

Effect of Different B20 Fuels on Laboratory-Aged Engine Oil Properties

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ABSTRACT

Biodiesel-blended fuel is increasingly becoming available for diesel engines. Due to seasonal and economic factors, biodiesel available in filling stations can be sourced from varying feedstocks. Moreover, biodiesel may not contain the minimum oxidative stability required by the time it is used by the automotive consumer. With fuel dilution of engine oil accelerated by post-injection of fuel for regeneration of diesel particulate filters, it is necessary to investigate whether different biodiesel feedstocks or stabilities can affect engine oil properties. In this work, SAE 15W-40 CJ-4 is diluted with B20 fuel, where the B20 was prepared with soy methyl ester (SME) B100 with high Rancimat oxidative stability, SME B100 with low oxidative stability, and lard methyl ester (LME). The oils were then subjected to laboratory aging simulating severe drive cycles. At intermediate aging times, samples were obtained and additional B20 was added to simulate on-going fuel dilution. Gas chromatographic and FTIR analyses were performed to monitor fatty acid methyl ester (FAME) content and oil degradation, respectively, while ball-on-flat sliding tests (HFRR) were run to assess friction, antiwear film formation, and wear protection capability under boundary lubrication conditions.

The results generally showed no differences in film formation, friction, and degree of wear with these three different sources. Friction, film formation, and wear were very similar before, during, and after aging. Oxidation of polyunsaturated FAMES in SME and LME occurred, but did not appear to adversely impact the tribological results. Oil degradation as measured by FTIR was also similar for the different B20s.

INTRODUCTION

Fuel dilution occurs when fuel is injected late in the combustion cycle ("post-injection") to regenerate the diesel particulate filter (DPF) for trapping particulate emissions. Under normal engine operating conditions, a small amount of dilution is always seen, but post-injection can bring upwards of 20 wt% dilution before the oil is drained¹. As a direct effect, this reduces engine oil viscosity (and hence oil film thickness) and the concentration of oil additives, which can potentially impact oil life and increase engine wear. With biodiesel usage, the impact may be greater, since biodiesel is more oxidatively unstable than mineral diesel and its oxidation can potentially produce more undesired chemical reactions and products.

The effects of fuel dilution with biodiesel has been investigated by several workers^{2, 3, 4, 5, 6}, including oil and additive suppliers⁷. Results are varied, but this could also be due to the levels of dilution and biodiesel type used. In general, excess wear did not result with biodiesel usage, although lead corrosion, increased oil oxidation, and increased deposits were sometimes observed.

A 12-year experiment using 50% rapeseed methyl ester (RME) biodiesel in heavy trucks and light vehicles did not result in increased wear or deposits in rings and crankcases². Engine dynamometer tests conducted by Blackburn et al.³ with 100% soybean methyl ester (SME) biodiesel did result in copper/lead (Cu/Pb) bearing corrosion and increased oxidative degradation of the oil. Tests from the API CJ-4 category conducted by Devlin et al.⁴ to evaluate oil oxidation, deposit formation and wear showed that using SME significantly increased oxidation and deposits in fuel-diluted engine oil, and Pb corrosion. The study by Thornton et al. saw no obvious lubricant aging effects attributed to

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Table 1. List of oil samples prepared. Percentages are by weight.

Oil Sample Name	% FAME	%ULSD	%Oil
Original SME B20	4	16	80
Degraded SME B20	4	16	80
LME B20	4	16	80

SME⁵. Lastly, the study by Sem⁶ concludes that increased deposits caused by biodiesel dilution can be reduced by engine oils with higher additive levels.

We also investigated how fuel dilution affects wear protection capability and degradation of engine oil at different dilution levels using ULSD and B10-B30 (SME/ULSD). Chemical analyses of surface films were employed to explain the tribological results. This work will be published at a later date⁸.

This current investigation is focused on comparing the effects of two feedstocks on engine oil properties, friction, and wear. Since filling stations typically contain biodiesel sourced from various feedstocks depending on price and availability, and since biodiesel blends reaching the consumer may have different oxidative stabilities, we extended our prior work and evaluate the effect of using different biodiesels with different stabilities on engine oil properties.

EXPERIMENTAL

A. SAMPLE PREPARATION

Three types of B20 fuels were used: “Original SME B20”, “Degraded SME B20”, and “LME B20”. The “Original SME B20” was prepared using SME B100 from Haltermann Products. “Degraded SME B20” was prepared using SME B100 sampled from the fuel tank of a truck that filled up with B100 from fuel stations supplying B100, but was degraded by heating the fuel at temperatures less than 90°C for several days while bubbling air through the fuel. The fuel turned a clear, dark orange color after several hours; it was originally a pale yellow color. Since the degradation was performed in open air, lower boiling degradation components would be absent. This may yield a different product from the degradation of biodiesel in closed containers and/or lower temperatures. The “Original SME B20” and “Degraded SME B20” fuel samples were prepared by mixing 20% of the SME with 80% of ultra-low sulfur diesel by weight, or approximately 21% by volume. The third B20 fuel (“LME B20”) was obtained from a Meijer fuel station at Ann Arbor-Saline Rd., Ann Arbor, MI. The feedstock for the biodiesel in this B20 (measured as % by volume) was found to consist primarily of lard. (See Section IIIC below.)

The Rancimat oxidation stability test (EN 14112, ASTM D2274) was used to assess the oxidation of the two SME biodiesel samples and the three B20 blends. The Rancimat test measures the time (“induction period”, IP) before rapid oxidation begins in a fuel sample heated to 110°C. Purified air is bubbled through the heated sample and then through a water bath that traps volatile organic acids generated from oxidation of the sample. The accumulation of organic acids in the water bath is measured by conductivity. The SME B100 from Haltermann Products had a Rancimat IP of 3.5 h, which meets the minimum oxidation stability requirement (3 hr Rancimat IP) specified in ASTM D6751 for B100. The degraded SME B100 had a Rancimat IP of 0.5 h, which had been reduced from a value of 1.2 h by the degradation process described above. Blending into ULSD increased the Rancimat IP values of the Original SME B20 and Degraded SME B20 to 6.2 h and 1.4 h, respectively. The LME B20 sample had a Rancimat IP of 3.6 h, intermediate between the two SME B20 samples.

The “Original SME B20” and “Degraded SME B20” oil samples (100 ml in volume) were prepared by mixing each of the B20s with SAE 15W-40 API CJ-4 oil. A mixture of 20% by weight of B20 in oil was prepared. [Table 1](#) summarizes these samples.

B. OIL AGING PROCEDURE

Oil aging was performed using the Ford Oil Aging Test (FOAT), which was previously developed to simulate the Sequence IIIE engine dynamometer test in terms of viscosity increase⁹. The apparatus consisted of a stainless steel reactor (Parr 4564 Bench Top Mini Reactor) attached to a temperature control unit capable of maintaining the operating temperature to $\pm 2^\circ\text{C}$. 100 ml of the sample was mixed with ~ 60 ppm iron (as ferric octanoate) to simulate the presence of wear metal, which can catalyze oil degradation. The mixture was placed in the reactor and heated to 160°C. Simulated blowby gas in the form of 300 ppm NO₂ in air was bubbled into the oil at a rate of 200 ml/min with constant stirring at 350 rpm. The reactor operated at atmospheric pressure.

The oil samples were aged for a total of 48 h each, where 44 h of aging corresponded to approximately 5000 miles of

severe taxi (gasoline) service in terms of kinematic viscosity and FTIR oxidation changes based on an internal study. 6.5 ml of the oil was withdrawn at intermediate intervals - 0 h (immediately after the oil reached 160°C), 7 h, 24 h, and 31h - for analysis. After sample withdrawal, 6.5 ml of the particular B20 used was added back to the oil in the reactor vessel, to simulate the periodic fuel addition that occurs when the DPF is regenerated in actual operation.

C. FRICTION AND WEAR EVALUATION

Friction and wear experiments were conducted using the High Frequency Reciprocating Rig (HFRR) manufactured by PCS Instruments. The apparatus provided a ball-on-flat contact operating under boundary lubrication conditions. A harder ball (650-670 Hv, 6 mm diameter) reciprocated against a softer disk (190-210 Hv, 10 mm diameter) immersed in an oil bath under a normal load of 9.8 N. This provided an initial contact stress of 1.3 GPa at the start and 0.5 - 1 GPa at the end of the test. These stresses are similar to the maximum stresses experienced at the cam and tappet contact in the valvetrain. Stroke length was 1 mm and the reciprocation frequency was 20 Hz. The oil temperature was kept at 105°C and each test was run for 3 h. For each oil sample, two, and occasionally three, runs were performed. Experiments conducted with different ball and disk materials with this load show reasonable correlations with engine dynamometer testing.

The electrical resistance at the sliding contact was measured by the electrical contact resistance (ECR) technique¹⁰ which provided an indication of the formation of lubricant-derived, electrically-insulating films. ECR was converted to electrical voltage between contact surfaces by a voltage divider circuit. A zero contact voltage indicated metal-to-metal contact or the presence of electrically-conductive film between the two sliding surfaces, corresponding to 0% open circuit voltage (closed circuit). When the electrical contact voltage reached a maximum value which meant an open circuit, the asperities are completely separated by insulating films, and 100 % open circuit voltage was recorded. The voltage drop across the contact surfaces was thus an indication of the formation of insulating anti-wear films between two contact surfaces¹¹. However, this did not provide any indication of film thickness or distribution.

The wear volume on the disk was measured using the Wyko NT3300 optical profiler.

D. OIL ANALYSIS

FTIR

Oil degradation was monitored using a differential absorbance technique using FTIR. Oxidation, nitration, and

sulfation were determined for the 18 oil samples. Fresh SAE 15W-40 API CJ-4 oil was used to obtain the reference spectrum, which was subtracted from the aged oil spectrum. Peaks at $\sim 1150\text{ cm}^{-1}$ were considered to be sulfation products, at 1630 cm^{-1} nitration products, and near 1700 cm^{-1} organic oxidation products.

Sulfation measures the formation of sulfate compounds from sulfur from diesel fuels or oxidation of sulfur-containing compounds in the oil or additives. Nitration is a measure of nitrogen oxide fixation into the oil. Finally, oxidation is a measure of the formation of carboxylic acids, aldehydes, ketones, and esters.

Note that values obtained for oxidation and sulfation in biodiesel-diluted oil should not be interpreted in the same way as those from oil without biodiesel. Biodiesel is composed of esters with a strong C=O stretch at 1741 cm^{-1} which will increase the measured oxidation result and a C-O stretch at 1169 cm^{-1} which will increase sulfation.

Oxidation, sulfation, and nitration were also measured for both Original and Degraded SME B100. Table 2 lists these values. Note the large contributions of the biodiesel to oxidation and sulfation, as explained in the preceding paragraph. These add an offset to the values for oxidation and sulfation at 0h and beyond for the B20-containing oil samples [See Figs. 5 and 7]. These were not subtracted from FTIR measurements of the oil/fuel samples, since these values represent carbonyl contributions of fresh biodiesel. Doing so would have assumed that FAME concentration was constant during the aging process, which is not the case as the results of the GC analysis will show.

One unexpected result is the slightly lower FTIR oxidation obtained for Degraded SME B100. Apparently, degradation of the biodiesel as measured by the Rancimat test does not correlate at all with degradation as measured by FTIR oxidation.

Gas Chromatography

Biodiesel content and composition were quantified by gas chromatography. Approximately 0.010 g (about one drop) of oil or fuel sample was first diluted in 10 ml of dichloromethane, with 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 μl) 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- μm film thickness. Oven temperature was initially 130 °C for 1 min, then ramped to 170 °C at 6.5 °C/min, then ramped to 215 °C at 2.75 °C/min and held for 12 min, then ramped to 270 °C at 40 °C/min and held for 3 min. Helium carrier gas was held at constant pressure of 14.5 psi.