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Gaseous and Particulate Emissions from Diesel Engines at Idle and under Load: Comparison of Biodiesel Blend and Ultralow Sulfur Diesel Fuels

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Abstract

Diesel exhaust emissions have been reported for a number of engine operating strategies, after-treatment technologies, and fuels. However, information is limited regarding emissions of many pollutants during idling and when biodiesel fuels are used. This study investigates regulated and unregulated emissions from both light-duty passenger car (1.7 L) and medium-duty (6.4 L) diesel engines at idle and load and compares a biodiesel blend (B20) to conventional ultralow sulfur diesel (ULSD) fuel. Exhaust aftertreatment devices included a diesel oxidation catalyst (DOC) and a diesel particle filter (DPF). For the 1.7 L engine under load without a DOC, B20 reduced brake-specific emissions of particulate matter (PM), elemental carbon (EC), nonmethane hydrocarbons (NMHCs), and most volatile organic compounds (VOCs) compared to ULSD; however, formaldehyde brake-specific emissions increased. With a DOC and high load, B20 increased brake-specific emissions of NMHC, nitrogen oxides (NO_x), formaldehyde, naphthalene, and several other VOCs. For the 6.4 L engine under load, B20 reduced brake-specific emissions of PM_{2.5}, EC, formaldehyde, and most VOCs; however, NO_x brake-specific emissions increased. When idling, the effects of fuel type were different: B20 increased NMHC, PM_{2.5}, EC, formaldehyde, benzene, and other VOC emission rates from both engines, and changes were sometimes large, e.g., PM_{2.5} increased by 60% for the 6.4 L/2004 calibration engine, and benzene by 40% for the 1.7 L engine with the DOC, possibly reflecting incomplete combustion and unburned fuel. Diesel exhaust emissions depended on the fuel type and engine load (idle versus

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Supporting Information

Methods and materials for emission measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

loaded). The higher emissions found when using B20 are especially important given the recent attention to exposures from idling vehicles and the health significance of PM_{2.5}. The emission profiles demonstrate the effects of fuel type, engine calibration, and emission control system, and they can be used as source profiles for apportionment, inventory, and exposure purposes.

1. INTRODUCTION

The use of biodiesel blends and other alternative fuels has grown rapidly in recent years. These fuels have the potential to reduce emissions of the “regulated” pollutants, e.g., particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_x), and nonmethane hydrocarbons (NMHC).¹ In addition, these fuels may improve energy security, and some may reduce CO₂ emissions. In the U.S., ultralow sulfur diesel fuel (ULSD, sulfur content less than 15 ppm) has been phased in since 2006 for on-road diesel vehicles,² and biodiesel blends have become widely available. While most heavy-duty (HD) vehicles are diesel, currently only a small fraction of light-duty vehicles in the U.S. are diesel.^{3,4}

Due to environmental and health concerns, increasingly stringent regulations have been imposed on diesel engine exhaust emissions.^{5–7} Emissions depend on the fuel, engine type, emission control technology, engine age, and maintenance among other factors, and many control technologies are used to meet emission standards for regulated pollutants.⁸ For example, exhaust gas recirculation (EGR) reduces NO_x, which is primarily formed by the reaction of nitrogen and oxygen at high temperatures, by recirculating a portion of the exhaust gas, thus reducing excess oxygen in the engine as well as peak combustion temperatures. Diesel oxidation catalysts (DOCs) oxidize CO, gas phase hydrocarbons, and some of the soluble organic fraction of diesel particulate matter.⁹ Diesel particle filters (DPFs), which require ULSD fuel, physically trap and remove PM from the exhaust stream and achieve reductions of 90% or more of PM in engine exhaust.¹⁰

While designed to reduce emissions and comply with emission limits, the use of biodiesel and other fuels in conjunction with emission controls can change the composition and toxicity of exhaust emissions.^{1,11–13} Engine performance with biodiesel blends and conventional diesel fuels is generally similar except that brake-specific fuel consumption increases using biodiesel due to its lower energy content.^{1,12,13} Biodiesel also reduces smoke opacity, PM, CO, and NMHC emissions, although NO_x may increase, depending on operating conditions.^{1,11,14–16}

Diesel engine exhaust also includes toxic unregulated pollutants, such as volatile organic compounds (VOCs) like benzene and formaldehyde and polycyclic aromatic hydrocarbons (PAHs) like benzo(a)pyrene. Unregulated pollutants also include ozone precursors and bioaccumulative and toxic compounds. Information pertaining to these emissions in diesel engine exhaust is much less complete than that for the regulated pollutants. While lower emissions of unregulated pollutants might be expected for biodiesel blends given results observed for PM and NMHC, the literature is inconsistent. The U.S. EPA (2002) has identified 11 toxics in diesel exhaust (acetaldehyde, acrolein, benzene, 1,3-butadiene, ethyl benzene, formaldehyde, n-hexane, naphthalene, styrene, toluene, and xylene) and stated that emissions could “increase or decrease when biodiesel is blended with diesel fuel, and of

those (species) that decrease, the magnitude of that decrease will vary from one toxic to another”.¹⁷ Tests of diesel engine emissions of carbonyl compounds, e.g., acetaldehyde and formaldehyde, have shown both increases^{18–20} and decreases.^{21–23} Information pertaining to unregulated pollutants is especially scarce for biodiesel fuels that meet current ULSD requirements, for modern engines with EGR and aftertreatment systems, and for various engine loads.

This study investigates exhaust emissions of both regulated and unregulated pollutants from diesel engines and specifically compares emissions obtained using ULSD and a biodiesel blend. Results are presented for two engines at idle and three load conditions, both with and without aftertreatment systems, and with calibrations similar to the stock settings. A range of pollutants are measured, including several toxic and diesel marker compounds. The information presented can be used for developing emission inventories, apportioning air pollutant sources, and estimating exposures and risks.

2. METHODS AND MATERIALS

2.1. Test Engines, Emission Controls, and Fuels

Two engines were used (described in Table 1). The first is a General Motors (GM) 2002 1.7 L displacement engine manufactured by Isuzu, which is used in passenger cars in Europe and Asia. This engine is equipped with EGR and a platinum-based DOC.²⁴ The second engine is a Ford 2008 6.4 L “Power Stroke” engine manufactured by International, which is used in pick-up trucks, school buses, tow trucks, and other vehicles. This engine also has an EGR system and is further equipped with a DOC and a catalyzed DPF that meets 2007 emissions regulations.

Tests were conducted using a midcetane U.S. specification ultralow sulfur diesel (ULSD, sulfur content <15 ppm) certification fuel and a custom-blended B20, which contained 20% soy methyl ester biodiesel (Peter Cremer North America, Cincinnati, OH) and 80% ULSD mixed by volume. Fuel properties of ULSD and soy methyl ester biodiesel (B100) were analyzed by Paragon Laboratories (Livonia, MI) and are listed in Table S1 in the Supporting Information. Fuel properties of the custom-blended B20 were not available.

2.2. Test Conditions

The experiments used 26 test conditions (Table 2). The 1.7 L engine was operated at conditions similar to its 2002 emission calibration in all tests, which included idle and three load conditions expressed in brake mean effective pressure (BMEP): 200 kPa BMEP at 1500 rpm, 600 kPa BMEP at 1500 rpm, and 900 kPa BMEP at 2500 rpm, each with and without the DOC, and each with ULSD and B20 fuels. The fuel injection strategy for this engine used an advanced single injection. Engine speed and BMEP were the only two parameters adjusted. Other parameters were controlled by the manufacturer's engine control unit, e.g., fuel amount, injection timing, and EGR percentage.

The 6.4 L engine was operated under both 2004 and 2007 calibrations. For the 2004 calibration, the engine was operated under idle and two load conditions (600 kPa BMEP at 1500 rpm and 900 kPa BMEP at 2500 rpm), without the DOC and catalyzed DPF, each with

the two fuels. Other than setting the engine speed and BMEP, the main injection timing was set as at 3.5° after top dead center (ATDC) for all conditions. For the 2007 calibration, the engine was operated under idle and one load condition (900 kPa BMEP at 2500 rpm) with the DOC and catalyzed DPF and with the two fuels. Again, the engine speed and BMEP were the only parameters adjusted. Other parameters were controlled by the manufacturer's engine control unit, e.g., the injection timing, which was at 3.0° before top dead center (BTDC) for load conditions and 5.0° ATDC for idling conditions.

The measured power output and EGR percentage for each test are listed in Table 2. For the 1.7 L engine, the EGR was turned off manually during the 900 kPa BMEP tests due to an EGR cooler limitation. Each engine was fully warmed up before each test (including idle tests). To avoid contamination, the engine's lubricant oil (Mobil One 10W-30 for the 1.7 L engine and Shell Rotella-T 15W-40 for the 6.4 L engine) was changed after switching fuels.

2.3. Emission Measurements

Figure 1 shows a schematic of the sampling and analysis system. Two engine test systems were located in different test rooms that were similarly configured. Sampling probes were placed in the exhaust pipe, approximately 1 m after the engine, or the same distance after the aftertreatment systems. All sampling lines were heated and maintained at 190 °C. After each engine operating condition stabilized, the sampling sequence was as follows.

A combustion emission bench (CEB II, AVL North America, Inc., Plymouth, MI) measured criteria pollutants CO, NO_x, and non-methane hydrocarbons (NMHC), a smoke meter measured reflectance from PM collected on filter media (AVL 415S, North America, Inc., Plymouth, MI), and a Fourier transform infrared (FTIR) spectrometer (2030-HS high speed multigas analyzer, MKS Instruments, Inc., Andover, MA) quantified formaldehyde concentrations. Next, a partial flow dilution system (model BG-2, Sierra Emissions System, Inc., Dewitt, MI) collected two PM_{2.5} samples, first on a Teflon filter (46.2 mm diameter, PTFE membrane with support ring, model 7592-104, Whatman Inc., Piscataway, NJ), then on a quartz filter (47 mm diameter, Type R-100, binder free, SKC Inc., Eighty Four, PA). Volatile organic compounds (VOCs) were then sampled on adsorbent-filled thermal desorption tubes (TDT, stainless steel, 10 cm × 4 mm; Scientific Instrument Services, Inc., Ringoes, NJ) containing 160 mg of Tenax GR and 70 mg of Carbosieve SIII. Finally, the emission bench, smoke opacity, and FTIR measurements were repeated. For the 6.4 L engine, the emission bench was not fully functional at the time of testing, thus CO and NO_x measurements from the FTIR were used and NMHC measurements were unavailable. (Further details of the measurements are provided in the Supporting Information and Table S2.)

To determine mass concentrations, Teflon filters were weighed before and after use to 1 µg precision after conditioning at constant temperature and humidity. Quartz filters were analyzed using an automated thermal optical analysis (TOA, Sunset Laboratory Inc., Tigard, OR) for organic carbon (OC) and elemental carbon (EC). OC data was excluded due to absorption artifacts and sampling unit limitations. While the use of two sequential filters can help to compensate for the artifacts,^{25–27} this was not possible in the sampling system. Black carbon (BC) was derived from the filter smoke number (as detailed in the Supporting

Information, eq A.1). VOC analysis protocols, described elsewhere,^{28–30} included spiking each TDT with 2 μL of an internal standard (containing 1 ng/ μL each of fluorobenzene and *p*-bromofluorobenzene), followed by thermal desorption (Scientific Instrument Services, Inc., Ringoes, NJ), gas chromatography and mass spectrometry (GC 5973/MS 6890, Agilent, Palo Alto, CA). Over 100 target VOCs were quantified, including alkanes, aromatics, halogenated, and phenols. The quality assurance and quality control (QA/QC) program included laboratory and field blanks, spiked and duplicate samples. Method detection limits (MDLs), established using seven low concentration spiked samples, ranged from 0.04 to 2 $\mu\text{g}/\text{m}^3$ depending on the VOC. Speciated VOC emissions were averaged from the two sequential samples for each condition and fuel. Duplicate precision was usually less than 15%.

2.4. Data Analysis

Engine load was described in BMEP (in kPa), rather than torque or power. BMEP normalizes power output across different engine displacements and facilitates comparisons between different engines. Emissions were expressed in terms of the brake-specific emissions (e.g., g/kWh or mg/kWh) for loaded conditions and in terms of the emission rate (e.g., g/h or mg/h) for idling conditions (which have brake-specific power near zero). Comparisons between idle and loaded conditions use emission rates.

FTIR and smoke meter measurements were averaged over two or three tests for each engine condition. For these measurements, differences between ULSD and B20 fuels, both with and without aftertreatment, were evaluated using paired *t* tests (two-tailed, significance level $p = 0.05$). For some conditions, only a single $\text{PM}_{2.5}$ and EC sample could be collected (applying to the 1.7 L engine for all test conditions and the 6.4 L/2007 calibration engine), and only one or two VOC samples could be collected for each test. In these cases, statistical evaluations were not possible.

3. RESULTS

Table 3 summarizes brake-specific emissions obtained using the 1.7 L/2002 calibration engine (with and without the DOC) and the 6.4 L engine at both 2004 and 2007 calibrations (the latter with the DOC and catalyzed DPF). To compare results for idle and load conditions, emission rates are expressed in units of mass per time. Table S3 in the Supporting Information summarizes results for all pollutants, and Figure 2 shows six pollutants. Table 4 lists percentage differences between the two fuels for 8 selected pollutants and 13 test conditions. Although B20 has slightly lower energy content than ULSD, engine performance measurements of brake-specific power, brake-specific fuel consumption, and thermal efficiency did not differ statistically between the two fuels. Thus, emission comparisons for each test condition were valid across fuels and after-treatment devices. The following presents results by pollutant.

3.1. PM, BC, and EC Emissions

For the 1.7 L engine, brake-specific emissions of $\text{PM}_{2.5}$, BC, and EC increased markedly with load for both fuels, both with and without the DOC (Table 3). Brake-specific emissions

were lower with B20 than with ULSD by 7–24% for $PM_{2.5}$, 16–31% for BC, and 14–28% for EC and reductions depended on both load (600 and 900 kPa BMEP) and presence or absence of the DOC (Figure 3a). At idle, $PM_{2.5}$ emission rates were 1.5 to 2 times higher than at 200 kPa BMEP but much lower than at the two higher loads. Idling emission rates of BC and EC were low compared to loaded conditions and comprised only 6–8% of $PM_{2.5}$ (Table S3 in the Supporting Information, Figure 2a,b). With B20, idling emission rates of $PM_{2.5}$ increased by 31–33%, probably due to unburned fuel in the organic fraction of $PM_{2.5}$. With B20, idling emission rates of EC increased by 5% without DOC and 34% with DOC; however, emission rates of BC decreased by 3% without DOC and increased by 14% with DOC.

For the 6.4 L engine/2004 calibration (without DOC/DPF), $PM_{2.5}$, BC, and EC brake-specific emission trends resembled those of the small engine (Table 4 and Figure 3b). Compared to ULSD at load, B20 lowered brake-specific emissions $PM_{2.5}$ by 24–28%, BC by 34–48%, and EC by 34–46%. At idle, emission rates of these three pollutants were the lowest among the tests, although B20 increased the $PM_{2.5}$ emission rate by 87% (Table S3 in the Supporting Information and Figure 2a), which indicates that $PM_{2.5}$ emissions were likely comprised primarily of unburned fuel and oil as well as products of incomplete combustion. BC and EC comprised only 3–4% of $PM_{2.5}$. With B20 at idle, emission rates of BC and EC increased 15 and 50%, respectively. For the 2007 calibration (with the DOC/DPF) at load and idle, BC and EC measurements were below the method detection limits. $PM_{2.5}$ measurements were detected at load, but given the low brake-specific emissions, differences between fuels could not be distinguished. However, at idle, B20 decreased emission rates of $PM_{2.5}$ by 82%.

BC and EC measurements from the two engines were highly correlated ($r = 0.98$ – 0.99) and slopes were near 1 (0.94 – 1.04) across tests and fuels. However, at idle, BC measurements were systematically higher than EC. Idling is a low soot condition, but unburned fuels and oils or other pollutants collected on the filter may affect light reflectance and bias the BC measurement. While high correlation was shown between BC and EC measurements, including the tests at idle, BC determinations based on contrasts in optical absorption, like those in the present study, are surrogate measurements that depend on optical properties of the collected aerosol that can have a higher degree of uncertainty. In contrast, the TOA method used for EC, which is very sensitive and has a large dynamic range, should be unaffected.

Biodiesel blends have been shown to lower emissions of PM and soot compared to petroleum diesel due to their lower content of aromatic hydrocarbons, which serve as soot precursors.^{1,11,14–17} Biodiesel blends also have higher oxygen content and a higher cetane number, which may lead to more complete combustion, further reducing PM emissions and potentially aiding the oxidation of already formed soot.^{1,31} However, the present study shows that B20 increased idle emission rates of $PM_{2.5}$ and EC compared to ULSD. While the literature regarding emission rates while idling for current ULSD and biodiesel blends is very limited, our results show higher emission rates during idling with biodiesel blends, an important result given the recent attention to exposures from idling vehicles. (Idling emissions are further analyzed in the Discussion.)

3.2. Nitrogen Oxides (NO_x)

For the 1.7 L engine at load, NO_x brake-specific emissions were highest at 200 kPa BMEP and comparable at 600 and 900 kPa BMEP (Table 3 and Figure 4a). Effects of fuel type for engine-out emissions were inconsistent, but B20 slightly increased DOC-out brake-specific emissions (by 2–8%) under load (Table 3). NO_x emission rates were the lowest at idle (Table S3 in the Supporting Information), and effects of fuel were not significant.

For the 6.4 L engine using both 2004 and 2007 calibrations, B20 increased brake-specific emissions of NO_x by 15–23% compared to ULSD for all test conditions (Table 3 and Figure 4b). Notably, at 900 kPa BMEP, brake-specific emissions with the 2007 calibration exceeded by 2.4 times those with the 2004 calibration. At idle, NO_x emission rates were low, especially for the 2007 calibration (Table S3 in the Supporting Information and Figure 2c). All of these differences, including those during idling, were statistically significant ($p < 0.05$).

Biodiesel fuels have been reported to increase NO_x emissions, a result of the fuel's viscosity, density, compressibility, and other properties that advance the injection timing, which promotes NO_x formation.^{1,11,14–17}

3.3. Carbon Monoxide (CO)

For the 1.7 L engine at load, engine-out CO brake-specific emissions at 200 kPa BMEP were much higher, by 6–12 times, than emissions at 600 or 900 kPa BMEP, reflecting the less complete combustion occurring at low load (Table 3 and Figure 5a). B20 lowered engine-out CO brake-specific emissions by 3 and 13% at 200 and 600 kPa BMEP, respectively, but CO brake-specific emissions increased by 6% at 900 kPa BMEP (Table 4). At idle, CO emission rates were up to 3–15 times higher than under load (Table S3 in the Supporting Information) and unaffected by the DOC due to cool exhaust. B20 increased CO emission rates at idle by 11–13% (Table 4 and Figure 2d).

For the 6.4 L engine/2004 calibration at 900 kPa BMEP, B20 reduced CO brake-specific emissions by 14% (Table 3 and Figure 5b). At idle, however, B20 increased CO emission rates by 21%. Under the 2007 calibrations and at 900 kPa BMEP, CO brake-specific emissions were greatly reduced and compare to the 2004 calibrations. With this configuration, B20 reduced CO brake-specific emissions by 28% at 900 kPa BMEP. Idling CO emission rates were high relative to the loaded conditions (Table S3 in the Supporting Information), and B20 lowered CO emission rates by 15%.

Biodiesel fuels are generally believed to decrease CO emissions due to its higher oxygen content and cetane number.^{1,11,14–17,31} At idle, however, B20 appeared to increase idling emissions for the 2002 and 2004 engine configurations.

3.4. Nonmethane Hydrocarbons (NMHC)

For the 1.7 L engine, engine-out NMHC brake-specific emissions were 4–6 times higher at 200 kPa than at 600 and 900 kPa BMEP, reflecting less complete combustion at low load (Table 3 and Figure 6). B20 lowered engine-out NMHC brake-specific emissions by 5–21%

at load (Table 4). With the DOC and the two higher loads, B20 increased NMHC brake-specific emissions by 103–144%, possibly because this device was optimized for ULSD, and conversion efficiencies for B20 were relatively low. At idle, NMHC emission rates were 4–15 times higher than under load (Table S3 in the Supporting Information) and largely unaffected by the DOC. B20 increased the NMHC emission rates while idling by 11%. (NMHC measurements were unavailable for the 6.4 L engine.)

Biodiesel fuels generally decrease NMHC emissions under load due to the fuel's higher oxygen content and advanced fuel injection, which leads to a more complete combustion and lower NMHC emissions.^{1,32}

3.5. Target Volatile Organic Compounds

VOCs detected in exhaust emissions included 18 aromatics and 9 nalkanes (Table 2). Benzene, toluene, naphthalene, and 1,2,3-trimethylbenzene were the top four aromatic compounds, and C_{9–13} n-alkanes were most abundant. The total of target VOCs (TTVOCs) represented from 7 to 22% of NMHCs, a percentage which depended on fuel, test condition, and DOC. Similar fractions (4–22%) have been reported previously when sampling exhaust using Tenax adsorbents.^{23,33–36}

For the 1.7 L engine under load, TTVOC brake-specific emissions were highest at 200 kPa BMEP (Table 3). B20 lowered engine-out TTVOC brake-specific emissions by 2, 22, and 25% at 200, 600, and 900 kPa BMEP, respectively (Table 4). Brake-specific emissions of most individual VOCs followed the TTVOC trends. For example, engine-out brake-specific emissions with B20 were generally lower than with ULSD, and 15 VOCs showed (statistically) lower brake-specific emissions at 600 and 900 kPa BMEP, e.g., benzene was reduced by 2–25% and toluene and *p,m*-xylene were reduced by 22–32% compared to ULSD. At low load, B20 increased brake-specific emissions of a few VOCs (naphthalene, 1,3,5-trimethylbenzene, and C_{12–16} n-alkanes). At idle, the two fuels had similar engine-out VOC emission rates and compositions (Figure 2f).

Installing the DOC on the 1.7 L engine decreased TTVOC and VOC brake-specific emissions with ULSD; however, with B20, TTVOC brake-specific emissions increased by 43–46% at the two higher loads (relative to ULSD using the DOC), mostly due to increases in naphthalene and *n*-alkane brake-specific emissions (Table 3). At idle with the DOC, emission rates using ULSD decreased, but emissions with B20 were largely unchanged (Figure 2f). Thus, comparing the two fuels, B20 resulted in 46% higher TTVOC emission rates due to increases in all target VOCs, including naphthalene (73% increase), ethylbenzene (60%), benzene (55%), C_{11–16} n-alkanes (48–94%), 1,2,3-trimethylbenzene (46%), and toluene (38%). The reason for these differences is unclear. The DOC was not expected to affect emissions while idling due to low exhaust temperature, although it appeared to remain somewhat active for the target VOCs with ULSD. B20 may deactivate the DOC at idle, and while experimental error can contribute to differences, sequential samples for target VOCs in these tests showed good precision (within 5%). However, no differences in NMHC were seen.

The same VOCs, along with one additional *n*-C₇ alkane, were detected for the 6.4 L engine (Table 3). For the 2004 calibration engine, B20 reduced TTVOG brake-specific emissions by 13–32% under load and by 24% at idle (Table 4). At idle and 600 kPa BMEP tests, benzene and toluene were the top two aromatics and *n*-nonane and *n*-decane were the top aliphatic compounds. At 900 kPa BMEP, the composition shifted to naphthalene, 2-methylnaphthalene, 1,2,4-trimethylbenzene, *n*-dodecane, and *n*-tridecane. B20 decreased emissions of most VOCs (by 14–58%), but benzene emission rates increased by 9% while idling and by 52% (brake-specific emissions) at 900 kPa BMEP.

The 2007 calibration (with the DOC/DPF) significantly lowered VOC brake-specific emissions under load (900 kPa BMEP), e.g., reductions were 83–99% using B20 and 42–99% for ULSD, depending on the VOC. Compared to ULSD, B20 reduced TTVOG brake-specific emissions by 76%, and individual VOCs were reduced by 13–88%. (The idling tests using the 2007 calibration failed, a result of a long sampling time that allowed an excessive accumulation of water in the sampling tube.)

As noted earlier, biodiesel fuels can aid combustion and lower the fraction of aromatics in exhaust emissions. However, higher emissions of at least some VOCs reflect biodiesel's lower volatility and the tendency for unburned fuel to remain in exhaust gases, especially for fuel components with high boiling points.^{1,19}

3.6. Formaldehyde

For the 1.7 L engine at load, engine-out brake-specific emissions of formaldehyde showed the same trend as CO, NMHC, and target VOCs: low load (200 kPa BMEP) produced much higher brake-specific emissions (by a factor of 15–30 times) than at high load (600 and 900 kPa BMEP), reflecting the less complete combustion occurring at low load (Table 3 and Figure 7a). Compared to ULSD, B20 slightly increased (by 1–11%) engine-out brake-specific emissions of formaldehyde at load (Table 4). B20 produced larger changes with the DOC: formaldehyde brake-specific emissions increased 51 and 8% at 600 and 900 kPa BMEP, respectively, but decreased by 10% at 200 kPa BMEP. At idle, formaldehyde emission rates were up to 13 times higher than at load, and B20 increased emission rates by 17 and 28% with and without the DOC, respectively (Table S3 in the Supporting Information).

Formaldehyde brake-specific emissions trends for the 6.4 L engine under 2004 and 2007 calibrations differed from those of the smaller engine (Table 3 and Figure 7b). At idle, emission rates were not high, rather, both B20 and ULSD gave similar or slightly lower brake-specific emissions than those at 600 and 900 kPa BMEP (Table S3 in the Supporting Information). This applied to both 2004 and 2007 calibrations. B20 significantly reduced emissions for all conditions except idling under the 2004 calibration, where formaldehyde emission rates increased by 29% (Table S3 in the Supporting Information and Figure 2e). Compared to the 2004 calibration, the 2007 calibration (with the DOC/DPF) lowered formaldehyde brake-specific emissions by 50% for both fuels. Idling produced similar trends, although reductions were lower, and B20 yielded a greater reduction of formaldehyde (by 30%) than ULSD (Table 4).

The literature shows the potential to increase emissions of formaldehyde and other oxygenated compounds with biofuels due to their greater oxygen content, although the decomposition of esters in the fuel can decrease concentrations of oxygenated combustion intermediates.^{1,18–20,35} The results obtained for the two engines suggest that differences in formaldehyde emissions between fuels are engine-specific.

4. DISCUSSION

4.1. Summary and Comparison of Idle Emissions

The tests allow direct comparisons of the two engines at idle using emission rates, and at load using brake-specific emissions (at 900 kPa BMEP). Emission rates from the smaller engine using the 2002 calibration were higher than those from the larger engine using the newer (2004 and 2007) calibration that meets more stringent emission standards.^{37,38} Comparisons at idle are particularly interesting. At idle, emission rates of regulated and unregulated pollutants from the smaller engine exceeded those from the 6.4 L engine for both fuels (Table S3 in the Supporting Information and Figure 2), except for PM_{2.5} with B20 (535 and 580 mg/h for the 1.7 engine and 6.4 L engine/2004 calibration, respectively). This included NO_x emission rates using either fuel, despite a higher EGR ratio in the small engine (27 versus 2%). The smaller engine also had higher (and sometimes much higher) emission rates of most VOCs, e.g., benzene and naphthalene emission rates were 3 and 25–30 times higher, respectively.

The literature on idling emission rates, which has focused on heavy-duty diesel vehicles (HDDVs), simple emission control systems, and older fuels (not ULSD or biodiesel blends), shows widely ranging results. Testing of 75 HDDVs from 1969 to 2005 without EGR, DOC, or DPF had average emission rates of 20–35 g/h of CO, 48–86 g/h of NO_x, 6–23 g/h of NMHC, and 1–4 g/h of PM₁₀.³⁹ Several years later, the same researchers examined 19 medium HDDVs from 1974 to 2001 (again without EGR, DOC, or DPF) and reported a wider range of emission rates, e.g., 10–45 g/h of CO, 34–161 g/h of NO_x, 1–20 g/h of NMHC, and up to 4 g/h of PM₁₀.⁴⁰ Measurements using six school buses (model years from 1997 to 2004, Caterpillar engines equipped with DOCs) showed idling emission rates of 30 g/h of CO, 65 g/h of NO_x, 17 g/h of NMHC, and 0.35 g/h of PM₁₀.⁴¹ In the present study, the 1.7 L engine had higher idle emission rates of CO and NMHC but much lower emission rates of NO_x and PM_{2.5}, while the 6.4 L/2004 calibration engine had lower emission rates of NO_x, CO, and PM_{2.5} that were comparable to Kinsey et al.⁴¹ These results suggest that newer engine calibrations and fuels have effectively lowered idling emission rates of NO_x and PM_{2.5}, but have only slightly changed CO and NMHC, probably because combustion is incomplete and the DOC is inactive at idle (idle temperatures ranged from 59 to 129 °C).

Idling emissions have drawn considerable attention in recent years, and a variety of management strategies have been developed, especially for school buses.⁴² As examples, California requires 2008 and newer HDDVs to have a nonprogrammable engine system that automatically shuts down the engine after idling for five minutes,⁴³ and many school districts have retro-fitted school buses with DPFs to reduce children's exposure to diesel exhaust.^{44,45} Still, very limited information exists regarding idling emissions for current fuels, including ULSD and biodiesel blends. Results for the 1.7 L engine in the present study

show that engine-out emission rates of PM_{2.5}, CO, NMHC, and formaldehyde at idle could exceed emission rates at load (on a mass/time basis). In contrast, emission rates of BC, EC, NO_x, and TTVOC were lower at idle. Smaller changes were seen for the 6.4 L engine; however, idling with the 2004 calibration produced formaldehyde emission rates similar to those under load, and idling under the 2007 calibration (with the catalyzed DPF) produced higher CO emission rates than under load.

B20 was not necessarily advantageous for idling emissions. For the 1.7 L engine, both with and without the DOC, B20 increased idle emission rates of CO, PM_{2.5}, NMHC, EC, formaldehyde, and benzene compared to ULSD. For the 6.4 L engine using the 2004 calibration, B20 increased idle emission rates of CO, NO_x, PM_{2.5}, EC, formaldehyde, and benzene. For the 6.4 L engine using the 2007 calibration, B20 increased idle emission rates of only NO_x. As noted, idle emissions and the resulting exposures may differ from those under load since DOCs and potentially other technologies do not reach the operating temperature required for conversion, and unburned fuel and products of incomplete combustion may represent a significant fraction of emissions. In addition, idling tests that follow current protocols may result in some artifacts and increase variability since sampling line temperatures that exceed exhaust temperatures may evaporate liquid phase exhaust components in the sample lines.

4.2. Summary and Comparison of Emissions under Load

At a load of 900 kPa BMEP, brake-specific emissions from the 1.7 L engine greatly exceeded those from the larger engine, e.g., brake-specific emissions of CO, EC, PM_{2.5}, formaldehyde, and TTVOC from the smaller engine with the 2002 calibration (no DOC) were 1.7 to 5.6 times higher than those from the 6.4 L engine with the 2004 calibration. Further reductions in brake-specific emissions from the larger engine were obtained with the 2007 calibration with the exception of NO_x, which exceeded emissions obtained using the 2004 calibration and also exceeded emissions from the 1.7 L engine. The high NO_x emissions from the 6.4 L engine likely result from injection timing issues: the 2007 calibration used an advanced injection, which promoted NO_x formation, while the 2004 calibration used a late injection, which reduced NO_x production. These results indicate that the 6.4 L engine with the 2007 calibration requires further adjustments to control NO_x emissions.

In practice, emissions are measured and reported using several methods, such as the U.S. transient federal test procedure (FTP), the new European driving cycle (NEDC), and the steady-state conditions used in the present study. Results can vary widely due to differences among engines, test conditions, and measurement approaches. Thus, the following discussion emphasizes general trends and differences between fuels and aftertreatment technologies.

Biodiesel blends have been shown to lower emissions of CO, NMHC, VOCs, and PM₁₀ but to increase NO_x.^{1,11,14–17,46} On the basis of correlations for CO, NMHC, PM₁₀, and NO_x developed from measurements of 43 unmodified HD engines using the transient FTP, the U.S. EPA predicted that B20 would reduce emissions of CO, NMHC, and PM₁₀ by 12, 20, and 15%, respectively, and increase NO_x by 1.9% compared to diesel fuel with ~300 ppm

sulfur.¹⁷ Some of our results were similar, e.g., B20 lowered CO and PM_{2.5} brake-specific emissions by 14 and 28%, respectively; however, NO_x brake-specific emissions increased by 20% for the 6.4 L/2004 calibration engine at 900 kPa BMEP.

Effects of biodiesel fuels on formaldehyde emissions remain uncertain. Compared to petroleum diesel, formaldehyde emissions using biodiesel blends have both decreased^{17,21,23} and increased.^{18–20,33} In the present study, B20 increased form-aldehyde brake-specific emissions from the 1.7 L engine under all conditions but decreased brake-specific emissions from the 6.4 L/2004 calibration engine under load.

Compared to petroleum diesel, biodiesel blends generally reduce emissions of aromatics, NMHC, and TT VOC, but benzene and other VOCs sometimes increase.^{1,19,47–51} The U.S. EPA has reported reductions for ethylbenzene, naphthalene, and xylene using biodiesel but did not draw conclusions for benzene, toluene, and styrene given the variation in the literature.¹⁷ In the present study, B20 generally reduced total speciated VOC brake-specific emissions compared to ULSD.

Emissions from DOC-equipped engines using biodiesel blends are expected to depend on the engine, fuel, and test conditions, although supporting literature is scarce. Using a Detroit Diesel Corporation (DDC) series 50 HD engine and the U.S. FTP cycle, DOC conversion rates were only 20% for total C_{1–12} VOC emissions with B20 compared to 40% for diesel.⁵⁰ B20 increased formaldehyde emissions regardless of fuel and engine.⁵⁰ For a Golf 1.9 L engine under the new European driving cycle (NEDC), a DOC with B100 significantly lowered PM and EC, although the organic fraction of PM was not reduced, compared to regulated diesel (sulfur <50 ppm) without a DOC.⁵² The present study shows similar trends, e.g., the 1.7 L diesel engine at load with active DOC had lower conversion efficiencies for B20 than for ULSD and increased brake-specific emissions of NMHC, formaldehyde, the organic fraction of PM, and some speciated VOCs.

The combination of the catalyzed DPF and ULSD on HD engines clearly reduces emissions of CO, PM, NMHC, aromatics, alkenes, carbonyls, polycyclic aromatic hydrocarbons (PAHs), hopanes, and steranes compared to earlier diesel fuels and engines without aftertreatment.^{25,34,52–54} However, form-aldehyde emissions using ULSD or B20 can increase.⁴⁹ In the present study, the 6.4 L/2007 calibration engine had significantly lower brake-specific emissions of most pollutants compared to the 2004 calibration, and reductions were slightly greater with B20. However, the 2007 calibration increased NO_x brake-specific emissions, a result that applied to both fuels.

5. CONCLUSIONS

Diesel exhaust emissions for a wide range of pollutants were contrasted for two engines and aftertreatment systems, B20 and ULSD fuels, and idle and load conditions. At idle, B20 increased engine-out and DOC-out emission rates of CO, NMHC, PM_{2.5}, EC, formaldehyde, benzene, and other VOCs for both the 1.7 L/2002 calibration and 6.4 L/2004 calibration engines. For the 6.4 L engine, B20 also increased emission rates of NO_x. At load, brake-specific emission trends depended on engine and aftertreatment systems. For the 1.7 L

engine, B20 reduced PM_{2.5}, EC, NMHC, TTVOG, and benzene brake-specific emissions without the DOC; however, with the DOC, B20 increased brake-specific emissions of NO_x, NMHC, form-aldehyde, and several VOCs. For the 6.4 L/2004 calibration engine (without a DOC/DPF) at load, B20 lowered CO, PM_{2.5}, EC, formaldehyde, and TTVOG brake-specific emissions, but NO_x brake-specific emissions increased by about 20%. The 2007 calibration (with the DOC and DPF) on the same engine significantly reduced brake-specific emissions of CO, PM_{2.5}, EC, formaldehyde, benzene, and TTVOG brake-specific emissions, but brake-specific emissions of NO_x increased under load. B20 provided slightly greater reductions of most pollutants. Comparing the two engines on the basis of brake mean effective pressure (BMEP), the 6.4 L engine had lower brake-specific emissions of all pollutants except NO_x.

The study measurements show that the new engine calibrations and aftertreatment systems significantly reduce emissions of most pollutants. However, emission reductions under load do not necessarily portray trends while idling if the DOC does not attain its operating temperature. Although B20 decreased emissions of most pollutants, emissions of unregulated pollutants, including formaldehyde and benzene, increased with the 1.7 L DOC-equipped engine. Ideally, engine and control systems would reduce both regulated and unregulated emissions during both idle and load conditions and with both regulated and biodiesel fuels. While unregulated pollutants comprise a small fraction of the total emissions, pollutants such as benzene, formaldehyde, and PAHs are important due to their toxicity. These emissions strongly depend on fuel and exhaust gas treatments and perhaps more so than the regulated pollutants. Future studies might be designed to evaluate the origin of these emissions.

This work demonstrates how emissions of regulated and unregulated pollutants in diesel exhaust depend on fuel, load, engine calibration, and exhaust aftertreatment technology. In addition to providing new information on emissions during idling and using B20, the results include a number of toxic species that can be used in emission inventories and as emission profiles in receptor models that are used to apportion air pollutant sources.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic of engine test system showing sampling and analysis components.

Figure 2.

Emission rates for the 1.7 and 6.4 L engines at idle. Panels show (a) PM_{2.5}, (b) elemental carbon (EC), (c) nitrogen oxides (NO_x), (d) carbon monoxide (CO), (e) formaldehyde, and (f) sum of target VOCs. *Indicate engine with aftertreatment.

Figure 3.

Total brake-specific PM_{2.5} emissions (whole bar) and EC component (lower portion of bar). (a) 1.7 L engine at three load conditions under 2002 calibration; (b) 6.4 L engine at two load conditions under 2004 calibration and at one load condition under 2007 calibration (bars C and D, brake-specific PM_{2.5} emissions were below 1 mg/kWh; and brake-specific EC emissions were below the method detection limit).

Figure 4.

NO_x brake-specific emissions: (a) 1.7 L engine at three load conditions under 2002 calibration and (b) 6.4 L engine at two load conditions under 2004 calibration and at 900 kPa BMEP conditions under 2007 calibration with DPF and DOC.

Figure 5.

CO brake-specific emissions: (a) 1.7 L engine at three load conditions under 2002 calibration (For both fuels, brake-specific CO emissions were below the method detection limit with DOC.) and (b) 6.4 L engine at two load conditions under 2004 calibration and at 900 kPa BMEP conditions under 2007 calibration with DPF and DOC.

Figure 6. NMHC brake-specific emissions of the 1.7 L engine at three load conditions under 2002 calibration.

Figure 7.

Formaldehyde brake-specific emissions: (a) 1.7 L engine at three load conditions under 2002 calibration and (b) 6.4 L engine at two load conditions under 2004 calibration and at 900 kPa BMEP conditions under 2007 calibration with DPF and DOC.

Table 1**Engine Specifications**

manufacturer	General Motors	Ford
model year	2002	2008
number of cylinders	4	8
displacement (L)	1.7	6.4
compression ratio	16:1	16.7:1
bore (mm)	79	98
stroke (mm)	86	105
connecting rod length (mm)	133.5	176
piston geometry	bowl-in	bowl-in
no. of valves per cylinder	4	4
fuel injection system	direct-injection common rail	direct-injection, high pressure common rail, piezoelectric actuation
injector location	centrally located	centrally located
injector nozzle number of holes	6	6
exhaust gas recirculation (EGR)	EGR cooler, flow controlled with poppet-style control valve	dual EGR coolers with EGR exhaust catalysts
turbocharger	variable geometry turbocharger	two compound turbochargers, smaller turbo uses variable geometry turbine
horsepower	100 bhp at 4400 rpm	350 bhp at 3000 rpm

Table 2

Summary of Experimental Design and Test Conditions for the Two Engines

test	engine	fuel	calibration	BMEP (kPa)	speed (rpm)	aftertreatment	power (kW)	EGR (%)	exhaust temperature (°C)	injection timing (°BTDC)
1	1.7 L	ULSD	2002	idle	800	none	0	27	129	3.0
2	General			200	1500	none	4	20	210	3.9
3	Motors			600	1500	none	13	17	368	1.2
4				900	2500	none	32	0	434	5.6
5				idle	800	DOC	0	27	126	2.6
6				200	1500	DOC	4	20	207	7.9
7				600	1500	DOC	13	17	372	1.4
8				900	2500	DOC	32	0	448	17.7
9		B20	2002	idle	800	none	0	27	125	3.2
10				200	1500	none	4	20	211	4.3
11				600	1500	none	13	17	368	1.8
12				900	2500	none	32	0	439	9.2
13				idle	800	DOC	0	27	127	2.8
14				200	1500	DOC	4	20	213	5.9
15				600	1500	DOC	13	17	372	1.4
16				900	2500	DOC	32	0	444	18.8
17	6.4 L	ULSD	2004	idle	665	none	0	2	74	-3.5
18	Ford			600	1500	none	49	10	265	-3.5
19				900	2500	none	120	19	320	-3.5
20			2007	idle	665	DOC + DPF	0	2	59	-5.0
21				900	2500	DOC + DPF	120	15	319	3.0
22		B20	2004	idle	665	none	0	2	72	-3.5
23				600	1500	none	49	10	262	-3.5
24				900	2500	none	120	19	314	-3.5
25			2007	idle	665	DOC + DPF	0	2	62	-5.0
26				900	2500	DOC + DPF	120	15	316	3.0

Table 3

Summary of Emission Measurements for the Two Engines and 26 Tests^a

test	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
engine and calibration	1.7 L, 2002 calibration																									
fuel	ULSD													B20												
	idle	200	600	900	idle	200	600	900	idle	200	600	900	idle	200	600	900	idle	600	900	idle	900	idle	600	900	idle	900
condition (BMEP in kPa)																										
aftertreatment	none	none	none	none	DOC	DOC	DOC	DOC	none	none	none	none	DOC	DOC	DOC	DOC	none	none	none	DOC + DPF	DOC + DPF	none	none	none	DOC + DPF	DOC + DPF
EGR (%)	27	20	17	0	27	20	17	0	27	20	17	0	27	20	17	0	2	10	19	2	15	2	10	19	2	15
exhaust temperature (°C)	129	210	368	434	126	207	372	448	125	211	368	439	127	213	372	444	74	265	320	59	319	72	262	314	62	316
unit	(g/h)				(g/h)			(g/Kwh)	(g/h)			(g/Kwh)	(g/h)			(g/Kwh)	(g/h)			(g/Kwh)	(g/h)			(g/Kwh)	(g/h)	(g/Kwh)
CO	69.46	20.46	1.79	3.01	76.08	22.10	0.00	0.00	78.57	19.80	1.56	3.19	84.30	19.86	0.00	0.00	28.82	1.46	1.01	21.96	0.03	34.83	1.49	0.87	18.66	0.02
NO _x	14.98	5.98	4.20	3.79	11.18	5.17	3.17	3.49	14.34	6.62	3.65	3.63	11.14	5.60	3.23	3.75	9.50	4.88	3.50	2.90	8.58	10.43	5.59	4.23	3.55	9.87
NMHC	75.06	3.16	0.50	0.60	72.38	2.60	0.04	0.15	83.11	2.51	0.42	0.57	80.63	1.85	0.10	0.31	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
formaldehyde	3.11	0.69	0.023	0.043	3.74	0.90	0.001	0.013	3.97	0.69	0.024	0.048	4.38	0.805	0.002	0.014	1.29	0.027	0.020	0.87	0.010	1.66	0.024	0.018	0.62	0.008
unit	(mg/h)				(mg/h)			(mg/Kwh)	(mg/h)			(mg/Kwh)	(mg/h)			(mg/Kwh)	(mg/h)			(mg/Kwh)	(mg/h)			(mg/Kwh)	(mg/h)	(mg/Kwh)
PM _{2.5}	404.70	72.25	111.03	186.52	404.83	31.80	113.83	173.06	530.71	62.10	84.03	156.75	540.21	36.06	102.39	161.49	310.87	56.73	108.50	22.51	0.60	580.94	43.35	78.44	4.09	0.75
BC	51.57	15.75	86.15	120.99	48.15	10.59	87.03	174.72	49.99	13.86	63.31	101.54	54.65	15.92	70.39	120.54	23.74	31.73	79.90	<MDL	<MDL	27.21	16.49	52.56	<MDL	<MDL
EC	33.43	20.60	87.24	145.00	24.08	14.96	81.22	170.28	35.21	20.53	71.00	124.37	32.37	18.83	64.06	122.24	11.88	31.31	77.18	<MDL	<MDL	17.85	16.91	50.71	<MDL	<MDL
benzene	110.79	41.74	8.99	12.40	79.75	34.27	0.11	0.88	128.93	37.90	6.72	12.14	123.96	NA	0.10	0.86	35.39	0.75	0.72	NA	0.02	38.53	0.64	1.10	NA	0.01
toluene	48.53	16.84	2.16	4.05	37.47	16.51	0.15	0.38	49.81	13.15	1.46	3.01	51.64	NA	0.10	0.35	21.10	0.45	0.80	NA	0.11	18.22	0.32	0.78	NA	0.03
ethylbenzene	5.59	1.64	0.22	0.40	4.09	1.70	0.04	0.05	6.18	1.35	0.17	0.31	6.55	NA	0.03	0.07	4.31	0.10	0.19	NA	0.05	3.56	0.07	0.18	NA	0.01
<i>p</i> -, <i>m</i> -xylene	11.03	3.35	0.43	0.86	8.65	4.21	0.10	0.13	10.51	2.63	0.30	0.59	10.89	NA	0.07	0.15	11.83	0.33	0.61	NA	0.16	7.98	0.20	0.52	NA	0.03
<i>o</i> -xylene	5.55	1.56	0.20	0.40	4.22	1.96	0.04	0.06	5.27	1.27	0.15	0.28	5.34	NA	0.03	0.06	4.85	0.14	0.24	NA	0.08	3.37	0.09	0.21	NA	0.01
4-ethyltoluene	6.04	1.56	0.21	0.46	4.52	1.81	0.05	0.09	5.75	1.38	0.18	0.35	5.70	NA	0.03	0.09	6.08	0.20	0.43	NA	0.18	4.12	0.12	0.35	NA	0.02
2-ethyltoluene	4.75	1.15	0.15	0.35	3.63	1.36	0.03	0.07	2.73	1.12	0.15	0.29	4.37	NA	0.02	0.06	3.30	0.11	0.25	NA	0.11	2.25	0.07	0.20	NA	0.01
1,2,3-trimethylbenzene	36.45	9.24	2.50	5.19	21.89	6.90	0.23	0.68	33.64	8.39	1.87	3.46	31.99	NA	0.21	0.75	4.59	0.21	0.50	NA	0.27	3.07	0.15	0.43	NA	0.03
1,2,4-trimethylbenzene	6.23	1.68	0.29	0.61	4.58	2.02	0.07	0.13	5.94	1.60	0.26	0.48	5.67	NA	0.05	0.13	8.32	0.35	0.81	NA	0.39	5.54	0.24	0.69	NA	0.05
1,3,5-trimethylbenzene	1.34	0.38	0.08	0.14	1.05	0.48	0.02	0.03	1.28	0.43	0.08	0.13	1.16	NA	0.01	0.03	2.82	0.11	0.23	NA	0.10	1.80	0.07	0.19	NA	0.01
styrene	9.42	3.14	0.61	1.25	6.89	3.56	0.04	0.16	10.64	2.64	0.45	0.99	12.24	NA	0.03	0.15	2.49	0.13	0.24	NA	0.00	1.04	0.11	0.25	NA	0.00
isopropylbenzene	0.55	0.16	0.02	0.04	0.44	0.19	<MDL	<MDL	0.59	0.14	0.02	0.03	0.54	NA	<MDL	<MDL	1.26	0.03	0.06	NA	0.02	0.85	0.02	0.05	NA	0.00
<i>n</i> -propylbenzene	1.99	0.55	0.07	0.18	1.50	0.63	<MDL	0.03	2.20	0.55	0.07	0.15	2.27	NA	0.01	0.04	2.27	0.07	0.15	NA	0.06	1.62	0.05	0.14	NA	0.01
<i>p</i> -isopropyltoluene	1.11	0.30	0.08	0.15	0.71	0.26	0.01	0.02	1.05	0.28	0.06	0.11	0.99	NA	0.01	0.02	0.91	0.04	0.11	NA	0.04	0.60	0.02	0.08	NA	0.01

test	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
	1.7 L, 2002 calibration														6.4 L, 2004 calibration										6.4 L, 2007 calibration	
engine and calibration	ULSD														B20										B20	
fuel	ULSD														B20										B20	
condition (BMEP in kPa)	idle	200	600	900	idle	200	600	900	idle	200	600	900	idle	200	600	900	idle	600	900	idle	900	idle	600	900	idle	900
<i>n</i> -butylbenzene	7.15	1.87	0.54	1.15	3.95	1.26	0.05	0.15	6.62	1.77	0.43	0.83	6.57	NA	0.05	0.19	1.25	0.06	0.15	NA	0.09	0.94	0.05	0.13	NA	0.01
naphthalene	62.20	11.30	3.86	14.02	29.85	7.98	0.75	1.50	62.92	16.24	3.78	11.34	51.67	NA	1.32	3.45	2.52	0.25	0.89	NA	0.49	2.13	0.22	0.85	NA	0.12
2-methylnaphthalene	2.11	0.30	0.14	0.52	1.01	0.33	0.02	0.04	2.31	0.55	0.12	0.43	1.59	NA	0.04	0.11	2.07	0.17	0.80	NA	0.36	1.75	0.15	0.86	NA	0.13
1-methylnaphthalene	0.84	0.12	0.07	0.24	0.40	0.15	0.01	0.02	0.97	0.26	0.06	0.21	0.57	NA	0.02	0.05	1.25	0.10	0.48	NA	0.22	1.00	0.09	0.51	NA	0.08
<i>n</i> -heptane	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	NA	<MDL	<MDL	2.42	0.09	0.16	NA	0.02	1.76	0.06	0.13	NA	0.02
<i>n</i> -octane	0.91	0.71	0.36	0.27	0.68	0.86	0.04	0.08	<MDL	0.66	0.20	0.25	<MDL	NA	0.10	0.17	3.58	0.19	0.33	NA	0.03	1.67	0.09	0.22	NA	0.03
<i>n</i> -nonane	82.22	28.77	8.36	11.54	65.71	22.31	0.38	1.51	76.44	22.20	5.96	7.71	74.96	NA	0.43	1.36	18.68	0.95	1.72	NA	0.25	10.26	0.48	1.34	NA	0.08
<i>n</i> -decane	65.59	22.00	6.90	9.97	43.83	17.53	0.38	1.37	59.80	18.46	5.15	6.81	57.64	NA	0.34	1.09	17.61	1.03	2.04	NA	0.58	10.73	0.63	1.64	NA	0.09
<i>n</i> -undecane	57.68	17.68	6.24	10.46	32.86	14.97	0.48	1.57	52.74	16.01	4.70	7.19	48.71	NA	0.52	1.53	9.46	0.74	1.99	NA	0.82	6.37	0.51	1.67	NA	0.14
<i>n</i> -dodecane	59.80	16.18	6.73	14.14	29.36	11.94	0.65	1.80	57.78	17.50	5.35	10.00	48.41	NA	0.98	2.63	5.02	0.66	2.86	NA	0.84	3.38	0.43	1.89	NA	0.21
<i>n</i> -tridecane	95.38	20.93	10.47	26.48	43.38	12.98	1.08	2.52	95.22	27.81	8.71	19.58	72.35	NA	2.02	5.18	4.64	0.51	2.22	NA	1.08	3.36	0.40	2.11	NA	0.37
<i>n</i> -tetradecane	19.81	3.37	2.12	7.03	7.30	1.73	0.19	0.50	19.54	5.59	1.75	5.09	12.87	NA	0.39	1.18	3.29	0.36	1.60	NA	0.61	2.40	0.24	1.33	NA	0.18
<i>n</i> -pentadecane	5.85	0.86	0.67	3.34	1.37	0.27	0.06	0.28	5.60	1.82	0.62	2.47	2.66	NA	0.13	0.59	2.82	0.33	1.34	NA	0.53	1.99	0.22	1.07	NA	0.12
<i>n</i> -hexadecane	3.10	0.38	0.44	3.75	0.52	0.06	0.08	0.23	3.60	1.38	0.62	2.54	0.83	NA	0.15	0.60	1.54	0.27	0.95	NA	0.49	1.09	0.18	0.89	NA	0.07
TTVOC	712.0	207.7	62.9	129.4	439.6	168.2	5.0	14.3	708.1	203.1	49.4	96.8	642.1	NA	7.2	20.9	186.5	8.7	22.9	NA	8.0	142.1	6.0	19.9	NA	1.9

^aNA: data not available, < MDL: below method detection limit.

Table 4

Percentage Change in Emissions Using B20 Relative to ULSD for 13 Test Conditions^a

engine	calibration	BMEP (kPa)	aftertreatment	CO	NO _x	NMHC	PM _{2.5}	EC	formaldehyde	benzene	TTVOC
1.7 L	2002	idle	none	13	-4	11	31 ^c	5	28	16 ^b	-1
General		200	none	-3	11	-21	-14	0	1	-9	-2
Motors		600	none	-13	-13	-17	-24 ^c	-19	4	-25 ^b	-22 ^c
		900	none	6	-4	-5	-16 ^c	-14	11	-2 ^c	-25 ^c
		idle	DOC	11 ^b	0	11	33	34	17	55	46
		200	DOC	-10	8	-29	13	26	-10	NA	NA
		600	DOC	NA	2	144	-10 ^c	-21	51	-9	43 ^b
		900	DOC	NA	8 ^b	103	-7 ^c	-28	8	-2	46 ^c
6.4 L	2004	idle	EGR	21 ^b	10 ^b	NA	87 ^b	50	29 ^b	9	-24 ^b
Ford		600	EGR	2	15 ^b	NA	-24 ^b	-46	-13	-14	-32 ^c
		900	EGR	-14 ^b	21 ^b	NA	-28 ^b	-34	-7 ^b	52	-13 ^c
	2007	idle	DOC + DPF	-15 ^b	23 ^b	NA	-82	NA	-29 ^b	NA	NA
		900	DOC + DPF	-28 ^b	15 ^b	NA	25	NA	-23 ^b	-30	-76

^a Positive numbers indicate greater emissions with B20. Idle conditions compare emission rates in g/h or mg/h; load conditions compare emission rates in g/kWh or mg/kWh.

^b Denotes statistical significance ($p < 0.05$; t test).

^c Denotes statistical significance for combined 600 and 900 kPa BMEP conditions ($p < 0.05$; t test, paired).