Effects of Biodiesel, Biodiesel Blends, and a Synthetic Diesel on Emissions from Light Heavy-Duty Diesel Vehicles

THOMAS D. DURBIN,* JOHN R. COLLINS, JOSEPH M. NORBECK, AND MATTHEW R. SMITH

Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, California 92521

Over the past several years, there has been increased interest in reformulated and alternative diesel fuels to control emissions and provide energy independence. In the following study, a California diesel fuel was compared with neat biodiesel, an 80% California diesel/20% biodiesel blend, and a synthetic diesel fuel to examine the effects on emissions. Chassis dynamometer tests were performed on four light heavy-duty diesel trucks using each of the four fuels. The results of this study showed that biodiesel, the biodiesel blends, and the synthetic diesel produced generally lower THC and CO emissions than California diesel. NO_x emissions were comparable over most of the fuel/vehicle combinations, with slightly higher NO_x emissions found for the two noncatalyst vehicles on 100% biodiesel. Particulate emissions were slightly higher for two test vehicles and significantly higher for a third test vehicle on the biodiesel fuels. Chemical analyses showed elemental and organic carbon to be the primary constituents of the diesel particulate, accounting for 73−80% of the total mass for the four vehicles. Neat biodiesel had the highest organic carbon fractions for each of the test vehicles. PAH emissions for all fuel combinations were relatively low, probably due to the low fuel PAH levels.

Background

Over the past several years, there has been considerable effort to develop reformulated and alternative diesel fuels in California and throughout the United States. One of the primary motives for this effort has been to reduce diesel emissions. Another important objective in developing alternative diesel fuels is to promote independence from imported petroleum sources. Two fuels that have received attention recently as potential alternative fuels for diesel engines are biodiesel and synthetic diesel fuels such as Fischer−Tropsch (F−T) diesel. These fuels offer the important advantage that they can be produced domestically and can be derived from renewable sources. These fuels also have properties similar to those of traditional diesel such that they can be substituted for diesel fuel with little or no engine modification. Under the Energy Policy Act (EPACT), the U.S. Department of Energy (DOE) has established several programs to develop and evaluate possible alternatives to conventional diesel blends, such as biodiesel and F−T and other synthetic diesel fuels. Also, Congress has passed legislation allowing Federal and State fleet managers to meet the EPACT's alternative fuel vehicle (AFV) acquisition requirements by using biodiesel added to conventional diesel at blends of 20% and higher.

Given the possibility of increased use of biodiesel or synthetic diesel fuels, it is important to quantify any potential emissions benefits or liabilities of these fuels. To date, several studies have shown that biodiesel and F−T synthetic diesels can provide emissions reductions relative to standard petroleum diesel (*1*−*6*). Much of this work has focused on comparisons with Federal diesel rather than California reformulated diesel (RFD). More recently, several studies have also made emissions comparisons between both biodiesel and F−T diesel and California diesel. Recent work on a 1994 7.3-L Navistar diesel engine by researchers at West Virginia University (WVU) showed reductions in total hydrocarbons (THC), carbon monoxide (CO), and nitrogen oxides (NO_x) for an F−T diesel in comparison with a California diesel (*4*). Comparisons with other biodiesel data presented in this study also indicate that biodiesel blends could provide reductions in particulate matter (PM), THC, and CO in comparison with the California RFD, with some increases in NO_x. Starr conducted research on a Detroit diesel series 60 engine and found a 20% biodiesel blend with Federal no. 2 diesel to have slightly lower PM but higher NO_x emissions than a California low-aromatic diesel fuel (*7*). Similar results also were found by other researchers comparing biodiesel blends with California and Federal diesel for engine tests and chassis dynamometer tests on a diesel bus (*8*). Researchers at the National Renewable Energy Laboratory (NREL) and WVU showed reductions in THC, CO, NO_x, and PM emissions for an F−T diesel in comparison with a California RFD using chassis dynamometer tests on diesel trucks (*9*). Schaberg et al. also showed emission reductions for a Sasol's Slurry Phase Distillate (SSPD) diesel and SSPD blends as compared with California RFD using a Detroit diesel series 60 engine (*10*).

The present program was designed to further investigate the effects of alternative diesel fuels on exhaust emission rates in comparison with California diesel. In this project, a representative California diesel was compared with a 100% biodiesel, an 80/20 (California diesel/biodiesel) blend, and a synthetic diesel fuel for emissions performance. Chassis dynamometer tests were performed on four light heavy-duty diesel vehicles using each of the four fuels. For these tests, emissions measurements were collected for THC, CO, NO_x, and PM. Additional measurements were also performed to provide chemical characterization of the exhaust PM including elemental and organic carbon; ions, trace elements, and metals; and semivolatile and particulate phase polynuclear aromatic hydrocarbons (PAHs).

Experimental Procedures

Vehicle Recruitment. Four light heavy-duty diesel vehicles were recruited for vehicle testing. These vehicles were chosen to represent major manufacturers of light heavy-duty diesels (Ford and Dodge) and two catalyst classes (noncatalyst and oxidation catalyst). The test vehicles and their characteristics are listed in Table 1.

Test Fuels. Each vehicle was tested on a series of four test fuels. The test fuels were as follows:

(a) A 10% aromatic diesel fuel representative of the general diesel reference fuel for California (*11*). Similar fuels are used

* Corresponding author phone: (909)781-5794; fax: (909)781-5790; e-mail: durbin@cert.ucr.edu.

10.1021/es990543c CCC: $19.00 © 2000 American Chemical Society
Published on Web 12/21/1999

TABLE 1. Vehicle Descriptions for Test Fleet[a]

model year	make	model	odometer (mi)	GVW (lb)	engine size (L)	fuel, air system	catalyst
1996	Dodge	Ram 2500 PU	9 838	8800	5.9	DFI, turbo	OC
1995	Ford	F-350 PU	33 217	9000	7.3	DFI, turbo	OC
1990	Dodge	Ram 250 PU	115 734	8510	5.9	DFI, turbo	none
1988	Ford	F-250 PU	76 469	8800	7.3	IDI, non-turbo	none

[a] DFI, direct fuel injection; IDI, indirect fuel injection; OC, oxidation catalyst.

TABLE 2. Selected Fuel Properties[a]

	Cal. Ref.	biodiesel	80/20 blend	synthetic diesel
API gravity	38.7	28.2	36.0	45.2
aromatics, vol %	9.5	NA[b]	NA	10.1
PAHs	0.17 wt %	NA	NA	<0.1 vol %
Cetane Index	49.0		NA	51.4
cetane number		53.0	NA	
distillation				
T50, °F	479	NA	510	
T90, °F	550		641	610
free glycerin, mass %	NA	0.006	NA	NA
total glycerin, mass %	NA	0.147	NA	NA
sulfur, ppm	330	40	280	<10

[a] A number of the standard tests could not be performed on all fuels. Biodiesel is approximately a single boiling point compound, and thus distillation tests are not applicable. The calculated Cetane Index, which is based on diesel distillation properties, is also not applicable. Biodiesel also includes nonaromatic compounds that interfere with the standard method for measuring aromatics. Biodiesel is expected to have negligible levels of aromatics however. The glycerin test is applicable only to biodiesel. [b] NA, not available.

by California refiners for comparative testing to certify alternative diesel fuel blends. The fuel was obtained from Phillips Chemical Co. in Borger, TX, and as such was produced from Texas crude sources, as opposed to straight-run California diesel fuel as specified in the California regulations. Overall, this fuel has a lower aromatic and PAH content than average in-use California diesel, which averages 20% and 2.1%, respectively, for aromatics and PAHs (*12*). The fuel sulfur content is also higher than that of typical California in-use diesel, which averages between 90 and 160 ppmw (*12*, *13*).

(b) A 100% biodiesel fuel, Envirodiesel, obtained from Taurus Lubricants Corporation in Lowell, MA.

(c) A blend of 80% RFD and 20% biodiesel, splash-blended from the two fuels above.

(d) A synthetic diesel fuel obtained from Mossgas Ltd. in Mossel Bay, South Africa. This fuel was produced using the Mossgas conversion of olefins to distillate (COD) process. This process uses the light olefin byproducts from a F−T conversion but is not a direct F−T conversion. The olefin byproducts include propene, butene, pentene, and hexene. These light olefins are catalytically oligomerized over a zeolite catalyst to form gasoline and a distillate, which is then hydrotreated. This fuel was also used in a study by researchers from NREL and WVU, where buses from the Port Authority of Allegheny County, Pennsylvania, were tested (*6*).

Specifications for each of the test fuels are provided in Table 2.

Protocol for Vehicle Testing. All vehicles were tested over the Federal Test Procedure (FTP) to obtain mass emission rates for total PM, THC, CO, and NO_x. THC measurements were collected using a heated sample line as specified in the Code of Federal Regulations (CFR) for diesel vehicles (§86.110−94). Vehicles were preconditioned prior to the first test on any new fuel over two back-to-back iterations of the LA4 driving schedule followed by an overnight soak at a temperature of approximately 72 °F. Each vehicle was tested at least twice on each of the four test fuels. In some cases, additional tests were conducted to verify the observed emissions trends. All tests were conducted in the University of California at Riverside, Bourns College of Engineering—Center for Environmental Research and Technology (CE-CERT) Vehicle Emission Research Laboratory (VERL) equipped with a Burke E. Porter 48-in. single-roll electric dynamometer and a 12-in. diameter dilution tunnel for diesel vehicles. A CVS flow rate of 856 standard feet per cubic meter was used for testing, resulting in dilution ratios ranging from 16 to 38 depending on the vehicle and the test phase.

To meet the program objectives regarding fuel effects on exhaust composition, reactivity, and toxicity, additional sampling was conducted during a subset of FTP tests. Particle samples were collected for analysis of elemental and organic carbon, trace elements and metals, ions, particulate and semivolatile PAHs, and particle size distribution. Gas-phase samples were collected for analysis of detailed hydrocarbon species and carbonyls. The detailed hydrocarbon speciation, carbonyl, and size distribution results are presented elsewhere (*14*). Table 3 shows the type of analyses conducted for each fuel/vehicle combination.

Particulate Sampling and Analysis. Particulate samples were collected using a 12-in. diameter dilution tunnel fitted with three sampling probes. Samples for total particulate mass determinations were collected for each phase using 47 mm 2.0 μm Gelman Teflon membrane filters. These filters were weighed before and after sampling to determine the collected mass using an ATI Orion ultra-microbalance. Prior to each weighing, filters were equilibrated in a constant temperature and humidity environmental chamber.

Samples for chemical analysis were collected on Teflon membrane filters and prefired Pallflex 2500 QAT-UP quartz fiber filters. Samples for chemical analysis were collected cumulatively over the entire FTP. The Teflon membrane filters were utilized for chemical analysis of metals and other trace elements and sulfate, nitrate, and ammonium ions. Metals and other trace elements were analyzed using X-ray fluorescence (XRF). Filters were extracted in a 60:40 mixture of isopropyl alcohol and distilled, deionized water for nitrate and sulfate analyses using ion chromatography. A separate extraction with distilled, deionized water was used for analysis of ammonium ions. The quartz fiber filters were used for elemental and organic carbon analyses using the Thermal Optical Reflectance (TOR) method (*15*). All analyses were conducted by the Desert Research Institute (DRI), Reno, NV.

For the 1988 Ford, the quartz filters were backed up using a vapor-phase trap for collection of PAHs consisting of XAD-4 resin (polystyrene, divinylbenzene polymer) sandwiched between two polyurethane foam (PUF) plugs. The PUF/XAD vapor trap and the quartz fiber filter for each test were extracted separately for PAH analysis to allow separation of semivolatile (PUF/XAD) and particulate PAHs (quartz filter). The PUF plugs were Soxhlet extracted with 10% diethyl ether in hexane, while the filters and XAD resin were microwave extracted with dichloromethane. The PUF and XAD extracts were then combined into one semivolatile extract. The semivolatile extract and the particulate extract from the quartz

TABLE 3. Sample Collection and Analysis Matrix

vehicle	fuel	FTP 3-phase: PM, gases	FTP 3-phase: C_1-C_4, C_4-C_{12}	FTP 3-phase: C_8-C_{20}	FTP 3-phase: carbonyl	cumulative over 3 phases: ions, XRF EC, OC	cumulative over 3 phases: PAH
96 Dodge	Cal. Ref.	√				√	
96 Dodge	synthetic	√				√	
96 Dodge	80/20 blend	√				√	
96 Dodge	100% BioD	√				√	
95 Ford	Cal. Ref.	√				√	
95 Ford	synthetic	√				√	
95 Ford	80/20 blend	√				√	
95 Ford	100% BioD	√				√	
90 Dodge	Cal. Ref.	√	√		√	√	
90 Dodge	synthetic	√	√		√	√	
90 Dodge	80/20 blend	√	√		√	√	
90 Dodge	100% BioD	√	√		√	√	
88 Ford	Cal. Ref.	√	√	√	√	√	√
88 Ford	synthetic	√	√	√	√	√	√
88 Ford	80/20 blend	√	√	√	√	√	√
88 Ford	100% BioD	√	√	√	√	√	√

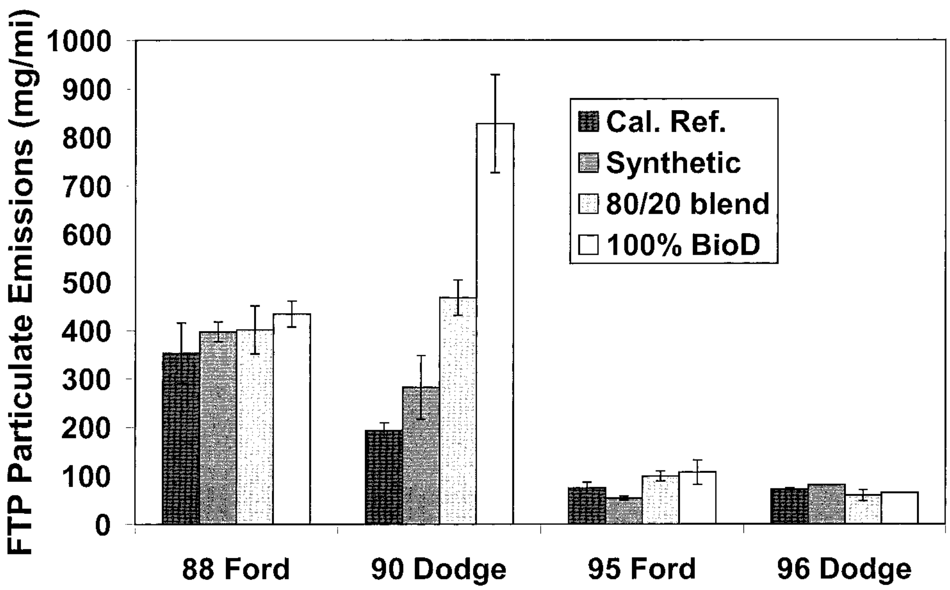

FIGURE 1. FTP particulate emissions.

filter were then reduced to a volume of ~1 mL by rotary evaporation and analyzed by GC/MS in selected ion monitoring mode. PAH extractions and analyses were conducted by DRI.

Emissions Test Results

Mass Emission Results. The FTP-weighted PM and gaseous mass emission rates for each vehicle/fuel combination are presented in Figures 1−4. These data represent the average of all tests conducted for each vehicle/fuel combination. The error bars in Figures 1−4 were calculated from the replicate tests for each vehicle/fuel combination as 2 times the standard deviation of the mean.

The effect of fuel on PM emission rates varied significantly from vehicle to vehicle. PM emissions for the 1996 Dodge Ram were comparable for the different fuel types. For the 1995 Ford F350, the 100% biodiesel and biodiesel blends produced slightly higher emissions than the California diesel while the synthetic diesel produced the lowest emissions. For the 1988 Ford F250, the biodiesel fuels and the synthetic diesel all produced higher PM emissions than the California diesel. The most dramatic effect on PM emissions on both an absolute and a relative scale were observed for the 1990 Dodge Ram. For this vehicle, PM emissions for all of the alternative fuel blends were significantly higher than those of the California diesel, with dramatic increases observed for the 100% biodiesel and the 20% biodiesel blend. It should be noted that the 1990 Dodge was brought back and retested over the test sequence on the California diesel, 100% biodiesel, and 20% biodiesel blend to verify the trends observed in the PM emissions. Similar results were observed over both testing periods and for replicate tests, indicating that the trends were very repeatable. This trend for the 1990 Dodge may, however, indicate that this vehicle is anomalous and not representative of the overall light heavy-duty vehicle fleet.

THC emissions were generally lower for the 100% biodiesel, the 20% biodiesel blend, and the synthetic diesel as compared with the California diesel with the exception of the 20% biodiesel blend for the 1990 Dodge Ram. The 100% biodiesel fuel had the lowest THC emissions, with THC emissions considerably lower than those for the other fuels for all vehicles but the 1988 Ford F250. THC emissions for the 1988 Ford F250 were comparable for the different fuels.

CO emissions were significantly lower for the all the alternative blends as compared with the California diesel for the 1995 Ford F350. Lower CO emissions were also observed for the alternative fuels for the 1988 Ford F250 and the 1996 Dodge Ram, although these reductions were not as significant. For the 1990 Dodge Ram, CO emissions were slightly higher on the biodiesel fuels and blends and slightly lower

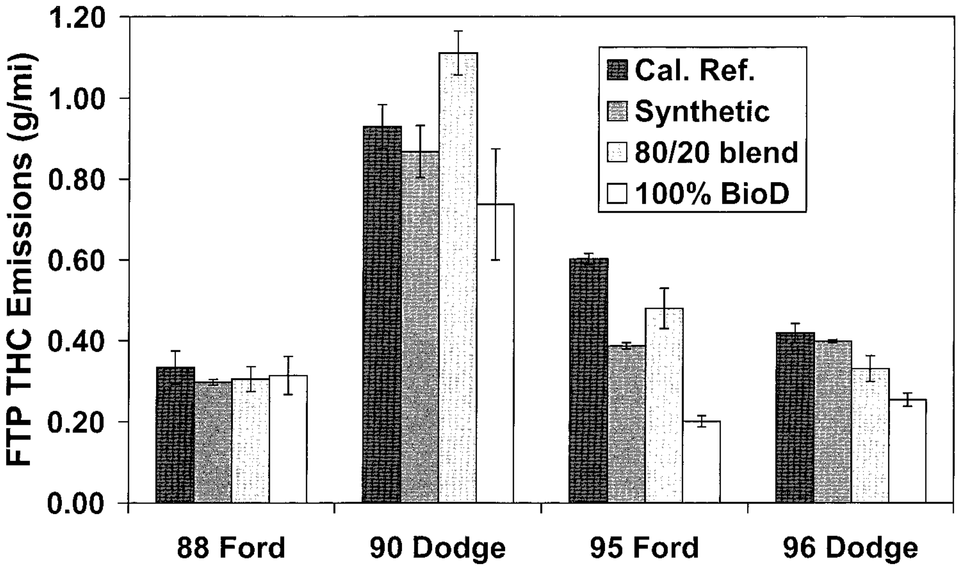

FIGURE 2. FTP THC emissions.

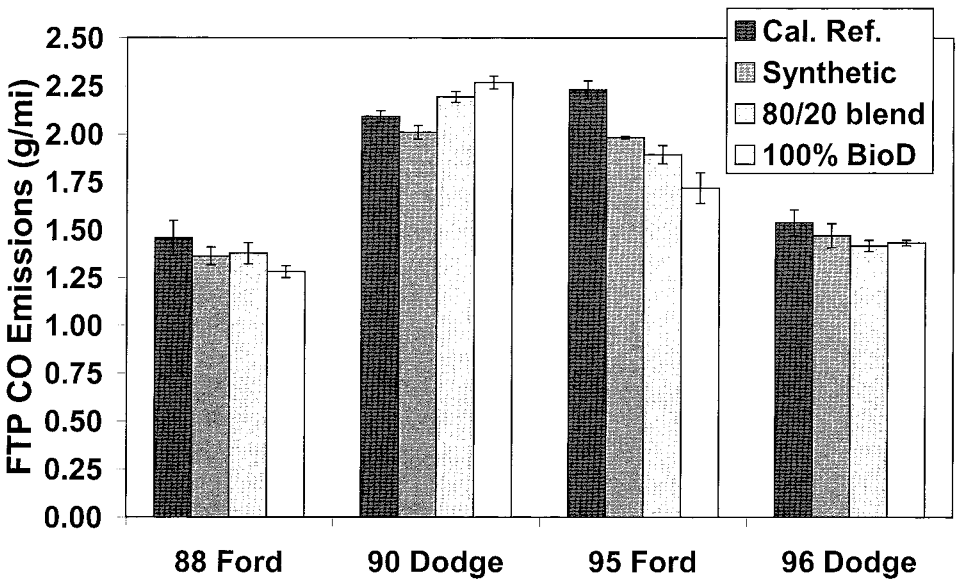

FIGURE 3. FTP CO emissions.

on the synthetic diesel as compared with the California diesel. The slightly higher CO emissions for the 1990 Dodge Ram on the biodiesel blends could be related to the higher particulate emissions discussed above, although the magnitude of the increase in CO emissions is considerably less than that for the particulate emissions.

NO_x emissions for the alternative fuels and the California diesel were comparable for the two newest vehicles, the 1995 Ford and 1996 Dodge. Slightly higher NO_x emissions were found for the 1990 Dodge and 1988 Ford on 100% biodiesel, while NO_x emissions were slightly lower using the synthetic diesel fuels on the 1990 Dodge.

Chemical Analysis Results

Chemical Species. Chemical analyses were performed on one test for each vehicle/fuel combination to determine emissions for elemental and organic carbon, ions, and trace elements. The mass emissions results for the most important species are presented in Table 4. Mass emission rates that are at least twice the analytical uncertainty are shown in bold.

Table 5 gives elemental carbon and organic carbon as a percentage of total carbon and the fractions of total carbon, inorganic compounds, and PAH as percentage of total particulate mass. The results show that elemental and organic carbon are the primary constituents for diesel particulate, consistent with the observations of other researchers (*16, 17*). Total carbon accounted for an average of 73.3−79.9% of the total mass for the four vehicles. The elemental and organic fractions varied from vehicle to vehicle and for the different fuel types. Biodiesel had the highest fraction of organic carbon for each of the test vehicles. The 80/20 blend had the next-highest organic fraction for two of the four test vehicles, but this trend was not consistent over the other two test vehicles. The 1988 Ford F250 had the highest organic fractions for each of the test fuels. Inorganic species including ions and elements represented a smaller portion of the composite total, with averages ranging from 0.7 to 1.6% of the total particulate for different vehicles. Nearly all inorganic species had emission rates of less than 1 mg/mi for each test vehicle, with the only species with average emission rates of greater than 0.1 mg/mi for each of the test vehicles being SO_4^{2-}, NH_4^+, Si, S, Ca, and Zn. The most significant vehicle differences are the higher ion and element emissions for the 1990 Dodge Ram and the 1988 Ford F250, consistent with their higher overall higher PM emission rates.

TABLE 4. PM Emission Rates for Chemical Species (mg/mi)[a]

vehicle	96 Dodge				95 Ford				90 Dodge				88 Ford			
fuel	Cal. Ref.	synthetic	80/20 blend	100% Bio	Cal. Ref.	synthetic	80/20 blend	100% Bio	Cal. Ref.	synthetic	80/20 blend	100% Bio	Cal. Ref.	synthetic	80/20 blend	100% Bio
FTP PM	**74.0**	**79.7**	**52.6**	**63.6**	**76.9**	**50.0**	**107.8**	**106.3**	**180.9**	**314.2**	**455.7**	**872.0**	**396.8**	**385.8**	**464.3**	**451.2**
organic C	**28.0**	**38.7**	**22.0**	**32.0**	**39.5**	**26.5**	**56.8**	**64.6**	**93.0**	**147.5**	**268.0**	**436.9**	**296.2**	**291.1**	**320.1**	**363.1**
elemental C	**29.0**	**31.8**	**23.3**	**18.6**	**24.2**	**24.2**	**26.6**	**18.5**	**84.1**	**112.6**	**103.8**	**56.6**	**52.9**	**44.1**	**54.7**	**34.9**
total C	**56.9**	**70.5**	**45.3**	**50.5**	**63.7**	**50.6**	**83.4**	**83.1**	**177.1**	**260.2**	**371.8**	**493.5**	**349.1**	**335.3**	**374.8**	**398.0**
NO_3^-	0.00	0.00	**0.15**	**0.14**	0.00	**0.27**	0.08	0.00	**0.42**	**0.17**	**0.26**	0.00	**0.16**	**0.43**	**0.16**	**0.69**
SO_4^{2-}	**0.41**	**0.22**	**0.38**	**0.42**	**0.45**	**0.17**	**0.53**	**0.28**	**1.18**	**0.20**	**1.43**	0.03	**0.85**	**0.14**	**0.85**	**0.39**
NH_4^+	**0.13**	0.09	0.08	**0.11**	**0.13**	0.06	**0.14**	**0.10**	**0.54**	**0.14**	**0.63**	**0.22**	**0.50**	**0.25**	**0.45**	**0.24**
Na	−0.06	0.00	−0.06	−0.01	−0.06	−0.06	−0.06	−0.06	0.16	−0.01	−0.06	−0.06	−0.06	−0.06	−0.06	−0.06
Mg	0.00	−0.01	−0.02	−0.03	0.00	0.00	**0.03**	**0.04**	0.03	−0.01	−0.04	−0.04	−0.04	−0.05	−0.01	0.01
Al	**0.03**	0.01	**0.03**	0.00	0.01	0.01	−0.01	0.00	**0.05**	0.00	0.01	0.00	0.00	−0.01	0.01	0.03
Si	**0.28**	**0.10**	**0.22**	**0.20**	**0.17**	**0.10**	**0.16**	**0.09**	**0.44**	**0.30**	**0.35**	**0.31**	**0.17**	**0.14**	**0.18**	**0.12**
P	**0.03**	**0.02**	**0.04**	**0.07**	**0.05**	**0.03**	**0.04**	**0.15**	**0.05**	**0.03**	**0.05**	**0.10**	**0.37**	**0.29**	**0.40**	**0.50**
S	**0.30**	**0.18**	**0.23**	**0.25**	**0.27**	**0.10**	**0.26**	**0.14**	**0.75**	**0.23**	**0.83**	**0.54**	**1.27**	**0.54**	**1.26**	**0.73**
Cl	**0.03**	**0.02**	**0.09**	**0.12**	**0.04**	**0.02**	**0.06**	**0.08**	0.03	**0.02**	**0.05**	**0.17**	**0.08**	**0.09**	**0.05**	**0.12**
K	0.00	0.00	0.01	**0.04**	0.01	−0.01	0.00	**0.02**	0.00	0.00	0.00	**0.06**	−0.01	−0.01	0.01	**0.18**
Ca	**0.16**	**0.12**	**0.11**	**0.14**	**0.14**	**0.07**	**0.14**	**0.15**	**0.13**	**0.09**	**0.11**	**0.15**	**0.96**	**0.74**	**0.90**	**1.04**
Fe	**0.02**	**0.05**	**0.02**	**0.04**	**0.01**	**0.01**	**0.02**	**0.05**	**0.01**	**0.02**	**0.03**	**0.10**	**0.05**	**0.04**	**0.06**	**0.27**
Cu	0.00	0.00	**0.01**	**0.01**	0.00	0.00	**0.01**	**0.02**	0.00	0.00	**0.00**	**0.01**	**0.01**	0.00	**0.01**	**0.02**
Zn	**0.12**	**0.10**	**0.20**	**0.33**	**0.12**	**0.07**	**0.16**	**0.43**	**0.09**	**0.08**	**0.15**	**0.32**	**0.84**	**0.61**	**0.80**	**1.08**
Br	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.00**	0.00	0.00	0.00	0.00
Pb	**0.01**	0.00	0.00	**0.01**	0.01	0.00	**0.02**	**0.11**	0.00	0.00	0.00	**0.02**	**0.02**	0.00	0.01	**0.04**

[a] FTP PM emission rates are cumulative for the test. The mass emission rates are tunnel blank corrected and, as a result, include some negative values. Mass emission rates that are at least twice the analytical uncertainty are shown in bold.

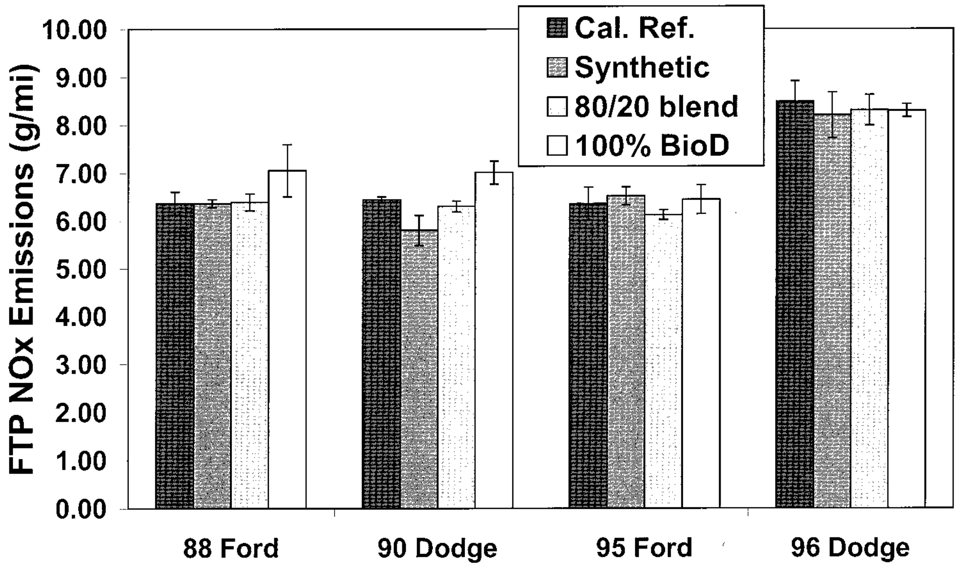

FIGURE 4. FTP NO_x emissions.

TABLE 5. Particle Mass Fractions

vehicle	fuel	FTP PM (mg/mi)	OC % of TC[a]	EC % of TC	TC % of PM	elements + ions % of PM	total PAH % of PM[b]
96 Dodge	Cal. Ref.	74.0	49.1	50.9	67.7	1.5	
96 Dodge	synthetic	79.7	54.9	45.1	87.1	0.9	
96 Dodge	80/20	52.6	48.5	51.5	73.0	2.0	
96 Dodge	100% Bio	63.6	63.3	36.8	65.7	2.1	
	average	67.5	54.0	46.1	73.4	1.6	
95 Ford	Cal. Ref.	76.9	62.0	38.0	73.4	1.4	
95 Ford	synthetic	50.0	52.2	47.8	85.0	1.2	
95 Ford	80/20	107.8	68.1	31.9	74.0	1.2	
95 Ford	100% Bio	106.3	77.7	22.3	76.4	1.3	
	average	85.3	65.0	35.0	77.2	1.3	
90 Dodge	Cal. Ref.	180.9	52.5	47.5	78.5	1.6	
90 Dodge	synthetic	314.2	56.7	43.3	87.4	0.4	
90 Dodge	80/20	455.7	72.1	27.9	78.4	0.7	
90 Dodge	100% Bio	872.0	88.5	11.5	49.0	0.2	
	average	455.7	67.5	32.6	73.3	0.7	
88 Ford	Cal. Ref.	396.8	84.8	15.2	75.1	1.1	0.3
88 Ford	synthetic	385.8	86.8	13.2	86.5	0.8	0.3
88 Ford	80/20	464.3	85.4	14.6	80.7	1.0	0.3
88 Ford	100% Bio	451.2	91.2	8.8	77.2	1.0	0.2
	average	424.5	87.1	13.0	79.9	1.0	0.3

[a] TC, total carbon. [b] Semi-volatile and particulate PAH.

Regarding fuel differences, there is a trend of higher sulfate and sulfur emissions for the California diesel and 80/20 blend fuels. This is consistent with the higher fuel sulfur levels in the California diesel as compared with the synthetic diesel and 100% biodiesel. Overall, the sulfate and sulfur emissions for the California diesel are similar to those observed in previous studies of light and light heavy-duty diesels with similar fuel sulfur levels (*18*). It should also be noted that the particulate sulfate and sulfur emissions represent a relatively small fraction of the total particulate mass for all fuel/vehicle combinations. The California diesel and 80/20 blend also have higher NH_4^+ emissions than the synthetic diesel and 100% biodiesel for the two noncatalyst vehicles. The neat biodiesel is the only fuel that emits K, which was found in the exhaust of all four vehicles. K is frequently used as a tracer for vegetative burning, which is consistent with the vegetative source of the biodiesel. The neat biodiesel also generally has higher emissions of Zn, Fe, Cl, P, and Pb than the other fuels, although the trends are not always strong.

PAH Emission Results. PAH emissions were collected for the 1988 Ford F250 for each fuel type. Total semivolatile PAH emissions were relatively low and comparable for all of the test fuels. Semivolatile PAHs averaged 0.91 mg/mi for the four tests with a range from 0.82 to 1.02 mg/mi. This represents 0.2−0.3% of the total particulate mass. The distribution of PAHs consists primarily of naphthalene, 2-methylnaphthalene and 1-methylnaphthalene with a profile similar to that expected for semivolatile PAHs from vehicles (*19*). The semivolatile PAH distributions showed only minor differences between different fuels, such as lower emissions of methylbiphenyls for the biodiesel as compared with the other fuels. Additional samples and vehicles would be required to determine whether these minor differences are characteristic of the fuel.

The contribution from the particulate PAHs was near background levels for nearly all components despite the relatively substantial overall particulate levels. Particle PAH totals ranged from 0.17 to 0.22 mg/mi for the different fuels. Among the particle PAHs, the single largest component was pyrene. The remaining measurable compounds consisted primarily of various methyl, dimethyl, and unsubstituted phenanthrenes. The overall low levels of both semivolatile and particulate PAHs can probably be attributed to the low levels of PAHs in all four of the test fuels. Since most commercially available diesel fuels in California have higher levels of PAHs than the diesel used in this study, it is suggested that additional tests be conducted on California diesel blends with higher PAH contents.

Acknowledgments

The authors acknowledge the contribution and support of the following individuals during the course of this project. Dave Martis, Joesph Calhoun, and Ross Rettig of the Vehicle Emissions Research Laboratory (CE-CERT) performed the emissions testing on the vehicles. Kathy Cocker (CE-CERT) performed all of the particulate collection and mass analysis. Clifton Frazier, Barbara Zielinska, Barbara Hinsvark, and Ewa Uberna of the Desert Research Institute performed the particulate chemical analyses. We thank the South Coast Air Quality Management District for its financial support of this project.

Literature Cited

(1) Sharp, C. A. *Characterization of Biodiesel Exhaust Emissions for EPA 211(b)*; Final Report for the National Biodiesel Board, by the Southwest Research Institute, San Antonio, TX; 1998.

(2) McDonald, J. F.; Purcell, D. L.; McClure, B. T.; Kittelson, D. B. *Emissions Characteristics of Soy Methyl Ester Fuels in an IDI Compression Ignition Engine*; SAE Technical Paper 950400; SAE: Warrendale, PA, 1995.
(3) Graboski, M. S.; Ross, J. D.; McCormick, R. L. *Transient Emissions from No. 2 Diesel and Biodiesel Blends in a DDC Series 60 Engine*; SAE Technical Paper 961166; SAE: Warrendale, PA, 1996.
(4) Clark, N. N.; Atkinson, C. M.; Thompson, G. J.; Nine, R. D. *Transient Emissions Comparisons of Alternative Compression Ignition Fuels*; SAE Technical Paper 1999-01-1117; SAE: Warrendale, PA, 1999.
(5) Smith, J. A.; Endicott, D. L.; Graze, R. R. *Biodiesel Engine Performance and Emissions Testing*; Final Report to the National Biodiesel Board, by Caterpillar; May 1998.
(6) Norton, P.; Vertin, K.; Clark, N. N.; Lyons, D. W.; Gautam, M.; Goguen, S.; Eberhardt, J. *Emissions from Buses with DDC 6V92 Engines using Synthetic Diesel Fuel*; SAE Technical Paper 1999-01-1512; SAE: Warrendale, PA, 1999.
(7) Starr, M. E. *Influence on Transient Emissions at Various Injection Timings, using Cetane Improvers, Biodiesel, and Low Aromatic Fuels*; SAE Technical Paper 972904; SAE: Warrendale, PA, 1997.
(8) Spataru, A.; Romig, C. *Emissions and Engine Performance of Soya and Canola Methyl Esters Blended with ARB #2 Diesel Fuels*; Final Report to Saskatchewan Canola Development Commission, Saskatoon, Saskatchewan, Canada, by The ADEPT Group, Inc., Los Angeles, CA; 1995.
(9) Norton, P.; Vertin, K.; Bailey, B.; Clark, N. N.; Lyons, D. W.; Goguen, S.; Eberhardt, J. *Emissions from Trucks using Fischer–Tropsch Diesel Fuel*; SAE Technical Paper 982526; SAE: Warrendale, PA, 1998.
(10) Schaberg, P.; Myburgh, I. S.; Botha, J. J.; Roets, P. N.; Viljoen, C. L.; Dancuart, L. P.; Starr, M. E. *Diesel Exhaust Emission using Sasol Slurry Phase Distillate Fuels*; SAE Technical Paper 972898; SAE: Warrendale, PA, 1997.
(11) California Code of Regulations. *The California Diesel Fuel Regulations*, Title 13, Sections 2281 and 2282.
(12) Simeroth, D. *Overview of California Diesel Fuel Regulations*; Presented at the California Air Resources Board's Advisory Committee to Address Toxic Air Contaminants from Diesel-Fueled Vehicles; March 1999.
(13) Peckham, J. Calif. Refiners Already Producing Fuel Good for Ultra-low Emissions. *Diesel Fuel News*, Sep 7, 1999, p 1.
(14) Durbin, T. D.; Collins, J. R.; Norbeck, J. M.; Smith, M. R. *Evaluation of the Effects of Alternative Diesel Fuel Formulations on Exhaust Rates and Reactivity*; Final report to the South Coast Air Quality Management District, Contract 98102; 1998.
(15) Chow, J. C.; Watson, J. G.; Pritchaett, L. C.; Pierson, W. R.; Frazier, C. A.; Purcell, R. G. *Atmos. Environ.* **1993**, *27A*, 1185.
(16) Hildemann, L. M.; Markowski, G. R.; Cass, G. R. *Environ. Sci. Technol.* **1991**, *25*, 744.
(17) Watson, J. G.; Chow, J. C.; Lowenthal, D. H.; Prichett, L. C.; Frazier, C. A.; Neuroth, G. R.; Robbins, R. *Atmos. Environ.* **1994**, *28*, 2493.
(18) Calde, S. H.; Mulawa, P.; Ragazzi, R. A.; Knapp, K. T.; Norbeck, J. M.; Durbin, T. D.; Truex, T. J.; Whitney, K. A. *Exhaust Particulate Matter Emissions from In-Use Passenger Vehicles Recruited in Three Locations*; CRC Project E-24; SAE Technical Paper 99FL-215; SAE: Warrendale, PA, 1999.
(19) Norbeck, J. M.; Durbin, T. D.; Truex, T. J. *Measurement of Primary Particulate Matter Emissions from Light-Duty Motor Vehicles*; Coordinating Research Council Project E-24-2 Final Report; December 1998.

Received for review May 12, 1999. Revised manuscript received October 4, 1999. Accepted October 25, 1999.

ES990543C