BIODIESEL FEEDSTOCK AND BLEND LEVEL SENSING USING VISIBLE LIGHT SPECTRA AND NEURAL NETWORK

A. Zawadzki, D. S. Shrestha

ABSTRACT. *Even after biodiesel meets ASTM D6751 specifications, biodiesels from different feedstocks may have different properties. Biodiesel blend level influences the fuel properties, such as cloud point and emissions. Therefore, whether for performance reasons or other reasons, it is often required to detect the biodiesel percentage in a diesel-biodiesel blend. This research used a spectrophotometer to scan the blends of U.S. No. 2 diesel and biodiesel from three different feedstocks (rapeseed, soybean. and mustard oil) in the visible wavelength range of 380-530 nm. It was found that the shape of the absorption curve varied according to biodiesel feedstock; however, relative absorbance was proportional to the blend level. If the absorbance of the parent biodiesel can be measured, such as in a blending facility, then a single wavelength between 470 and 490 nm could be used to measure the biodiesel blend level with ±1.85% standard error at 95% confidence interval. A neural network was trained to measure the blend level when the parent biodiesel spectrum was unknown. It was concluded that even if the absorption spectrum of the parent biodiesel is not known, the absorption spectrum of the blend from 380-530 nm can be used along with a neural network to detect the biodiesel feedstock and for rough blend level estimation.*

Keywords. *Absorbance, Biodiesel, Neural network, Sensor, Spectrophotometer.*

All vegetable oils and animal fats are primarily triglycerides (triacylglycerols), which are esters of glycerol and long-chain fatty acids. Biodiesel is produced by transesterification of the triglycerides with alcohol, usually methanol or ethanol. Chemically speaking, biodiesel is the mono-alkyl esters of the fatty acids. The composition of vegetable oil varies with the plant source (Van Gerpen et al., 2006). Since biodiesel is made primarily from vegetable oil, its properties also depend on the fatty acid profile and other constituents. Biodiesels from different feedstock have different properties in terms of their cold weather properties and emissions characteristics (Peterson et al., 2000).

Average refined bleached and deodorized vegetable oil contains about 95% triacylglycerols, 2% phospholipids, 1.5% unsaponifiable matter, 0.5% free fatty acids, and 1% trace metals. Composition of crude soybean and rapeseed oil is shown in table 1.

Natural fats and oils from plants and animals contain pigments exhibiting visible absorption (O'Connor, 1960). These coloring pigments are primarily chlorophyll, phytosterols, and carotenoids (part of the unsaponifiable matter). The concentration of these pigments varies among different oils and also from crude to processed oil. For example, the chlorophyll and unsaponifiable matter content of crude soybean and rapeseed oil are different (table 1), and it is expected that the light absorption pattern of these two oils in the visible spectrum will be different. On the other hand, pure aliphatic acids, esters, water, and glycerides are colorless substances and do not affect absorption in the visible range. Despite the fact that absorption in the visible range of light is not affected by the primary constituents of biodiesel, it is possible to distinguish biodiesel feedstocks and blends by utilizing the light absorbance of the coloring pigments.

Biodiesel must meet the ASTM D6751 (ASTM, 2007) quality standard in the U.S. (or EN 14214 in Europe), which also defines the test methods for each of the specified biodiesel properties. However, ASTM D6751 does not specify the required cloud point (CP) of biodiesel. Differences in fatty acid profiles and the presence of impurities cause CP of biodiesels to vary. For instance, CP for palm oil biodiesel could be as high as 16°C, compared to -3°C for canola biodiesel (Mittelbach and Remschmidt, 2005). When biodiesel is blended with diesel fuel, blend level as well as choice of feedstock affects CP of the blended fuel. Therefore, in order to estimate CP of blended biodiesel, determination of both the blend level and the type of parent feedstock are important.

It has been reported that the actual biodiesel content in fuel sold at gas stations can be significantly different from the nominal blend level. A 2% nominal blend was found to actually contain anywhere between 0% and 8% biodiesel (Ritz

Table 1. Constituents of soybean and rapeseed oil (Przybylski and Mag, 2002).

Components	Soybean	Rapeseed
Triacylglycerols (%)	93.0 to 99.2	91.8 to 99.0
Phospholipids (%)	Up to 4.0	Up to 3.5
Free fatty acids	0.3 to 1.0	0.5 to 1.8
Unsaponifiable matter (%)	0.5 to 1.6	0.5 to 1.2
Tocopherols (ppm)	1700 to 2200	700 to 1000
Chlorophyll (ppm)	Trace	5 to 55
Sulfur (ppm)	Nil	5 to 35

Submitted for review in August 2008 as manuscript number FPE 7652; approved for publication by the Food & Process Engineering Institute Division of ASABE in March 2009.

The authors are **Artur Zawadzki, ASABE Member Engineer,** Graduate Student, and **Dev S. Shrestha, ASABE Member Engineer,** Assistant Professor, Department of Biological and Agricultural Engineering, University of Idaho, Moscow, Idaho. **Corresponding author:** Dev S. Shrestha, P.O. Box 442060, Moscow, ID 83844; phone: 208-885-7545; fax: 208-885-8923; e-mail: devs@uidaho.edu.

  ISSN 0001-2351

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 5.6°C above its cloud point, it does not mix well with diesel, causing a rich mixture in one portion of the tank versus 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 bring down the overall blend level of biodiesel. Biodiesel is usually sold at a higher price than diesel fuel; therefore, the price of fuel is dependent on the blend level.

Knothe (2001) showed that near-infrared (NIR) spectroscopy and nuclear magnetic resonance (NMR) can be used to detect biodiesel blend level. However, the NMR method depends on the biodiesel fatty acid profile, and 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 2083-2174 nm. Since aromatic compounds produce strong and sharp infrared bands due to their relatively rigid molecular structure (Workman, 2001) and diesel fuels have varying amounts of aromatics, between 20% and 35% (Song et al., 2000), absorbance alone may not directly correlate to the percentage of biodiesel.

Tat and Van Gerpen (2003) used a commercially available dielectric fuel composition detector to find biodiesel blend level. The authors 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 CETANE 2000 diesel fuel analyzer, a commercial instrument capable of measuring cetane number, cetane index, total aromatic, polynuclear aromatic, and biodiesel blend level 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. Zawadzki et al. (2007) developed a method of detecting biodiesel blend using ultraviolet absorption spectroscopy.

With recent developments in information technology and the availability of low-cost optical sensing technology, it may be well worth exploring the use of visible wavelengths to detect biodiesel type and blend level. When light is transmitted through a liquid such as biodiesel, that light is absorbed at specific wavelengths due to the presence of certain chemicals within the liquid. By monitoring the light absorption at particular known wavelengths, it is possible to identify the concentrations of the chemicals absorbing the light. This technique could potentially be used to determine biodiesel feedstocks and blend levels.

The objective of this work was to develop a methodology to detect biodiesel-diesel blend level and the type of biodiesel feedstock by using a visible light spectrum, which is easy to generate, measure, and implement.

Materials and Method

Biodiesel from each of five different feedstocks (three cultivars of rapeseed, one of mustard, and one of soybean) were prepared at the Biological and Agricultural Engineering Laboratory at the University of Idaho. They are referred to here as rapeseed methyl ester (RME), mustard methyl ester (MME), and soybean methyl ester (SME). The biodiesel after the reaction was water-washed and dried to remove excess soap, catalyst, free glycerol, and methanol. The final biodiesel was then tested for ASTM D6751 and found to be within the specifications.

Blends of 5%, 10%, 20%, 30%, 50%, and 80% of biodiesel by volume with commercial U.S. No. 2 diesel were prepared. The absorption spectra of the biodiesels and biodiesel-diesel blends without any dilution or solvent were measured using a general purpose UV/vis spectrophotometer (model DU 520, Beckman Coulter, Fullerton, Cal.) for visible absorption spectra from 380 to 530 nm. The spectra were recorded at intervals of 1 nm.

Since each type of biodiesel gave a different absorption curve, the curve shapes and position features were extracted to train an artificial neural network. The measured absorption spectra of the biodiesels from 380 to 530 nm were fitted with a second-degree polynomial. It was observed that the shape and position information of the absorbance curves could be adequately captured by a quadratic equation.

A three-layer neural network with a sigmoidal transfer function in two hidden layers and a linear transfer function in the output layer was employed to distinguish between the different kinds of biodiesel blended in different proportion with regular diesel. Five neurons were used in the first hidden layer and three in the second one. The number of neurons in each layer and the number of layers were optimized by trial and error. Three coefficients of the best fit quadratic equation for each curve were used as inputs to the network. The network had two outputs since there were two expected variables: the amount of biodiesel in the sample, and the biodiesel feedstock type. The resilient back-propagation algorithm (Demuth and Beale, 1998) was used for network training in MATLAB (The MathWorks, Inc., Natick, Mass.). The network was trained with biodiesel blends B0, B5, B10, B20, B30, B50, B80, and B100 from three different feedstocks. Two different batches of rapeseed biodiesel and their blends were used as a validation set.

Results and Discussion

The different feedstocks used for biodiesel production have different amounts and kinds of pigments (table 1). Pigments make the color of one vegetable oil different from that of others. Part of those pigment constituents remain in the biodiesel as impurities. The shape and position of the absorbance curve in the visible range was used to distinguish between biodiesels from different feedstocks (fig. 1).

The absorption of vegetable oils in the visible region is usually due to lipid-soluble pigments such as carotenoids and chlorophylls (Angioni et al., 2002). Pure aliphatic acids, esters, water, and glycerides are colorless substances and do not affect absorption in the visible range. Therefore, the characteristic absorption of biodiesel in the visible range (fig. 1) is caused by pigments but not by other impurities such as glycerol and alcohol.

When the absorbances of RME from different sources were recorded, they were similar but did not overlap with each other (fig. 1). However, the overall shape of the

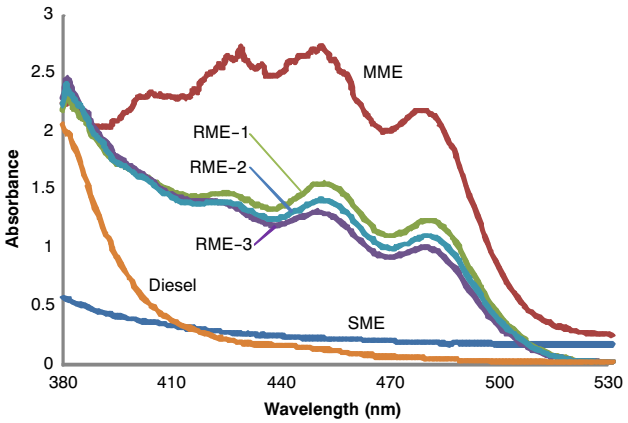

Figure 1. Absorption spectra of MME, SME, diesel, and three different sources of RME in the visible range.

absorbance curves was similar. Therefore, it was concluded that absolute absorbance is inadequate to predict the percentage of biodiesel in blends of biodiesel and diesel, as the absorbance of parent biodiesels from similar feedstocks may vary.

When biodiesel was mixed with diesel in various proportions, it was observed that the characteristic shape of the absorbance curve did not change; only the magnitude of absorbance was reduced. The characteristic peaks were gradually worn off as more of diesel was used in the blend (fig. 2).

When the absorbance of the parent biodiesel and diesel are known, such as in a blending facility, the absorbance of the blended fuel at one particular wavelength could reveal the percentage of biodiesel in the mixture. This method could potentially be used to check if the fuel has been blended properly by taking fuel samples from different parts of the storage tank. In order to evaluate which wavelengths would perform better in estimating the blend level, the expected absorbance of the blended fuel was calculated as:

$$ABS_{pred} = ABS_{BD} \times BD + ABS_D \times (1 - BD) \qquad (1)$$

where ABS_{pred} is the predicted absorbance for a blend, ABS_{BD} is the absorbance of the parent biodiesel, BD is the fraction of biodiesel in the mixture, and ABS_D is the absorbance of diesel fuel at a particular wavelength. For the diesel fuels used in this study, the absorbance varied for one fuel to another. However, the absorbance of the blended fuel always followed the linear model given in equation 1. In addition, no diesel fuel had the characteristic peaks as in the case of biodiesel (fig. 2). Since diesel fuel is hard to characterize, as its detailed composition may vary from one source to another, no attempt was made to distinguish between different diesel fuels.

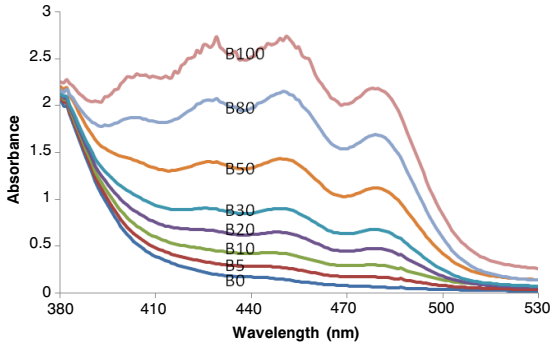

Figure 2. Absorption spectra of mustard methyl ester (MME) with diesel blends.

The predicted absorbance for B5, B10, B20, B30, B50, and B80 from equation 1 was then plotted against the corresponding measured absorbance, and a linear equation was fitted. The coefficient of determination (R^2) was then calculated for each of the wavelengths and plotted for each biodiesel blend (fig. 3). Since the absorbance curve for SME intersects with that of diesel fuel, the R^2 value dropped to about 0.01 at around 415 nm. Considering the best linear fit, the wavelengths between 470 and 490 nm gave the highest R^2 value and were considered as the best choice of wavelength to predict the blend level when absorbance of the parent biodiesel is known. The maximum standard error of mean ABS_{pred} in the range of 470 to 490 nm was found to be 0.02 for MME.

This standard error in absorbance measurement translated into 0.94% standard error in blend level predicted from measured absorbance. Assuming a normal distribution, the actual blend level could be measured within ±1.85% accuracy at 95% confidence interval. Therefore, equation 1 was modified to predict the biodiesel as:

$$BD = \frac{ABS - ABS_D}{ABS_{BD} - ABS_D} \times 100 \pm 1.85\% \qquad (2)$$

where ABS is the measured absorbance of the biodiesel blend. Equation 2 is valid to be used to predict biodiesel using any of the wavelengths between 470 and 490 nm.

Analysis of Biodiesel Spectra with Application of the Artificial Neural Network

The characteristic shapes of the biodiesel absorption spectra in the visible range indicated that this information could be used to detect the biodiesel feedstock. Differences in position of the absorption spectra gave information about biodiesel blend level with regular diesel. A feed-forward neural network was a logical choice for using these spectrum shape and position parameters to identify biodiesel feedstock and blend level. The method used the characteristics shape of the biodiesel absorption spectra and compensated for biodiesel type in predicting blend level when absorption of the parent biodiesel is not known.

The network was trained with biodiesel from one batch of RME, one of MME, one of SME and their blends. The absorbance data from the other two batches of RME were used to verify the network performance. Initial random weights and

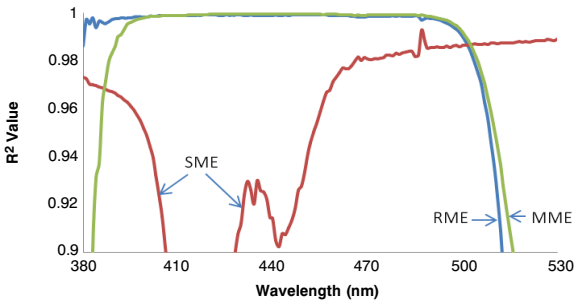

Figure 3. R^2 value for the linear line fitted between ABS_{pred} (eq. 1) and actual absorbance for blends from B5 to B80.

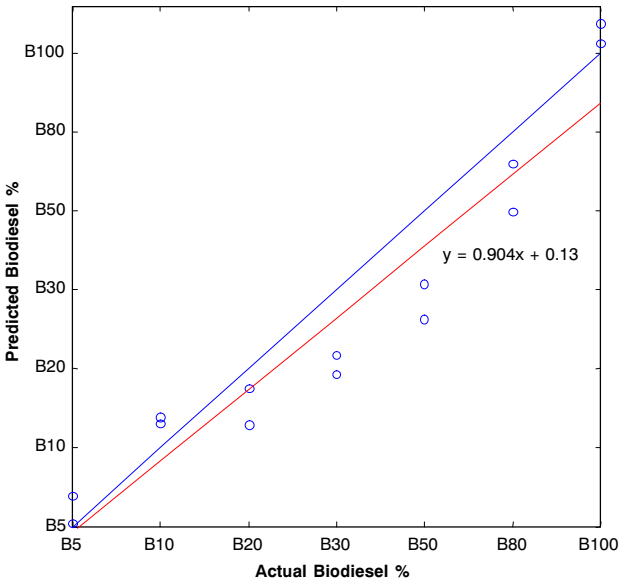

Figure 4. Regression analysis between the network response and the corresponding biodiesel blend levels. The perfect fit (1:1 line) is indicated by the upper line; the lower line indicates the best linear fit.

biases of the neurons influenced the network performance. However, 2000 epochs were usually sufficient to reduce the error to a stable level.

The network-predicted biodiesel blend levels were plotted against the actual blend levels (fig. 4). The best-fit linear regression line had a slope of 0.9 ± 0.18 and an intercept of 0.13 ± 0.93 at 95% CI. The coefficient of determination (R^2) of the regression line was 0.91. The slope and intercept of the line were not statistically significant from 1 and 0, respectively. However, it should be noted that although the predicted blend on average was close to the actual blend level, individual measurements could be off by as much as 25% from the measured value. This can be seen in figure 4; predictions for B50 were as low as B25. Even though the blend level was not recognized correctly in all cases, the neural network was able to correctly recognize the feedstock. Therefore, it was concluded that the visible spectrum in conjunction with a neural network could be used for feedstock recognition and for rough blend level estimation.

Conclusions

The visible spectrum of light was investigated to predict biodiesel blend levels. Presence of chlorophyll, phytosterols, carotenoids, and other coloring pigments give characteristic colors and absorption spectra to biodiesels made from various oil sources. When the absorbance of the parent biodiesel being blended with diesel is known or can be measured, such as in a biodiesel blending facility, the absorbance of the blended fuel was found to be the weighted average of the absorbance of neat biodiesel and diesel. Considering the best linear fit, wavelengths between 470 and 490 nm gave the highest R^2 value and are recommended as the best choice of wavelength to predict the blend level when absorbance of the parent biodiesel is known. The 95% confidence interval of standard error for the measured blend level was found to be within ±1.85% of the predicted value. This method could potentially be used to determine if a fuel has been blended properly by taking samples from different parts of the storage tank.

The characteristic shapes of biodiesel absorption spectra in the visible range indicated that this information could be used to detect the biodiesel feedstock. The absorbance curve was approximated with a second-order polynomial equation, and coefficients of the polynomials were used as network inputs. It was concluded that a single wavelength of the visible spectrum between 470 and 490 nm can be used for accurate blend level sensing if the spectrum of the parent biodiesel is known. When the spectrum of the parent biodiesel is unknown, the absorbance spectrum from 380 to 530 can be used with a neural network for feedstock recognition and rough blend level estimation.

References

Angioni, E., G. Lercker, N. G. Frega, G. Carta, M. P. Melis, E. Murru, S. Spada, and S. Banni. 2002. UV spectral properties of lipids as a tool for their identification. *European J. Lipid Sci. and Tech.* 104(1): 59-64.

ASTM. 2007. D 6751-07be1: Standard specification for biodiesel fuel (B100) blend stock for middle distillate fuels. In *ASTM Vol. 05.04 Petroleum Products and Lubricants*. West Conshohocken, Pa.: American Society for Testing and Materials.

Demuth, H., and M. Beale. 1998. *Neural Network Toolbox for Use with Matlab.* 3rd ed. Natick, Mass.: The MathWorks, Inc.

Knothe, G. 2001. Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber-optic near-infrared spectroscopy and H-1 nuclear magnetic resonance spectroscopy. *J. American Oil Chem. Soc*. 78(10): 1025-1028.

Mittelbach, M., and C. Remschmidt. 2005. *Biodiesel the Comprehensive Handbook*. 2nd ed. Vienna, Austria: Boersedruck.

NBB. 2005. Biodiesel cold weather blending study. Jefferson City, Mo.: National Biodiesel Board.

O'Connor, R T. 1960. Chapter 5: Spectral properties. In *Fatty Acids, their Chemistry, Properties, Production, and Uses*, 394-497. K. Markley, ed. New York, N.Y.: Interscience Publishers.

Peterson, C. L., J. S. Taberski, J. C. Thompson, and C. L. Chase. 2000. The effect of biodiesel feedstock on regulated emissions in chassis dynamometer tests of a pickup truck. *Trans. ASAE* 43(6): 1371-1381.

Przybylski, R., and T. Mag. 2002. Chapter 4: Canola/rapeseed oil. In *Vegetable Oils in Food Technology: Composition, Properties and Uses*, 98-127. F. D. Gunstone, ed. Boca Raton, Fla.: CRC Press.

Ritz, G. P., and M. C. Croudace. 2005. Biodiesel or FAME (fatty acid methyl ester): Mid-infrared determination of ester concentration in diesel fuel. Houston, Tex.: Petroleum Analyzer Company (PAC). Available at: www.hdscientific.com.au/media/Biodiesel.pdf. Accessed 12 March 2009.

Song, C, C. S. Hsu, and I. Mochida. 2000. Introduction to chemistry of diesel fuel. In *Chemistry of Diesel Fuels*, 1-60. New York, N.Y.: Taylor and Francis.

Tat, M. E., and J. H. Van Gerpen. 2003. Biodiesel blend detection with a fuel composition sensor. *Applied Eng. in Agric.* 19(2): 125-131.

Van Gerpen, J, R. Pruszko, D. Clements, B. Shanks, and G. Knothe. 2006. *Building a Successful Biodiesel Business: Technology Considerations, Developing the Business, Analytical Methodologies.* 2nd ed. Dubuque, Iowa: Biodiesel Basics.

Workman, J. 2001. Interpretive spectroscopy for near infrared. In *Handbook of Organic Compounds* 1: 143-182. San Diego, Cal.: Academic Press.

Zawadzki, A., D. Shrestha, and B. He. 2007. Biodiesel blend level detection using ultraviolet absorption spectra. *Trans. ASABE* 50(4): 1349-1353.