Biodiesel Performance with Modern Engines

Cooperative Research and Development Final Report

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In accordance with Requirements set forth in Article XI, A(3) of the CRADA agreement, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: National Biodiesel Board

CRADA Number: CRD-05-153

CRADA Title: Biodiesel Performance with Modern Engines

Joint Work Statement Funding Table Showing DOE Commitment:

Estimated Costs	NREL Shared Resources
Year 1	$ 1,665,000.00
Modification 2	$ 20,000.00
Modification 4	$ 500,000.00
Modification 5	$ 500,000.00
Modification 6	$ 200,000.00
Modification 7	$ 400,000.00
Modification 9	$ 100,000.00
Modification 10	$ 100,000.00
Modification 12	$ 100,000.00
TOTALS	$ 3,585,000.00

Abstract of CRADA Work:

NREL and the National Biodiesel Board (NBB) will work cooperatively to assess the effects of biodiesel blends on the performance of modern diesel engines and emissions control systems meeting increasingly strict emissions standards. This work will include research to understand the impact of biodiesel blends on the operation and durability of particle filters and NOx control sorbents/catalysts, to quantify the effect on emission control systems performance, and to understand effects on engine component durability. Work to assess the impact of biodiesel blends on real world fleet operations will be performed. Also, research to develop appropriate ASTM standards for biodiesel quality and stability will be conducted. The cooperative project will involve engine testing and fleet evaluation studies at NREL using biodiesel from a variety of sources. In addition, NREL will work with NBB to set up an Industrial Steering Committee to design the scope for the various projects and to provide technical oversight to these projects. NREL and NBB will cooperatively communicate the study results to as broad an audience as possible.

Summary of Research Results:

Research was performed under this CRADA on several aspects of biodiesel compatibility with engines, vehicles, and fuel handling infrastructure.

Biodiesel Performance with New Technology Diesel Emission Controls. Early work under this CRADA examined performance of generic biodiesel blends with new diesel emission control technologies over the short term. Williams and coworkers [1] demonstrated that biodiesel increased the reactivity of particulate matter (PM) in a diesel particle filter (DPF), resulting in lower light-off temperature and easier DPF regeneration. Research on biodiesel performance with urea selective catalytic reduction (SCR) systems for reducing NOx emissions showed no negative impact of biodiesel [2] and demonstrated that unburned biodiesel adsorbed on the zeolite-based catalyst would not result in thermal excursions capable of causing catalyst damage [3]. Research on an alternative NOx reduction system called a NOx adsorber catalyst (NAC) demonstrated increased NOx conversion for biodiesel because biodiesel leads to reduced exhaust temperature. The lower operation temperature for the NAC increased the amount of NOx adsorbed and subsequently higher NOx reduction was achieved [4].

Additional research has examined long-term durability impacts of biodiesel on these systems. Engine dynamometer testing that simulated 120,000 miles of use in a light-duty car showed no negative impacts on DPF or NAC durability for a commercial biodiesel (B20 blend) [4]. Similar testing of an SCR catalyst demonstrated no catalyst activity loss in comparison to conventional diesel, although both systems experienced a relatively high degree of catalyst deactivation such that the car could not meet the Tier 2 Bin 5 emission standards at end of test [5]. Subsequently, engine and catalyst manufacturers expressed concern about residual metals (Na, K, Mg, and Ca) that can be present in biodiesel and how these metals might impact catalyst durability. In a follow up study the SCR system on a Ford F250 truck was exposed to the equivalent of 150,000 miles of biodiesel (B20) exhaust containing Na, K, or Ca [6]. The system also included a diesel oxidation catalyst (DOC) and a DPF. Over the course of the catalyst aging no activity loss or increase in emissions from the truck were observed. However, detailed investigation of the fate of the metals on the catalyst parts and the activity at different locations in the catalyst parts showed significant impact on the diesel oxidation catalyst. These results imply the possibility that heavy-duty (HD) truck systems with longer lifetime and exposure to larger volume of exhaust may prove more sensitive. The metals aging study accelerated catalyst exposure by doping of the fuel with high levels of metal. A related task investigated the possibility that this approach to acceleration created deactivation modes that would not be observed at normal fuel metal levels [7]. Results showed that beyond a certain threshold, the acceleration rate creates an artificial mechanism for catalyst deactivation.

Research has also examined the impact of biodiesel metals on HD catalyst system deactivation. A 2007 model year HD engine was subjected to a 1,000 hr durability test using market biodiesel. No issues with the fuel injection or emission control systems were noted [8]. Fuel doped with high levels of biodiesel metals was burned in an engine and used to expose HD catalyst parts to the equivalent of 435,000 miles of metals [9]. No evidence of SCR catalyst deactivation was observed, however there was some degradation of DOC activity and of DPF thermal shock resistance. However, at the time this task was conducted HD emission control systems were in development and not yet commercially available. Engine and catalyst manufacturers anticipated that occasional temperature excursions to 850°C could occur and a fraction of catalyst aging time was spent at this very high temperature. After introduction of these systems into the market in 2010, manufacturers determined that temperatures above 650°C were rarely if ever encountered. Thus, the catalyst and filter degradation observed in our study may have been an artifact of the very high temperatures utilized (chemical reaction rates typically double with a 10°C increase in temperature, thus for a 200°C increase in temperature reaction rates could increase by a factor of 220, or 1 million).

One of the final tasks in the CRADA was to re-examine HD emission control systems using more realistic temperatures and other method improvements developed over the past several years. A 2010 model year Cummins HD engine with a fully engineered emission control system was employed. The engine and catalyst parts were exposed to the equivalent of 435,000 miles of Na assuming that the engine utilized B20 prepared from B100 at the 5 ppm alkali metal specification limit its entire full-useful life. Some degradation of NOx conversion was observed over the 1,000 hr aging cycle, as well as significant buildup of pressure drop over the DPF. Detailed post-test analysis of the system components suggested that engine lube oil components were negatively impacting the ability of the DOC to oxidize NO to NO_2. Additionally, the SCR was found to be contaminated with Pt, which likely originated in the DOC or DPF during high temperature excursions. No evidence of deactivation caused by Na was observed in these components. There is a potential issue with DPF ash loading being significantly higher for B20 at the specification limit than would be the case for an engine operating for 435,000 miles on ultra-low sulfur diesel. High ash loading could lead to the need for a DPF cleaning event to occur at significantly lower mileage than baseline. The implications of this result are still being examined by the industrial steering committee. These results have not yet been published.

Advanced emission control systems utilize fuel injected into the exhaust for temperature control during DPF regeneration as well as for NAC regeneration. This can, in some cases, result in high levels of lube oil dilution by the fuel. In two tasks the potential for high levels of biodiesel in the lubricant was examined. In a study utilizing a light-duty vehicle with DPF and NOx control systems, for operation of the NAC, biodiesel oil dilution levels ranged from 5%-10% [10]. For operation with an SCR system biodiesel oil dilution ranged from 2%-5%. The rate of lubricant total base number (TBN) decrease with oil age was identical for the SCR and NAC systems, indicating that the main factor affecting TBN loss is simply lubricant age, not biodiesel content. Additional experiments were conducted on both a HD engine and a second light-duty car [11]. In this study a new lube oil analysis method was developed for improved quantitation of both diesel and biodiesel content of the oil. Analysis of the HD lube-oil samples showed only 1.5% to 1.6% fuel dilution for both fuels during continuous operation under DPF regeneration events, suggesting that lube oil dilution from late in-cylinder injection is not an issue for this engine design. However, for B20 the fuel in the oil was 36% biodiesel. After 4,000 miles of LD vehicle operation with ULSD, fuel dilution in the lube-oil was 4.1% diesel. After 4,000 miles of operation with B20, total fuel in oil dilution level was 6.7% consisting of 3.6% diesel and 3.1% biodiesel. Extrapolation to the 10,000-mile oil drain interval with B20 suggests that the total fuel content in the oil could reach 12%, compared to 5% for operation on ULSD.

Effect of Biodiesel on Engine-Out NOx and DPF Performance. A 2002 model year Cummins ISB 300 engine was used to examine the effects of shifting engine parameters from their stock settings on the performance of a 20% biodiesel blend (B20) [12]. The objective of this work was to determine if it is possible to use a more optimal engine calibration to eliminate the small fuel economy and NOx emission penalties typically observed for B20 in comparison to petroleum diesel, while preserving the significant reduction in PM emissions that is also typically observed. Tests were conducted at multiple steady-state operating modes. Two engine parameters were modified: a 1° advance in fuel injection timing and a 4% exhaust gas recirculation valve position increase. For B20, the simple calibration changes yielded an average decrease in NOx emissions of 2% with a brake-specific fuel consumption penalty of less than 1%, while still reducing PM emissions overall in comparison to B0 and the stock calibration. In comparison, the stock calibration resulted in an average 5% increase in NOx emissions, and a 2% increase in fuel consumption with B20.

A second study investigated which biodiesel fuel properties impact soot reactivity in a DPF [13]. 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 and soot oxidation was studied by thermo-gravimetric 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 provided a more effective form of oxygen than the methyl-esters of biodiesel for improving soot reactivity.

B20 In-Use Fleet Evaluation. The objective of this project was to evaluate the extended in-use performance of transit buses employing engines equipped with exhaust gas recirculation (EGR), a newer engine technology than those assessed in prior studies [14]. Specific objectives were to compare fuel economy, vehicle maintenance costs, reliability, and lube oil performance in comparison to ULSD. The buses were operated by St. Louis Metro from October 2006 to April 2008. Thus, the initiation of this test coincided with the introduction of ULSD that occurred in most of the United States in October 2006. We examined 15 model year (MY) 2002 Gillig 40-foot transit buses equipped with MY 2002 Cummins ISM engines. The engines met 2004 U.S. emission standards. For 18 months, eight of these buses operated exclusively on B20 and seven operated exclusively on ULSD. The B20 and ULSD study groups operated from different depots of the St. Louis (Missouri) Metro, with bus routes matched for duty cycle parity.

The B20- and ULSD-fueled buses exhibited comparable fuel economy, reliability (as measured by miles between road calls), and total maintenance costs. Engine and fuel system maintenance costs were also the same for the two groups after correcting for the higher average mileage of the B20 group. Fuel filter plugging during unseasonably cold temperatures was more prevalent for the B20 group. Lube oil samples were collected over a wide range of mileage within the drain interval, and analyses indicate reductions in soot loading and wear metals in the B20 buses. Viscosity loss and lead corrosion were greater in the B20 group, while the total base number (TBN) loss was not significantly changed.

Biodiesel Oxidation Stability. Longer-term storage stability of biodiesel and blends was studied in experiments simulating up to one year for 100% biodiesel (B100) and three years for blends [15]. Aging was simulated by holding samples at 43 °C to accelerate oxidation (ASTM method

D4625). Biodiesels were treated with antioxidants before and after aging, with continued aging after antioxidant treatment. Treating aged biodiesel was effective at restoring stability; however, antioxidant effectiveness was decreased relative to fresh biodiesel. Blends were prepared at B5 (5 vol.%) and B20 (20 vol.%) with biodiesel having either 3- or 6-hour Rancimat induction time and low or high polyunsaturated ester content with two diesels produced from hydrocracked or hydrotreated feedstocks. All B5s were stable for the entire storage time regardless of B100 induction time. B20s were unstable if prepared from high polyunsaturated ester biodiesel with a 3-hour induction time. Base diesel stability had considerable effect on blend stability. All but the lowest-stability B20s remained within specification, indicating that long-term storage of biodiesel blends is possible if the biodiesel has high oxidative stability and storage conditions are clean. Induction time decreases indicated loss of stability (consumption of antioxidant) prior to blend degradation; therefore, induction time monitoring is recommended for predicting quality changes during storage.

Adoption of high-pressure common-rail (HPCR) fuel systems, which subject diesel fuels to higher temperatures and pressures, has brought into question the veracity of ASTM International specifications for biodiesel and biodiesel blend oxidation stability, as well as the lack of any stability parameter for diesel fuel. A controlled experiment was developed to investigate the impact of a light-duty diesel HPCR fuel system on the stability of 20% biodiesel (B20) blends under conditions of intermittent use and long-term storage in a relatively hot and dry climate [16]. B20 samples with Rancimat induction periods (IPs) near the current 6.0-hour minimum specification (6.5 hr) and roughly double the ASTM specification (13.5 hr) were prepared from a conventional diesel and a highly unsaturated biodiesel. Four 2011 model year Volkswagen Passats equipped with HPCR fuel injection systems were utilized: one on B0, two on B20-6.5 hr, and one on B20-13.5 hr. Each vehicle was operated over a one-hour drive cycle in a hot running loss test cell to initially stress the fuel. The cars were then kept at Volkswagen's Arizona Proving Ground for two (35°C average daily maximum) to six months (26°C average daily maximum). The fuel was then stressed again by running a portion of the one-hour dynamometer drive cycle (limited by the amount of fuel in the tank). Fuel rail and fuel tank samples were analyzed for IP, acid number, peroxide content, polymer content, and ester profile. The HPCR fuel pumps were removed, dismantled, and inspected for deposits or abnormal wear. Analysis of fuels collected during initial dynamometer tests showed no impact of exposure to HPCR conditions. Long-term storage with intermittent use showed that IP remained above 3 hours, acid number below 0.3 mg KOH/g, peroxides low, no change in ester profile, and no production of polymers. Final dynamometer tests produced only small changes in fuel properties. Inspection of the HPCR fuel pumps revealed no deposits or abnormal wear for any fuel. The results provide some confidence that the ASTM D7467 stability requirement of 6 hr minimum IP for B6 to B20 blends provides adequate protection for modern engine fuel systems.

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<u>Subject Inventions Listing</u>:

None

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