dryness. All extracts were stored frozen (-18 ± 4 °C) until they were divided into aliquots for Ames assay and PAH analysis.

Particle Size Measurements. Exhaust particle number concentrations for nine particle size intervals were measured for each fuel and OCC combination using a TSI electrical aerosol analyzer (EAA). Use of the EAA for particle size measurement of dilute samples of fine particles was described in detail by Liu and co-workers (15, 16). Particle size measurements were taken from the mini-dilution tunnel approximately 6 m (~ 0.5 s) downstream from the entrance of the tunnel. Exhaust samples were drawn from the dilution tunnel and further diluted with clean, dry air prior to entering the EAA. The final dilution ratio of the sample entering the EAA was approximately 280–360:1, depending on the steady-state speed and load condition. The electrical charge on the sampled particles was reduced to approximately the Boltzmann equilibrium charge distribution by passing the sample through a Kr-85 neutralizer upstream of the EAA.

The particle number concentrations and number size distributions were derived from the EAA current signal and the resultant electrical mobility distribution of the aerosol

using a Simplex minimization method developed by Kapadia (17). Particle volume concentrations and volume size distributions were determined from the particle number data using the methods of Hatch and Choate (18). The detectable size range of particles measured by the EAA was approximately 0.01–1.00 μm . EAA particle size measurements have been found to agree well with other particle size measurement techniques for TPM (19–21).

PAH and Nitro-PAH Quantification. The PAH and nitro-PAH compounds chosen for quantification were fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BP), 1-nitropyrene (1-NP), 2-nitrofluorene (2-NF), 6-nitrochrysene (6-NC), and the dinitropyrenes (1,6-DNP and 1,8-DNP). These compounds were chosen either because they were specified by the U.S. Environmental Protection Agency in the Fuels and Fuel Additives Regulations (22), because of their interest due to their health effects (23), or because of their potential to be converted to compounds with known or suspected health effects.

The SOF or XOC samples were first separated into three fractions (aliphatics, PAH, and nitro-PAH) using a two-column procedure (24); the PAH and nitro-PAH fractions were then analyzed via reverse-phase high-performance liquid chromatography (HPLC) with fluorescence detection (25). The nitro-PAH were reduced to fluorescent amines using the postcolumn method first reported by MacCrehan et al. (26). The HPLC parameters are summarized in Tables S-3 and S-4 in the Supporting Information. The calibration and reference standard materials are described in detail in Bagley et al. (25).

Mutagenicity Assays. Mutagenic activity of the SOF and XOC samples was determined using a version of the microspore suspension (micropreincubation) modification of the *Salmonella typhimurium*/microsome mutagenicity bioassay or Ames test (25). Tester strain TA98 was provided by Dr. B. Ames (University of California, Berkeley) and tester strains TA98NR and TA98 – 1,8-DNP₆ (TA98DNP) were provided by Dr. E. McCoy (Case Western Reserve University, Cleveland, OH). Rat liver S9 from Arochlor 1254-induced male Sprague–Dawley rats was purchased from Molecular Toxicology, Inc. (Annapolis, MD). After solvent removal, dimethyl sulfoxide (DMSO) was added to an aliquot of known mass for use in mutagenicity testing.

The modified, small dish (60 × 15 mm) microspore suspension assay was conducted following previously described procedures (25). All samples were first tested with TA98 – S9; if sufficient mass was available and the sample demonstrated activity with TA98 – S9, the sample was tested again with TA98NR – S9 and TA98DNP – S9. Some of the samples were also tested with the S9 mammalian liver enzyme activation system. The mean (and coefficient of variation, CV) spontaneous revertant levels (revertants/plate) without S9 were 26.8 (32%) for TA98, 31 (1.4) for TA98NR, and 20.5 (3.4) for TA98DNP. Mean (and CV) revertant levels with 2-NF (400 ng/plate) without S9 were 740 (11) for TA98, 98.5 (14) for TA98NR, and 341 (7.9) for TA98DNP; revertant levels with 1-NP (40 ng/plate) were 795 (13) for TA98, 95 (15) for TA98NR, and 668 (9.0) for TA98DNP.

Experimental Design and Data Analysis. The engine was operated with the D2 fuel and the biodiesel fuel, with and without the OCC. At least six samples (three filters and three aliquots of XAD-2) were obtained for each fuel and control device. Particle size measurements were repeated at least four times at each steady-state speed and load condition, and three sets of steady-state test cycles were completed for each condition of fuel and exhaust aftertreatment evaluated.

Statistical comparisons were made between data with differing conditions of fuel and exhaust aftertreatment by applying a two-sided Students *t*-test to test for significant differences between sample set means. Differences between mean values at a level of $p = 0.05$ (95% confidence level) were considered statistically significant. The PAH, nitro-PAH, and mutagenic activity data sets for which the levels were found to be either less than the minimum detection limit (PAH and nitro-PAH) or not above background levels (mutagenic activity) were not statistically analyzed.

Results and Discussion

TPM, SOF, and XOC Levels. Emissions of TPM, SOF, and XOC are presented on a brake-specific (work normalized) basis in Figure 1 for all of the combinations of fuel and exhaust aftertreatment that were evaluated using the light-duty cycle. The SOF during operation on the biodiesel fuel was 60 and 80% of the TPM emissions when measured with and without the OCC, respectively. The increased SOF with the biodiesel fuel is consistent with earlier studies and is due to a shift to higher carbon number, less volatile fuel-related organic species in the exhaust than is typical of petroleum-based, D2-type fuels (1, 2). The SOF for the D2 fuel was 40% with the OCC and 57% without the OCC. Compared to the baseline case of the D2 fuel with no OCC, use of the biodiesel fuel with the OCC resulted in greater reductions in TPM levels but slightly lower reductions in SOF levels than when using the D2 fuel with the OCC. The TPM reductions for both fuels with the OCC from the baseline case were significant at a level of $p < 0.001$. Trends in XOC levels with the OCC as compared to the D2 fuel with no OCC were similar to the SOF trends (Figure 1). These changes were also found to be significant ($0.001 < p < 0.002$). It should be noted that both of the test fuels had very low sulfur content (0.01% mass) and that this particular OCC was designed specifically with a low reactivity for the oxidation of SO_2 to sulfate. Particulate sulfate emissions were not measured as part of this work but contributed no more than 3% of the TPM emissions in previous work with the same fuels and OCC (27) where the only measurable particulate sulfate was for the condition of no. 2 diesel fuel with the OCC, during the heavy-duty transient cycle.

Although the levels of the solid, carbonaceous component (SOL) of the TPM were not specifically determined as part of this study, SOL levels are generally calculated as the difference between the TPM levels and the sum of the SOF and sulfate levels. As mentioned above, fuel sulfur and sulfate aerosol levels were very low with both fuels, so the SOL levels can be approximated by the difference in TPM and SOF levels. This SOL component of particulate matter, in particular, has been linked in recent studies to potential increases in adverse health effects (28). The biodiesel fuel produced TPM with significantly lower SOL compositions than the D2 fuel, with or without use of the OCC (Figure 1). The differences were significant at a level between $0.002 < p < 0.01$. The reduction in TPM with biodiesel as compared to the D2 fuel, along with the higher SOF and lower solids levels, was as expected based on previous results from other evaluations of mono-ester biodiesel fuels (1, 2, 4–7).

A similar pattern of TPM, SOF, and XOC results was also obtained for the heavy-duty cycle (data presented in Figure S-1 in the Supporting Information). The key differences between the two sets of data were that TPM, SOF, and XOC levels were lower with the OCC for the heavy-duty versus the light-duty cycle. These differences in levels would be expected given that the heavier-duty cycle with its higher exhaust temperatures should promote more oxidation of the organic compounds, resulting in lower SOF and XOC levels.

Particle Size. Particle concentrations and size distribution parameters for the diluted exhaust samples at the tested

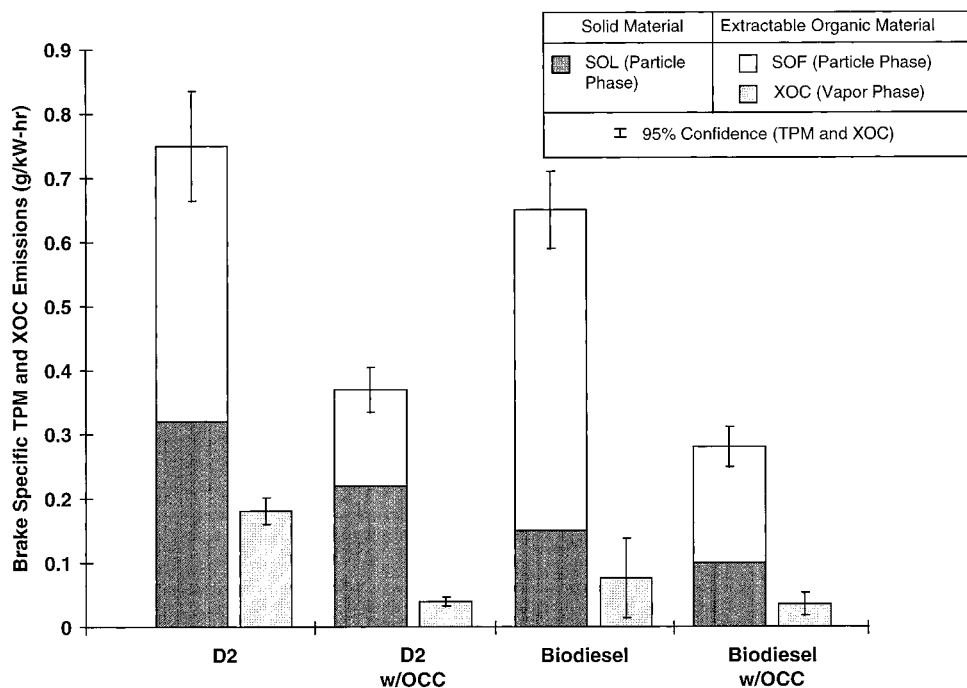


FIGURE 1. Brake-specific total particulate matter (TPM) emissions with the relative contributions of the soluble organic fraction (SOF), solid, insoluble material (SOL), and vapor-phase organic material (XOC) emissions over the light-duty transient test cycle. [The 95% confidence interval (CI) is expressed as 2.5% confidence based on the *t*-distribution.]

TABLE 2. Particle Number Concentration (N), Number Mean Diameter (NMD), and Geometric Standard Deviation for Diluted Diesel Exhaust

test conditions			particle characteristics		
fuel	OCC	speed/load (rpm/% full load)	N^a (no./cm ³)	NMD ^b (μm)	σ_g^c
D2	no	2200/100	3.48×10^7	0.070	1.90
D2	no	1500/100	5.28×10^7	0.083	1.85
D2	no	1500/50	1.13×10^8	0.057	1.77
D2	yes	2200/100	1.19×10^8	0.041	2.00
D2	yes	1500/100	1.43×10^8	0.044	1.81
D2	yes	1500/50	5.64×10^8	0.094	2.12
biodiesel	no	2200/100	8.73×10^7	0.034	1.94
biodiesel	no	1500/100	4.44×10^7	0.064	1.77
biodiesel	no	1500/50	1.22×10^8	0.055	1.74
biodiesel	yes	2200/100	8.47×10^7	0.036	1.76
biodiesel	yes	1500/100	1.01×10^8	0.034	2.05
biodiesel	yes	1500/50	9.87×10^7	0.050	1.74

^a Accumulation mode number concentration. ^b Number mean diameter. ^c Geometric standard deviation.

conditions are presented in Table 2. Nuclei mode particles were evident in particle size number distributions for most of the tested conditions. Particles present in the nuclei mode have electrical mobility diameters (D_{em}) of approximately 0.002–0.03 μm. The nuclei mode particles are composed of sulfuric acid, water, and organic aerosols with solid carbonaceous particles (21, 29, 30). Analysis of nuclei mode particles was somewhat limited by the detectable particle size range of the EAA (~0.01–1.0 μm). Nuclei mode particles within the particle size range measured by the EAA contributed less than 2% to the total particle volume concentrations in the exhaust for the tested conditions.

Accumulation mode particles (D_{em} of approximately 0.02–1 μm) contributed the most to the particle volume concentrations for the tested conditions. Accumulation mode particles are composed primarily of nonvolatile, solid carbon (21, 29) and adsorbed organic material (30).

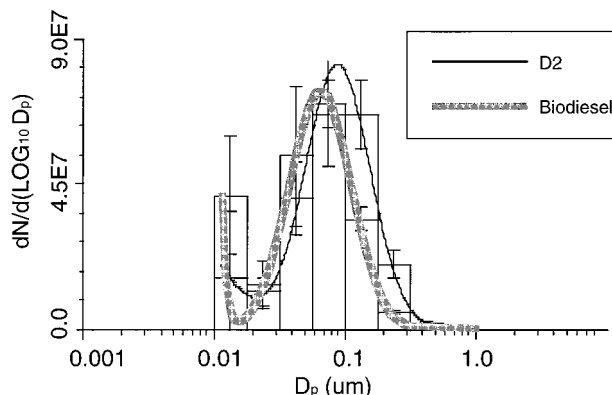


FIGURE 2. Particle size number distribution for D2 and biodiesel fuels at 100% load, 1500 rpm.

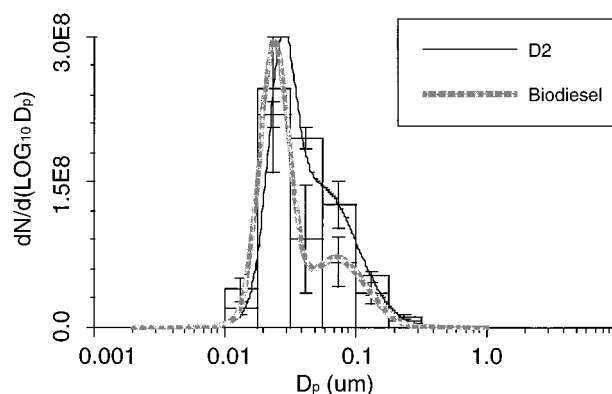


FIGURE 3. Particle size number distribution for the OCC with the D2 and biodiesel fuels at 100% load, 1500 rpm.

A shift was found in the particle size number distribution of nuclei mode particles toward larger particle sizes when the various fuels were tested with the OCC at the 100% load/1500 rpm condition (Figures 2 and 3). There was a general trend shifting the number mean diameter (NMD) of the

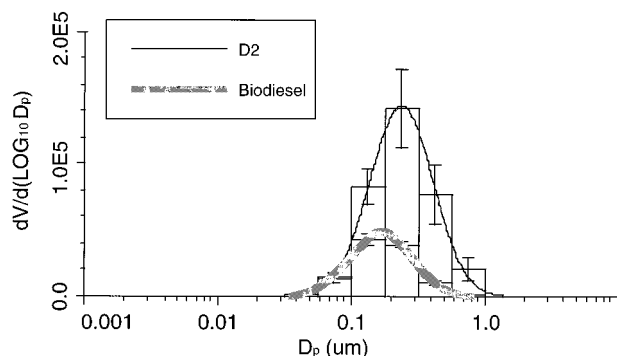


FIGURE 4. Particle size volume distribution for D2 and biodiesel fuels at 100% load, 1500 rpm.

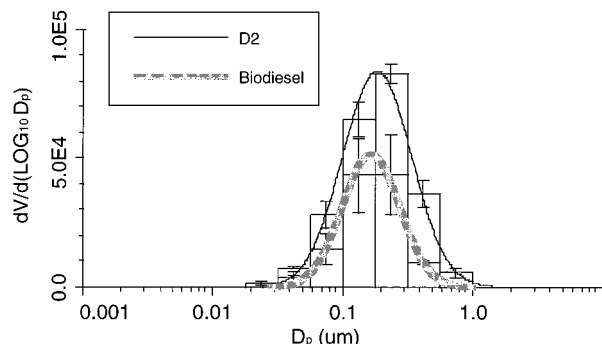


FIGURE 5. Particle size volume distribution for the OCC with the D2 and biodiesel fuels at 100% load, 1500 rpm.

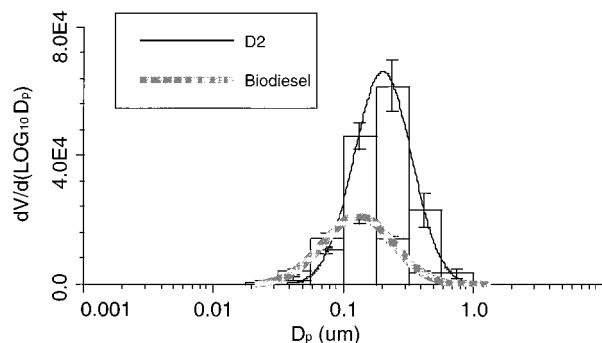


FIGURE 6. Particle size volume distribution for D2 and biodiesel fuels at 100% load, 2200 rpm.

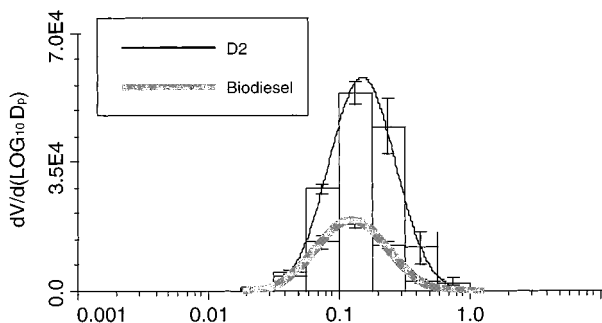


FIGURE 7. Particle size volume distribution for the OCC with the D2 and biodiesel fuels at 100% load, 2200 rpm.

accumulation mode to smaller particles when the OCC was used at several of the tested conditions with both fuels (Table 2). Use of the OCC reduced the total particle volume concentrations by 40–45% for all of the fuels at the 100% load/1500 rpm condition (Figures 4 and 5), but did not significantly affect total particle volume concentrations at 100% load/2200 rpm condition (Figures 6 and 7) or the 50% load/1500 rpm condition.

Particle volume concentrations for the biodiesel fuel were reduced by approximately 45–65% as compared to the D2 fuel at the same conditions of exhaust aftertreatment for the range of speed and load conditions evaluated. The observed reduction in particle volume concentration in the diluted exhaust during operation on the biodiesel fuel agreed fairly well with the reductions in SOL measured by gravimetric analysis. The reductions are also in good general agreement with reductions in nonvolatile, solid particulate matter that were found in other studies of biodiesel using this particular engine (1, 2). The particle size volume distributions of accumulation mode particles measured during operation on the biodiesel fuel exhibited a slight trend toward smaller particles relative to D2 fuel.

For fine particles with D_{em} of 0.2 μm , a high degree of particle deposition occurs within the pulmonary (gas exchange) region of the lungs (31). Use of the biodiesel fuel reduced particle volume concentrations (and thus, mass concentrations) by 50–70% in the 0.01–0.2 μm size range both with and without the OCC.

PAH and Nitro-PAH Levels. Brake-specific emissions ($\mu\text{g}/\text{kW}\cdot\text{h}$) of PAH and nitro-PAH associated with the particle and vapor phases are presented in Figures 8 and 9, respectively, for compounds present above the minimum detection limits. These data indicate that both particle-associated and vapor-phase PAH levels are generally reduced with biodiesel compared to the D2 fuel without the OCC, whether an OCC is used with biodiesel fuel. Levels of particle-associated PAH were usually lower (for both fuels) when the OCC is used as compared to PAH levels without the OCC. The finding of quantifiable PAH from combustion of the biodiesel fuel containing no aromatics indicates that these PAH compounds were either produced during the combustion process or were derived from the lubricating oil. Similar findings were reported in studies with a rapeseed methyl ester (RSME) fuel (7, 32).

Seven of the nine PAH compounds (FLU, PYR, BaA, CHR, BbF, BkF, and BaP) in the test matrix were found in quantifiable levels in all the SOF samples analyzed, i.e., the D2 and biodiesel samples obtained both with and without the OCC. There were a number of statistically significant differences between PAH levels between sample sets. Comparing the biodiesel fuel with the OCC to D2 fuel without it, all of the PAH levels were significantly lower ($0.01 < p < 0.02$), with the biodiesel fuel plus OCC producing PAH levels that were reduced by 85–90% (Figure 8). The use of the OCC with the D2 fuel was also associated with reduced levels (62–74%) of particle-associated PAH. Of the seven compounds for which all values were above detection limits, all except for PYR and FLU were significantly different ($0.02 < p < 0.05$) when these two groups were compared. When biodiesel fuel was used either with or without the OCC, there were relatively few differences in particle-associated PAH levels as compared to D2 fuel with the OCC.

Of the nitro-PAH compounds analyzed, only one compound (1-NP) was found in quantifiable levels in all SOF samples (Figure 8). It is important to note that the levels of 1-NP reported here may include any 1,3-DNP also present (as 1,3-DNP and 1-NP coelute in the method used for this study); thus, the amount of 1-NP reported may be artificially high by the amount of 1,3-DNP present, if any. Levels of 1-NP were reduced by 89% when the biodiesel fuel was used with the OCC as compared to the D2 fuel with no OCC ($0.01 < p < 0.02$). Although the use of the OCC with the D2 fuel also reduced 1-NP (by 66%), this difference was not significant at the $p \leq 0.05$ level. There were no significant differences when 1-NP levels with biodiesel fuel with or without the OCC were compared to the level of 1-NP with the D2 fuel and the OCC.

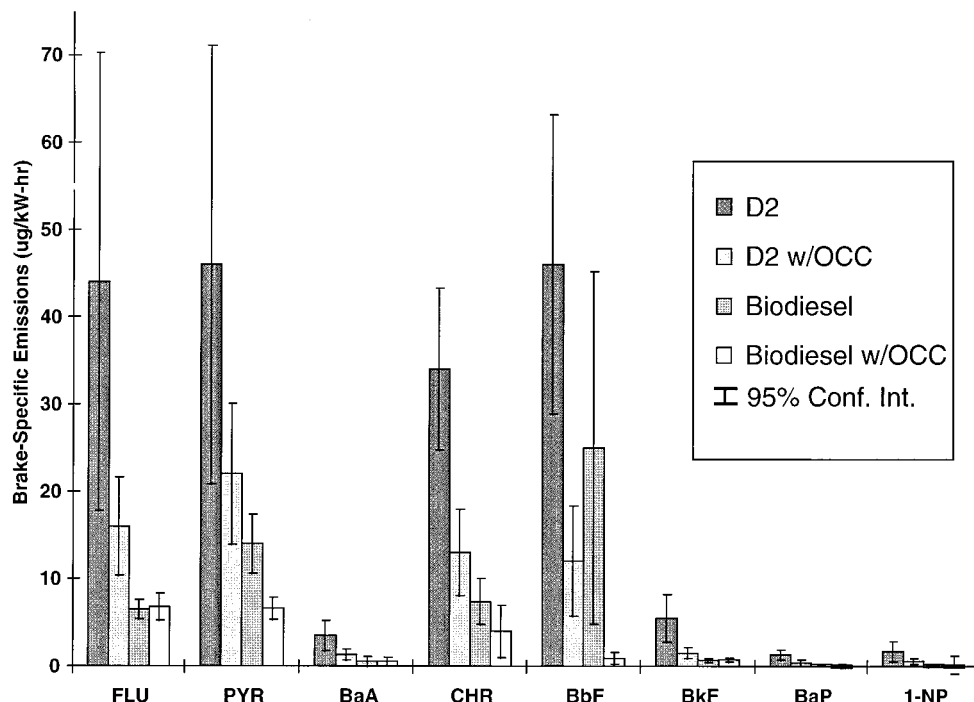


FIGURE 8. Brake-specific emissions of particle-associated (SOF) PAH and 1-nitropyrene compounds over the light-duty transient test cycle. [The 95% confidence interval (CI) is expressed as 2.5% confidence based on the *t*-distribution.]

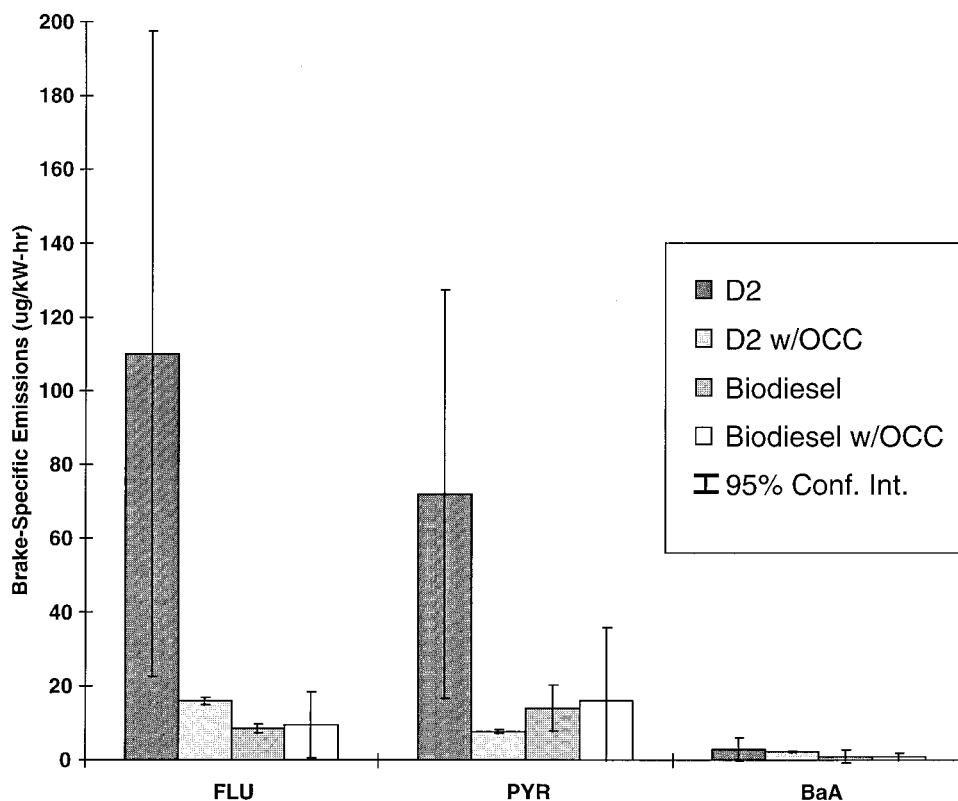


FIGURE 9. Brake-specific emissions of vapor-phase (XOC) PAH compounds over the light-duty transient test cycle. [The 95% confidence interval (CI) is expressed as 2.5% confidence based on the *t*-distribution.]

The statistical analysis of vapor-phase (XOC) PAH levels showed fewer significant differences between sample sets (Figure 9). There were only three PAH compounds found in quantifiable levels in all of the samples: FLU, PYR, and BaA. Significant differences (all within $0.02 < p < 0.05$) were found in FLU and PYR levels obtained with the D2 fuel or the

biodiesel fuel with the OCC, as compared to D2 without an OCC. When the OCC was used with the D2 fuel, vapor-phase FLU and PYR levels were reduced 85 and 89%, respectively. Reductions for these two compounds for biodiesel fuel plus the OCC as compared to the D2 fuel with no OCC were 91 and 78%, respectively. There were no

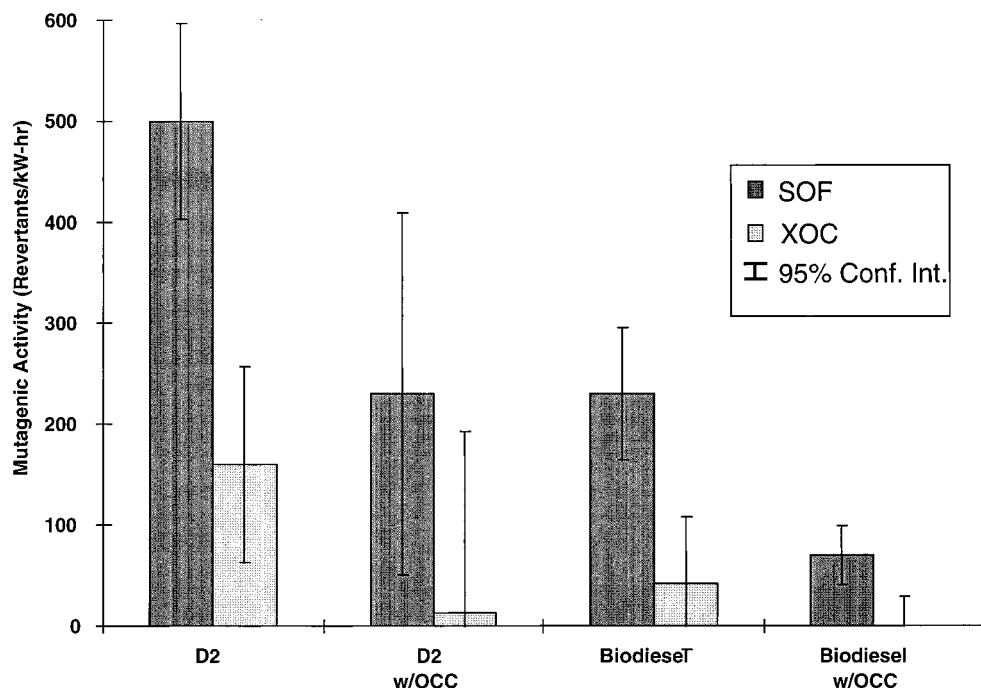


FIGURE 10. Brake-specific emissions of particle (SOF) and vapor phase (XOC) associated mutagenic activity over the light-duty transient test cycle. [The 95% confidence interval (CI) is expressed as 2.5% confidence based on the *t*-distribution.]

differences between measurable PAH levels in the XOC between fuels when the biodiesel fuel data with and without the OCC were compared to D2 fuel data with the OCC.

It is interesting to note the similarities in PAH and nitro-PAH levels obtained from use of the biodiesel fuel with or without the OCC. As the levels of SOF and XOC decreased with OCC use, the amount of PAH and nitro-PAH per unit mass of SOF or XOC actually increased with OCC use for the biodiesel fuel. This is in contrast to what was found with the D2 fuel, where the reductions in PAH levels, in particular, are similar to the reductions in SOF and XOC levels (Figure 1).

The results of this study indicate that there are lower levels of some of the commonly analyzed diesel exhaust PAH compounds when either biodiesel fuel or the OCC is used as compared to a low sulfur diesel fuel without a catalyst. The OCC likely oxidizes some of the PAH in the gas phase. The lower PAH levels seen with the biodiesel fuel are no doubt due to the fuel composition itself, as there are essentially no aromatics and no sulfur in the unburned fuel. In a recent study (33), a correlation was found between fuel PAH and PAH emissions, adding to the body of evidence that exhaust PAH originate mainly from unburned fuel. In another study of emissions using RSME, sulfur-free diesel, and low sulfur diesel fuels (7), PAH emissions were found to increase with the concentration of triaromatics in the fuel. Interestingly, the PAH exhaust levels found in that study seem to be correlated with fuel sulfur levels as well.

Mutagenic Activity Determinations. The results of analyses of the light-duty cycle particle-associated (TPM) and vapor-phase (XOC) samples are presented in Figure 10 on a brake-specific (revertants/kW-h) basis. The activity values on a mass basis (revertants/g) are presented in Table S-5 in the Supporting Information.

Use of the OCC resulted in 50% or greater reductions in both particle and vapor phase-associated mutagenic activity, with significant effects for all fuels for the particle-associated activity ($0.02 < p < 0.05$ for D2, $0.002 < 0.01$ for biodiesel). Greater reductions were detected with the biodiesel fuel than for the D2 fuel despite increased levels of SOF (Figure 10), as the SOF had lower levels of mutagenic activity (revertants/

TABLE 3. Effects of Nitro-Containing Compounds and Metabolic Activation on Mutagenic Activity, Light-Duty Engine Test Cycle^a

fuel	OCC	sample type	TA98NR ^b (% TA98-S9)	TA98DNP ^b (% TA98-S9)	TA98+S9 ^c (% TA98-S9)
D2	no	SOF	31	17	ND ^d
D2	yes	SOF	22	27	98
biodiesel	yes	SOF	IS ^d	IS	165
biodiesel	yes	XOC	ND	ND	NC ^d

^a Compared to activity with TA98-S9. ^b Nitroreductase-deficient tester strain, without S9 metabolic activation. ^c Tested with the S9 metabolic activation system. ^d ND, not determined for these samples; IS, insufficient sample mass available for testing; NC, not calculated, no response above background levels for samples with and without S9.

g; Table S-5). The TPM-associated activity for the biodiesel fuel with the OCC was also about 25% of that detected without the OCC. This difference was primarily due to effects of the OCC on reducing SOF levels. Assays for effects of PAH (requiring the S9 metabolic activation system) indicated little effect of these types of compounds (Table 3). On the basis of the results with other tester strains (Table 3), nitro-PAHs would make greater contributions to the observed mutagenic activity with the D2 fuel than with the biodiesel fuel. The results reported for 1-NP (Figure 8) appear to correlate well with these mutagenic activity results.

Use of the OCC with the D2 fuel also had a significant effect (92% reduction, $0.01 < p < 0.02$) on the XOC-associated mutagenic activity. This was due both to a reduction in activity on a mass basis (Table S-6) and a reduction in XOC emissions (Figure 1). No vapor phase-associated mutagenic activity was detected with the biodiesel fuel with the OCC, although low-level mutagenic activity was detected with the biodiesel fuel without the OCC (about 25% that of the D2 fuel without the OCC). Overall, biodiesel fuel used with an OCC would be expected to have similar or reduced levels of particle or vapor phase-associated mutagenic activity as compared to use of D2 fuel with an OCC.

Large reductions in SOF- and XOC-associated mutagenic activity levels were also found with use of the OCC use for

the heavy-duty cycle (Figure S-2), although the changes were not always found to be significant at the $p \leq 0.05$ level. Similar reductions (64–70%) in SOF-associated mutagenic activity with the OCC were found for both fuels, in large part due to the combined effects of the OCC and the low levels of SOF produced at this heavier load operating cycle. Unlike the results from the light-duty cycle, mutagenic activity was detected with all of the heavy-duty cycle vapor-phase (XOC) samples (Figure S-2). Similar changes in activity (about 90% reductions) were found with the D2 and biodiesel fuels when the OCC was used.

Particle (SOF)-associated mutagenic activity was also monitored in an earlier study comparing a RSME fuel and petroleum diesel fuels varying in parameters such as sulfur and aromatics contents (7). All tests were conducted without OCCs or any other types of aftertreatment devices. The results were generally similar to those found in this study with the soy methyl ester biodiesel fuel. The mutagenic activity with the RSME fuel was about half or more than that of the low sulfur, petroleum diesel fuels on a mass basis (revertants/g) but was equivalent or greater on a brake-specific basis (revertants/kW-h) due to the large increases in SOF with the RSME fuel. As with this study, at least some of the mutagenic activity observed with the RSME fuel could be attributed to nitro-PAH formed during or after the fuel combustion, based on responses with the nitroreductase-deficient tester strains.

The combination of reduced particle-associated PAH, 1-NP, and mutagenic activity levels, lower SOL emissions, and reduced emissions of particles with deep lung penetration would support the use of this biodiesel fuel for TPM control with diesel engines in confined spaces. The increased SOF emissions using biodiesel fuel will necessitate the use of an OCC for these applications. Further testing of this fuel in the field with an appropriate OCC is warranted, and it will be necessary to determine the effects of the fuel and the OCC on diesel particulate matter in the ambient air.

Acknowledgments

The authors thank Dr. B. T. McClure, David Purcell, and the technical staff of the USBM Diesel Technology Group for their assistance with project planning and the engine test-cell portion of this project. At MTU, the authors extend thanks to Barbara Heard, Department of Mechanical Engineering—Engineering Mechanics, who conducted portions of the chemical analysis laboratory work, and Greg Kleinheinz, Department of Biological Sciences, who assisted in conducting the mutagenicity analyses. Funding for this project was provided by the USBM, the National Biodiesel Board (Jefferson City, MO), the Agricultural Utilization Research Institute (Marshall, MN), and the U.S. Department of Agriculture—CSRS.

Supporting Information Available

Five tables giving the engine specifications, fatty acid distribution, HPLC method parameters, and the effects of fuels, OCC, and engine operating conditions and two figures showing the brake-specific emissions (9 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$21.00 for photocopy (\$23.00 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via

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Received for review March 12, 1997. Revised manuscript received January 5, 1998. Accepted February 9, 1998.

ES970224Q