

Effects of B20 versus ULSD Fuel on Diesel Engine PM Emissions and Aftertreatment Performance

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ABSTRACT

A detailed study is undertaken to examine how 2010+ diesel engine exhaust emissions change when a soybean derived B20 biodiesel fuel is used instead of a conventional ultra-low sulfur diesel fuel and to investigate how these changes impact the aftertreatment system. Particulate matter (PM) emissions for each fuel are characterized in terms of mass emissions, size distributions, organic versus soot fraction, metals content, and particle morphology. PM mass recorded by Dekati Mass Monitor, thermal analysis of quartz filters, and calculated from particle size distributions consistently shows a 2 - 3 fold decrease in engine-out soot emissions over a wide mid-load range when changing from ULSD to B20 fuel. This is partly due to a decrease in particle number and partly to a decrease in average size. HC and NO_x emissions, in contrast, exhibit little change with fuel type. "Hot" dilution sampling, consistent with exhaust conditions, was employed as opposed to regulatory methods suited for post-DPF emissions levels. Under these conditions, the particles are ~90% soot, 10% semivolatile and with little metal content from either fuel. Similar fractal-like geometries and primary particle dimensions are observed for the soot from both fuels. HC and NO_x aftertreatment is equally efficient for both fuels, and exhibits little influence on particle emissions. DPF loading is slower for B20 fuel, as expected from the lower soot content. The loading is non-linear for both fuels, likely due to some passive regeneration. Active DPF regeneration is achieved in 15 minutes for both fuels.

INTRODUCTION

Combining the inherent fuel efficiency of diesel combustion with the use of renewable biofuels presents an attractive midterm path towards an environmentally sustainable future for transportation and improved energy security. Modern aftertreatment technology shows great promise in eliminating major drawbacks of diesel engines, namely their particulate matter (PM) and NO_x emissions. The diesel particulate filter (DPF) has overachieved in its ability to reduce PM emissions [1], and recent developments in selective catalytic reduction (SCR) and lean NO_x traps (LNT) are closing in on the very low NO_x targets posed by near-term regulations [2].

Biofuels have received considerable attention from a number of perspectives ranging from economic viability to regulated and unregulated emissions. A review of the subject by Graboski and McCormik includes discussion on the economics of biofuel production, a comparison of biofuel and conventional diesel fuel properties, as well as the impact on emissions [3]. A number of deleterious effects, such as deposits, corrosion, and pour point problems, make the direct use of fats and oils problematic. Rather these raw materials are refined into the form of fatty acid methyl (or ethyl) esters. The latter fuels still exhibit many differences from conventional diesel fuel, for example, ~10 wt% oxygen content, negligible sulfur and aromatic content, and higher viscosity and bulk modulus. As discussed by Lapuerta et al. [4], some of these lead to advantages, and others disadvantages, relative to conventional fuel.

There is general consensus that biodiesel reduces HC, CO, and PM emissions [5, 6, 7,8]. However, there are differences from one study to another regarding the extent of the benefits, including reports of only small changes in these emissions [9]. NO_x emissions, in contrast, are often reported as increasing slightly, by 2 - 4% with B20 biofuel use [10]. While this seems like a small effect, it exacerbates the already difficult task of meeting upcoming NO_x emissions standards. Again, reports vary as to the extent of the increase. Thus, a recent meta analysis concludes that, whereas the 2 - 4% increase applies to heavy duty engines, the increase may be 10 - 15% for light duty diesels [8]. A number of mechanisms have been proposed to explain the NO_x increase [4,11]. In reality there are likely a number of competing factors at play [12].

The modern pairing of engine and aftertreatment technology represents a complex system that must be carefully optimized to achieve mandated emissions standards; thus, engine-out emissions alone do not dictate the benefits or disadvantages of a particular fuel. An important aspect of the problem is to understand how changes in fuel composition affect aftertreatment performance. This is especially true for PM, since this pollutant is in general a complex mixture in both physical characteristics (solid versus liquid) and chemical composition. While there may seem little reason to believe that DPF efficiency depends on fuel type, potential chemical and structural differences in biodiesel derived soot may alter DPF loading rates and regeneration, as well as hydrocarbon and NO_x aftertreatment performance [13]. SCR function is sensitive to hydrocarbons. Williams et al. found Fe-Zeolite SCR to absorb more B100 hydrocarbons relative to ULSD, but that overall catalyst performance was less affected due to faster recovery [14].

The aim of the present paper is to examine biodiesel fuel's impact on the performance of 2010+ intent engine and aftertreatment technologies, both gaseous and particulate. As described in the next section, a number of tools are employed to investigate the size, composition, and morphology of the PM. These tools are applied in a manner consistent with interrogating exhaust PM at the levels and under the conditions that exist in a modern diesel vehicle exhaust system. The methods do not follow EPA Part 1065 [15] and are not appropriate for the very low PM levels found post DPF where semivolatile and nucleation mode PM may play a relatively more dominant role. Consequently post-DPF PM data are not discussed, except to state that they are typically ~1 mg/mile or lower, substantially below the 10 mg/mi emissions standard. The results are presented in two phases, first to explore changes in the soot produced by the engine running on a B20 biodiesel blend versus ultra-low sulfur diesel (ULSD) fuel, and second to investigate how this impacts the aftertreatment system.

EXPERIMENTAL METHODS

ENGINE AND FUELS

Comparison of exhaust emissions from ultra-low sulfur diesel fuel (ULSD) versus B20 biodiesel fuel was made using a prototype 6.5 L, 8 cylinder, 4 valve, turbocharged, common-rail, diesel engine. The engine has 99 mm bore, 105 mm stroke, and 15.8 compression ratio. The aftertreatment system includes a diesel oxidation catalyst (DOC) followed by copper based urea selective catalytic reduction (SCR) and an 8" × 12" (9.88 L) catalyzed diesel particulate filter (DPF). The DOC and SCR were oven aged for 64 hours at 800 °C and 670 °C, respectively, prior to testing. The DPF was temperature cycled by repeating six times a 30-minute highway speed/load point (1828 rpm & 217 N-m), followed by a 15 minute DPF regeneration. The target exhaust gas temperature for regeneration was 600 °C at the DPF inlet. No calibration changes were made between the two fuels for normal operation, but, post-injection fuel quantities were changed to achieve the desired ~600 °C DPF inlet temperature for filter regeneration with both fuels. Actual fueling increased by an average of 4.1% for the B20 fuel. This is somewhat higher than the 2.9% decrease in net heating value, but accounts for the slightly higher average actual regeneration temperature of 605 °C for B20 versus 580 °C for ULSD fuel.

Fuel properties are compared in [Table 1](#) and metals contents are provided in [Table 2](#) (below). The lube oil used was the manufacturer specified low-ash oil. Diesel certification fuel is used as the ULSD fuel; whereas a soybean derived biodiesel was blended by Haltermann with diesel development fuel (US727A) to produce the B20 fuel. Both fuels have similar cetane numbers and a sulfur level of ~10 ppm. The distillation points are somewhat higher for the B20 fuel. But the principal differences are the 2.3% weight content of oxygen and 45% volume content of aromatics in the B20 blend, as compared to 0% oxygen and 27% aromatics for the ULSD fuel. For reasons that remain unknown, the B20 aromatic content is anomalously high; other batches of this blend typically have 32% - 37% aromatic content. The US727A fuel is often used for development work to challenge aftertreatment systems as representative of marketplace fuels with potentially higher emissions.

To avoid interference from the two different fuels, separate, but identically specified, aftertreatment systems were employed in the emissions testing. In addition, separate fuel lines were run into the dynamometer cell for each fuel. Fuel change was then accomplished by switching fuel tanks, interchanging aftertreatment systems, and running the engine at highway speed/load for 30 minutes to purge the engine mounted fuel delivery system. While there may be some variability even between aftertreatment systems comprised of identical components, this was deemed less problematical

than potential interference from two different fuels used with the same aftertreatment system.

Table 1. Fuel properties

Characteristic	ULSD	B20
Cetane Number	45.4	43.5
10% recovery dist. T	211.3 °C	213.9 °C
50% recovery dist. T	253.8 °C	272.4 °C
Hydrogen weight %	12.94%	12.69%
Oxygen weight %	< 0.05%	2.28%
Carbon weight %	87.06%	85.03%
Ester Content	0%	21.8% (from soy)
Sulfur	9 ppm	11 ppm
Net Heating Value (MJ/kg)	42.79	41.57
Aromatics (%vol)	27.2	45.1

EMISSIONS MEASUREMENTS

The results presented below derive from tests performed in an engine dynamometer cell equipped with standard emissions analyzers for total hydrocarbons (HC), nitrogen oxides (NO_x), O₂, and CO₂. These data are augmented by a number of specialized measurements aimed to characterize the PM emissions. These include a scanning mobility particle sizer (SMPS) to determine PM size distributions, Dekati mass monitor (DMM) for real time PM mass measurement, Horiba 1370 thermal analyzer to provide semivolatile organic versus soot particle composition, ion coupled plasma analysis (ICP) of filter collected soot for metal content, and high resolution transmission electron microscopy (HRTEM) for soot particle morphology.

Sampling

Exhaust was sampled from 2 locations: engine-out and post SCR. A custom dilution system was used to sample exhaust directly from the exhaust pipe and provide diluted room temperature input for size measurement by SMPS and DMM. This system is based on Dekati ejector pumps, but designed to operate over a wide range of pressure and temperature, up

to 4000 mbar and 200 °C [16]. It consists of two ejector pumps in series followed by an optional axial diluter. Nitrogen (or air) acts as both the working fluid for the ejector pumps and the diluent. The upstream diluter is heated to 200 °C and supplied with 200 °C nitrogen. This likely suppresses semivolatile particle nucleation and condensation, as compared to other sampling methods [17], but is logically consistent with the aim to examine how changes in emissions might affect the aftertreatment system, which is likewise at similarly elevated temperatures.

Exhaust is sampled into the primary ejector pump at 5 L/min through a ~1.3 m long, 0.63 cm diameter, heated line at 191 °C. This temperature effectively inhibits thermophoretic losses, and the ~0.5 s residence time is sufficiently short that calculated diffusion losses are <10% at 10 nm and that the predicted increase in mean particle diameter from coagulation is <2% [18]. The second ejector and axial diluters operate at room temperature to bring the diluted exhaust to near room temperature. Each ejector pump nominally provides a factor of eight dilution. The precise value for the primary diluter is determined second by second from pressure and temperature readings at the ejector inlet, which are calibrated against the ratio of O₂ levels measured upstream versus downstream of the ejector pump (possible with the use of N₂ diluent). Because of the buffering provided by the primary diluter, a constant dilution factor, calibrated by direct flow measurements, is used for secondary dilution. The axial diluter supplies additional air or nitrogen coaxially to the sample. Here, the diluent flow is maintained constant with a flow controller, and the dilution factor is measured by a Gilibrator-2 flowmeter.

Soot samples for thermal semivolatile / soot measurement are collected onto quartz filters, and for metals analysis onto Teflo filters, by direct sampling of raw exhaust at 7.5 L/min through a short (< 0.5 m) heated line (191 °C). The filter holders themselves were not heated. Thermophoretic losses to the filter are inconsequential because filter efficiency is already above 99%. Normally dilution is used to avoid water condensation onto the filter media. The impact of water is minimized by allowing the filters to equilibrate for > 2 hours prior to analysis, and by the fact that both the thermal and ICP analyses are much less sensitive to water than gravimetric measurements. The benefit is a higher rate of soot collection at temperature conditions relevant to conditions inside the tailpipe. Quartz filters are cleaned prior to use by baking in air at 1000 °C for 20 minutes.

SMPS

A TSI model 3936 scanning mobility particle sizer is used to record particle size distributions for exhaust PM under steady state engine operation. This instrument employs a ²¹⁰Po neutralizer to bring the particle population into a Boltzmann charge distribution [19], the “long” differential mobility

analyzer to classify particle mobility diameter, and a model 3025 ultrafine condensation particle counter. The classifier is run at 10 L/min sheath flow and 1 L/min aerosol flow, which covers the size range from 7.6 to 289 nm. The size distributions are corrected for multiply charged particles produced in the neutralizer and diffusion losses within the SMPS.

DMM

Second by second PM mass emissions are measured with a Dekati mass monitor, model DMM-230. Particles first pass by a corona discharge for unipolar charging, next through an electric field where particles are segregated by electrical mobility, and finally through a six stage cascade impactor which separates particles according to aerodynamic diameter. Electric currents deposited by the particles are measured in the mobility and each of the impactor stages. The total current scales with particle surface area. The relative currents between mobility and impactor stages provide an estimate of particle mean mobility diameter, and the relative impactor currents give the aerodynamic diameter. Comparison of these two diameters allows an estimate of particle density. PM mass is then be calculated based on the total current, particle size, and particle density. In our experience the DMM overestimates PM mass by 0 - 30% relative to the gravimetric measurement. This appears to be a systematic effect that varies from one testing campaign to another, but is generally stable over each campaign. Other researchers report similar behavior [20,21]. In the present study the DMM data are consistent with thermally derived PM mass collected onto quartz filters.

Semivolatile organic / soot analysis

The relative contributions of semivolatile material and soot to the total PM is ascertained using the Horiba MEXA-1370 PM. In this instrument PM collected onto quartz filters is successively heated in a nitrogen atmosphere and in oxygen. Gas evolved in the first step is then oxidized, and the resulting CO₂ is assigned to semivolatile organic material, corrected by a factor of 1.15 to account for an approximately CH_{1.8} average hydrogen content in the organic species. CO₂ evolved in the second step is attributed to soot. As has been discussed before, this is a somewhat operational definition, because it is difficult to avoid pyrolysis in the first step, which leads in the second step to some amount of semivolatile material being misclassified as soot. And the amount depends on the specifics of the protocol being used [22]. In spite of this, the total PM mass ascertained by this thermal method correlates well with gravimetric PM mass [23].

Metals analysis

PM samples collected onto Teflo filters are measured for Na, K, Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn content using

ion coupled plasma analysis. Sample digestion and analysis followed established methods [24]. The support ring of the Teflo filter is removed and the center portion is vortexed for 2 minutes in trace-metal grade nitric acid to dislodge PM from the filter. It is then refluxed for 2 hours at 105 °C. A blank filter is processed in parallel as a control. Metals are recorded using a Perkin-Elmer Optima 3300 dual-view spectrometer, which is calibrated over concentrations of 0.005 mg/L to 10 mg/L.

Transmission electron microscopy

PM samples for TEM analysis are collected onto holey grids by placing them on the lower stages of a MOUDI impactor and sampling diluted exhaust for ~5 minutes. Soot particle are imaged either with a FEI Tecnai F20 TEM/STEM at 200 KeV and a 7.2 Mpixel Gatan camera, or with a JEOL 3011 high resolution TEM at 300 KeV and a Gatan 794 1.6 Mpixel Slow Scan CCD TV camera.

RESULTS

The presentation of results is divided into two parts. The first examines how engine-out emissions differ from the combustion of conventional diesel and a 20% biodiesel blend. The second part looks at how these differences affect exhaust aftertreatment. Tailpipe PM emissions were not measured in the present study, but from other aftertreatment and vehicle testing these are consistently < ~1 mg/mile over the FTP drive cycle. Emissions measurements are presented for both steady state and transient engine operation. Steady state tests were performed at the 10 speed / load conditions listed in [Table 2](#). The various measurements were not always performed in parallel, but were repeated in two or more separate tests for most operating conditions. At each test point the engine was stabilized for at least 10 minutes followed by 10 minutes of DMM data collection. SMPS data are reported as the average and standard deviation of typically 4 SMPS scans. Horiba 1370 data are presented as the average and standard deviation of 3 - 5 filter measurements. Transient tests were conducted over the cold-start bag 1 and urban driving bag 2 of the FTP drive cycle.

Table 2. Steady state engine operating points.

Engine speed (rpm)	Load (N-m)	Exhaust flow (Kg/hr)
750	80	95
1250	200	210
1450	160	230
1450	320	315
1450	400	360
1450	500	430
1828	217	350
1828	400	480
2280	200	510
2280	437	720

Engine-out hydrocarbon concentrations are virtually independent of fuel choice within the data scatter. NO_x levels likewise are nearly identical, except at the 2280 rpm / 437 N-m point, where levels are higher with the ULSD fuel. PM mass concentrations exhibit greater test-to-test repeatability than HC and NO_x emissions for reasons that are not entirely clear. The superposition of data from two engine rpms at the 200 and 400 N-m test points contributes some scatter, but doesn't explain the variability at the other loads. It is clear, however, that B20 fuel leads to a 2 - 3 fold reduction in PM mass relative to ULSD at low and mid loads, whereas the emissions become comparable at loads above 400 N-m.

ENGINE-OUT EMISSIONS

PM, NO_x and HC

Steady state PM mass, NO_x, and hydrocarbon (HC) exhaust concentrations for ULSD and B20 fuels are compared in [Figure 1](#) as a function of engine load. At 200 and 400 N-m data are plotted from measurements at two different rpms. But, multiple data points at all other loads represent repeat measurements from separate tests. As discussed below, variability from repeat measurements during the same test are within the symbol width; thus, the data scatter in [Figure 1](#) originates with test to test repeatability.

Both fuels exhibit similar emissions trends. Hydrocarbon concentrations decline with increasing load. Translated to units of brake specific emissions, the decrease is somewhat steeper, falling from 1.5 to 0.15 g/kWh from idle to 500 N-m. NO_x exhaust concentration rises with increasing load, but the brake specific emissions are relatively flat, with data scattered in the 1 - 3 g/kWh range. PM mass data from the DMM (solid symbols) and thermal analysis of quartz filter samples (open symbols) are consistent and exhibit similar test-to-test scatter. PM emissions are lowest at idle and high load, and relatively flat, but with considerable scatter, over the mid loads. The brake specific emissions range from 0.1 - 0.9 g/kWh for ULSD and 0.1 - 0.5 g/kWh for B20 fuel.