

Properties of Butanol-Biodiesel-ULSD Ternary Mixtures

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ABSTRACT

The use of butanol as an alternative biofuel blend component for conventional diesel fuel has been under extensive investigation. However, some fuel properties such as cetane number and lubricity fall below the accepted values as described by the ASTM D 975 diesel specifications. Blending 10% butanol with #2 ULSD decreases the cetane number by 7% (from 41.6 to 39.0). At higher butanol blend levels, i.e., 20% v/v, the cetane number decrease cannot be compensated for; even with the addition of a 2000 ppm level commercial cetane improver. The decreased cetane number, or in other words, increased ignition delay, can be attributed to the increased blend level of low cetane butanol as well as the critical physical properties for better atomization of fuels during auto ignition such as viscosity. The kinematic viscosity dropped sharply with increasing butanol blend level up to 25 % v/v, then increased with further increase of butanol blend level. Also, the addition of butanol decreases the lubricity properties of conventional diesel. Interestingly, blending biodiesel (fatty acid methyl esters) with butanol-diesel mixtures restores the required properties of diesel fuel for compression ignition. In this study, biodiesel and butanol were blended with commercial diesel fuel at different ternary mixture compositions to characterize the key fuel properties of the blends such as cetane number, viscosity, lubricity, flash point and cold filter plugging point. An optimum ternary mixture of biodiesel-butanol-diesel will be developed based on the physical properties which can be used in CI engines without altering engine parameters or the addition of performance enhancers. In addition the feasibility of using green diesel (hydrotreated animal fats) as a matrix for butanol blending was also investigated.

INTRODUCTION

The world's energy still primarily relies on the limited petroleum reserves. As the dwindling fossil fuel sources and the increasing dependency of the USA on imported crude oil and the environmental impacts resulting from fossil fuel combustion has become severe. Recently there has been a growing trend towards employing modern technologies to produce a wide range of biofuels from biomass resources, which are becoming cost-wise competitive with fossil fuels. The commitment by the US government to increase bioenergy three-fold in 10 years has added impetus to the search for viable biofuels. The European Union (EU) has also adopted a proposal for a directive on the promotion of the use of biofuels with measures ensuring that biofuels account for at least 5.75% of the market for gasoline and diesel sold as transport fuel by the end of 2010.

Biofuels, including bioethanol, biomethanol, vegetable oils, biodiesel, biogas, bio-synthetic gas (bio-syngas), bio-oil, bio-char, Fischer-Tropsch liquids, and biohydrogen, are liquid or gaseous fuels for transport produced from biomass [1]. Bioethanol, as one the most important biofuels, can be used in gasoline or diesel engines with a form of ethanol-gasoline blend (called gasohol) or ethanol-diesel blend (called e-diesel) [2]. However, the use of bioethanol suffers from a series of limitations [3, 4]: it has lower energy density compared with petroleum, relatively low boiling point leading to excessive evaporation at elevated temperatures, low miscibility with petroleum which may cause phase separations with catastrophic consequences, and high water absorption which tends to corrode normal distribution pipelines.

Butanol or butyl alcohol (sometimes also called biobutanol when produced biologically), is a primary alcohol with a 4 carbon structure and the molecular formula of $C_4H_{10}O$. Recently, butanol as a biofuel alternative to ethanol got a big

boost with the news of a partnership between DuPont (DP) and British Petroleum (BP) to make biobutanol. Compared with ethanol, butanol has many advantages, such as higher energy content (giving it 88 percent of the mileage of petroleum, versus ethanol's 70 percent), lower water absorption, less corrosive to pipelines, better blending ability, and use in conventional combustion engines without modification [4]. There have been several studies [5, 6, 7, 8] on the butanol/gasoline blends performance since the 1990s. Butanol/diesel blends as an alternative for petroleum diesel was also studied as early as 1986 [9]. Recently there have been several reports published on the use of butanol blends in diesel engines [10, 11, 12]. Considering the physical properties mentioned earlier [13] and all of the previous studies indicated that butanol can be a better alternative biofuel than ethanol.

Like ethanol, butanol can be produced fermentatively or petrochemically. Current crude oil prices render the biotechnological process economic again. An example of this process is the so-called ABE (acetone butanol ethanol) fermentation from renewable agricultural crops such as corn, sugar and starch [14]. Non-fermentative methods of using metabolic engineering approach to produce higher alcohol [15] and new fermentation processes that can convert the fermentation of syngas (a mixture of CO and H₂), obtained from gasification of unconverted biomass to ethanol and butanol, are being developed [16]. In these methods production of biobutanol from renewable biomasses is possible.

When considering an alternative fuel for use in diesel engines, a number of issues are important. These issues include supply and distribution, integrity of the fuel being delivered to the engine, emissions, and engine durability. These issues largely depend on the properties of fuel. The effects of low density and low viscosity synthetic aviation fuel on a power generator run on a CI engine was explained in our recently published work [17, 18]. The purpose of this paper is to discuss the properties and specifications of butanol blended with petroleum based diesel fuel (Ultra low sulfur diesel, ULSD) and bio based diesel fuels such as FAME and Green Diesel with special emphasis on the factors critical to the potential commercial use of these blends. These factors include blend properties such as cetane number (ignition delay), stability, viscosity and lubricity, and safety.

MATERIALS AND EXPERIMENTAL SECTION

Materials

Soybean oil based biodiesel (BD) was obtained from G. E. Wacker Inc. (Manchester, MI). Certification #2 ultra low sulfur diesel (ULSD) was obtained from Haltermann Products (Channelview, Texas). Analytical grade Butanol

(Bu) was purchased from Sigma-Aldrich. A sample of Green Diesel (hydrotreated animal fats) was provided by the National Automotive Center, US Army (Warren, Michigan). Reagent grade 2-ethylhexyl nitrate, which is the most widely used cetane improver for ULSD was also purchased from Sigma Aldrich.

The blends were made on a volume basis and stored in glass bottles at room temperature. Butanol was used as neat (Bu100) or in a blend with petroleum diesel. Bu 2 represents a blend of 2 % butanol with 98 % ULSD, by volume. Similarly butanol was blended with green diesel. The ternary mixtures of biodiesel-butanol-ULSD were also prepared and represented as BD: Bu: ULSD.

FUEL PROPERTY TESTING METHODS

Kinematic viscosity

The viscosity at 40 °C of each fuel blend 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.

Cetane Number Measurement

The derived cetane number (DCN) was determined with the Ignition Quality Tester (IQT™, Advanced Engineering Technology, Inc, Ottawa, Canada). A complete sequence comprised 15 preliminary combustion 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 cyclohexane and heptane as primary reference fuels. The average value of three trials is presented.

Lubricity Measurements

A High Frequency Reciprocating Rig (HFRR) (PCS Instruments, London, England) was used to measure lubricity based on ASTM D 6079. Specifically, a 2-mL sample was placed in the test reservoir at 60 °C and a steel ball and steel disk which were submerged in the test fuel were brought into contact with each other. The steel ball is placed in a vibrator arm which was loaded with a 200 g mass. The steel ball was contacted against the stationary disk with a stroke length of 1 mm at a frequency of 50 Hz for 75 min. The wear scar generated on the test ball, with the average of X and Y direction measured under a calibrated optical microscope was termed as wear scar diameter (WSD, μm), and was considered to be a measure of the lubricating property of the

Table 1. Several properties of neat fuels used in this study. ASTM D 975 specifications are also included for comparison.

Property	ASTM D 975 Limit	# 2 ULSD	Butanol	Biodiesel	Green Diesel
Lubricity (μm)	520	437.00	N/A	196.50	341.00
Derived Cetane Number	40	41.60	24.80	54.79	71.10
Cloud Point ($^{\circ}\text{C}$)	Report	-26.00	N/A	0.00	-8.00
Pour Point ($^{\circ}\text{C}$)	Report	<-33.00	N/A	0.00	-6.00
Cold Filter Plugging Point ($^{\circ}\text{C}$)	Report	-26.00	N/A	-3.00	-7.00
Flash Point ($^{\circ}\text{C}$)	52	53.50	35.00	64.00	N/A
Kinematic Viscosity at 40 $^{\circ}\text{C}$ (mm^2/s)	1.9 - 4.1	2.15	2.24	3.96	2.64

fuel. All the experiments were repeated twice and repeatability was demonstrated to be less than 20 μm .

Cloud Point, Pour Point and Cold Filter Plugging 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.

Flash Point (FP) Measurements

FP measurements were conducted using Herzog HFP 339 Automated Pensky Martens closed cup flash point tester (PCS Instruments, London, England) according to the ASTM D93 test method. The results are automatically corrected for barometric pressure and displayed on a display.

RESULTS AND DISCUSSIONS

Analysis of Fuel Properties

The properties of fuel depend on the bulk chemical composition of hydrocarbons and some trace compounds present in the fuel. These fuel properties strongly affect the engine performance, durability and emission characteristics. Several important properties of neat fuels used in this study relevant to the ASTM D 975 diesel fuel specification are shown in Table 1. Although the required fuel properties of biodiesel and biodiesel blends are specified under different ASTM specifications, the properties listed in Table 1 are useful when using ULSD blends with new blend components in CI engines. These results are consistent with previously published properties of ULSD [17,19] butanol [12] and biodiesel [18].

The composition of ULSD is aromatics 27.5%, saturated hydrocarbons 70.8%, and olefins 1.7% by volume. The

biodiesel used in this study contains 99% of fatty acid methyl esters (FAME). The FAME profile consists of methyl stearate (methyl-octadecanoate C18:0) (4.2 %), methyl oleate (methyl-9Z-octadecanoate C18:1) (22.6%), methyl linoleate (methyl-9Z, 12Z-octadecadienoate C18:2) (55%), as the predominant FAME, methyl linolenate (methyl-9Z, 12Z, 15Z-octadecatrienoate C18:3) (7.2%) and methyl palmitate (methylhexadecanoate C16:0) (11%) [20]. Anhydrous 1-butanol (99.8%) with the molecular formula $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ was used in this study. The flash point and boiling point of this butanol are 35 $^{\circ}\text{C}$ and 117.7 $^{\circ}\text{C}$ respectively. The exact composition of the green diesel used in this study is not known. However, green diesel produced from hydrotreating contains saturated hydrocarbons with a C-14 to C-18 chain length.

Properties of Butanol Blends

Cetane Number

The cetane number (CN) is the most significant property for measuring the auto ignition quality of fuels for CI engines. It is actually a measure of the ignition delay (ID) of a diesel fuel. This is the time period between the start of injection (SOI) and the start of combustion (SOC) of the fuel. Lower cetane numbers mean longer ignition delays. The cetane number affects cold-starting, combustion noise, and exhaust emissions. A fuel with lower cetane number can shift the timing of combustion considerably, especially at high speed - light load operating conditions, causing incomplete combustion and elevated emissions [21]. The Derived Cetane Numbers (DCN) of all the fuels was measured using an Ignition Quality Tester according to the ASTM D6890 test method. The DCNs of all fuels except butanol in Table 1 meets the ASTM 975 specification of 40. The relatively higher cetane number (shorter ignition delay) of Green Diesel can be attributed primarily to the presence of saturated, straight long chain hydrocarbons and a lack of aromatic components. The oxygenated nature, long and straight hydrocarbon chain (C14-C18) of biodiesel and the presence

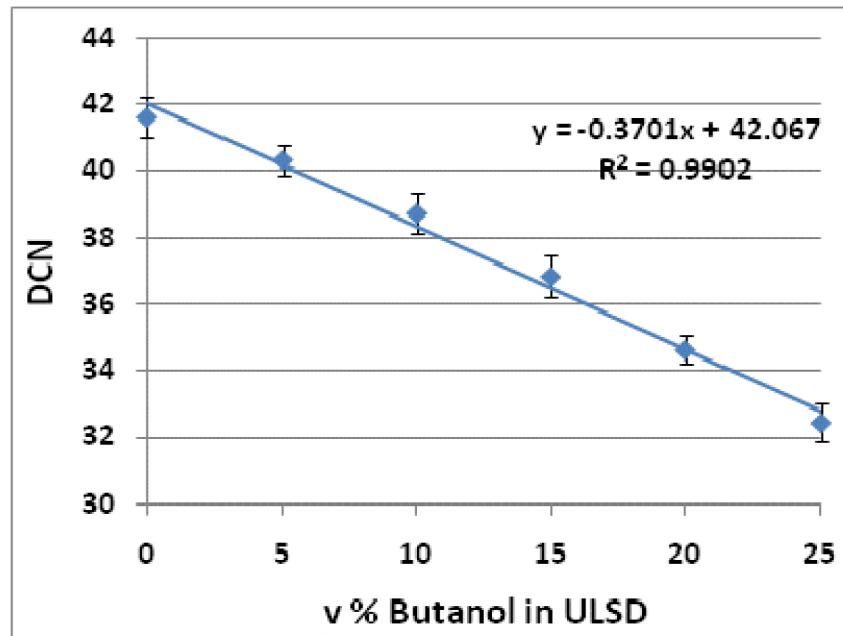


Figure 1. Derived cetane number of butanol-ULSD blends as a function of butanol percentage.

of trace oxidative products account for the high CN of biodiesel [21].

The measured CN of butanol is well below that of ULSD. Although the cetane measurement below 30 is not reliable the value of 24.8 given here is in agreement with the previous data [13]. The change in CN of ULSD as a function of butanol blend amount is presented in Figure 1.

As shown in this figure, a linear and significant decrease of CN was observed. The addition of one volume % butanol can decrease the cetane number of ULSD by 0.37 cetane units. According to these data, butanol levels above 6% by volume decrease the CN to below the ASTM specified value of 40 for diesel fuel. The addition of cetane improvers is necessary to achieve the ASTM required CN. The CN of 20% butanol in ULSD dropped to 34.64 ± 0.43 . The effect of 2-ethylhexyl nitrate (EHN), the most widely used cetane improver, on the cetane number of selected butanol-ULSD blend levels are presented in Figure 2. For comparison purposes the CN of ULSD with EHN is also presented in Figure 2. At a 10% butanol blend level, adding 1000 ppm EHN resulted in 42.9 ± 0.57 CN. However, 2000 ppm of EHN was required in this butanol blend to get the ASTM required CN. The decrease of the effect of 2-EHN on ULSD CN by the addition of 20% butanol was 17.2 %, which is close to the decrease of ULSD CN by the addition of 20% butanol (16.7%). The calculated CN at 20% butanol blend level assuming the linear combination of neat butanol and ULSD values is 38.29.

It has been reported by our group and several other research groups that fatty acid methyl ester based biodiesel has a higher cetane number than ULSD. Therefore the effect of

biodiesel on the CN of above mentioned butanol-ULSD mixtures was studied. The CNs of selected BD:Bu:ULSD ternary mixtures are given in Figure 3. The CN of the B100 biodiesel used in this study is 54.79 ± 1.07 , which is 54% higher than the CN of ULSD. According to Figure 3, equal or higher amount of biodiesel compared to butanol in biodiesel-butanol-ULSD ternary mixtures can result in CNs' higher than 40. For example, 20:20:60, 10:10:80 and 15:5:80 biodiesel:butanol:ULSD ternary mixtures had CNs' of 40.5, 42.0 and 43.9 respectively. These results suggest the addition of biodiesel can compensate for the reduced CN of butanol-ULSD blends.

Recently, the use of hydrotreated triglycerides derived from vegetable oil and animal fat as a biofuel has been under extensive investigation. Due to the renewable nature of these biofuels, they are often called Green Diesel or sometimes as Super Cetane diesel due to their high cetane numbers. The cetane numbers of butanol-Green Diesel blends were also investigated in this project. The CN of neat green diesel is 71.10 ± 1.17 (Table 1). The changes of CN of green diesel with increasing butanol blend amounts are presented in Figure 4. As shown in this figure, similar to ULSD-butanol mixture (Figure 1), a linear and significant decrease of CN was observed. The addition of one volume % butanol decreases the cetane number of green diesel by 0.74 cetane units. Although this value is higher than that for butanol-ULSD blends, the CN of even 25% butanol in green diesel is much higher than the ASTM required CN.

According to these observations, green diesel could be a better matrix for blending butanol. However, the use of all the fuel blends mentioned above in CI engines depends on