

Soy Biodiesel Oxidation at Vehicle Fuel System Temperature: Influence of Aged Fuel on Fresh Fuel Degradation to Simulate Refueling

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ABSTRACT

An experimental study of the effects of partially-oxidized biodiesel fuel on the degradation of fresh fuel was performed. A blend of soybean oil fatty acid methyl esters (FAMES) in petroleum diesel fuel (30% v:v biodiesel, B30) was aged under accelerated conditions (90°C with aeration). Aging conditions focused on three different degrees of initial oxidation: 1) reduced oxidation stability (Rancimat induction period, IP); 2) high peroxide values (PV); and 3) high total acid number (TAN). Aged B30 fuel was mixed with fresh B30 fuel at two concentrations (10% and 30% m:m) and degradation of the mixtures at the above aging conditions was monitored for IP, PV, TAN, and FAME composition. Greater content of aged fuel carryover (30% m:m) corresponded to stronger effects. Oxidation stability was most adversely affected by high peroxide concentration (Scenario 2), while peroxide content was most reduced for the high TAN scenario (Scenario 3). However, changes in TAN and FAME composition were modest with all four scenarios reaching a plateau in TAN formation at similar times and FAME concentrations showing similar declines. The results are discussed with respect to the chemistry of biodiesel fuel aging under high-temperature diesel fuel system conditions and considerations associated with the mixing of aged fuels with fresh fuels following vehicle refueling.

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INTRODUCTION

Biodiesel is a renewable fuel used as an alternative to petroleum diesel. Biodiesel is commonly defined as fatty acid alkyl esters, typically methyl esters (FAMES), produced from bio-derived feedstocks including plant oils, animal fats, waste cooking oils, and potentially other oleaginous sources such as algae [1, 2]. Acid- or base-catalyzed transesterification with methanol converts fatty acids in triacylglycerides into FAMES and glycerol.

Greater biodiesel consumption in recent years has been spurred by desires for alternative energy sources and reduced greenhouse gas emissions. Biodiesel blends with petroleum diesel are conventionally identified using the biodiesel volume percentage, e.g. B30 for 30% v:v biodiesel. Many compression ignition engines for light-duty and medium-duty cars and trucks are designed to tolerate up to B20 levels [3]. The B30 content used in this study was selected to be fully protective for possible variability in biodiesel content in B20 fuels.

Biodiesel composition is determined by the feedstock from which it is derived and its functional properties can vary. Biodiesel is composed of saturated, monounsaturated, and polyunsaturated FAMES. Monounsaturated FAMES contain one carbon-carbon double bond, while polyunsaturated FAMES contain two or more carbon-carbon double bonds. Individual FAMES are often identified using YY:Z notation; where YY is the number of carbon atoms and Z is the number of double bonds, respectively, in the fatty acid chain. In some

cases, the geometric configuration of the double bond (*cis* or *trans*) is added after the number of double bonds; unless specified, all double bonds are generally assumed to be in the *cis* configuration. Biodiesel from the most common feedstocks is primarily comprised of five FAMES: methyl palmitate (16:0), methyl stearate (18:0), methyl oleate (18:1), methyl linoleate (18:2), and methyl linolenate (18:3).

Oxidation Stability

Oxidation stability is a fuel property that relates to the propensity of a fuel, especially biodiesel and particularly polyunsaturated FAMES, to react with oxygen in a series of free radical reactions. The oxidation of biodiesel typically generates degradation products such as peroxides, acids, alcohols, ethers, aldehydes, and ketones [4, 5, 6, 7]. The dynamics of the oxidation of biodiesel and biodiesel blends have been described in detail elsewhere [4, 5, 6, 7, 8, 9]. Briefly, an initial loss of oxidation stability is followed by a transient increase in peroxides, followed closely by an increase in more stable oxidation products such as acids, and then a decrease in peroxides as the stable oxidation products continue to increase. Some of these products polymerize, generating larger compounds [10,11]. These oxidation products can compromise fuel quality and lead to adverse effects on fuel system materials and engine performance. Hydroperoxides are known to be reactive, causing materials compatibility issues. Acids are corrosive and can cause metal leaching. Polymers increase fuel viscosity and can agglomerate, forming buildups and creating blockages [12].

Considerable research has been conducted on the oxidation of biodiesel fuels, but primarily at temperatures typical of ambient temperatures for fuel storage. Studies to better characterize biodiesel oxidation at higher temperatures simulating diesel engine fuel system temperatures are relatively few in number [9,13, 14, 15, 16, 17, 18, 19].

In a recent study by the Coordinating Research Council (CRC) [18] fuel system conditions were monitored and changes in fuel stability were investigated in two diesel engine vehicles (one passenger car, one light truck) during both chassis dynamometer and real-world operation. During on-road operation, fuel rail pressures up to 29,800 psi (205,000 kPa) were recorded, while temperatures reached 88 °C and 81 °C in the fuel supply systems and 72 °C and 55 °C in the fuel tanks in the two vehicles. Higher temperatures (up to 104 °C in the fuel rail and 87 °C in the fuel tank) were observed during heated dynamometer testing. Elevated temperature and oxygen availability are key factors affecting oxidation stability, while higher pressure likely has a secondary impact.

Key fuel factors affecting biodiesel oxidation stability include FAME composition, the presence of antioxidants, and catalytic contaminants. In terms of FAME composition, the number and location of double bonds in a given FAME is critical. The methylene carbon atoms on either side of a carbon-carbon double bond are defined as allylic sites, while carbon atoms between two double bonds are *bis*-allylic. The *bis*-allylic sites are considerably more susceptible to oxidation than the allylic sites, which are in turn considerably more susceptible than other methylene carbon atoms not adjacent to double bonds. Methyl linolenate, considered the most oxidatively unstable of typical FAMES, has four allylic sites of which two are also *bis*-allylic sites [20]. Overall, saturated FAMES are the most stable, followed by monounsaturated FAMES, and finally polyunsaturated FAMES, which are the least stable.

The reaction pathways for FAME oxidation can be broken down into several steps, with hydroperoxides formed as initial products and acids and polymers generated as secondary products. Radical initiation, typically at *bis*-allylic or allylic sites, is the first step in the reaction pathway. Isomerization of the allylic radicals gives conjugated diene intermediates that add oxygen to give peroxy radicals. Peroxy radicals abstract hydrogen atoms from other FAMES leading to hydroperoxides. The hydroperoxides homolytically cleave to yield an alkoxy radical and a hydroxyl radical. These two radicals can then abstract hydrogen atoms from allylic carbon atoms in other FAMES resulting in a chain reaction of FAME oxidation [12, 21]. Decomposition and reactions of hydroperoxides lead to formation of aldehydes, ketones, acids, alcohols, and oligomers [22]. The primary oxidation products can subsequently react to form a range of secondary higher molecular weight compounds (e.g. acids and alcohols can yield esters) [5].

Antioxidants are compounds that delay the onset of oxidation and can be found naturally in biodiesel or can be produced synthetically. These compounds contribute to the overall oxidation resistance or oxidation reserve in the fuel. Antioxidants help maintain fuel stability by scavenging radicals as they form, preventing the chain reaction that forms a larger pool of radicals. Natural antioxidants, such as tocopherols, depend on the biodiesel feedstock and are generally less

effective than synthetic antioxidants. Synthetic antioxidants are commonly added to increase oxidation stability to acceptable limits. Metals are known to increase the rate of fuel oxidation. Storage tanks and fuel systems present opportunities for fuel to contact metals such as iron, zinc, aluminum, chromium, and copper that can act as catalysts that accelerate fuel deterioration [12, 20].

The objective of this study is to investigate possible changes in oxidation stability and oxidation product patterns associated with vehicle refueling. In this real-world situation, fresh fuel is added to older fuel that may have already been oxidized to some extent and that contains reactive oxidized products (e.g. hydroperoxides). While the aging duration (up to 20 days at 90 °C) is certainly longer than what would be experienced during normal vehicle operation, the results allow an assessment of oxidation reactions in highly aged fuel and considerations associated with mixing aged fuels and fresh fuels during refueling.

EXPERIMENTAL METHODS

Fuel

Soybean oil methyl ester (SME) biodiesel, previously blended with ultra-low sulfur petroleum diesel (<10 ppm sulfur) in a 30% v:v blend (B30) was obtained from Gage Products Company (Ferndale, Michigan). The neat biodiesel (B100) met ASTM D6751 specifications [23]. No synthetic antioxidants were added to the SME biodiesel or the petroleum diesel. Fuel properties of the fresh B30 fuel are given in Table 1.

Table 1. Fresh B30 fuel properties

Property	Value	Test Method
Specific gravity (@ 60 °F, 15.6 °C)	0.862	ASTM D4052 [24]
Ester content	29.9 % v:v	GC/FID
TAN	0.1 mg KOH/g	ASTM D974 [25]
Induction period (Rancimat)	7.8 hr	EN 15751 [26]
Water content	64 ppm	ASTM E1064 [27]
Initial boiling point	189 °C	ASTM D86 [28]
T10	218°C	ASTM D86 [28]
T50	287°C	ASTM D86 [28]
T90	334°C	ASTM D86 [28]
Final boiling point	341°C	ASTM D86 [28]

Experimental Procedures

All fuels were aged using the apparatus described in ASTM method D2274 [29], consisting of a 1-liter glass tube equipped with an air supply tube (100 mL/min of ultrapure, dry air) and a mushroom condenser cap (cooling water maintained at 20°C) to minimize loss of semi-volatile compounds. The 1-liter tubes initially containing 400 mL fuel were placed in an aluminum heating block (Lawler Manufacturing Corp., Edison, NJ) and heated at 90°C. Samples collected for analyses were analyzed immediately after sampling and stored at 4 °C in glass sample vials with nitrogen-purged headspace

to prevent further oxidation and analyzed at a later date. Rancimat oxidation stability induction period (IP), peroxide value (PV), total acid number (TAN), and FAME composition were measured.

The experiment consisted of four steps, as shown in Figure 1: 1) initial aging of fresh fuel, 2) collecting fuel aliquots after three characteristic aging periods, 3) mixing fresh fuel with the three aged fuels at two volume ratios, and 4) aging of the six resulting fuel mixtures.

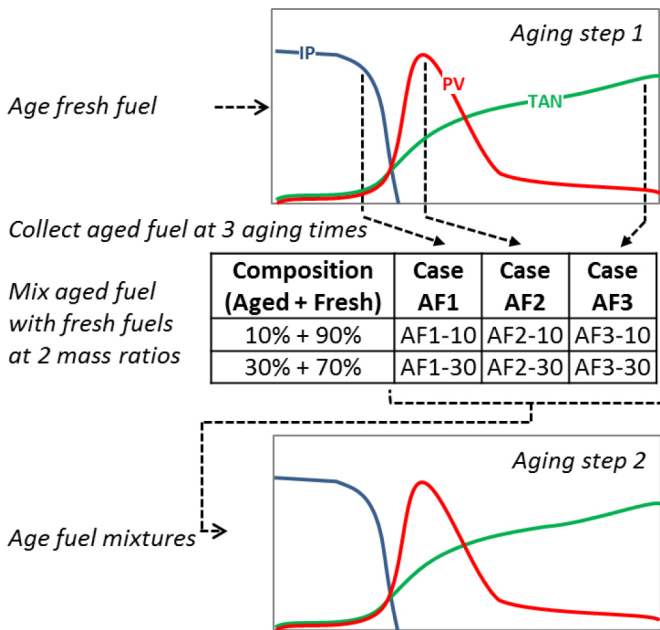


Figure 1. Schematic description of experimental approach: IP, induction period; PV, peroxide value; TAN, total acid number; AF, aged fuel.

As detailed in Table 2, samples of the initially-aged fuel (AF) were collected at three different degrees of deterioration (three elapsed time periods): Case AF1 had ~20% reduction in oxidation stability, Case AF2 had approximately the highest PV value, and Case AF3 had high TAN concentrations after PV had declined. After each of the three aged fuel samples were collected, they were immediately mixed into fresh fuel at both 10:90 and 30:70 mass ratios (aged:fresh) and then aged again. Due to differences in the density of the aged fuel, volumetric concentrations of aged fuel were as follows: Case AF1, 9.9% and 29.6% v:v; Case AF2, 9.8% and 29.4% v:v, and Case AF3, 9.2% and 28.1% v:v.

Four methods (Rancimat IP, peroxides, FAME concentrations, and TAN) were used to follow the oxidative stability of fresh fuels added to fuels that have previously been exposed to oxygen and elevated temperatures - conditions that could be found in vehicle fuel systems. Each of these methods can be considered as metrics for oxidation stability. Three methods (IP, peroxides, FAME concentrations) involve the formation of peroxides from the reaction of oxygen primarily with unsaturated FAMES. The fourth method (TAN) involves the subsequent degradation of the peroxides to acids.

The induction period, a measure of oxidation stability, was measured using the Biodiesel 873 Rancimat (Metrohm AG) at 110 °C using zero-grade air at 10 L/h [30]. Volatile acids (products of biodiesel degradation) are trapped in deionized water and measured by conductivity. The IP is determined from the second derivative of

conductivity versus time. The IP was measured for each sample until the IP dropped to the lower limit of detection (0.6 hr) and was not measured thereafter. Peroxide analysis followed a modified version of ASTM method D3703 [31] using a Titrand 836 with dual Pt-electrode and Tiamo software (Metrohm AG). Peroxides in the sample are reduced by potassium iodide in a decanol-acetic acid solution, releasing an equivalent amount of iodine which is titrated with an aqueous sodium thiosulfate solution. Total acid number (TAN) was measured using ASTM method D664 [32]. The solvent was spiked with oleic acid to provide a suitable baseline response to improve accuracy at low TAN concentrations. FAME concentrations were determined by gas chromatography with flame ionization detection (GC-FID) in an Agilent Technologies 7890A gas chromatograph equipped with a J&W DB-23 column (30m × 0.310 mm × 0.25 µm). GC parameters included: inlet temperature, 200 °C; initial oven temperature, 30 °C with 15 °C/min ramp to 150 °C, 10 °C/min ramp to 240 °C, and hold at 240 °C for 10 minutes; 1 mL/min He carrier gas flow; 25:1 split ratio; and 0.2 µl injection volume. FAME identification and quantification were based on reference standards of the methyl esters of palmitic, stearic, oleic, vaccenic, linoleic, and linolenic fatty acids (Supelco, Bellefonte, PA).

Table 2. Fuel properties for fresh fuel, aged baseline fuel, and mixtures of aged and fresh fuel

Fuel ID	Description	IP (hr)	PV (meq O ₂ /kg)	TAN (mg KOH/g)
Baseline	Fresh B30 fuel	7.8	<0.6	0.1
AF1	Baseline fuel aged 1.3 days to reduced IP	6.4	20	0.1
AF2	Baseline fuel aged 4.0 days to high PV	<0.6	356	2.5
AF3	Baseline fuel aged 14.1 days to high TAN	n.d. ^a	28	20
AF1-10	10% aged fuel with reduced IP + 90% fresh fuel (m:m)	7.5	3.8	0.1
AF1-30	30% aged fuel with reduced IP + 70% fresh fuel (m:m)	7.0	7.8	0.1
AF2-10	10% aged fuel with high PV + 90% fresh fuel (m:m)	3.4	41	0.4
AF2-30	30% aged fuel with high PV + 70% fresh fuel (m:m)	1.5	115	0.7
AF3-10	10% aged fuel with high TAN + 90% fresh fuel (m:m)	7.9	5.5	1.9
AF3-30	30% aged fuel with high TAN + 70% fresh fuel (m:m)	6.3	10.0	5.5

a. Not determined

RESULTS AND DISCUSSION

The effect of the presence of previously aged biodiesel fuel on the aging dynamics of fresh biodiesel fuel following vehicle refueling has not been investigated under vehicle-specific conditions. In the present study, this effect was studied using mixtures of aged fuels and fresh fuel that were subjected to aging at 90 °C with aeration. The fuel mixtures consisted of aged fuel and fresh fuel combined in 10:90 and 30:70 mass:mass ratios, consistent with a range of typical refueling practices. The three initial aging cases involved varying degrees of oxidation as shown in Figure 1. Case AF1 involved a 20% reduction in IP of the aged fuel with relatively little accumulation of peroxides or secondary oxidation products. Case AF2, with the highest level of peroxides in the aged fuel, provides insight into the impact of peroxides on fresh fuel. For example, hydroperoxides can