

Effect of Biodiesel (B20) on Vehicle-Aged Engine Oil Properties

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ABSTRACT

High concentrations of diesel fuel can accumulate in the engine oil, especially in vehicles equipped with diesel particle filters. Fuel dilution can decrease the viscosity of engine oil, reducing its film thickness. Higher concentrations of fuel are believed to accumulate in oil with biodiesel than with diesel fuel because biodiesel has a higher boiling temperature range, allowing it to persist in the sump. Numerous countries are taking actions to promote the use of biodiesel. The growing interest for biodiesel has been driven by a desire for energy independence (domestically produced), the increasing cost of petroleum-derived fuels, and an interest in reducing greenhouse gas emissions.

Biodiesel can affect engine lubrication (through fuel dilution), as its physical and chemical properties are significantly different from those of petrodiesel. Many risks associated with excessive biodiesel dilution have been identified, yet its actual impact has not been well quantified. In this study, diesel engine oil samples were collected from a fleet of prototype medium-duty trucks with diesel particulate filters running on either ULSD (ultra low sulfur diesel) or B20 (20 vol% biodiesel in ULSD) fuel to determine the effect of biodiesel on engine lubrication. The study consisted of three parts: 1) oil analysis, 2) laboratory friction and wear testing with the vehicle-aged oil samples, and 3) chemical analysis of the wear-protective tribofilms that formed on ferrous substrates during laboratory friction and wear testing. Results showed B20 dilution caused increased lead corrosion, fuel dilution, and oxidation, and decreased viscosity. Laboratory wear test results showed increased wear with vehicle miles for both ULSD and B20 fuels. However, increased wear is not directly related to decreased viscosity resulting from fuel dilution.

INTRODUCTION

Modern diesel vehicles are equipped with emissions control equipment to help meet stringent particulate matter and NO_x emissions regulations. Diesel particle filters (DPFs) are used to help meet stringent particulate matter emissions regulations. As the pores of DPFs become blocked with soot particles, the filter is cleaned through regeneration. Regeneration is currently accomplished by post injection of fuel into the engine cylinders, which heats the DPF to high temperatures required for regeneration of the DPF. However, late fuel injections create higher levels of fuel dilution of the engine oil.

Fuel dilution decreases the viscosity of the engine oil, reducing its film thickness, and also decreases the concentration of oil additives. Higher concentrations of fuel are believed to accumulate in the oil with biodiesel than with petrodiesel because biodiesel has a higher boiling temperature range, allowing it to persist in the sump¹. The wear protection capability of engine oil is primarily influenced by 1) the oil film thickness and 2) the nature of the additive-derived film that forms on the surface of ferrous substrate materials in contact with each other. The film thickness decreases as viscosity decreases. The viscosity of both ultra low sulfur (<15 ppm sulfur) diesel (USLD) and B20, a blend of 20 vol% biodiesel blended with 80 vol% ULSD, (1.9-4.1 cSt at 40 °C^{2, 3}) is much lower than Ford's recommended SAE 15W-40 API CJ-4 service fill diesel oil (116 cSt at 40 °C), increasing the potential for excessive wear with fuel dilution.

Pure biodiesel fuel is referred to as B100. It has significantly different physical and chemical properties from ULSD. This raises concerns over the effect of biodiesel on the performance of engine oil. Biodiesel is composed of fatty

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acid methyl esters (FAMES) produced from the transesterification reaction of triglycerides containing long chain fatty acids and alcohol (usually methanol). The composition of the FAMES varies with the feedstock, and affects the properties of biodiesel such as pour point and oxidation stability⁴. Common biodiesel feedstocks in the US include vegetable oils, such as soy and corn oil, and animal fats. A biodiesel blend, designated as BXX, is a blend of XX % biodiesel with petrodiesel. Ford warranty policy currently accepts biodiesel blends of B5 or less for use in any of its diesel engines. Biodiesel blends up to B20 are approved for the new 6.7L V-8 turbocharged diesel engine. Other original equipment manufacturers are cautiously recommending various biodiesel blends⁵.

Numerous countries worldwide are taking actions to promote the use of biodiesel. The new Renewable Fuel Standard of the U.S. Energy Independence and Security Act of 2007 mandates the use of alternative, renewable fuels such as biodiesel. This legislation will greatly increase the use of biodiesel in the marketplace. It requires a volume of 500 million gallons of biomass-based diesel (which includes biodiesel) into the nation's fuel supply in 2009, growing to 1 billion gallons by 2012⁶. In comparison, the U.S. consumes about 45 billion gallons of diesel fuel for transportation per year⁷. More biodiesel in the marketplace leads to a greater potential risk of engine lubrication issues.

The growing interest for biodiesel has been driven by a desire for energy independence (domestically produced), the increasing cost of petroleum-derived fuels, and an interest in reducing greenhouse gas emissions⁸. Biodiesel can affect engine lubrication (through fuel dilution), as well as combustion characteristics and emissions. Many risks associated with excessive biodiesel dilution have been identified, yet its actual impact has not been well quantified.

Limited information has been published on the impact of biodiesel on the durability of modern engines in cases with high fuel dilution. Laboratory oil aging studies have reported the effect of biodiesel dilution on engine oil^{9, 10, 11, 12}. Work at Ford Research⁹ has shown that fuel dilution resulted in increased oil degradation, and biodiesel has a greater effect on degradation than ULSD dilution. Bench tests with the laboratory-aged oil with simulated fuel dilution showed wear increases as oil age increases, but wear was not any worse with biodiesel than with ULSD. Work by Watson et al.¹⁰ indicated that fuel dilution would be greater with biodiesel than ULSD, and biodiesel dilution increased oil degradation and copper corrosion. A bench test used to qualify oil as API CJ-4, High Temperature Corrosion Bench Test (HTCBT), conducted with B20 showed increased levels of lead corrosion¹¹. A laboratory study by Fang et al.¹² using

mixtures of base oil, zinc dithiodialkyl phosphate (ZDDP), and fuel showed an increase in wear as the concentration of aged biodiesel increased. The authors suggested partially degraded biodiesel interacts with ZDDP, an anti-wear additive, to hinder wear protection. Wear did not increase as the amount of fresh biodiesel increased, indicating no problematic interaction between ZDDP with fresh biodiesel.

Engine tests with significant levels of fuel dilution have been run to study the impact of biodiesel dilution on engine lubrication^{11, 13, 14, 15, 16}. The general conclusions have been consistent, in that biodiesel dilution causes increased fuel dilution¹³, increased oil degradation^{14, 15}, increased lead corrosion^{11, 14, 15}, and increased engine deposits^{11, 14}. These findings have supported reduced oil drain interval recommendations for vehicles running on biodiesel blends greater than B5. Despite these findings, excessive engine wear has not been observed with biodiesel^{11, 14, 16}. Additionally, Devlin et al.¹⁶ observed that soot particles in the oil from B20 and ULSD were of similar size and hardness. The latest ACEA European specifications for heavy duty engine oils require OM646LA¹⁷ and OM501LA¹⁸ engine tests to be run with B5 to ensure that the oil is able to adequately protect the engine in the presence of biodiesel.

Fleet evaluations have been run with B20, but the level of fuel dilution in these studies was either minimal or unreported^{19, 20, 21, 22}. Proc¹⁹ and Barnitt²⁰ reported lower concentrations of soot in the engine oil with vehicles fueled with B20, probably due to reduced particulate matter emissions with B20¹.

In this study, several engine oil samples were collected from a fleet of prototype medium-duty trucks running on either ULSD or biodiesel to determine the effect of biodiesel on engine lubrication. The study consisted of three parts: 1) oil analysis, 2) laboratory friction and wear testing with the vehicle-aged oil samples, and 3) chemical analysis of the wear-protective tribofilms that formed on ferrous substrates during laboratory friction and wear testing.

EXPERIMENTAL

VEHICLE AGING

Diesel engine oil samples were collected between 2-3 times per week from a fleet throughout a given oil change interval. The fleet consisted of six prototype medium-duty trucks equipped with V-8 diesel engines. The vehicles were equipped with an experimental urea selective catalytic reduction (SCR) aftertreatment system, and used a post-injection strategy for active DPF regeneration. The experimental aftertreatment configuration did not include any means of passive regeneration of the DPF, such as a



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continuously regenerating trap (CRT), which shortened the usual DPF regeneration interval. The trucks accumulated miles rapidly, as they were driven on a specified route between Grand Rapids, MI and Dearborn, MI in a light load cycle that included roughly 80% highway and 20% city driving. Motorcraft SAE 15W-40 diesel engine oil was used, which meets the current API CJ-4 specification.

The ULSD and B20 trials were run in series for this experiment, first with ULSD and then with B20. A total of 42 oil samples were collected throughout seven oil drain intervals from the fleet during the ULSD trial, which was run in August. The odometer reading of the vehicle fleet ranged from 74,000 to 87,000 miles at the start of the ULSD trial, thus the vehicles were well broken-in. Vehicle #142 was not available during the ULSD trial. Subsequently, 49 oil samples were collected throughout six oil drain intervals from the same fleet while it was running on B20 fuel. The odometer reading of the vehicle fleet ranged from 99,000 to 126,000 miles at the start of the B20 trial, which was run in November. B20 fuel was obtained from the Ann Arbor-Saline Road Meijer fuel station in Ann Arbor, MI. Oil samples were collected at regular intervals throughout the duration of an oil change interval. The volume of each oil sample was four ounces, which was small enough to ensure that the engine did not have to be topped off with any additional fresh oil. The normal oil drain interval for this fleet was 7,500 miles. Four of the thirteen oil change intervals in this study were extended to ~12,000 miles, in which special care was taken to drain a portion of the oil after 7,500 miles to prevent the sump from overflowing from excessive fuel dilution. Vehicles #144 and #145 had an extended oil drain interval with ULSD, and Vehicles #140 and #143 had an extended drain interval with B20. The bulk engine oil temperature during vehicle operation generally ranged from 85-95 °C (Figure 1) and did not exceed 100 °C. Slightly lower bulk oil temperature with B20 is most likely due to the lower ambient temperature during the B20 trial in November.

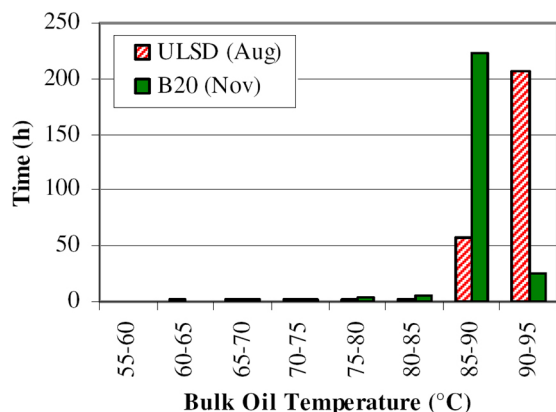


Figure 1. Histogram of bulk oil temperature for Vehicle #143.

The vehicles were equipped with sensors to monitor certain regeneration characteristics. On average, the regeneration interval was 50% longer with B20, compared to ULSD (Figure 2). The fact that regenerations were not required as frequently with B20 implies that the pores of the DPF were not plugged as rapidly with the use of B20. The vehicles were calibrated to regenerate the DPF when either the pressure reached a certain level, or after a certain number of miles travelled. With the use of B20, the mileage backstop usually triggered regenerations. However, this difference was partially offset by the fact that a greater mass of fuel was post-injected with B20 than with ULSD during each DPF regeneration event (Figure 3). The average mass of fuel consumed during a DPF regeneration event was 1,900 g and 2,500 g for ULSD and B20, respectively (including both fuel for running the engine and regenerating the DPF over an interval of several minutes). This was due to several factors including cooler ambient temperatures during the B20 trial, lower energy density of B20, engine speed and load operation shift due to energy density change, and a longer regeneration event duration for the mileage backstop. Both the DPF regeneration interval and the mass of fuel injected per regeneration affect the fuel dilution rate. If the B20 trial was run at the same ambient temperature as the ULSD trial, it is likely that the mass of B20 injected per regeneration would decrease, and thus the B20 dilution rate would also decrease.

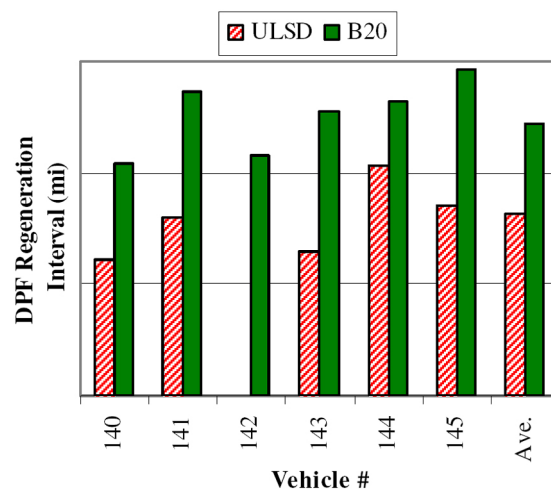


Figure 2. Average DPF regeneration interval for each vehicle.

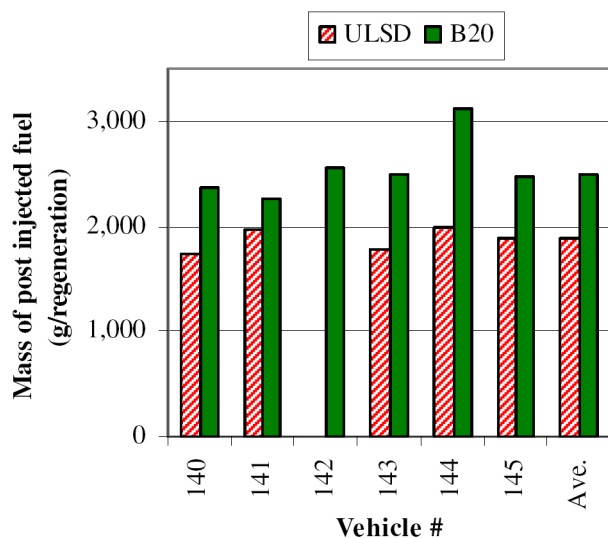


Figure 3. Average mass of post injected fuel per regeneration for each vehicle.

ENGINE OIL ANALYSIS

Vehicle-aged oils were analyzed for several properties including: fuel dilution, kinematic viscosity, metal content, oxidation, total acid number (TAN), total base number (TBN), and soot content. Analysis of the biodiesel fraction and oxidation measurements were conducted at the Ford Research and Innovation Center, and all other oil properties were determined at Intertek. Intertek's oil analyses were based on in-house methods that are similar to the ASTM methods. Fuel dilution determination was similar to ASTM D3524, a gas chromatography (GC) method. Elemental analysis was done similarly to ASTM D5185, and kinematic viscosity was based on ASTM D445. Water concentration was determined through Karl Fischer analysis, based on ASTM D6304.

Oxidation was determined by differential IR analysis using the fresh oil as a reference and the IR peak near 1700 cm^{-1} with a Nicolet Avatar 360 FTIR and OMNIC Integra analysis software. In the case of biodiesel-containing samples, the interference of esters on oxidation was removed, as described later. Oil oxidation products are composed of many different carbonyl-containing compounds including esters, aldehydes, ketones, and carboxylic acids. Oxidation can cause viscosity increase, sludge formation, additive depletion, TAN increase, and base oil breakdown. TAN and TBN were determined by titration methods similar to those described in ASTM D664 and ASTM D4739, respectively. TAN refers to the amount of acid species in the oil, and is an indicator of the potential to have corrosion problems. TBN indicates the total base components remaining in the oil to neutralize the buildup of harmful acidic species in the oil.

The biodiesel fraction of vehicle-aged oil samples was measured and compared with the use of two different methods, a differential IR method similar to ASTM D7371, and a second GC method. The differential IR method uses the differential height of the ester peak near 1746 cm^{-1} , which grows linearly with increasing concentration of fresh biodiesel in fresh oil. Due to possible oil and/or fuel degradation with aging or possible oil/fuel interactions that could interfere with the IR peak at 1746 cm^{-1} , the biodiesel dilution of selected samples was verified through a GC method, using a GC column optimized for biodiesel measurement, rather than petrodiesel, as described below.

The identity and concentration of individual FAMES in oil and fuel were quantified by GC. Approximately 0.010 g (about one drop) of oil or fuel sample was first diluted in 10 mL of dichloromethane, with the actual amounts determined gravimetrically. The diluted sample was then analyzed using a Model 7890A GC (Agilent Technologies) equipped with a flame ionization detector and autosampler. Injections ($1\text{ }\mu\text{L}$) were in split mode (50:1 split ratio) onto a DB-23 capillary column (J&W Scientific) having 30-m length, 0.32-mm outer diameter, and $0.25\text{-}\mu\text{m}$ film thickness. Oven temperature was initially $130\text{ }^{\circ}\text{C}$ for 1 min , then ramped to $170\text{ }^{\circ}\text{C}$ at $6.5\text{ }^{\circ}\text{C/min}$, then ramped to $215\text{ }^{\circ}\text{C}$ at $2.75\text{ }^{\circ}\text{C/min}$ and held for 12 min , then ramped to $270\text{ }^{\circ}\text{C}$ at $40\text{ }^{\circ}\text{C/min}$ and held for 3 min . Helium carrier gas was held at constant pressure of 100 kPa . Injector and detector temperatures were $270\text{ }^{\circ}\text{C}$ and $280\text{ }^{\circ}\text{C}$, respectively. Nitrogen was used as the detector make-up gas. For quantification and peak identification, peak areas and retention times were compared to those of known FAME standards.

The GC data were used to provide information on total biodiesel content (sum of all detected FAME concentrations), the composition (speciation) of the FAMES, and the location and cis-trans isomerism of carbon-carbon double bonds. The type of feedstock used to produce biodiesel can be determined from the composition of the resulting FAMES. Typically, a biodiesel feedstock oil is comprised of triglycerides containing a variety of different fatty acids, each having different carbon chain length and/or number of carbon-carbon double bonds in its chain. Typical biodiesel in the US, made from soy oil, corn oil, or animal fat, is composed of FAMES with carbon chain lengths of 16-18 carbon atoms, and 0-3 double bonds. The notation commonly used is Cx:y , where x is the chain length and y is the number of double bonds. For example, methyl linoleate (also known as linoleic acid methyl ester) is identified as C18:2 , indicating a carbon chain length of 18 and 2 double bonds.

Biodiesel feedstock determination was accomplished by comparing the FAME composition of samples (normalized to 100% of identified FAMES) to the fatty acid profiles of reference materials in published sources^{23, 24}. The sum of

squared errors between the two was used to determine goodness of match. In cases where a reasonably good fit was not obtained with a single feedstock, combinations of up to three common feedstocks (soy oil, corn oil, or lard) were used and best-fit proportions were again determined by minimizing the sum of squared errors.

FRICITION AND WEAR TESTING

Friction and wear protection capability of vehicle-aged oils were evaluated with a High Frequency Reciprocating Rig (HFRR) from PCS Instruments. HFRR is a bench test to study wear in the boundary lubrication regime. HFRR allows for fast, inexpensive testing of a large number of samples, and only requires an oil volume of 2 mL. In the bench test, a non-rotating steel ball (6 mm diameter) slides against a stationary steel disk (9.8 mm diameter). The ball material is AISI E-52100 steel with hardness of 58-66 HRC, and the disk material is AISI E-52100 steel with hardness of 190-210 HV 30. The rubbing interface is submerged in oil. The test conditions used in this study were selected to represent severely loaded engine contacts. They include a 1,000 g normal load, 20 Hz reciprocating frequency, 1,000 micron stroke length, and three hour test duration. The oil temperature was 105 °C. The initial contact stress with a 1,000 g load is 1.3 GPa. A new ball and disk were used in each test. Generally, oil with better boundary wear protection will produce a smaller wear scar.

Prior to testing, the steel balls and disks were ultrasonically cleaned in hexane for five minutes, and then rinsed again with hexane. The friction coefficient and the electrical contact resistance (ECR) are measured by HFRR during testing. The reported friction coefficient and ECR values are the average values over the three hour test duration. ECR provides a measure of the formation of an electrically insulating film at the sliding contact. It does not provide an indication of film thickness. Zero percent ECR can be interpreted as either metal-to-metal contact, or the presence of an electrical conducting film. One-hundred percent ECR indicates the formation of a fully insulating film between the sliding surfaces. After the completion of testing, wear was determined by measuring the volume of material that was removed from a steel disk during a test using a Wyko NT3300 optical profilometry instrument from VEECO and Vision software program. The surface of each steel disk was rinsed with hexane to remove all residual oil and non-adherent material prior to the wear measurement.

SURFACE FILM ANALYSIS

The chemical constituents of lubricant-derived films that formed on selected HFRR disks were analyzed through UV and visible Raman spectroscopy. Details of Raman analysis have been described earlier²⁵. Raman spectroscopy provides information on the identities of molecular species. UV (244

nm) and visible (532 nm) Raman spectroscopy are both utilized because of differences in penetration depth and differences in resonance enhancement which can lead to observations of different components when both laser wavelengths are used. The continuity of a film can be assessed with Raman, as it has a spatial resolution of ~1-2 µm in diameter. Multiple spectra were taken from each sample to ensure the results were not out of the ordinary.

RESULTS

OIL ANALYSIS

Fuel Dilution

Fuel dilution in the oil (based on the ASTM D3524 method) reached higher levels with the use of B20, compared to ULSD (Figure 4). After 12,000 miles, the fuel dilution with B20 and ULSD reached roughly 35% and 25%, respectively. At low mileage, the dilution levels were similar. The difference between B20 and ULSD dilution levels grew as oil miles increased, due to the slower evaporation rate of biodiesel at the oil temperatures in this study. In addition, the oil sump temperature with B20 was lower, which would further reduce the evaporation rate. Other factors that were described earlier, including the frequency of DPF regenerations and the mass of fuel post injected into cylinders, were seen to vary with fuel type, which also affect the fuel dilution rate. Initial oil samples that were collected right after an oil change contained ~5% fuel dilution, which is partly attributed to carryover from the previous oil drain. It is also possible that light ends of the oil were counted as fuel.

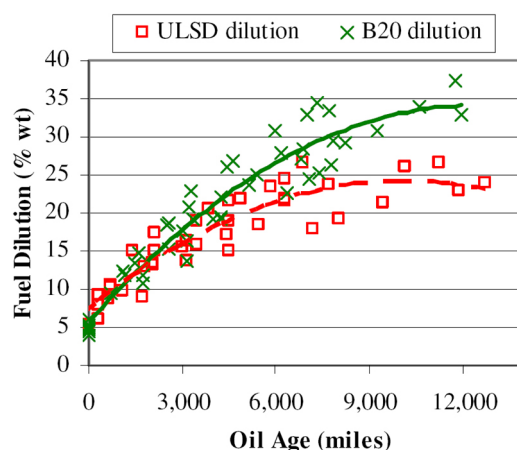


Figure 4. Fuel dilution vs. mileage.

The fuel in the oil samples from vehicles that ran with B20 consists of both ULSD and biodiesel. The biodiesel concentration in oil (measured by differential IR) reaches ~13% after 12,000 miles (Figure 5). Initial biodiesel accumulation in oil was ~2-3% wt. per 100 gallons of B20 consumed. Of the total fuel accumulated in the oil after 7,000 miles, the biodiesel fraction was ~40% wt. while the other

~60% wt. is ULSD (Figure 6), as calculated from the ratio of biodiesel concentration (Figure 5) to total fuel concentration in oil (Figure 4). Multiple samples of the fresh B20 fuel from the fuel station were analyzed to confirm that fresh fuel pumped into the fuel tank was indeed B20, or 20% biodiesel. In other words, the fuel pumped into the fuel tank is B20, but the fuel in the oil resembles B40 because ULSD boils off at a lower temperature range than biodiesel, and ULSD is volatilized faster than biodiesel at the oil temperatures in this study. The slightly increasing trend shown in Figure 6 is attributed to ongoing evaporation of ULSD from the oil, and to ULSD dilution that was carried over from the previous oil drains.

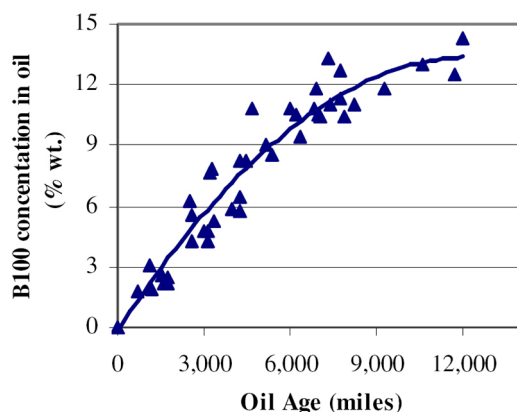


Figure 5. Biodiesel concentration in oil vs. mileage. The oil consists of oil, biodiesel, and ULSD.

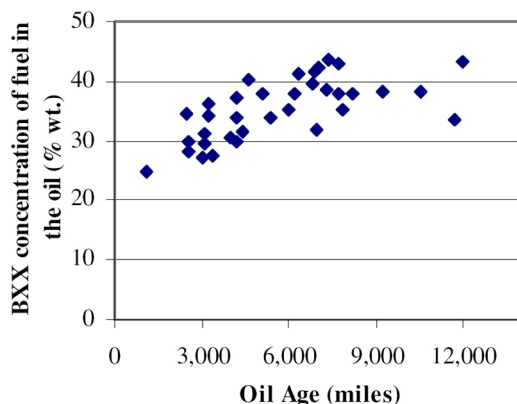


Figure 6. BXX concentration of fuel in the oil vs. mileage. The fuel consists of biodiesel and ULSD.

The biodiesel concentration shown in Figures 5 and 6 was measured with a differential IR method. Oil degradation could interfere with the accuracy of the IR method, so the biodiesel dilution of selected samples was confirmed through a GC method. Results from the two methods show high correlation and good absolute agreement (Figure 7). The agreement suggests that the methyl ester absorptions at 1746

cm^{-1} of IR spectra were not greatly disturbed by the absorption of oxidation products near 1700 cm^{-1} .

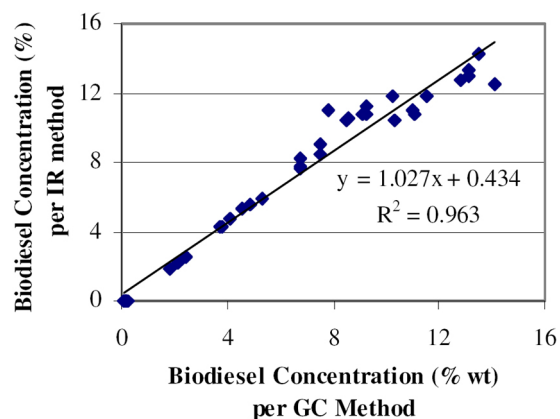


Figure 7. Comparison of IR vs. GC biodiesel measurement methods.

Additionally, the speciation of FAMES in biodiesel-containing oils changed only modestly and the location and cis-trans isomerism of carbon-carbon double bonds in unsaturated FAMES did not change with age. The fatty acid ester composition of the biodiesel fraction of oil samples collected from Vehicle #143 is shown in Figure 8. After 1,499 miles, the oil contained 2.4 wt% biodiesel. The biodiesel was made up of 29.5% methyl linoleate (C18:2), 33.9% methyl oleate (C18:1), 16.6% methyl palmitate (C16:0), 10.1% methyl stearate (C18:0), 3.7% methyl linolenate (C18:3), 3.0% methyl palmitoleate (C16:1), and 3.1% other acid esters, suggesting a biodiesel feedstock containing about 40% soy oil and 60% lard (pig fat). As the biodiesel fraction in the oil increased to 5.3 wt% after 3,994 miles, the proportion of fatty acid esters remained the same, indicating the biodiesel feedstock did not change. At 5,398 miles, the proportion of fatty acid esters began to shift. The C18:2 fraction increased from 29.5% to 38.0%, whereas the fractions of C18:1, C16:0, and C18:0 decreased. The timing of the shift corresponded to when the fuel station supplying the B20 received a new batch of fuel. Based on the FAME composition of the new fuel (in a fuel sample collected on 11/24/08), the biodiesel contained a different feedstock mix (most closely matched by 20% soy oil, 20% lard, and 60% corn oil) than in the biodiesel used at the start of the B20 trial. After this change in fuel, the proportion of FAMES in the oil gradually shifted through the end of the oil interval, consistent with the accumulation/depletion of FAMES from the new fuel in the existing mixture from the prior fuel.

The poly-unsaturated FAMES (e.g., C18:3 and C18:2) are known to be considerably more oxidatively unstable than mono-unsaturated (e.g., C18:1, C16:1) and saturated FAMES (e.g., C18:0, C16:0). Given the change in B20 fuel FAME composition during the trial, determining whether the poly-