



Biodiesel Fuel Property Effects on Particulate Matter Reactivity

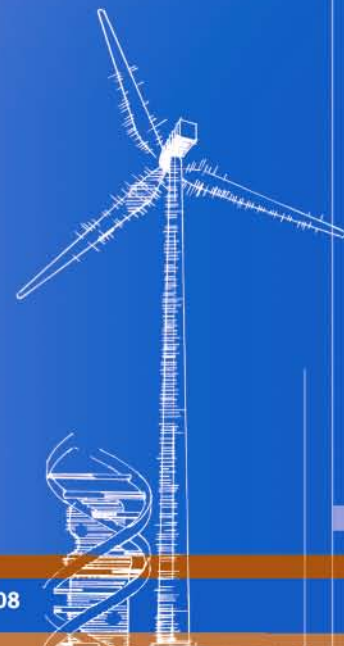
Conference Paper

NREL/CP-540-47286

June 2010

A. Williams, S. Black, and R.L. McCormick

*Presented at the 6th International Exhaust Gas and
Particulate Emissions Forum
Ludwigsburg, Germany
March 9–10, 2010*



NREL is operated for DOE by the Alliance for Sustainable Energy, LLC

Contract No. DE-AC36-08-GO28308



NOTICE

The submitted manuscript has been offered by an employee of the Alliance for Sustainable Energy, LLC (ASE), a contractor of the US Government under Contract No. DE-AC36-08-GO28308. Accordingly, the US Government and ASE retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Biodiesel Fuel Property Effects on Particulate Matter Reactivity

*A. Williams, S. Black, R. L. McCormick,
National Renewable Energy Laboratory
United States Department of Energy,
Golden, CO, USA*

Presented at the
6th International Exhaust Gas and Particulate Emissions Forum sponsored by AVL,
Ludwigsburg, Germany, March 9-10, 2010

Abstract

Control of diesel particulate emissions to the 2007 United States standard of 0.01 g/bhp-hr (0.013 g/kW-h) requires the use of a diesel particulate filter (DPF). The reactivity of soot, or the carbon fraction of particulate matter, in the DPF and the kinetics of soot oxidation are important factors in achieving better control of these aftertreatment devices. Earlier studies have shown that the presence of biodiesel in the fuel can increase soot reactivity. The purpose of this study was to investigate which biodiesel fuel properties impact reactivity. Three fuel properties of interest in this study included fuel oxygen content and functionality, fuel aromatic content, and the presence of alkali metals. To determine fuel effects on soot reactivity, the performance of a catalyzed DPF was measured with different test fuels through engine testing and thermogravimetric analysis (TGA). Experiments measured the time for DPF regeneration in an engine test and the onset temperature of soot combustion via TGA. Results showed no dependence on the aromatic content or the presence of alkali metals in the fuel. The presence and form of fuel oxygen proved to be the dominant contributor to faster DPF regeneration times and soot reactivity. The form of the oxygen functional group proved to play a role in DPF performance, and a long-chain alcohol (a carbon bonded to a single oxygen atom) provided a more effective form of oxygen than the methyl-esters of biodiesel (a carbon bonded to two oxygen atoms) for improving soot reactivity.

1 Introduction

The United States consumed approximately 450 million metric tonnes of gasoline, 200 million tonnes of diesel fuel, and 75 million tonnes of jet fuel in 2008. The U.S. currently imports 560 million tonnes of oil and petroleum products per year, 57% of consumption [1]. One strategy to increase domestic fuel production is the use of biodiesel, a fuel produced from lipid feedstocks such as vegetable oil, animal fat, and waste cooking oil. Biodiesel consists of mono-alkyl esters of fatty acids, which are typically methyl esters and are sometimes referred to as FAME, or fatty acid methyl esters. This renewable fuel is used primarily in the U.S. as a 2%- to 20%-by-volume blend with petroleum diesel. In 2008, the U.S. biodiesel industry produced 2.6 million tonnes [2]. Although reliable statistics on feedstocks are not available, sources in the biodiesel industry indicate that the largest fraction of U.S. biodiesel is produced from soy oil. A 2004 study indicates that U.S. resources are available to produce about 6 million tonnes of biodiesel annually [3]. A number of technologies may increase the available feedstock resource, including recovery of corn oil from dry mill ethanol production, the development of soybeans with higher oil content, new crops such as camelina and pennycress, as well as commercial production of algae.

1.1 U.S. Biodiesel Quality and Quality Specifications

For quality specification purposes in the United States, biodiesel must meet the requirements of ASTM standard D6751. The standard has been improved several times over the past few years, and the process continues today. The specification ensures that blends up to 20% are compatible with diesel engines and associated fuel system hardware. A

survey of B100 quality was conducted in 2007 to determine the degree to which U.S. biodiesel producers were meeting the D6751 specification [4]. Samples were tested for the most critical properties in D6751. Production volume information was used to estimate the volume percentage of biodiesel production passing or failing each requirement. The study found that 90% of the biodiesel was on specification.

Specifications have also been developed for biodiesel blends. ASTM D975, the specification for conventional diesel fuel, allows up to 5% biodiesel in the fuel. Fuel performance property requirements for petroleum diesel and blends up to 5% biodiesel are identical. Blends containing 6% to 20% biodiesel must meet the requirements of ASTM D7467. This includes additional requirements relative to D975, including a limit on acid value (0.3 mg KOH/g) and oxidation stability (6-hour minimum induction time by EN 15171). For any biodiesel blend, the biodiesel must meet D6751 prior to blending.

1.2 Emission Effects from the U.S. Perspective

In the United States, virtually all diesel fuel is used in heavy-duty vehicles. Diesel engines are significant contributors of oxides of nitrogen (NO_x) and particulate matter (PM) to air pollutant inventories. In the U.S., diesel vehicles produced 45% of mobile source NO_x and 60% of mobile source $\text{PM}_{2.5}$ in 2000 [5]. In contrast, diesel vehicles produced only approximately 7% of mobile-source volatile organic compound emissions and 5% of mobile-source carbon monoxide (CO). Although emission standards for NO_x and PM have become significantly more strict since 2000, diesel vehicles remain a significant source of those two pollutants. For this reason, the impact of biodiesel on NO_x and PM emissions is the primary concern. Heavy-duty engine emissions are regulated using an engine dynamometer test [6], and results are reported in g/bhp-h (0.7457 g/bhp-h = 1 g/kW-h). This is a transient test cycle lasting 20 minutes, plus a series of steady-state test points.

Allowable engine emission levels have been reduced dramatically over the past 25 years. The introduction of exhaust gas recirculation (EGR), higher pressure fuel injection, more advanced fuel injection control strategies, and NO_x emission control catalysts has been driven by a reduction in the allowable NO_x level from 4 g/bhp-h (5.4 g/kW-h) in 1998 to as low as 0.2 g/bhp-h (0.27 g/kW-h) in 2007. Additionally, beginning in 2006 the allowable level of sulfur in on-highway diesel fuel was lowered from 500 ppm to 15 ppm (ultra-low-sulfur diesel, or ULSD) to allow the introduction of diesel particle filters (DPF) and NO_x reduction catalysts. All 2007 and newer model-year on-highway heavy-duty engines in the United States are equipped with a DPF and meet a PM emission standard level of 0.01 g/bhp-h (0.013 g/kW-h), a factor of 10 lower than the previous standard of 0.1 g/bhp-h (0.13 g/kW-h).

An early review of biodiesel tailpipe emission impacts was published in 2002 and consisted almost entirely of data for HD engines in the 1988 to 1998 model-year range [7]. On average, the use of biodiesel as a blend or in neat form resulted in

substantial reductions in emissions of PM, CO, and total hydrocarbons (THC) for engines from this time period. The review also concluded that biodiesel caused a small increase in emissions of NO_x, but this conclusion is not as widely accepted, especially for blends of 20% or lower.

Table 1 summarizes the average emission changes resulting from the use of B20 for criteria pollutants, including results from more recent reviews. The first column of values was calculated in the early review, while the second and third columns are from Yanowitz and McCormick [8] and Robbins and coworkers [9], which are comprehensive reviews that include more recent biodiesel engine testing studies using biodiesel from a range of sources. All three studies found significant reductions in PM, CO, and THC, but the average effect of B20 on NO_x emissions appears to be small and dependent on the engine model and test conditions. Yanowitz and McCormick (2009) conclude that for the group of engines tested, it is not possible to state with any statistical certainty that B20 causes a change in NO_x emissions relative to petroleum diesel.

Table 1. Average Percent Change in Emissions for 20% Biodiesel (B20) Relative to Average Conventional Diesel Fuel for Heavy-Duty Engines

| Air Pollutant | U.S. EPA, 2002 [7] [†] | Yanowitz and McCormick, 2009 [8] | Robbins et al., 2009 [9] [†] |
|-----------------|---------------------------------|----------------------------------|---------------------------------------|
| NO _x | +2.1 | +2 (SD=4%) | -0.3 |
| PM | -10.1 | -15 (SD=10%) | -16.6 |
| CO | -11.0 | -14 (SD=13%) | -19.2 |
| THC | -21.1 | -16 (SD=18%) | -15.5 |

#Study did not include a statistical measure of uncertainty.
[†]SD = standard deviation.

1.3 DPF Performance

The previous discussion applies to engines that are not equipped with filter or catalyst technology to reduce air pollutant emissions. Control of diesel particulate emissions to the 2007 United States standard of 0.01 g/bhp-hr requires the use of a DPF. Like other standard automotive catalysts, a DPF uses a porous ceramic substrate monolith. However, in a DPF the monolith is a wall-flow filter consisting of parallel channels that are alternately plugged at either end in order to force the exhaust gases through the porous ceramic walls and allow for the capture of diesel soot. This capture of soot creates a longer residence time for oxidation. The volatile fraction of the particulate matter may oxidize easily at temperatures typically encountered in diesel exhaust.

The elemental carbon, on the other hand, requires much higher temperatures for oxidation. This typically requires exhaust fuel injection, in which diesel fuel is injected into the exhaust and ignited or oxidized over a catalyst, creating temperatures hot enough to oxidize the elemental carbon and regenerate the filter. Nitrogen dioxide in the exhaust can react with soot at lower temperatures, and many DPF designs use an oxidation catalyst upstream to convert NO to NO₂ and enhance passive regeneration at lower temperatures.

The drawback to using DPF aftertreatment technology is the increased backpressure from the stored soot and the fuel

economy penalty associated with the regeneration. Knowledge of soot reactivity in the DPF and the kinetics of soot oxidation are important in achieving optimal control of these devices.

Previous studies have shown improved DPF performance with the use of biodiesel blended fuels [10-14]. One such study measured two parameters used to gauge the performance of a DPF: balance point temperature and regeneration rate [12]. The balance point temperature is the temperature at which the rate of oxidation of stored soot is equivalent to the rate of soot accumulation. This study determined the balance point temperature to be 45°C lower for B20, when compared with petroleum-based ultra-low-sulfur diesel, or ULSD, for the catalyzed DPF used in the study.

The second parameter of interest, regeneration rate, is a measure of how quickly the DPF can be fully regenerated. This study also found improvements in the rate of DPF regeneration with the use of biodiesel. While biodiesel has been shown to reduce engine-out PM emissions and DPF balance point temperatures and to increase DPF regeneration rates, there is less published information regarding which properties of biodiesel contribute to these improvements. The purpose of this study was to investigate the effect of several fuel properties on the DPF regeneration rate. Three fuel properties of interest in this study include the fuel oxygen content and functionality, fuel aromatic content, and the potential presence of alkali metals.

Fuel Oxygen: While few studies have examined fuel property effects on soot reactivity, several studies have analyzed soot chemistry and morphology as they relate to the behavior of biodiesel-derived soot oxidation [10,12,13]. One study investigated the structure of soot at different levels of burnoff and cites three PM properties that are important to reactivity: the number of edge sites (amorphous structure), the number of surface oxygen groups, and the amount of volatile matter within the soot [10]. Based on this analysis, a unique oxidation progression model was proposed that explains the difference in oxidation rate of biodiesel blend-derived soot compared with that of ULSD soot. It concluded that surface oxygen sites, which are more prevalent in biodiesel soot, are the primary cause of more rapid soot oxidation.

Others have noted that the ester functional group is not the most efficient for reducing PM by oxygenates because two oxygen atoms are bonded to one carbon atom [15]. More efficient structures would have oxygen atoms distributed so that there is only one per carbon atom. Here we examine the effect of biodiesel (ester) at different blend levels on PM reactivity in a DPF and utilize an alcohol (1-decanol) blended with diesel fuel to have the same oxygen content as B20 (2.2 wt% oxygen).

Aromatics: Reducing diesel fuel aromatic content has correlated with reduced PM emissions in some studies, although not in modern, low-PM engines [16]; it has also correlated with reduced PM associated polycyclic aromatic hydrocarbon levels [17]. In studies with other fuels it is well established that fuel molecular structure can impact soot

properties [18]. We conjecture that hydrocarbon fuel properties can also affect soot reactivity. In this study, we examine diesel fuels with a range of aromatic content to determine if the reduction in aromatic content from biodiesel blending might have an effect on PM formation and reactivity in the DPF.

Alkali Metals: Fuel-borne catalysts, such as cerium [19], iron [20], and platinum [21], have been proven to assist in DPF regeneration by increasing the reactivity of particulate matter. The alkali metals that can result from the production of biodiesel are well known to catalyze carbon oxidation [22] and may act as a fuel-borne catalyst. Although recent fuel quality surveys typically show undetectable levels of alkali metals in the fuel (or less than 1 ppm) [4], sodium and potassium can be present because of the catalyst used for transesterification.

One study found longer distances between DPF regeneration events with the use of biodiesel in a vehicle test [11] and concluded that potassium methoxide found in the biodiesel led to a quasi-continuous regeneration of the filter. We have doped B20 to contain high levels of sodium and measured the impact on PM reactivity in the DPF.

2 Experimental Setup

Testing was conducted using a 2002 model year Cummins ISB mounted to a DC electric dynamometer. Properties for the test engine are shown in Table 2. The engine is designed and calibrated to meet U.S. 2004 emissions standards, employing cooled high-pressure EGR, a variable geometry turbocharger, and high-pressure common rail direct fuel injection. The engine was retrofitted with a 12-L diesel particulate filter. This is a passively regenerated DPF, utilizing Catalyzed Continuously Regenerated Technology (CCRT) provided by Johnson Matthey. The CCRT filter is a diesel oxidation catalyst followed by a wall-flow catalyzed soot filter. It is used in applications with average exhaust temperatures as low as 200°C-250°C.

The DPF is mounted 152 cm from the engine turbo flange outlet. The DPF was instrumented for inlet and outlet temperatures and pressures as well as differential pressure. Temperatures were measured with K-type thermocouples mounted 8 cm from the face of the pre-catalyst on the inlet side and 8 cm from the face of the DPF on the outlet side. Inlet and outlet pressures, as well as differential pressure, were measured from the same location. The overall setup and relative locations of all instrumentation are illustrated in Figure 1.

Engine-out NO_x and NO emissions were measured by a Horiba MEXA 1170-Nx chemiluminescence detection (CLD) analyzer. This is a dual detector with two CLDs for simultaneous measurement of NO_x and NO; NO₂ is determined by the difference. In addition, engine and emissions sampling systems were instrumented for measurement of all other critical temperatures and pressures.

Table 2. Cummins ISB Engine Specifications

| | |
|--------------------|---------------|
| Serial Number | 56993170 |
| Displacement (L) | 5.9 |
| Cylinders | 6 |
| Rated Power (kW) | 224 @ 2500rpm |
| Rated Torque (N-m) | 895 @ 1600rpm |
| Bore x Stroke (cm) | 10.2 x 12 |
| Compression Ratio | 16.5:1 |
| Fuel System | Common Rail |

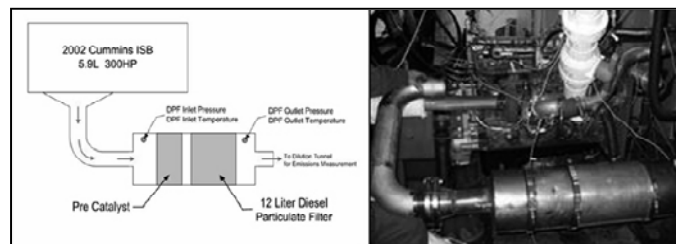


Figure 1. Engine and Emission Control System Setup (NREL photo)

Fuels used in this study are listed in Table 3. The base fuels included a 2007 certification ULSD and a low-aromatic ULSD. Blending components included a soy-based biodiesel, a distilled soy-based biodiesel, a straight-chain alcohol (1-decanol), and sodium oleate. In most tests, B100#1 was used for blending of B10 and B20. By calculation, B20 contains 2.2 wt% oxygen, and a blend of certification diesel and 23 volume percent (vol %) decanol was prepared to have the same oxygen content. The cetane number of 1-decanol is 50 [23], very close to the typical cetane number of soy biodiesel, 52 [24]. The ULSD #1 (30.7% aromatics) and ULSD #2 (17.2% aromatics) fuels cover a broad range of typical aromatic levels for diesel fuel. The ULSD #3 (24.6% aromatics) was prepared from a blend of these two fuels (55 vol% ULSD #1 + 45 vol% ULSD #2) to have an aromatic level equivalent to that of the B20 blend.

The distilled biodiesel was obtained from a large-scale producer that uses distillation to purify the crude biodiesel from transesterification. This material contains extremely low levels of impurities and is essentially pure methyl esters; it was of interest in this study because of its very low sodium (Na) content. To examine the impact of Na on soot reactivity, we compared a B20 prepared from the distilled biodiesel and the same fuel doped to 7 ppm Na using sodium oleate.

Table 3. Test Fuels

| Test Fuel | Base Fuels |
|---------------------------|---|
| ULSD #1 (30.7% aromatics) | 2007 certification ULSD |
| ULSD #2 (17.2% aromatics) | Low-aromatic ULSD |
| ULSD #3 (24.6% aromatics) | 2007 certification ULSD + low-aromatic ULSD |
| B100 #1 | Soy biodiesel |
| B100 #2 | Distilled soy biodiesel |
| B20 (24.6% aromatics) | 2007 certification ULSD + soy biodiesel |
| B10 | 2007 certification ULSD + soy biodiesel |
| B20 (<1 ppm Na) | Distilled soy biodiesel + 2007 certification ULSD |
| B20 (7 ppm Na) | Distilled soy biodiesel + 2007 certification ULSD + Na oleate |
| D23 | 2007 certification ULSD + 1-decanol (23 vol %) |

3 Test Procedures

To determine a fuel's effect on soot reactivity, the time for DPF regeneration was measured for the different test fuels. This is done in a two-step process. Mode 1 is loading the DPF with soot by operating at an engine set-point that creates high soot loads, but at exhaust temperatures low enough to avoid passive regeneration. Mode 1 engine operating conditions were 2000 rpm and 61 N-m. This was immediately followed by ramping the engine to Mode 2, a high-load condition in which exhaust temperatures are high enough to regenerate the soot-loaded filter. Mode 2 engine operating conditions were 1700 rpm and 650 N-m. Pressures and temperatures for a typical engine test are shown in Figure 2.

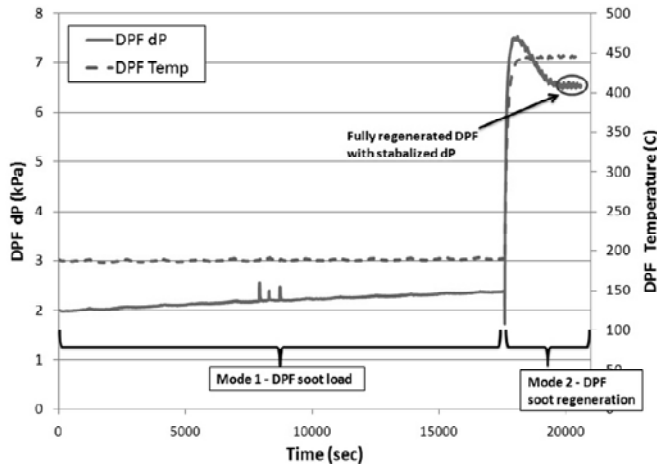


Figure 2. Regeneration Time Test Procedure

To make accurate comparisons of regeneration time, the filter was loaded to the same approximate soot load with each test fuel group. Because biodiesel results in lower engine-out soot emissions, it was necessary to load the DPF for a longer period of time to achieve the same soot load. The differential pressure (dP) of the DPF is used to approximate the state of soot loading on the filter. Thus, the duration of Mode 1 is varied for each fuel so that the differential pressure of the soot-loaded filter is the same. The time for DPF regeneration is then determined by operating at Mode 2. The dP of the DPF decreases as the filter is regenerated. The regeneration time is defined by the amount of time necessary for the dP to reach 98% of its fully regenerated pressure.

Conditioning the system between test fuels included a fuel swap and a full DPF regeneration. The fuel swap consists of draining the entire fuel system and then flushing three times the volumetric capacity of the system with the new test fuel. The full DPF regeneration to remove any soot accumulated with the previous test fuel included operating the engine for 30 minutes at full-load conditions. This is followed by removing the DPF from the engine and backflushing it with compressed air to remove any remaining soot or ash accumulation. Soot samples were collected from a loaded DPF by backflushing the DPF at room temperature with compressed air into a collection canister. These samples were then analyzed for reactivity by TGA. A TA Instruments Q500 TGA fitted with

platinum pans was employed. Approximately 2 mg of PM was loaded into the pans for analysis. The PM was heated at 100°C/minute to 400°C in a nitrogen flow of 40 mL/min. At 400°C, the gas was changed to air and the sample was combusted to 800°C at 30°/min.

Data analysis to determine weight loss during combustion and onset temperature was performed using TA Instruments Universal Analysis software. The onset temperature is defined as the temperature at the intersection of the baseline mass and the tangent drawn to the mass curve at the inflection point or point of greatest rate of mass loss.

4 Results

Prior testing with this engine-DPF system has shown that the DPF produces a greater than 99% reduction in PM emissions for both ULSD and B20 over the U.S. heavy-duty transient test [12]. The data presented here are the results of testing four different fuel groups to compare biodiesel blend content and fuel oxygen functional group, fuel aromatic levels, and fuel alkali levels. Cross comparisons of the regeneration time between these fuel groups cannot be made, because the DPF loading was not the same for each of the test campaigns.

4.1 Fuel Oxygen Content and Oxygen Functionality

Filter loading times as well as engine and exhaust conditions during regeneration (Mode 2) are shown in Table 4.

Table 4. Biodiesel Blend Level – Mode 2 Engine Conditions

| Test Fuel | DPF Loading Time (min) | Regen Time (sec) | DPF Temp (C) | NO _x :NO (ppm) | EGR Valve (% open) | Speed (rpm) | Torque (N-m) |
|-----------|------------------------|------------------|--------------|---------------------------|--------------------|-------------|--------------|
| ULSD | 244 | 1871 | 436 | 448:426 | 6.9 | 1700 | 651 |
| B10 | 269 | 1627 | 427 | 463:447 | 6.6 | 1700 | 651 |
| B20 | 311 | 1356 | 426 | 479:464 | 6.0 | 1700 | 651 |
| B100 | nm | 584 | 377 | 561:548 | 5.0 | 1701 | 649 |

nm = not measured

Test results for the regeneration time tests are shown in Figure 3, which shows the DPF dP as the filter is being regenerated.

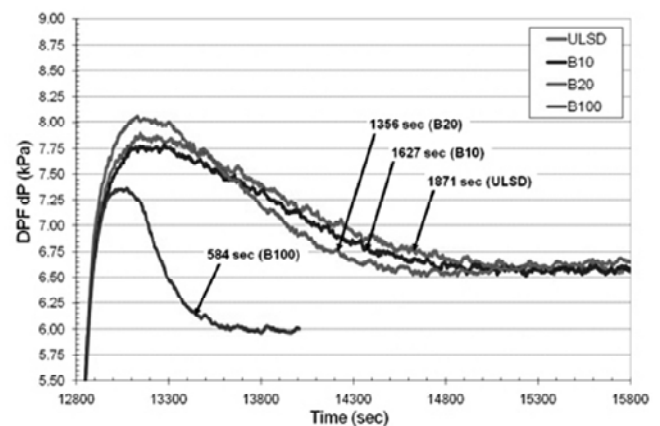


Figure 3. Biodiesel Blend Level – Regeneration Time Test Results

As expected based on previous studies, the DPF regeneration time shows an apparent dependence on biodiesel blend level. The DPF regenerated 13%, 28%, and 69% more quickly with B10, B20, and B100, respectively, in comparison to ULSD. The exhaust temperature at the regeneration condition for each of these fuels varied slightly, with lower temperatures occurring at higher biodiesel blend levels.

Engine-out NO_x emissions also varied between test fuels; NO_x trended upward along with increasing biodiesel blend levels. This is in part due to the EGR valve position changing as the biodiesel blend level increases (see Table 4). However, while total NO_x increased, engine-out NO_2 levels (estimated as $\text{NO}_x - \text{NO}$) actually decreased slightly as the biodiesel content increased. Nevertheless, given the increased NO , the diesel oxidation catalyst may have generated more NO_2 at the DPF inlet, reducing regeneration time for the biodiesel blends. The TGA tests, which were conducted in the absence of NO_2 , still show increased soot oxidation rate with B100. Figure 4 shows the soot mass fraction remaining as the oven temperature is ramped up to 800°C . At up to 400°C , the TGA feed gas is N_2 ; therefore, any mass loss is primarily due to evaporation of the volatile portion of the particulate matter. B100 shows a 4.5% mass loss under these conditions in comparison to 2.6% for ULSD, indicating a higher level of volatiles in the B100 particulate. Beyond 400°C , the TGA feed gas is air. The onset of combustion, as determined by the Universal Analysis software, is 590°C for the B100, in comparison to 635°C for the ULSD.

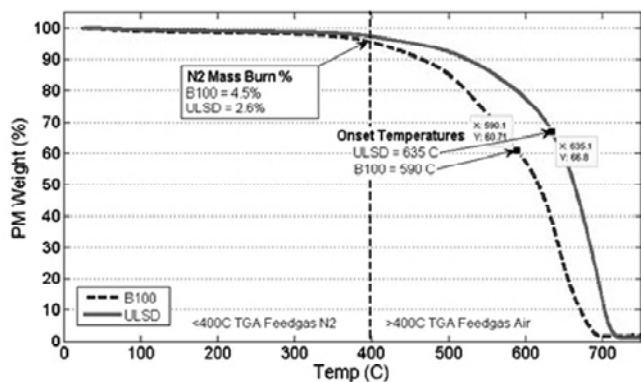


Figure 4. Biodiesel Blend Level – TGA Results

To test the hypothesis that shorter regeneration time is caused by properties of the soot loaded onto the filter and not the exhaust gas, we performed an experiment in which the DPF was loaded, using B20 as the fuel, and then regenerated after switching to ULSD #1. Results are shown in Figure 5, in which the regeneration times for B20 soot using either B20 fuel or ULSD fuel are compared. There is very little difference in the dP recovery curves for regeneration on the two fuels, indicating that the primary factors in achieving a shorter regeneration time are the properties of the soot.

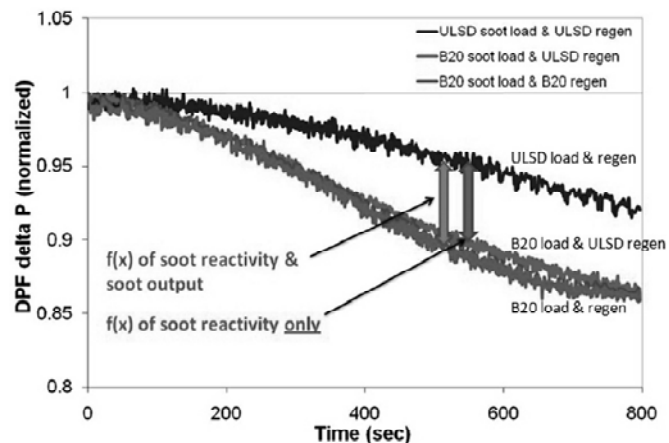


Figure 5. DPF Pressure Drop during Regeneration; Experiment Shows Regeneration of B20 Soot in Exhaust Gas Produced from ULSD

A second series of tests compared regeneration time for a B20 fuel produced using biodiesel and a second fuel produced using 1-decanol; both fuels had the same oxygen content (2.2% oxygen). These tests were conducted to determine if oxygenated fuels in general might reduce DPF regeneration time, and to determine if an oxygenate having carbon bonded to one oxygen atom rather than to two (as in biodiesel) might be more effective at increasing PM reactivity. Representations of the structures of the oxygen functional groups in biodiesel (methyl ester) and 1-decanol (primary alcohol) are shown in Figure 6.



Figure 6. Chemical Structure of Oxygen Functional Groups

This experiment is in part motivated by the work of Buchholz and coworkers [15], who showed that at equivalent oxygen content, molecules having each oxygen atom bound to a separate carbon atom were more effective at reducing PM emissions. Engine test results show that regeneration times were shorter when the decanol blended fuel was used (Figure 7 and Table 5), and NO_x emissions were slightly lower than those observed for B20 in other campaigns (see Tables 4, 6, and 7).

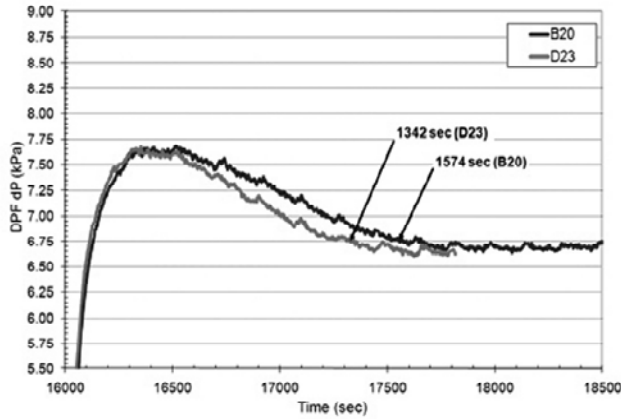


Figure 7. Fuel Oxygen Group – Regeneration Time Test Results

Table 5. Fuel Oxygen Group – Mode 2 Engine Conditions

| Test Fuel | DPF Loading Time (min) | Regen Time (sec) | DPF Temp (C) | NO _x :NO (ppm) | Speed (rpm) | Torque (N-m) |
|-----------|------------------------|------------------|--------------|---------------------------|-------------|--------------|
| B20 | 308 | 1574 | 426 | nm | 1700 | 651 |
| D23 | 305 | 1342 | 424 | 451:431 | 1701 | 649 |

Table 6. Aromatics Level – Mode 2 Engine Conditions

| Test Fuel (% Aromatics) | DPF Loading Time (min) | Regen Time (sec) | DPF Temp (C) | NO _x :NO (ppm) | Speed (rpm) | Torque (N-m) |
|-------------------------|------------------------|------------------|--------------|---------------------------|-------------|--------------|
| ULSD #1 (30.7%) | 144 | 2757 | 433 | 460:438 | 1700 | 651 |
| ULSD #2 (17.2%) | 182 | 2725 | 427 | 465:443 | 1700 | 649 |
| ULSD #3 (24.6%) | 156 | 2835 | 428 | 453:430 | 1701 | 648 |
| B20 (24.6%) | 194 | 2155 | 412 | 471:452 | 1700 | 649 |

Table 7. Na Level – Mode 2 Engine Conditions

| Test Fuel (ppm Na) | DPF Loading Time (min) | Regen Time (sec) | DPF Temp (C) | NO _x :NO (ppm) | Speed (rpm) | Torque (N-m) |
|--------------------|------------------------|------------------|--------------|---------------------------|-------------|--------------|
| B20 (0 ppm Na) | 312 | 1526 | 427 | 468:448 | 1700 | 651 |
| B20 (7 ppm Na) | 312 | 1440 | 425 | 472:452 | 1700 | 651 |

The TGA results (Figure 8) also indicate that a more reactive soot is created by combustion of the decanol/diesel blend. The decanol blended fuel yielded a soot combustion onset temperature of 612°C compared to 634°C for the B20. These results present a clear dependence on the chemical form of oxygen in the fuel, suggesting that the oxygen in decanol is more available for incorporation into the soot as reactive surface oxygen.

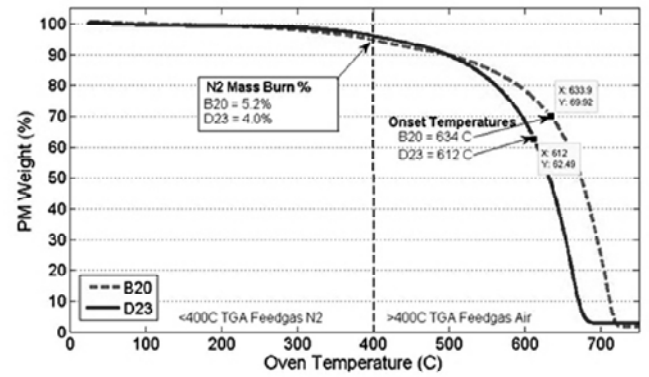


Figure 8. Fuel Oxygen Group – TGA Results

4.2 Fuel Aromatic Content

Regeneration times for three different ULSD fuels—high-level (30.7%), mid-level (24.6%) and low-level (17.2%) aromatics—are shown in Figure 9 and Table 6. The mid-level aromatics fuel was a blend of the high-level and low-level ULSDs to match the aromatic levels of a B20 test fuel produced using ULSD #1.

Testing shows an improvement in regeneration time for the B20 test fuel but not for the lower aromatic diesel fuels, indicating that the lower aromatic content of the biodiesel is not a contributor to soot reactivity. This is further supported by TGA results (Figure 10), which show no significant difference in soot combustion onset temperature between the low-level and high-level aromatic diesel soot.

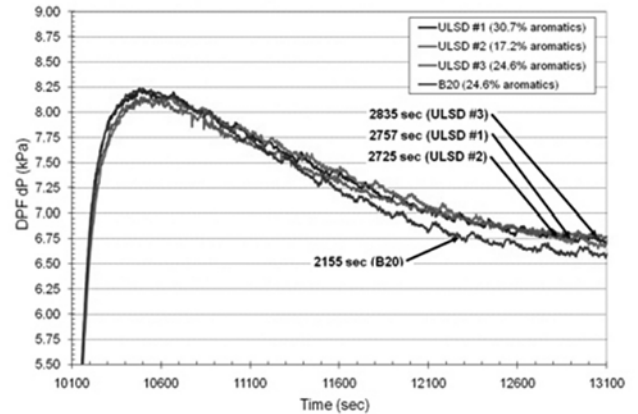


Figure 9. Aromatics Level – Regeneration Time Test Results

4.3 Fuel Sodium Content

Regeneration times for two B20 test fuels are shown in Figure 11. The first fuel is derived from a distilled biodiesel, which contains near-zero levels of impurities including alkali metals. The second test fuel was additized with sodium oleate, creating a B20 with 7 ppm Na. This level of Na is well above the 1-ppm total alkali metal level that could occur in a B20 made from specification-compliant B100.

Engine testing results (Figure 11) show a marginal decrease in regeneration time for the high Na B20. The aromatic diesel fuels, tested above, all had approximately the same regeneration time (i.e., fuel aromatic content had no effect on regeneration time; see Table 7).

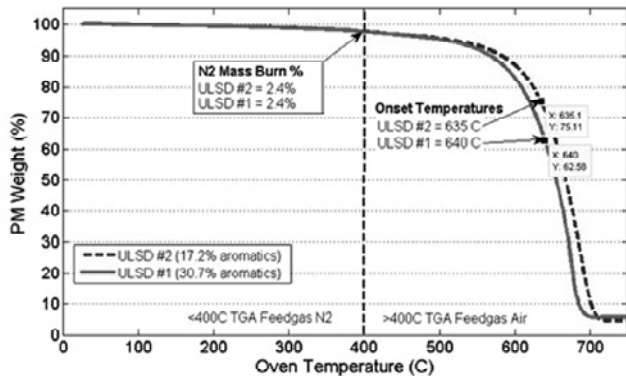


Figure 10. Aromatics Level – TGA Results

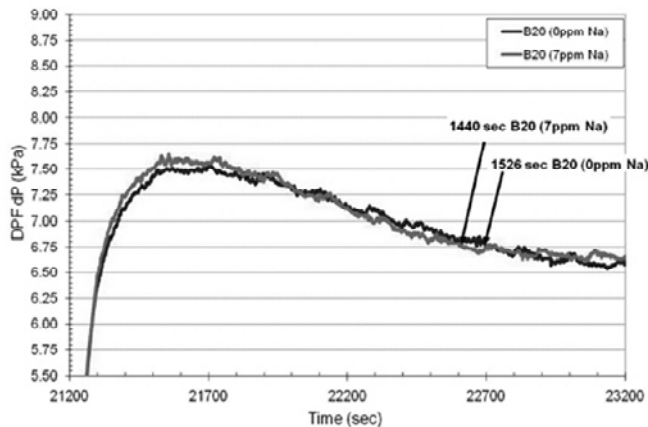


Figure 11. Na Level – Regeneration Time Test Results

Thus, to a good approximation, the aromatic diesel tests can be used as replicates to estimate repeatability. Regeneration times for these tests fall within 110 seconds (range of the data), and it is notable that the effects of B10 and B20 versus ULSD in general are larger, as was the effect of D23 versus B20. The effect of 7 ppm of Na was 86 seconds, so it is not likely a real difference under this assumption. Results from TGA (Figure 12) also reveal no difference in soot combustion onset temperature for the additized B20 soot. These results indicate that the potential for Na in the fuel, acting as a fuel-borne catalyst, is likely not the source of increased soot reactivity for biodiesel.

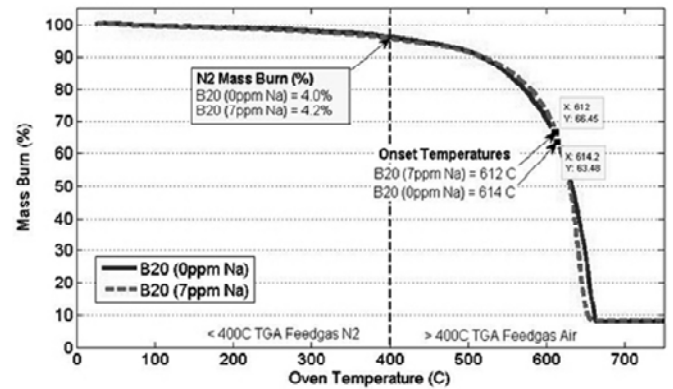


Figure 12. Na Level – TGA Results

5 Conclusions

In previous studies, biodiesel has been shown to reduce engine-out PM emissions and DPF balance point temperatures as well as to increase DPF regeneration rates. The purpose of this study was to expand the knowledge base regarding biodiesel particulate matter reactivity through engine testing and soot analysis. Three fuel properties of interest in this study were the fuel oxygen content and functionality, fuel aromatic content, and the potential presence of alkali metals.

To determine fuel effects on soot reactivity, the time for DPF regeneration was measured with different test fuels, controlling key fuel parameters. In addition, the onset temperature of soot combustion was measured through TGA analysis of collected soot samples. The conclusions of this work are as follows:

1. Different blend levels of biodiesel such as B0, B10, B20, and B100 showed an apparent difference in the regeneration time of the DPF, and performance improved with increasing biodiesel content.
2. The higher NO_x level found with increasing biodiesel content for this engine was not a factor in the improvement in DPF performance. This was demonstrated by the earlier onset of soot combustion found in TGA experiments, which were conducted in a NO_x-free environment, and by regenerating the DPF loaded with B20 soot using ULSD generated exhaust.
3. Neither lower aromatic levels nor the presence of alkali metals were found to be factors in the improvements in performance achieved with biodiesel. This was demonstrated by tests with controlled levels of aromatics and sodium, revealing no difference in the DPF regeneration time.
4. The presence and form of fuel oxygen proved to be the dominant contributor to faster DPF regeneration times and soot reactivity. The form of the oxygen functional group proved to play a role in DPF performance, and the long-chain alcohol (a carbon bonded to a single oxygen group) provided a more useful form of oxygen than the methyl-esters of biodiesel (a carbon bonded to two oxygen groups).

6 Acknowledgments

This work was supported by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

7 References

- [1] Energy Information Agency, www.eia.doe.gov/oil_gas/petroleum/info_glance/petroleum.html (accessed December 1, 2009).
- [2] Energy Information Agency, www.eia.doe.gov/emeu/mer/renew.html (accessed December 1, 2009).
- [3] Tyson, K.S., Bozell, J., Wallace, R., Petersen, E., and Moens, L. Biomass Oil Analysis: Research Needs and Recommendations; NREL Technical Report No. TP-510-34796, National Renewable Energy Laboratory, 2004.
- [4] Alleman, T.L., and McCormick, R.L. Results of the 2007 B100 Quality Survey, NREL Report No. TP-540-42787, National Renewable Energy Laboratory, 2008.
- [5] United States Environmental Protection Agency, National Air Quality and Emissions Trends Report, 2003 Special Studies Edition; report no. EPA 454/R-03-005 (2003).
- [6] United States Code of Federal Regulations, Title 40, Protection of the Environment, Part 1065.
- [7] United States Environmental Protection Agency, A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions; Draft Technical Report, EPA 420-P-02-001 (2002).
- [8] Yanowitz, J., McCormick, R.L. "Effect of Biodiesel Blends on North American Heavy-Duty Diesel Engine Emissions," *European J. of Lipid Science and Technology*, 111 (7), 763-772 (2009).
- [9] Robbins, C., Hoekman, S.K., Gertler, A., Broch, A. "Biodistillate Transportation Fuels 2. – Emissions Impacts." SAE Technical Paper No. 2009-01-2724 (2009).
- [10] Song, J., Alam, M., Boehman, A.L., Kim, U. "Examination of the Oxidation Behavior of Biodiesel Soot," *Combustion and Flame* 146, 589-604 (2006).
- [11] Yamane, K., Asakawa, T., Numao, H., Komori, M. "Characteristics of DPF for Diesel Engine Fueled with Biodiesel Fuel – First Report: Self-Regeneration Behavior on Vehicle Road Test and Engine Bench Rig Test," SAE Technical Paper No. 2004-01-1883 (2004).
- [12] Williams, A., McCormick, R.L., Hayes, R.R., Ireland, J., Fang, H. "Effect of Biodiesel Blends on Diesel Particulate Filter Performance," SAE Technical Paper No. 2006-01-3280 (2006).
- [13] Boehman, A.L., Song, J., Alam, M. "Impact of Biodiesel Blending on Diesel Soot and the Regeneration of Particulate Filters," *Energy and Fuels* 19, 1857-1864 (2005).
- [14] Jung, H., Kittelson, D.B., Zachariah, M.R. "Characteristics of SME Biodiesel-Fueled Diesel Particulate Emissions and the Kinetics of Oxidation," *Environmental Science and Technology*, 40 4949-4955 (2006).
- [15] Buchholz, B.A., Mueller, C.J., Upatnieks, A., Martin, G.C., Pitz, W.J., Westbrook, C.K. "Using Carbon-14 Isotope Tracing to Investigate Molecular Structure Effects of the Oxygenate Dibutyl Maleate on Soot Emissions from a DI Diesel Engine," SAE Technical Paper No. 2004-01-1849 (2004).
- [16] Tree, D.R., Svensson, K.I. Soot Processes in Compression Ignition Engines," *Progress in Energy and Combustion Science*, 33 (3), 272-309 (2007).
- [17] Westerholm, R., Christensen, A., Tornqvist, M., Ehrenberg, L., Rannug, U., Sjogren, M., Rafter, J., Soontjens, C., Almeñ, J., Gragg, K. "Comparison of Exhaust Emissions from Swedish Environmental Classified Diesel Fuel (MK1) and European Program On Emissions, Fuels and Engine Technologies (EPEFE) Reference Fuel: A Chemical and Biological Characterization, with Viewpoints on Cancer Risk," *Environmental Science & Technology*, 35, 1748–1754 (2001).
- [18] Vander Wal, R.L., Tomasek, A.J. "Soot Nanostructure: Dependence upon Synthesis Conditions," *Combustion and Flame*, 136, 129–140 (2004).
- [19] Kostoglou, M., Konstandopoulos, A.G., Burtscher, H. "Size Distribution Dynamics of Fuel-Borne Catalytic Ceria Nanoparticles," *Aerosol Science*, 38, 604–611 (2007).
- [20] Song, J., Wang, J., Boehman, A.L. "The Role of Fuel-Borne Catalyst in Diesel Particulate Oxidation Behavior," *Combustion and Flame*, 146, 73–84 (2006).
- [21] Hinot, K., Burtscher, H., Weber, A.P., Kasper, G. "The Effect of the Contact between Platinum and Soot Particles on the Catalytic Oxidation of Soot Deposits on a Diesel Particle Filter," *Applied Catalysis B: Environmental*, 71, 271–278 (2007).
- [22] Matarrese, R., Castoldi, L., Lietti, L., Forzatti, P. "Soot Combustion: Reactivity of Alkaline and Alkaline Earth Metal Oxides in Full Contact with Soot," *Catalysis Today*, 136, 11–17 (2008).
- [23] Freedman, B., Bagby, M.O. "Predicting Cetane Numbers of n-Alcohols and Methyl Esters from their Physical Properties," *J. American Oil Chemists Society*, 67, 565 (1990).
- [24] McCormick, R.L., Alleman, T., Ratcliff, M., Moens, L., Lawrence, R. Survey of the Quality and Stability of Biodiesel and Biodiesel Blends in the United States in 2004, NREL/TP-540-38836, October 2005.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

| | | | | | |
|---|------------------------------------|---|--|--|--|
| 1. REPORT DATE (DD-MM-YYYY) June 2010 | | 2. REPORT TYPE Conference Paper | | 3. DATES COVERED (From - To) | |
| 4. TITLE AND SUBTITLE Biodiesel Fuel Property Effects on Particulate Matter Reactivity | | | 5a. CONTRACT NUMBER DE-AC36-08-GO28308 | | |
| | | | 5b. GRANT NUMBER | | |
| | | | 5c. PROGRAM ELEMENT NUMBER | | |
| 6. AUTHOR(S) A. Williams, S. Black, and R.L. McCormick | | | 5d. PROJECT NUMBER NREL/CP-540-47286 | | |
| | | | 5e. TASK NUMBER FC08.9400 | | |
| | | | 5f. WORK UNIT NUMBER | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-540-47286 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) NREL | |
| | | | | 11. SPONSORING/MONITORING AGENCY REPORT NUMBER | |
| 12. DISTRIBUTION AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161 | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT (Maximum 200 Words) Control of diesel particulate emissions to the 2007 United States standard requires the use of a diesel particulate filter (DPF). The reactivity of soot, or the carbon fraction of particulate matter, in the DPF and the kinetics of soot oxidation are important in achieving better control of aftertreatment devices. Studies showed that biodiesel in the fuel can increase soot reactivity. This study therefore investigated which biodiesel fuel properties impact reactivity. Three fuel properties of interest included fuel oxygen content and functionality, fuel aromatic content, and the presence of alkali metals. To determine fuel effects on soot reactivity, the performance of a catalyzed DPF was measured with different test fuels through engine testing and thermo-gravimetric analysis. Results showed no dependence on the aromatic content or the presence of alkali metals in the fuel. The presence and form of fuel oxygen was the dominant contributor to faster DPF regeneration times and soot reactivity. | | | | | |
| 15. SUBJECT TERMS diesel particulate filter; DPF; emissions control; biodiesel; particulate matter; soot reactivity | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT UL | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
| a. REPORT Unclassified | b. ABSTRACT Unclassified | c. THIS PAGE Unclassified | | | 19b. TELEPHONE NUMBER (Include area code) |