

Deterioration of B20 from Compression Ignition Engine Operation

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ABSTRACT

Biodiesel has been widely accepted as an alternative for fossil-derived diesel fuel for use in compression ignition (CI) engines. Poor oxidative stability and cold flow properties restrict the use of biodiesel beyond current B20 blend levels (20% biodiesel in 80% ULSD) for vehicle applications. Maintaining the properties of B20 as specified by ASTM D7476-08 is important because, once out of spec, B20 may cause injector coke formation, fuel filter plugging, increased exhaust emissions, and overall loss of engine performance. While the properties of fresh B20 may be within the specifications, under engine operating and longer storage conditions B20 could deteriorate. In a diesel engine, the fuel that goes to the injector and does not enter the cylinder is recycled back to the fuel tank. The re-circulated fuel returns to the fuel tank at an elevated temperature, which can cause thermal oxidation. In this study, several critical fuel properties such as the oxidative stability, cetane number, viscosity, cold flow properties, and higher heating values of a B20 fuel on a CI engine, in a stationary power generator with a 200 gallon fuel tank, were measured as a function of engine run time. These property changes were compared with fuel stored in a commercial storage tank. The oxidative stability decreased by 50% within 60 hours of engine run time while the viscosity, cetane number, and acid number increased with time. B20 in the storage tank did not show significant fuel degradation. The thermal degradation of B20 is due to several factors, such as high temperature, depletion of reactivity of antioxidants, and dissolution of metals from engine parts at high temperatures. These property changes correlate with compositional changes. The effects of this fuel deterioration on the thermal efficiency and fuel consumption were also studied. Significant changes of thermal efficiency and fuel consumption were not observed during 60 hours of engine operation (without refueling the 200 gallon fuel tank). These

results will help understand the effects of oxidized biodiesel on engine performance and methods of minimizing degradation of B20 under engine operation conditions.

INTRODUCTION

Biodiesel, which is defined as fatty acid methyl esters (FAME), can be commercially produced through transesterification of renewable biological sources such as Soybean oil, Cottonseed oil, Rapeseed oil, various animal fats, and waste frying oil. Biodiesel is considered as a possible substitute for conventional diesel fuels; when blended with petroleum-based diesel fuel can be used in diesel engines without any significant modification to the engine [1,2,3]. There are several advantages of biodiesel over petroleum diesel such as improved lubricity, a higher flash point, lower toxicity, and biodegradability [4,5,6,7]. The properties of biodiesel as described in ASTM D 6751, biodiesel specification, depend on the individual FAME composition, which largely depends on the type of feedstock. Chemical structures that affect the fuel properties of FAME molecules are chain length, degree of unsaturation, and branching of the chain. These chemical structures render unique functionalities to biodiesel as a fuel. For example, biodiesel combustion is more complete and produces fewer harmful emissions and pollutants due to the oxygenated nature of FAME [8,9]. The higher lubricity of biodiesel is due to the ability of long chain FAME to form stable lubricating layers on metal surfaces [10]. However, the use of biodiesel is limited by some of its characteristics. Two important characteristics which are in question are the oxidation stability and cold-flow properties of biodiesel. The oxidation stability depends on the degree of unsaturation of the FAME chain [11]. The presence of high levels of unsaturated fatty acid methyl esters, especially polyunsaturated FAMES such as methyl linoleate (methyl-9Z, 12Z-octadecadienoate C18:2)

and methyl linolenate (methyl-9Z, 12Z, 15Z-octadecatrienoate C18:3), makes biodiesel very susceptible to oxidation when compared to petroleum diesel. Oxidative processes bring increased viscosity as a result of condensation reactions involving double bonds. This can lead to an insoluble formation, which can potentially plug fuel filters and injection systems. The increased acidity and increased peroxide value as a result of oxidation reactions can also cause the corrosion of fuel system components, hardening of rubber components, and fusion of moving components.

Factors which influence the oxidative stability of biodiesel include fatty acid composition, antioxidant content, the level of total glycerin, and the conditions of fuel storage such as temperature, exposure to light and air, and the materials of the tank. Additives such as antioxidants help improve the oxidation stability.

In a diesel engine the fuel that goes to the injector and does not enter the cylinder is recycled back to the fuel tank. The recycled fuel returns to the fuel tank at an elevated temperature, which can cause thermal oxidation. The exposure of hot biodiesel to metal parts in the return fuel path may facilitate the metal catalyzed oxidation of FAMES. The formation of secondary oxidative products such as aldehydes and carboxylic acid promote the corrosion of fuel injection system metal parts. The hydroperoxide radicals formed during initial oxidation can accelerate the polymerization reactions leading to viscous high molecular weight molecules. These compounds can deposit in the injection nozzle leading to injection instability and fuel filter plugging.

Oxidation of biodiesel (B100) and blends of biodiesel and changes of fuel properties has been studied extensively [12,13,14,15]. However, there are few reports on the effects of oxidized biodiesel on diesel engine performance and emissions [16]. In these reports, biodiesel was intentionally oxidized with different heat treatments and then run on engines. The degradation of re-circulated biodiesel through a fuel injection system under compression ignition operation conditions has not been reported.

The objective of this paper is to investigate the degradation of biodiesel during CI engine operation in a stationary power generator. The oxidation stability, derived cetane number, viscosity and FAME composition of biodiesel were evaluated as a function of engine runtime and compared with the properties of a biodiesel stored in a stainless steel container. The engine performances during the testing period are also reported.

MATERIALS AND EXPERIMENTAL SECTION

Materials

The B20 (20%v biodiesel in winter grade ULSD) was purchased from RKA Petroleum Corporation (Romulus, MI). Since the B20 experiments were performed during winter, ULSD was additized with “Cold Flo 6200RK” for winter conditions. To eliminate batch to batch variations, seven hundred gallons of B20 was purchased and stored in a commercial fuel storage tank just before the start of fuel testing.

Engine Description

The Titan Energy Sentry 5000 Mobile Utility generator set used in this study contains an inline five cylinder John Deere 5030TF270 diesel engine (3.0 L displacement, 3.4×4.1 inch bore and stroke), in conjunction with a Katolight D50FPJ4T2 50 kW generator. An external load bank (Liberty LPH65 AC, 75 kW, Avtron Manufacturing, Inc, Cleveland OH, USA) was coupled to the genset (generator engine set) to control loading of the engine. The fuel injection system in the John Deere 5030TF270 engine consists of a mechanically governed Pump-Line-Nozzle, “unit pump system”, manufactured by Stanadyne Corporation, which is calibrated for Diesel #2 fuel. The engine is turbocharged with a compression ratio of 19.1:1 and no exhaust gas recirculation (EGR). The exhaust system has no after-treatment devices but was modified to incorporate an inline Telonic Berkeley (M107, Laguna Beach CA, USA) smoke meter chamber for opacity and smoke density measurements. The engine was instrumented with two turbine type flow meters (Flow Technology, Tempe, AZ, USA) in both supply and return fuel lines.

Fuel was supplied to the engine from the two hundred gallon capacity fuel tank in the Sentry 5000 system. Under a steady load of 30 kW, the generator could run approximately 70 hours without a need to refuel the tank. The tank was refueled from the 500 gallon storage tank kept under the same ambient conditions.

Sampling of Fuel and Evaluation of Fuel Properties

About 200 mL of fuel samples were collected from the 200 gallon capacity generator tank at the end of each day (eight hours) of engine testing. Samples were collected for a total of 128 hours with one refueling in between. Also a sample of fuel was collected from the bottom of the 500 gallon commercial storage tank using the electric dispenser pump whenever the engine tank was refueled. These fuel samples were kept at 4 °C until all the testing described later had been completed.

Oxidative stability

Oxidative stability of B20 samples collected from the engine tank at the end of each day (eight hours of engine runtime per day) was analyzed according to the European standard EN 14214:2003 method using a Metrohm 743 Rancimat instrument (Herisau, Switzerland). Samples of 6 g were analyzed at a heating block temperature of 110 °C and a constant air flow of 10 L/h. The volatile compounds formed were collected in the conductivity cell of 60 mL of DI water. The inflection point of the derivative curve of conductivity as a function of time was reported as the induction period (IP).

Kinematic Viscosity

The viscosity at 40 °C of fuel blends was determined following ASTM D 445 using a Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England). In this test method the time is measured for a fixed volume of liquid to flow under gravity through a glass capillary of a calibrated viscometer. The kinematic viscosity is given by the product of the measured flow time and the calibration constant of the viscometer.

Cloud point, Cold Filter Plugging Point and Pour Point

The cloud point (CP), pour point (PP), and cloud filter plugging point (CFPP) measurements were done as per ASTM standards, D 2500-05, D 97-96a, and D 6371-05, respectively. A Lawler model DR-34H automated cold properties analyzer (Lawler Manufacturing Corporation, Edison, NJ) was used to measure the cold flow properties.

Derived Cetane Number

The derived cetane number (DCN) was determined with the IQT™ (Advanced Engineering Technology, Inc, Ottawa, Canada). A complete test sequence comprised of 15 preliminary cycles to provide equilibrium operating conditions and 32 further test cycles. The ignition delays for the last 32 cycles were averaged to produce the ID result. Each test consumes about 10 mL of sample volume. The IQT™ was calibrated with hexadecane and heptane as primary reference fuels. The average value of three trials is presented.

Metal Analysis

Metal analysis of B20 samples were carried out using a Perkin Elmer 2000 DV ICP OES system (Waltham, MA). This sample injection system consisted of a low-flow Gemcone nebulizer, cyclonic spray chamber, and a ceramic 1.2 mm ID injector to improve the atomization and fine mist formation of high viscosity B20 samples. Calibration standards were made using Conostan S-21 blended using deodorized sulfur free kerosene as the diluents and Co as the

internal standard. The relative standard deviations were less than 3%.

Heat of Combustion

The heat of combustion (higher heating value, HHV, MJ/kg) of B 20 samples was measured using IKA C2000 basic (IKA Works, Inc, Wilmington, NC). The instrument was calibrated using benzoic acid. All measurements were performed three times.

FAME Composition

The fatty acid composition of B20 was determined using a PerkinElmer Clarus 500 GC-MS with a split automatic injector and a Rtx-WAX (Restek, Bellefonte, PA) column (length: 60 meters; ID: 0.25 mm, coating: 0.25 µm). The column was held at 120 °C for 1 minute, then ramped to 240 °C at 20 °C/min, and finally held at 240 °C for 13 minutes. The transfer line between GC and MS was kept at 240 °C. Helium (99.9999%, Cryogenic Gases, Detroit, MI) was used as the carrier gas with a flow rate of 1.5 mL/min. Total Ion Count (TIC) was used for the quantification of each component. Details of calibration and quantification were described elsewhere.

Engine Performance Parameters and Data Acquisition

Data was recorded utilizing a Labview controller with data being input from two flow meters, two temperature probes (RTDs), pressure gauges for the fuel input and return lines, a differential pressure gauge across the fuel filter, and a temperature probe to monitor the exhaust temperature. The Labview data were collected at every five seconds and 100 data points were averaged. The BSFC in kg/kW-hr and brake thermal efficiency (BTE) were calculated to evaluate the engine performance during the testing period. Ambient conditions such as temperature, pressure and humidity were also recorded on an hourly basis.

RESULTS AND DISCUSSIONS

Composition and Physical Properties of B20 before Engine Testing

The volume % biodiesel in ULSD using GC-MS was found to be 19.5%, which is in a good agreement with the labeled blend level by the fuel distributor. The reactivity of biodiesel depends on the different chemical functionalities of FAME such as double bonds, triple bonds, allylic carbons, saturated carbon, carbon bonds, and ester groups. [Figure 1](#) illustrates the chemical structure of a typical FAME molecule showing different chemical functionalities.

Among these functionalities the most reactive site of FAME is the region with double bonds which can undergo oxidation.



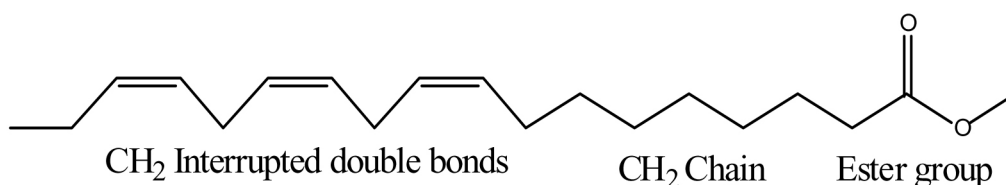


Figure 1. Chemical structure of C18:3 FAME showing chemical reactivity

Table 1. FAME composition of biodiesel in B20 (a) and fatty acid composition (% v/v) of common biodiesel feedstocks in North America (b) [19].

(a)

FAME	Volume %
C14:0	1.82
C16:0	24.1
C16:1	0.18
C18:0	14.74
C18:1	42.77
C18:2	16.39
Σ SFAME	40.66
Σ UFAME	59.34

(b)

Fatty Acid	Soybean	Cottonseed	Corn	Lard	Tallow
C14:0		0-2	1-2	1-2	3-6
C16:0	6-10	20-25	8-12	28-30	24-32
C18:0	2-5	1-2	2-5	12-18	20-25
C18:1	20-30	23-25	19-49	40-50	37-43
C18:2	50-60	40-50	34-62	7-13	2-3
C18:3	5-11	trace	trace	0-1	

resulting in numerous oxidative products and polymeric products [17], possibly resulting in problematic or out-of-specification biodiesel. The FAME composition of B20 used in this study is shown in Table 1(a) [18], where the abbreviation CX: Y is used, where X is the number of carbon atoms in the fatty acid chain and Y is the number of double bonds present in the fatty acid chain. The fuel distributor was unable to provide the feedstock of the biodiesel in B20, however according to the measured FAME profile (Table 1(a)) and comparing this with the fatty acid compositions of various oils and fats given in Table 1(b) [19] it is likely the biodiesel was animal fat based.

The FAME composition of animal fat based biodiesel differs greatly from the vegetable oil-based biodiesel where the predominant FAME was methyl oleate (methyl-9Z-octadecanoate C18:1) (35-45%), followed by methyl linoleate (methyl-9Z, 12Z-octadecadienoate C18:2) (20-30%), and methyl palmitate (methylhexadecanoate C16:0) (22%). The poly-unsaturated FAME composition of animal fat biodiesel is lower (15-20%) when compared to the poly unsaturated FAME compositions of vegetable oil based biodiesel, such as soybean based biodiesel (55-62%) and cottonseed based biodiesel (53%). The biodiesel component of B20 used in this study has higher methyl oleate (C18:1) composition (43%) than that of vegetable oil based biodiesels. The poly-unsaturated FAME composition in this biodiesel is only 16.7 %. There was no methyl linolenate (methyl-9Z, 12Z, 15Z-octadecatrienoate C18:3) observed in the B20.

The viscosity, CP, PP, CFPP, DCN, gross heating value, and induction period of B20 as received, together with the limits in biodiesel ASTM D7476-09 specifications are presented in Table 2. For comparison purposes those properties of winter grade ULSD are also included in Table 2. The fuel properties of B20 given here were all found to be within ASTM D7476-09 specifications. In fact the oxidation stability of original B20 was 16.3 hours which is well above the ASTM required value of six hours. This can be attributed to the addition of synthetic antioxidant into animal fat based biodiesel.

It should be noted that animal fat based biodiesel does not contain any natural antioxidant. A higher DCN value was observed for B20 compared to that of ULSD. It should also be noted that the winter grade ULSD in B20 contains a cold flow additive named “Cold Flo 6200RK”, which contains the cetane improver 2-ethylhexyl nitrate. The presence of this cetane improver and the inherited high cetane value of biodiesel are responsible for the higher cetane number of B20. The values of fuel properties of the original B20 given in Table 2 will be compared with those of B20 sample collected from engine tank as a function of engine run time.

Properties of the Fuels re-circulated thru the engine

As described in the introduction section, the re-circulated fuel can undergo thermal oxidation and metal catalyzed oxidation.