BIODIESEL BLEND LEVEL DETECTION USING ULTRAVIOLET ABSORPTION SPECTRA

A. Zawadzki, D. S. Shrestha, B. He

ABSTRACT. *Biodiesel is often blended with regular U.S. No. 2 diesel. The blending level influences engine performance, emissions, and fuel cold-flow properties. In this article, ultraviolet (UV) absorption spectroscopy is presented as a reliable and affordable technology for blend level detection based on the absorbance patterns of the aromatic compounds in the proposed spectrum. Blends of biodiesel from six different feedstocks and U.S. No. 2 diesels from five different sources were used to test the robustness of the method. Since the absorbance of undiluted samples was too high to measure reliably, the samples were diluted with n-heptane. It was found that the feedstock and alcohol used (methyl or ethyl) did not make a significant difference in the absorbance of diluted biodiesel in the 245 to 305 nm range, while absorbance from 254 to 281 nm was correlated with blend level with* $R^2 \geq 0.99$. *It was also observed that if the absorbance of the diesel source was known, then a single wavelength could be used to detect the biodiesel blend level. However, a single wavelength was inadequate when the diesel source was unknown because of variation in the level of aromatics in diesel fuel. Absorbances at 265, 273, and 280 nm were used to calculate the absorbance index, which was found to be independent of the diesel fuel used. Using three wavelengths captured the shape information of the absorbance curve and eliminated the variation from the aromatics content. The root mean square error in determining blend level with this method was estimated to be 2.88%, and the* R^2 *for the linear model was 0.99. The method worked well with biodiesel from the different feedstocks tested in this research and was independent of the diesel fuel used.*

Keywords. *Blend sensor, Diesel, Ester, Ethyl, Methyl, UV.*

Biodiesels are defined as fuels that comprise monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats and that are produced by transesterification of triglycerides with primary alcohols in the presence of a catalyst. Vegetable oils and animal fats are the only sources of triglycerides used in making biodiesel. Biodiesel and No. 2 diesel have many common characteristics, which make biodiesel suitable for use in diesel engines without any engine modification. However, there are some important differences between the two fuels. Because of these differences, many engine manufacturers have limited the recommended amount of biodiesel that can be blended with diesel fuel (EMA, 2003). The National Biodiesel Board provides details of individual engine manufacturers' limitations on biodiesel use (NBB, 2007).

The blend level (percentage of biodiesel in the biodiesel–diesel mixture) determines many important characteristics of the blended fuel. A higher-than-specified level of biodiesel may exceed the engine manufacturer's recommended limitation, compromising the engine performance. A lower blend level of biodiesel may reduce the expected benefits, such as fuel lubricity and tail pipe emission. In addition, cloud point and pour point of biodiesel are usually higher than that of diesel fuel, and a higher blend level makes the fuel unsuitable or difficult to use in cold weather conditions. Engine injection timing can be adjusted based on the blend level in order to improve the engine emission and performance (Tat and Van Gerpen, 2003).

It has been reported that the actual biodiesel content of blended biodiesel fuel sold at gas stations can be significantly different from the nominal blend level. A 2% nominal blend has been found to actually contain anywhere from 0% to 8% biodiesel (Ritz and Croudace, 2005). There are several reasons why the actual blend level may differ from the specified level. For instance, if biodiesel is blended at a temperature less than 10°F above its cloud point, it will not mix well with diesel, causing a rich mixture in one portion of the tank and a lean mixture in another portion (NBB, 2005). Other reasons for the discrepancy may include profit-driven fraud and involuntary mixing of diesel into the blend to lower the overall blend level of biodiesel. Biodiesel is usually sold at a higher price than diesel fuel; therefore, the price of the fuel is dependent on the blend level.

Knothe (2001) has shown that near-infrared (NIR) spectroscopy and nuclear magnetic resonance (NMR) can be used to detect biodiesel blend levels. However, the NMR method depends on the biodiesel fatty acid profile; hence, knowledge of the biodiesel feedstock is required before this method can be used. In addition, using NMR only to detect blend level may not be cost effective. For NIR spectroscopy, Knothe suggested using wavelengths around 1665 nm or 2083 to 2174 nm. Since aromatic compounds produce strong and sharp infrared bands due to their relatively rigid molecular

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structure (Workman, 2001) and diesel fuels have varying amounts of aromatics between 20% and 35% (Song et al., 2000), the absorbance of a blend may not directly correlate to the percentage of biodiesel. The absorbance is defined as the logarithm of the radiation intensities ratio, that is, before and after being absorbed by a sample.

Tat and Van Gerpen (2003) used a commercially available dielectric fuel composition detector to determine biodiesel blend level. They concluded that the sensor appeared to be usable for the development of a biodiesel flexible-fuel vehicle despite the fact that variability in response between the tested fuels might cause small errors in the blend level estimates. Ritz and Croudace (2005) discussed the use of the commercial diesel fuel analyzer CETANE 2000, which is capable of measuring cetane number, cetane index, total aromatics, polynuclear aromatics, and biodiesel simultaneously. The instrument uses infrared (IR) absorbance at 5731 nm (1745 cm^{-1}) and 8621 nm (1160 cm^{-1}), targeting at the C-O stretch. Since the CETANE 2000 is designed to detect several fuel parameters simultaneously, it may not be a cost-effective solution for a simple blend level detection application.

Diesel fuel is distilled from crude petroleum, which is composed primarily of hydrocarbons of the paraffinic, naphthenic, and aromatic classes. Each class contains a very broad range of molecular weights. One of the features of diesel fuel is the presence of 20% to 35% aromatic compounds by weight. Aromatics are a class of hydrocarbons that are characterized by a stable chemical ring structure. They are determined primarily by the composition of the crude oil feed, which is usually selected based on considerations of availability and cost (Chevron, 2006). On the other hand, biodiesel is a mixture of fatty acid esters. Fatty acids with 16 to 22 carbon chain lengths are predominant in oils and fats. The resulting mixture of fatty acid esters depends on the kind of feedstock used. Neat biodiesel contains essentially no aromatic compounds.

The presence of aromatics in diesel and their absence in biodiesel creates the possibility of distinguishing these two fuels using ultraviolet spectroscopy. Benzene, the simplest aromatic compound, has maximum absorption at 278 nm (Bruno and Svoronos, 2003). Biodiesel, which is esters of long-chain fatty acids when adequately diluted in *n*-heptane, has negligible absorbance compared to the aromatics at the same frequency. Hence, differences in biodiesel feedstocks will have a minimal impact on absorbance at this wavelength. The ultraviolet (UV) range between 200 and 380 nm is also referred to as near-UV. In general, light sources, filters, and detectors are less expensive for this vicinity of the spectrum than for IR at 8621 nm, as used by the CETANE 2000. Hence, near-UV spectroscopy may present a low-cost alternative method for biodiesel blend level sensing.

The purpose of this research is to identify the range of UV frequencies that can be used to detect biodiesel blend level. A low-cost detector can be constructed if such a wavelength or a range of wavelengths are able to measure the blend level.

Methodology

Since the amount of aromatic compounds varies with the source of diesel fuel and the sampling time, five samples of diesel were collected from different gas stations at different times of the year. Biodiesel was made from six different feedstocks at the Biological and Agricultural Engineering Laboratory at the University of Idaho. The six feedstocks chosen for biodiesel were canola, soybean, rapeseed, and three different cultivars of mustard. Seeds were crushed for oil using a mechanical oil expeller. Both methyl and ethyl esters were made for one variety of mustard to test the validity of the method with ethyl esters. Biodiesel blends of B5, B10, B20, B30, and B80 were prepared in 10 mL volumetric flasks and pipettes. Biodiesel blends have very high absorbance in the UV range. In order to bring the absorbance to the measurable range of a spectrophotometer, the samples were diluted with *n*-heptane. It has been reported that the error in absorbance measurement is lowest if the absorbance value is below 2 (Bauman, 1962). In order to reduce the amount of *n*-heptane and to reduce the error, the dilution was completed in three steps. In each step, 0.7 mL of sample was accurately mixed with 9.3 mL of *n*-heptane. The final dilution of all biodiesel diesel blends was 1:2915 v/v. This dilution reduced the absorbance in the 240 to 350 nm wavelength range to within 1.2 for all diesel samples. This concentration was chosen by trial and error to reduce the absorbance to the desired range of less than 2.

The UV absorption spectra of the biodiesel samples and the biodiesel blends with diesel were measured using a single-beam, general-purpose spectrophotometer (DU520, Beckman Coulter, Fullerton, Cal.). The absorption spectra in the range of 190 to 350 nm at 1 nm intervals of different biodiesel batches were scanned using standard 1 cm quartz cuvettes.

Results and Discussion

Figure 1 shows a typical family of absorbance curves for diluted soy methyl esters in the range of 240 to 320 nm. When the spectra were plotted for biodiesel from different sources and using the same diesel fuel, the variation in absorption intensity was found to be negligible. The absorbance for methyl and ethyl esters of mustard also produced very similar absorbances, with no statistically significant differences. Therefore, it was concluded that the absorbance in this band is not affected by the type of biodiesel, as blended biodiesel does

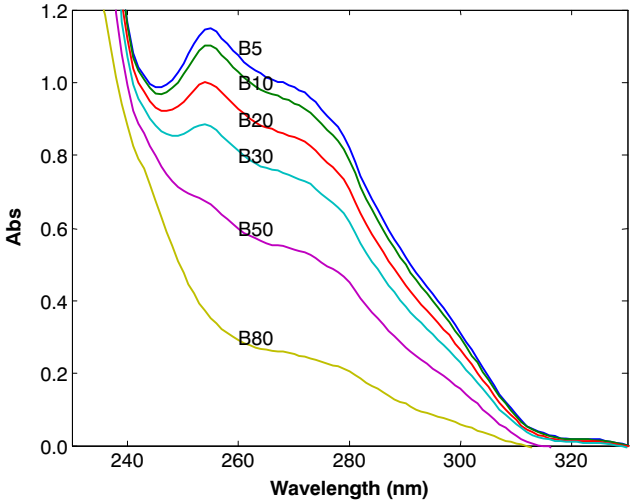

Figure 1. UV absorbance spectra of soy methyl ester and No. 2 diesel blend diluted 1:2915 in *n*-heptane.

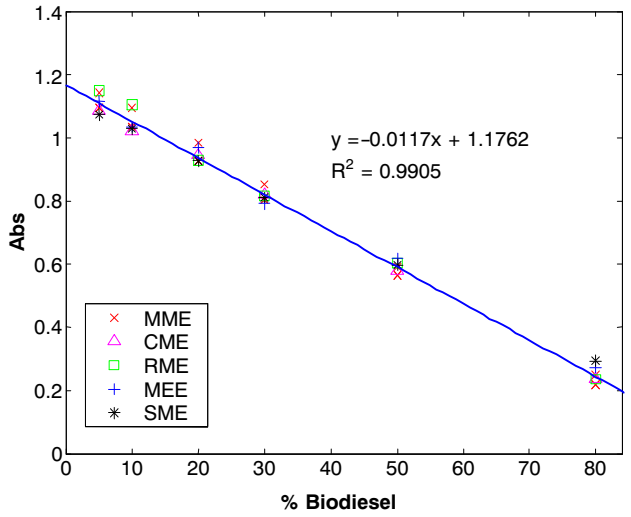

Figure 2. Absorbance of diluted biodiesel-diesel blends from different feedstocks at 260 nm wavelength (MME = mustard methyl esters, CME = canola methyl esters, RME = rapeseed methyl esters, MEE = mustard ethyl esters, and SME = soybean methyl esters).

not have chemical components that contribute to significant absorption in this range.

Analysis of the family of absorbance curves for various biodiesel feedstocks showed that a single wavelength in the UV range could be used to detect the blend level for a single diesel fuel. The absorbance decreased linearly with increasing blend level (fig. 2). When percent biodiesel was plotted against absorbance for any given wavelength between 245 and 305 nm, a linear relation was observed. This was attributed to the decreasing concentration of aromatic compounds in the diesel fuel. The difference in absorbance for B5 and B80 was highest in the vicinity of 260 nm (fig. 1).

A linear line fitted for absorbance versus percent biodiesel for all feedstocks at 260 nm (fig. 2) showed a high coefficient of determination (R^2 = 0.9905). The advantage of using this range over other ranges was that the relationship was independent of feedstock, as compared to the previously shown absorbance analysis in a visible range (Zawadzki et al., 2005; He and Thompson, 2004).

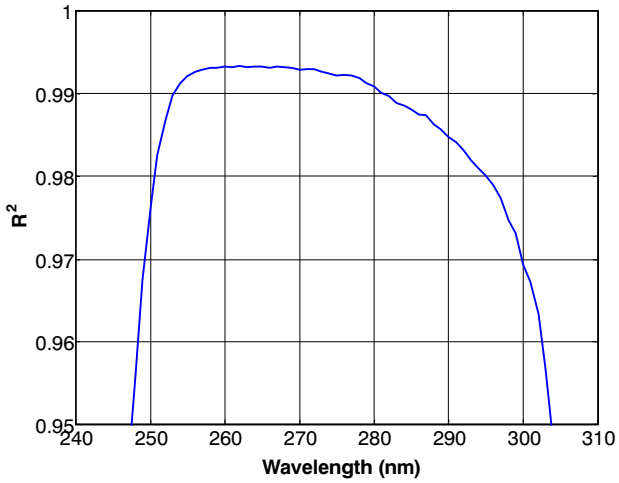

Figure 3. R^2 of linear relation of biodiesel percentage and absorbance as a function of wavelength.

In order to find the wavelength for the best correlation, R^2 was calculated by fitting a linear line for each wavelength from 245 to 305 nm and plotted against the corresponding wavelengths. It was found that the R^2 value was greater than 0.99 for the wavelengths from 254 to 281 nm and dropped sharply outside of this range (fig. 3).

The highest R^2 of 0.9933 was observed at 263 nm. Based on this analysis, it was concluded that a single wavelength between 254 and 281 nm can be used to detect the blend level regardless of the biodiesel feedstock. However, in field applications, it is expected that the aromatic content of the diesel fuel will vary from one fuel to another, and the absorbance from a single wavelength cannot be used. Therefore, an absorbance data transformation procedure, discussed in the following section, was developed to eliminate the differences in the absorbance intensity from different types of diesel fuel.

Accounting for Diesel Composition Variation

As mentioned earlier, the aromatic content of diesel fuel varies from 20% to 35%. Five diesel fuels collected locally from various gas stations at various times of the year were found to have different absorbance intensities (fig. 4). Samples were diluted with *n*-heptane in order to reduce the diesel absorption to the spectrophotometer range. As discussed earlier, the biodiesel and diesel blends showed a linear variation in absorbance, but the absorbance of the diesel fuel had to be known to correlate absorbance with blend level using a single point of measurement. A single-point measurement was not sufficient for blend level detection with an unknown diesel type, since the absorbance levels of diesel fuels vary.

According to Beer's law, the absorbance of a chemical component is proportional to its molar concentration (Bauman, 1962). When aromatic compounds are diluted with biodiesel, their absorbance at each wavelength decreases proportionately. When two quantities of different values decrease proportionately, their difference in absorption is reduced. What is preserved after dilution is the shape of the absorbance curve, with the amplitude attenuated. For instance, if the absorbances of diesel at 260 nm and 270 nm were 1 and 2, respectively, the difference in absorbance would be 1. When the diesel is mixed in equal proportion to biodiesel, it is expected that the absorbance would be 0.5 and 1 for the same wavelengths. The difference in absorbance is now only 0.5. However, for this method to work, all diesel

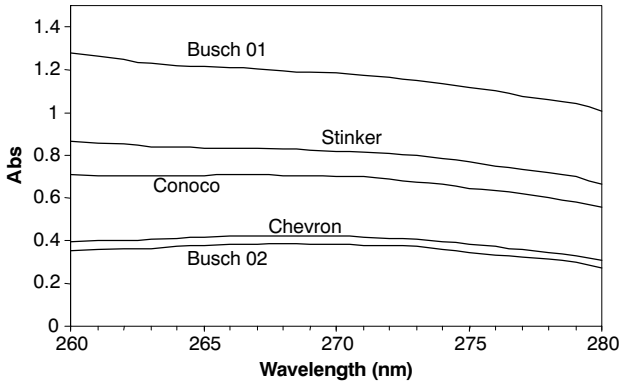

Figure 4. Absorbance of diesel diluted in *n*-heptane. Curves are marked with the name of the local gas stations where the samples were obtained. Busch01 and Busch02 were from the same station at different times of the year.

Table 1. Mean and coefficient of variation of AI for different biodiesel blends.

Blend	Mean AI	CV
B0	1.1135	3.70×10^{-3}
B5	1.1055	3.48×10^{-3}
B10	1.0976	1.23×10^{-3}
B20	1.0864	2.66×10^{-3}
B30	1.0766	1.69×10^{-3}
B50	1.0530	2.86×10^{-3}
B80	1.0226	3.45×10^{-3}

samples must have a similar shape of absorbance curve and the same amplitude difference between selected points.

It was observed that the shapes of the absorbance curves in the 265 to 280 nm range were consistent (fig. 4). Therefore, the absorbances at three wavelengths where the aromatics were best absorbed (265, 273, and 280 nm) were chosen to extract the absorbance index. The absorbance index is a measure of the shape of the absorbance curve and is defined as:

$$AI = 10^{\left(A_{273} - \frac{A_{265} + A_{280}}{2}\right)} \quad (1)$$

where AI is the absorbance index, and A_{xxx} is the absorbance at the *xxx* nm wavelength. The AI was found to be linearly correlated with the blend level.

The coefficients of variation (CV) of AI for the diesel fuels were found to be low. The values of AI were calculated at various blend levels from B5 to B80 using equation 1. The mean and CV of AI are shown in table 1.

The AI for all diesel fuels was found to be 1.1135, with CV of 3.70×10^{-3}. For B80, AI was 1.0226, with CV of 3.45×10^{-4}. Even though the absolute transformed value between neat diesel and B80 was small, very small CV values over the range of biodiesel blends made this method of blend level detection robust.

A linear line was fitted with all calculated AI values against percentage of biodiesel (fig. 5). The R^2 value of the fitted line was found to be 0.99. The root mean squared error (RMSE) of the linear line was 2.88%. The linear equation of the best fit line was:

$$BD = 984.7 - 886.6\ AI \quad (2)$$

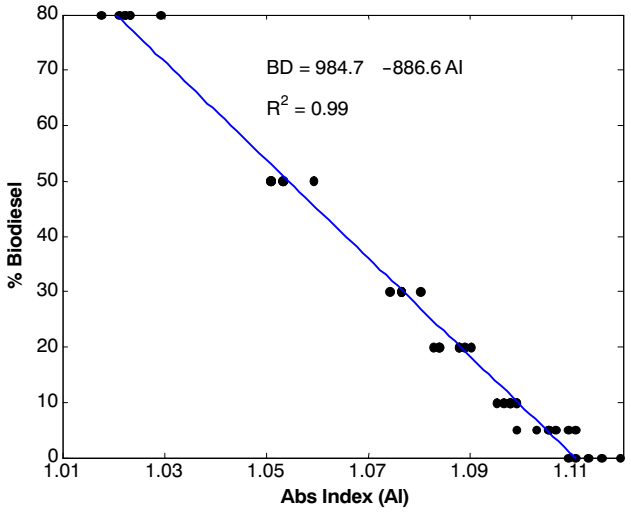

Figure 5. Transformed relation between blend level and absorbance index; dilution 1:2915.

where BD is the blend level, and AI is the absorbance index from equation 1. It is clear from equation 2 that the predicted blend level is very sensitive to AI. In fact, error in AI measurement is amplified 886.6 times in predicting BD. Fortunately, the CV in measuring AI was very small. From table 1, the maximum observed CV was 3.7×10^{-3}. This translates to maximum error in percent biodiesel prediction of 3.28%. This method determined the percentage of biodiesel with an average accuracy of 2.88%.

Conclusion

A method for sensing biodiesel-diesel blend level was proposed and evaluated. The method was based on the absorbance of diluted samples with *n*-heptane in the UV absorption range. The absorbance pattern, rather than the absolute absorbance of the aromatic content of the diesel fuel, was used to distinguish diesel from biodiesel. It was observed that biodiesel absorption in the near-UV range of 245 to 305 nm was unaffected by biodiesel from different feedstocks diluted with *n*-heptane. A linear relation was observed for the absorbances of various blend levels from 245 to 305 nm, and the correlation coefficient (R^2) was greater than 0.99 for the wavelengths from 254 to 281 nm. The highest correlation coefficient was observed for the absorbance around 260 nm.

When the absorbance of the diesel fuel was known, a single wavelength could be used to detect the blend level. However, since the amount of aromatics in the diesel samples varied, it was shown that a single wavelength was insufficient to detect the blend level with an unknown source of diesel. The absorbance index, calculated using absorbances at three different wavelengths, was proposed as a method to determine blend level with an unknown source of biodiesel and diesel. The transformation was found to have a very low coefficient of variance. The RMSE in determining blend level with this method was estimated to be 2.88%. The method was found to be applicable to any biodiesel feedstock and independent of the diesel fuel origins included in this research.

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