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Field Investigation of Biodiesel Fuel Particulate and Moisture Content

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Abstract

Due to enhanced sustainability, reduced environmental impact and local sourcing, expanded use of biofuels is an important part of the US strategic energy policy. En route from production to final use, it is difficult for biofuels to avoid exposure to moisture and particulates. The resulting contamination is a concern because it can lead to filter plugging, fuel injector fouling and engine damage. This research investigates the presence of water and particulates in commercial diesel fuel and how the bio-content of fuel affects quality. Biodiesel blends were gathered from truck stops and filling stations in Wisconsin and Illinois. The samples were tested for moisture using a submersible relative humidity (RH) sensor. A benchtop moisture analyzer was used to determine the water content in parts per million (ppm). Particulates were determined through the use of a laser particle counter. All samples complied with published moisture and particle count requirements. To determine the concentration of biodiesel, infrared spectroscopy analysis was conducted on each sample. Infrared analysis showed that the biofuel content was consistent with labels posted at the pump, however some fuel samples appear to contain high levels of free fatty acids that may impact engine performance.

Keywords: biodiesel, water, particulate

1. Introduction

The development of more industrially advanced nations has led to a growth in worldwide energy consumption. A report provided by the United States Energy Information Administration (EIA) states that the world's total energy consumption in 2000 was 406 quadrillion btu and is predicted to reach 769.8 quadrillion btu by 2035 [1]. Due to environmental concerns and the world's decreasing oil supply, countries are looking for environmentally considerate resources to power their economy sectors. Biodiesel, a bio-based fuel, is receiving more attention due to its sustainability and ability to serve as an alternative to diesel or petrol. In Fig. 1, the sustainability and biodegradability of biofuels is illustrated. Notice how the byproducts of combustion, water and carbon dioxide, assist in plant growth and photosynthesis. Currently, the U.S. Environmental Protection Agency (EPA) has proposed for the passage of a rule that will control the amount of bio-based fuels that must be blended into transportation fuel in the coming years [2]. The European Union has already implemented legislation favorable to the use of biodiesel and is leading the production of the majority of the world's biofuel supply [3]. Due to a history of inconsistency in biodiesel supplies, high production costs, incompatibility with cold weather, and filter/fuel injector plugging, biodiesel has been unable to gain widespread acceptance. In this study, the concentrations of various blends of biodiesel were determined in order to investigate the consistency between reported versus actual values. After, moisture and particulate content of various blends of biodiesel were examined and compared to that of ultra low sulfur diesel (ULSD) fuel in order to assist in understanding the extent of the effects of contaminants in biodiesel.

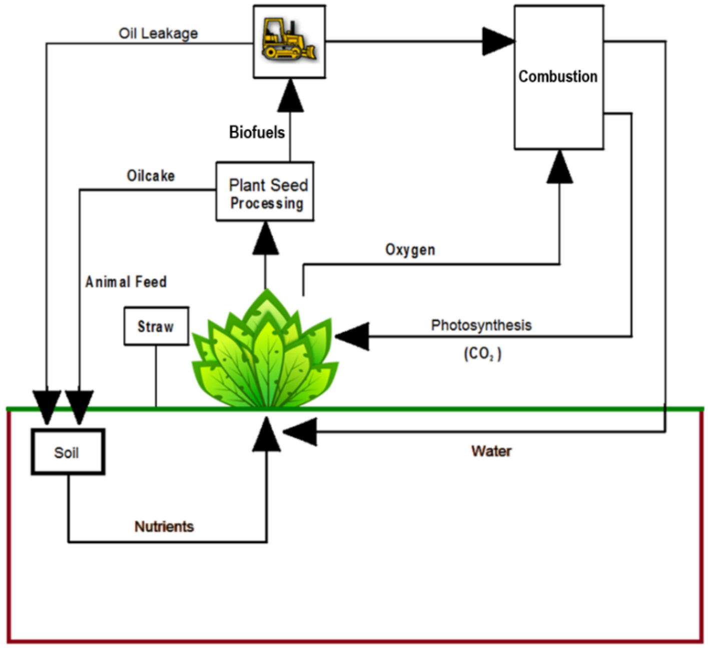

Fig. 1 The lifecycle of a biofuel is sustainable because combustion products are converted to biomass through photosynthesis

2. Background

2.1 Biodiesel Concentration

Biodiesel in its purest form is B100, meaning it contains one hundred percent biodiesel. In order to be used in various applications, a percentage of biodiesel is blended with ULSD. Most service stations sell biodiesel blends within the range of B5-B20. B20, twenty percent biodiesel and eighty percent ULSD, is the greatest amount of biodiesel that can be used without making engine modifications [4, 5]. Blends greater than B20 are associated with filter and fuel injector fouling amongst other problems. Anything below five percent biodiesel is considered to be diesel fuel [6]. Past quality surveys have reported discrepancies between the actual versus the reported values of biodiesel concentration. As a result, consumers may be purchasing fuel that can damage their engine or is simply diesel fuel.

2.2 Water Contamination

Water contamination is one of the greatest obstacles preventing biodiesel from becoming a more common fuel source. Moisture can enter fuel through fill ports, defective seals, corroded heat exchangers, and reservoir breathers in the form of rain water, cleaning solutions, process water, metalworking fluids, coolants, and humid air [7]. Once water is present, it can lead to a reduction of heat in combustion, corrosion, emulsions, cold filter plugging, and the growth of microbe colonies, thus resulting in machine damage [1]. The damage caused by the presence of moisture ultimately results in the premature wear and destruction of machinery. Prior research has acknowledged the presence of water in biodiesel. However, this study seeks to develop a relationship between the relative humidity and the actual water content (in ppm) of biodiesel.

2.3 Particulate Content

When transporting a fluid, particulate can enter at any point along the journey. Exposure to the environment coupled with residual sediment in storage tanks and on filter screens can lead to the contamination of fuels as well as an obstruction of fluid flow in mechanical systems [1]. Similar to water contamination, insoluble particulate can cause the plugging of filters and fuel injectors. Ultimately, particulate are responsible for causing moving parts to stick, wear, or leak. While previous research has analyzed particulate in biodiesel, this study seeks to compare particle contamination in biodiesel to that of ULSD.

3. Methods & Materials

3.1 Relative Humidity (RH) and Moisture Content

A submersible relative humidity sensor, the HYDAC Aqua Sensor 2000, and a moisture analyzer, the Computrac Vapor Pro Fx, were used to determine the RH and moisture content of the fuel samples. In both instruments, RH sensor technology was used to detect water. RH is the ratio of the amount of water vapor actually present in an air-water mixture to the amount of water vapor needed for saturation at the same temperature. The submersible RH sensor is made up of a parallel plate capacitor that consists of two platinum electrodes that are separated by a dielectric polymer. This assembly is sealed with a semi-permeable thermoset plastic onto a silicon substrate in order to prevent oil and particulate contamination from damaging the dielectric polymer. Through osmosis, water is diffused through the permeable plastic and into the dielectric polymer, resulting in a change in capacitance. This change is converted into an analog output reading of the RH (in terms of percent) and the temperature (in ºC). Sensor accuracy is within ±2% RH and response times depend on the material selection and sensor make up [7]. A sensor probe was immersed into each sample and stirred so the sample was agitated. RH and temperature readings were recorded once they stabilized after 3-5 minutes.

In order to determine the water content (in parts per million) the Computrac Vapor Pro Fx was used. The Vapor Pro is made up of a coiled tube heater, an automated sample injection system, a dry airflow supply, and a polymer capacitive RH sensor. Total water mass is detected using the outlet flow rate and sensor block temperature [7]. When testing the samples, the coil temperature read 110 ºC. The RH sensor value was set between 0.2 and 0.4% RH and the dry air flow rate was approximately 100±10 mL/min. Each sample was tested three times and the average was taken.

3.2 Particle Counter

A LaserNet Fines particle counter was used to determine the particulate content of the biodiesel blends. The counter consists of a tube that draws the sample into a flow cell. As the fluid traveled through the flow cell, it passed a pulsed laser that shone through a square space. If particulate was present, its silhouette would be projected onto a computer chip. The chip would process an actual pixel resolution of the particle, thus classifying the particle by its size and type [8]. Upon the completion of the test, an ISO reading consisting of three numerical values was reported. These numbers represent the ISO 4406 Rating and are Expressed as X / X / X. The first of the three numbers represented the numerical range of particles/mL ≥ 4 µm. Likewise, the second and third values represented the numerical range of particles/mL ≥ 6 µm and 14 µm.

Three series of tests were performed on each sample. An initial test was used to flush the system of any residual fluid or contaminants that may have been left by a previous test and was marked invalid. The data from the remaining two results was recorded and analyzed in the results.

3.3 Infrared Spectrometer

Fourier Transform InfraRed (FTIR) spectrometry was used to determine the biodiesel concentration in various fuel samples. In FTIR spectroscopy, absorption of infrared radiation by organic functional groups at characteristic frequencies is used to identify chemical composition. In this experiment, the presence of the C=O bond and the C-O bond indicated the existence of biodiesel in a sample. The C=O bond is found in the frequency range of 1690-1760 wavenumbers (cm^{-1}) while the C-O bond is found between 1080-1300 wavenumbers [9]. Fig. 2 shows these two regions found on an IR spectra.

A sealed liquid cell was used to mount the fuel samples in the IR spectrometer. This cell consisted of two KBr crystal windows with a 0.1 mm Teflon spacer between [10]. The fuel samples were injected into the cell and the cell was placed into the FTIR. A scan of the IR spectra was performed as different wavelengths of infrared radiation were transmitted through the fuel sample. [11]. The amount of IR radiation absorbed can be explained by Beer's law. This law relates the absorption of radiation by the sample to the concentration of a chemical compound and the path length through the sample. The results produced a spectra showing absorbance versus frequency (in terms of wavenumbers).

3.4 Biodiesel and ULSD

Fourteen diesel fuel samples were evaluated. The biodiesel blends and ULSD fuels were purchased from service stations in the states of Wisconsin and Illinois. The pumps were labeled B5-B20 or ULSD. The B5 and B100 were provided by Schroeder LLC Inc., an industry research partner. Samples were procured from the pump. Fuel was purged through the nozzle before a liter sample was gathered using a laboratory sample bottle.

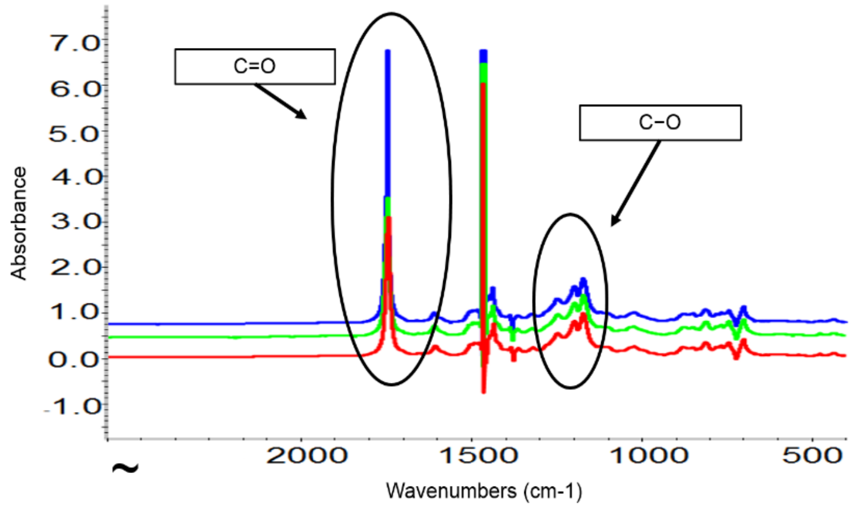

Fig. 2 Two IR peaks indicating the presence of C=O and C-O bonds served as markers for biofuels

The B100 and one of the ULSD samples were used to create five reference blends containing a half, five, ten, fifteen, and twenty percent biodiesel by weight. Volume percentage of biodiesel was determined using equation (1).

$$\text{Volume \% Biodiesel} = \frac{\frac{actual\ weight\ of\ biodiesel}{specific\ gravity\ of\ biodiesel}}{\frac{actual\ weight\ of\ biodiesel}{specific\ gravity\ biodiesel}+\frac{actual\ weight\ of\ ULSD}{specific\ gravity\ ULSD}} \tag{1}$$

The volume percentages of the five blends were plotted against the absorbance/cm at both 1200 and 1744 wavenumbers, creating two calibration curves. The curves were then used to determine the biodiesel concentration in the samples gathered from the various service stations at each respective wavenumber. In Fig. 3 the linear regressions relating absorbance to the concentration of biodiesel can be seen.

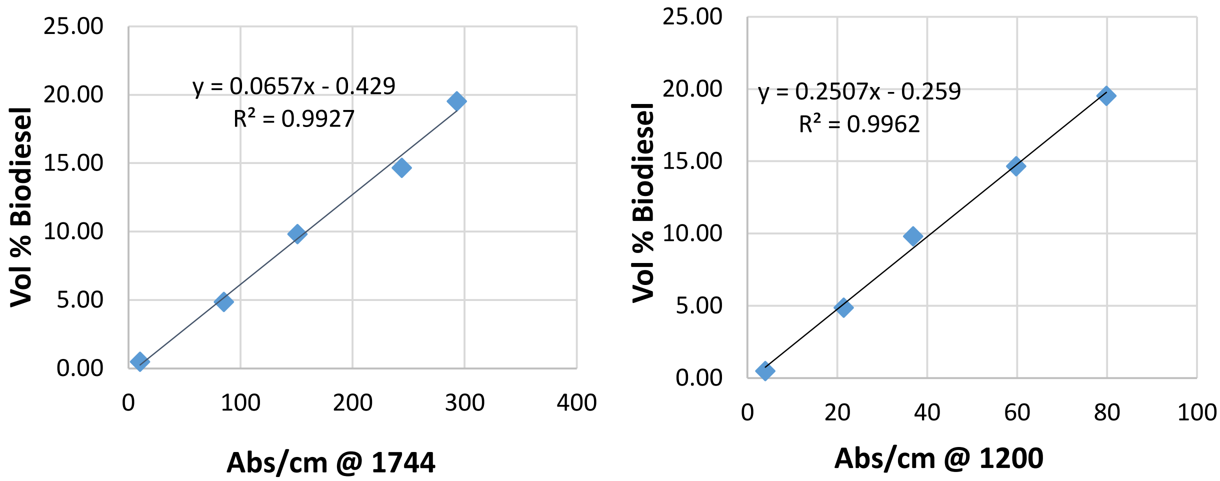

Fig. 3 Calibration curves were created by correlating the absorbance at 1200 and 1744 wavenumbers with known concentrations of biodiesel

4. Results & Discussion

4.1 Infrared Spectroscopy Tests

In the first tests using the infrared spectrometer, the absorbance values of the service station samples were reported at roughly 1744 wavenumbers and then converted to absorbance per centimeter. Using the equation produced by the calibration curve at 1744 wavenumbers, the biodiesel concentration of each field sample was analyzed. Fig. 4 compares the nominal values reported by the suppliers to the calculated values at 1744 wavenumbers. While most of the calculated values correlated with their nominal value, some were not consistent. The calculated concentration for sample 15099 more than half of its nominal value, B5. Although this is not ideal, this inconsistency will not cause any damage to an engine. However, the calculated values of samples 15086 and 15109 are shown to be twice the nominal values, B20. If these values are correct, these fuels could lead to significant engine problems.

To better understand the discrepancies found in samples 15086 and 15109, the calibration curve at 1200 wavenumbers was used. The concentration values calculated using this curve were then compared to both the nominal values and the calculated values at 1744 wavenumbers, as seen in Fig. 5. These results indicate that the two samples in question did in fact fall within the range of values reported by suppliers. It is hypothesized that a difference in the free fatty acid (FFA) content was responsible for the varying ratio of absorbance of at the two wavenumbers.

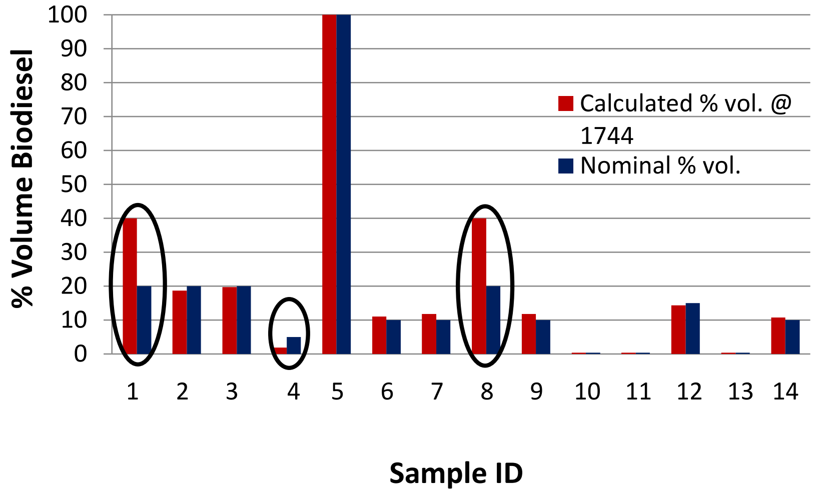

Fig. 4 The values that were calculated at 1744 wavenumbers indicated that three samples fell outside of the nominal values listed at the fuel pump

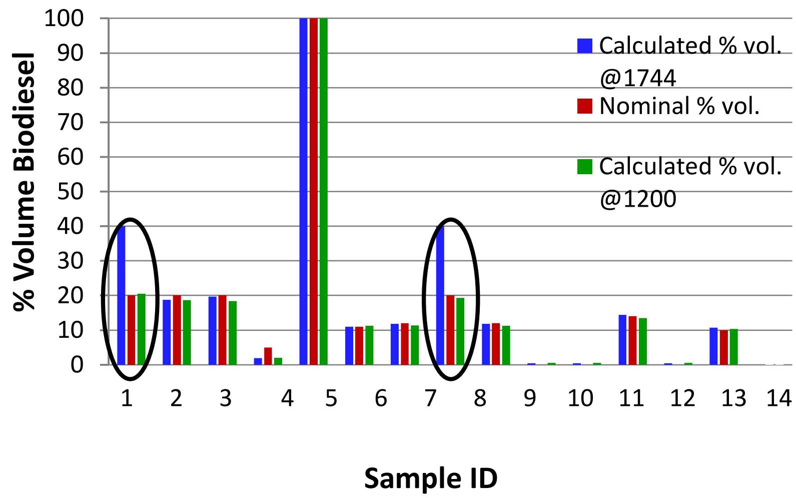

Fig. 5 The values calculated at 1200 wavenumbers showed that only one sample did not meet its nominal value

4.2 Relative Humidity and Moisture

Before conducting RH tests using the Aqua Sensor, it was hypothesized that if the RH readings were less than 60%, water contamination was not an issue in the fuel samples. However, if the RH readings were greater than 60%, the samples contained too much moisture and could damage engines. The results from the RH tests are shown in Fig. 6. All three of the ULSD samples had an RH reading greater than 60%. The two biodiesel samples above 60% were those labeled as B5 and the B100. It was expected that the B100 sample contains more water, because fatty acid methyl esters, the primary constituent of biodiesel, is water-loving ore hydrophilic. The B5 and ULSD samples were not expected to contain much moisture because diesel fuel is hydrophobic.

As shown in Fig. 7, all samples (except for B100) have a water content of less than 200 ppm, indicating that water contamination is not a concern. RH results were then compared to moisture content. In Fig. 8, the three highest RH readings are also the samples that contain the least water content. Previous research has found the RH technology useful in moisture analysis of lubricants, but these results indicate that RH is not useful in assessing the fuel quality of biodiesel fuels.

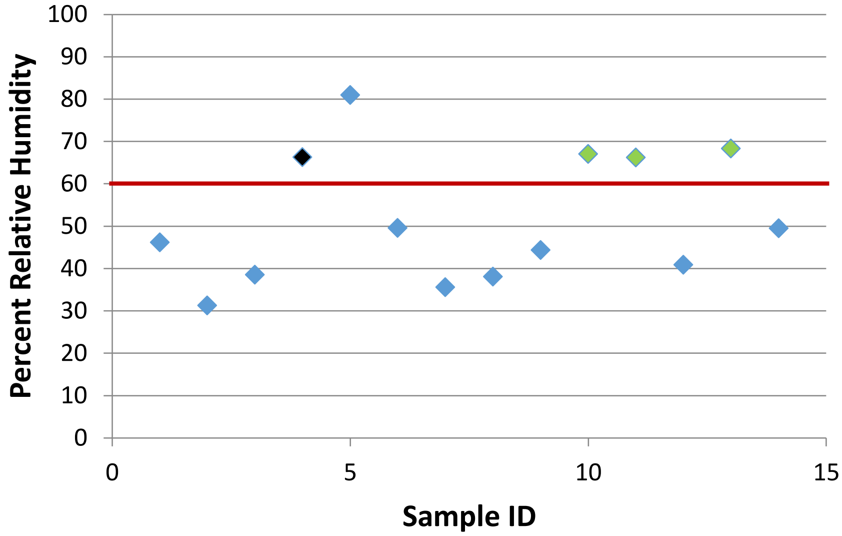

Fig. 6 RH measurements indicated that 5 samples had a high moisture content

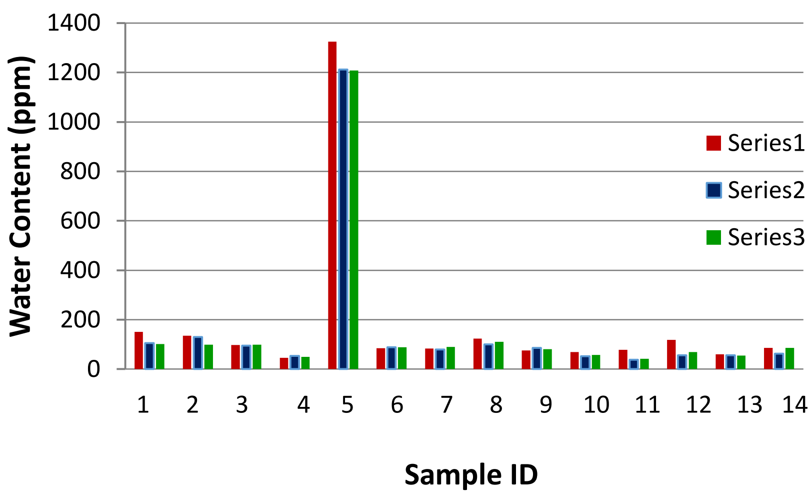

Fig. 7 Aside from sample 15100, which is pure biodiesel, all commercial fuel samples were found to have acceptable water content

4.3 Particulate

The particle content was determined using the LaserNet Fines particle counter. Each sample was run in triplicate. The values for the second and third runs were recorded. These values were then compared to the maximum ISO code standard for particulate cleanliness, 19/17/14. As shown in Fig. 9, all of the samples exhibit ISO codes below the upper limit. There were no differences in particulate observed between the ULSD and biodiesel samples.

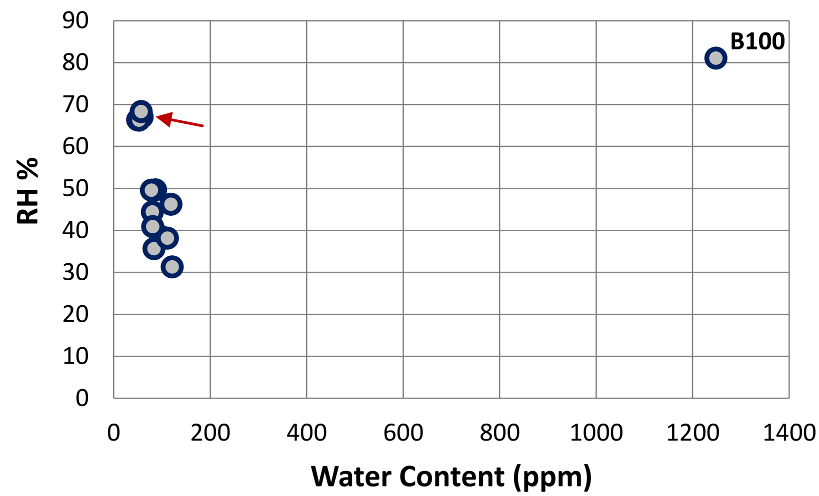

Fig. 8 The diesel fuel samples with the 3 highest RH readings had the lowest water content

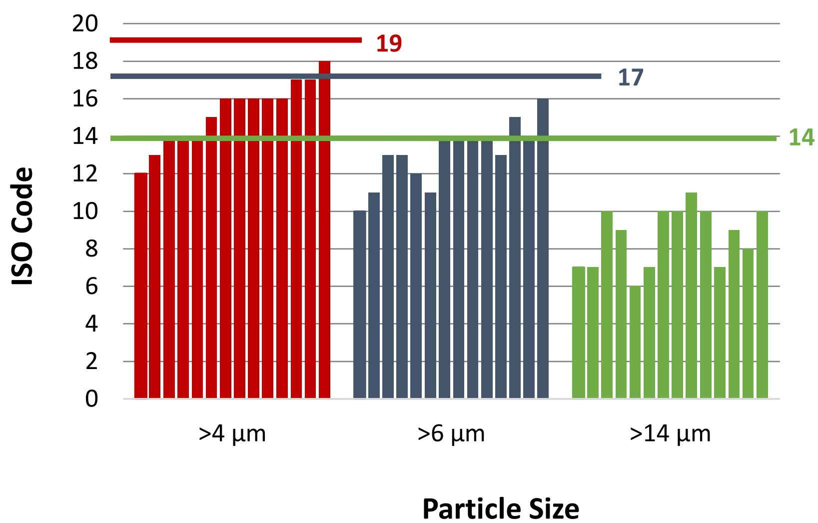

Fig.9 All samples meet fuel particle count limits

5. Conclusions

This research sought to understand how biodiesel impacts the quality of commercial diesel fuel supplies. Fourteen fuel samples were tested for water and particulate contamination. Moisture levels were acceptable for all of the commercial fuel samples. It was found that a submersible relative humidity sensor was not suitable for screening moisture content because it produced false-positive results for water contamination. There was no difference between the particulate content of biodiesel and ULSD. Chemical analysis via infrared spectroscopy showed that biofuel concentrations were consistent with labels posted at the pump, however some fuel samples appeared to contain high levels of free fatty acids that may impact engine performance. Commercial diesel fuel specifications do not provide limits for fuel acid number. A study of the free fatty acid content of commercial diesel fuel is suggested in the future.

6. Acknowledgments

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