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Ultraviolet absorption spectra for biodiesel quality sensing

Artur Zawadzki

Graduate Student, Biological and Agricultural Engineering Department, University of Idaho, Moscow, ID 83844-0904, USA, azawadzki@uidaho.edu

Dev Shrestha

Assistant Professor, Biological and Agricultural Engineering Department, University of Idaho, Moscow, ID 83844-0904, USA, devs@uidaho.edu

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Abstract. *Biodiesel fuels from different feedstock have different properties. A critical need in the increasingly emerging biodiesel industry right now is a reliable and rapid test for the determination of the blends of biodiesel in diesel fuel.*

Biodiesel from four different feedstocks: rapeseed, soybean, mustard, and canola oils were investigated. Their ultraviolet absorption spectra were compared and the suitability of those spectra for the use in biodiesel quality sensing was investigated. Different features of ultraviolet absorption spectra were observed after measuring various sample dilutions in n-heptane. Despite the fact that ultraviolet absorption spectra were affected mainly by diesel absorption in biodiesel-diesel blends, differences between spectra were significant. Those differences were not dependent on a kind of feedstock but only on the amount of biodiesel in blends.

Data from absorption measurements were analyzed. Absorption spectra of different feedstock and biodiesel blend samples from ultraviolet absorption range were fed to three different artificial neural network architectures. A feedforward neural system with Levenberg-Marquardt learning rule was a logical choice to input shape and position parameters of the spectra to identify the blend level. It was concluded that absorption spectra can be successfully used for biodiesel blend level sensing.

Keywords. absorption spectra, back-propagation, biodiesel, neural network, quality

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Introduction

Biodiesel is produced by transesterification reaction of triglycerides with alcohol in the presence of a catalyst. Vegetable oil and animal fats are a source of triglycerides which are esters of glycerol with long-chain fatty acids. Biodiesel itself is a mono-alkyl ester of fatty acids.

Biodiesel is most often blended with diesel and the blend composition is one of the properties of this fuel that needs to be determined. Distributors of the fuel rely on blend level determination as they need to keep certain level of the fuel blend. Also customers need to be able to verify expected level of biodiesel in purchased biodiesel-diesel blends. Additionally, engine injection timing can be adjusted based on the blend level in order to improve the engine emission and performance [9]. Fuel level is designated as BXX where XX is the percentage of biodiesel in the blend.

Biodiesel level in the biodiesel-diesel blends can be determined with the use of mainly spectroscopic or chromatographic methods. Blend level determination by Nuclear Magnetic Resonance (NMR) was reported in [10]. This method is suitable for producers who can use the same NMR instrument for biodiesel quality monitoring. However, when only information about the blend level is needed, the cost of NMR instrument is too high to utilize this method. A different approach to the blend level determination is the use of Near Infrared (NIR) Spectroscopy which is in good agreement with NMR data [10]. A blending equation that allows for calculation of the kinematic viscosity as a function of biodiesel fraction was presented in [13]. Also a sensor for testing of commercially available dielectric fuel composition, that was originally designated for the detection of the methanol concentration in methanol-gasoline blends, was reported in [9]. The authors concluded that the sensor appeared to be useable for the development of a biodiesel flexible fuel vehicle despite the fact that variability in response between the tested fuels might caused small error in the blend level estimate. The sensor caused small error in injection timing but it was closed to the manufacturing tolerance. Chromatographic methods such as gas chromatography or high pressure liquid chromatography (HPLC) produce complex chromatograms due to the complexity of biodiesel composition and generally spectroscopic methods may be more suitable to address the problem of blend level variety [11]. Application of visible absorption spectra to biodiesel blend level sensing was investigated in previous work [4]. Absorption in visible range depended on a kind of feedstock from which biodiesel was made. In case of different feedstock mixed together additional adjustment was suggested to be necessary.

UV-Vis spectroscopy presents a relatively simple and cost-effective method for biodiesel blend level sensing. When light is transmitted through a liquid such as biodiesel or diesel, it is noted that the light is absorbed at specific wavelengths due to the presence of certain characteristics within the liquid. Ultraviolet and visible spectroscopy produce spectra of organic compounds due to electronic excitations or transitions; for example, benzene (C_6H_6) absorbs strongly in ultraviolet range at characteristic wavelength of 184, 202, 255 nm, but characteristic wavelength for a compound may vary, depending on the solvent used [12]. Biodiesel and diesel constituents also show specific absorption characteristics.

Problem Description

The Quality of biodiesel is specified in ASTM D6751 standard, but procedures for the investigation of biodiesel quality are not widely implemented due to a need for expensive equipment such as a gas chromatograph. Cost effective solutions for the determination of

biodiesel quality and blend level are needed in an emerging biodiesel industry. Consumers need a reliable and inexpensive method to verify the fuel blend level that they purchased and producers need a qualitative method to control blend level to comply with the standard. Also, there is a need for the determination of blend level since important fuel properties like cold flow properties depend on the blend level. Because of this relation between pour point and blend level, pour point temperature could be predicted from biodiesel-diesel blend level. Therefore, the objective of this paper was to investigate a method of sensing biodiesel in biodiesel-diesel blends regardless of biodiesel feedstock using UV spectrophotometry. In our approach we were using a spectrophotometer, which is usually easily available in many laboratories. UV absorption spectra can be indicative of the amount of biodiesel in biodiesel-diesel blends.

Materials and methods of sample preparation

Several batches of biodiesel from different feedstock were prepared on site from rapeseed, mustard and canola oils. Biodiesel diesel blends were prepared by volume using 10ml volumetric flasks and volumetric pipettes. Samples were diluted in n-heptane (1:2915) because the dilution was necessary to achieve the absorption range within the spectrophotometer detection range.

The UV and visible absorption spectra of biodiesel samples and biodiesel blends with diesel were measured using Beckman Coulter DU520 (Fullerton, CA) General Purpose UV/Vis spectrophotometer. The absorption spectra in the range of 190-350 nm of five different biodiesel batches were measured.

Out of those six batches, three batches of mustard oil methyl ester (MME) were made from different mustard oil. Besides MME, one batch of mustard oil ethyl ester (MEE), canola methyl ester (CME) and rapeseed methyl ester (RME) were prepared. Blends of 5, 10, 20, 30, 50, 80% (v/v) of biodiesel with commercial No. 2 diesel were prepared (B5, B10, B20, B30, B50, B80, respectively). Additionally three samples of B7, B25 and B40 were prepared from MME. The spectra were recorded at 1 nm intervals.

Measurement results and discussion

The absorbance curves in the UV range 230-320 nm were used to distinguish between biodiesel-diesel blends. In this range biodiesel showed no absorbance while 100% diesel had characteristic absorption pattern. When biodiesel was mixed with diesel in various proportions, the shape of the absorbance curve did not change, but varied in magnitude. Characteristic peaks were blended off with the main curve as the amount of diesel in the blends decreased (Figure 1). Magnitude of characteristic peaks was used to determine the biodiesel blend level. When the amount of biodiesel in the samples increased, the magnitude of absorption curves decreased. This relation between absorption and the amount of biodiesel indicates that absorption of the samples diluted in n-heptane in this range is mainly because of the presence of diesel in the sample. Absorption curve of B100 diluted in n-heptane is almost flat in this region because of only a low amount of aromatic compounds present in biodiesel.

One of the features of chemical composition of diesel is the presence of aromatic compounds, such as benzene and naphthalene, that are absent in biodiesel. This feature is considered as one of the advantages of biodiesel quality [14]. Benzene has absorption maximum at 255 nm with molar absorptivity $E_{\max}=230 \text{ M}^{-1}\text{cm}^{-1}$ [12]. Absorption peak, which is observed for the blend samples in the UV range, corresponds to this maximum and is caused by the presence of

aromatic compounds like benzene in diesel fuel. The absorption due to the presence of those compounds is strong even in n-heptane diluted samples.

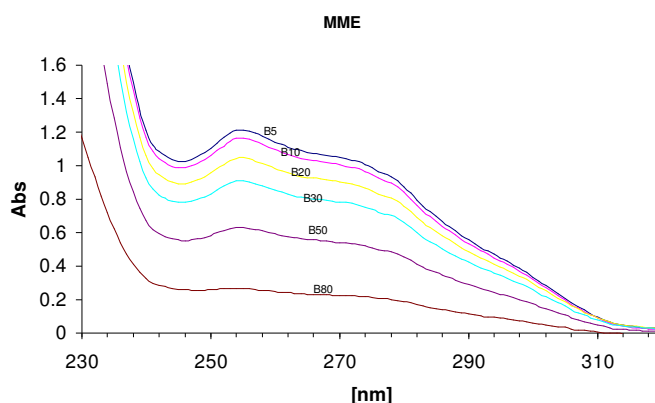


Figure 1. Ultraviolet absorption spectra of mustard methyl ester (MME) blended with diesel. B5 to B80 indicate 5-80% percent of biodiesel in the sample.

The pattern of absorption curves was consistent, but there was some variability between measurements. This variability was probably caused by dilution error or error of the spectrophotometer in higher absorption range; therefore, precise dilution was needed for all samples.

Differences in the shapes of absorption spectra in the UV range were used to detect the amount of biodiesel in biodiesel-diesel blends. Statistical methods and artificial neural networks were tools chosen to analyze the differences between spectra of different blends.

Statistical Approach

Statistical analysis allowed to investigate a method of sensing biodiesel in biodiesel-diesel blends from UV absorption spectra. General questions were addressed by applying statistical methods: Can biodiesel level be predicted from absorption spectra of biodiesel-diesel blend? Does this prediction depend on feedstock?

2-way MANOVA

To analyze if there are significant feedstock and blend level effects on absorption spectra of biodiesel-diesel blends, a two-way multivariate analysis of variance (2-way MANOVA) was applied. Experiment was designed and ran to see how feedstock and blend level effects absorption spectra of biodiesel-diesel blends. In the lab, 24 samples were prepared from 4 feedstock types with 6 biodiesel-diesel blend levels. After measuring the UV absorption spectra of biodiesel-diesel blends, the distinguishable features of those spectra were identified in the UV range. Each of the plots was characterized by 2 absorbance values for 255 nm and 280 nm: Abs_{255} , Abs_{280} .

In summary:

- Design: 2-way factorial in a completely randomized design with one observation per cell
- Treatments: Feedstock: MME, MEE, CME, RME; BXX-blend level: B5, B10, B20, B30, B50, B80

- Experimental units: batches of biodiesel-diesel blends
- Response variables: Abs255, Abs280.
- Model for 2-way factorial in a completely randomized design:

$Y_{ijk} = \mu + a_i + b_j + e_{ijk}$; where

μ - overall mean

a_i - effect of feedstock; $i = 1 \dots 4$

b_j - effect of blend level; $j = 1 \dots 6$

$e_{ijk} \sim \text{NID}_2(0, \Sigma)$; $k = 1 \dots 2$.

The data was skewed to the right; therefore, data transformation was performed using log function. Normality was assessed.

Multivariate test of main effects presented preliminary results for the data. Biodiesel blend level affects UV absorption spectra represented by values for two selected peaks. From the multivariate test, there was significant main effect of blend level; p -value < 0.001 . There was no significant main effect of feedstock on UV absorption spectra; from the multivariate test p -value was 0.0979 for Hotelling-Lawley trace. From Within 1st canonical variate, significant main effect of BXX was mainly due to Abs255. Two way factorial in a completely randomized design with one observation per cell allowed to test only main effects of feedstock and blend level. More observations are needed to test interaction which expected to be insignificant.

Discriminant Analysis

Discriminant analysis was applied for identifying samples of unknown biodiesel-diesel blends from UV absorption spectra. For developing a discriminant rule the same data as for multivariate analysis of variance were used. For this sample size, linear discriminant analysis was chosen. Equal priors were used and potential error was estimated using jackknife method. To test classification of blend level to one of six groups, additional samples of B7, B25 and B40 were used.

Discriminant analysis, as a statistical method, gave preliminary results about classification of samples. After the development of discriminant rule, most of the training samples were classified to the correct group, but not all 5% and 10% biodiesel blends were classified correctly. Overall jackknife error estimate was 0.1250. Linear discriminant rule was able to classify three unknown biodiesel-diesel blend samples: 7%, 25%, 40% to one of the nearest blend level group.

Application of Neural Network for blend level sensing

Data preparation

After measuring the UV absorption spectra of biodiesel-diesel blends, the distinguishable features of those spectra were identified in the range from 245 to 320 nm. Then, four absorbance values for the following wavelengths: 245 (valley), 255 (peak), 280 (peak), and 320 nm were selected. The plot was divided into three sections: 245-255, 255-280, 280-320 nm. For each of the sections the linear approximations were fitted, based on starting and ending values. Therefore, each of the plots was characterized by 8 variables: two coefficients for each line for

each of three sections and absorption values for 245 and 255 nm. Such approach allowed for describing the plot based on absorption measurements for only four different wavelength points.

The principal component analysis was performed, to reduce the dimensions of input vectors. However, the reduction of variables from eight to two increased uncertainty in blend level evaluation. Also some important features of the plots were lost after the application of principal components to reduce the input vector. If more measured absorption points were included into analysis, the transformation with the use principal component analysis could bring expected input vector reduction without compromising the results of the blend level estimation.

The use of other approaches for data preparation, like the second degree polynomial fitting for each plot is also possible. After measuring absorption spectra of the samples and sampling curves every five nanometers, second degree polynomials could be fitted for each curve. Polynomial coefficients could be presented to the network during the learning and testing phase. In case of polynomial fitting for the entire plot, more points from absorption plots have to be included, whereas the approach used in this work employed small amount of points.

Simulation results and discussion

Feedforward neural network solution

To evaluate features of the UV absorption spectra, including shape, peaks, and valleys, feedforward neural network with back propagation learning rule was used. The optimal structure of the network was needed to correctly sense the amount of biodiesel in unknown samples based on their absorption spectra. The neural network had 8 inputs and consisted of one hidden layer having 6 neurons with a sigmoidal transfer function and one output neuron with a linear transfer function. Input vector incorporated 8 variables describing features of the absorption plot. The amount of biodiesel in biodiesel-diesel blend was computed by the network as an output. Although other network structures were also possible (for example, 6-3-1), the 6-1 structure was chosen as the optimal as it gave stable, repeatable error throughout the learning stage. Network training was performed in MatLab environment.

To improve network generalization, an early stopping method was used. The data was divided into three sets: training, validation, and test data [6]. Training data was used for neural network training and the error of the validation set was monitored during training. The test data set was not used during training but it was used to compare the network performance (Figure 2).

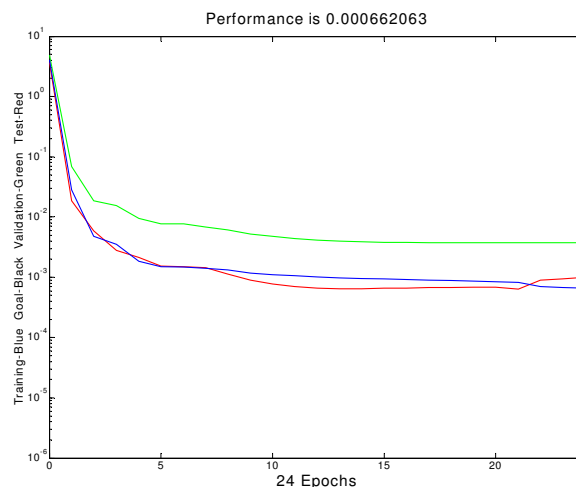


Figure 2. Results from the 6-1 neural network training using Levenberg-Marquardt algorithm: the total error for training, validation and test data set as a function of epoch number during the neural network training.

The samples consisted of 36 eight-dimension input vectors and 36 target responses for biodiesel-diesel blends B5, B10, B20, B30, B50, and B80. Additionally 3 samples of B7, B25 and B40 were prepared to evaluate network responses to unknown samples. The whole 39 sample set was divided into three groups, 24 samples were used for training, 6 to evaluate network responses and 9 as a test set. All data was normalized before applying to neural network. With normalized data, the network responses were more precise and learning time decreased.

Several algorithms such as error back propagation, steepest descent, resilient backpropagation, and Levenberg-Marquardt algorithm were tested. Levenberg-Marquardt (LM) algorithm was chosen as a training algorithm because it gave small error after small number of iterations and it was practical for a small network architecture. Although the LM algorithm combined speed with stability, its dependence on the initial randomly chosen weights was observed. Throughout supervised learning, the features of spectra of known biodiesel-diesel blend levels were presented to the network. When the unknown samples were later presented to the network, the network response indicated the amount of biodiesel in biodiesel-diesel blends. For example, after 24 epochs, the network achieved the total error $TE=7 \times 10^{-4}$ and was able to estimate the blend level correctly for the unknown samples (Figure 3). Thus for B25 and B40 samples that were never presented to the network before, the network responded with the correct blend level.

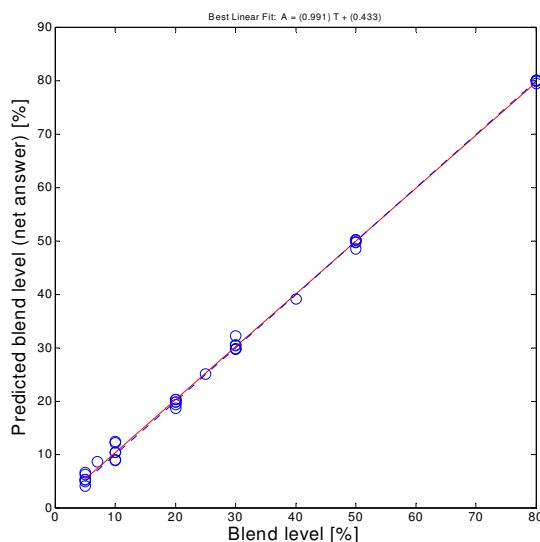


Figure 3. The neural network response and the corresponding actual blend levels of different kinds of biodiesel blended with diesel in different percentages: B5, B7, B10, B20, B25, B30, B40, B50, B80 where 5, 7, 10, 20, 25, 30, 40, 50, 80 are the percentage of biodiesel in the 39 sample set. The perfect fit is indicated by a dashed line; the solid line indicates the best linear fit.

Clustering algorithm solution using Kohonen learning rule

Another approach for sensing the correct blend level was the application of clustering algorithm. Clustering neural networks are able to categorize or cluster the data. Unsupervised classification learning was employed to teach the network to distinguish between different absorption spectra. Winner-Take-All learning rule was based on clustering of input data where network defined classes and boundaries between classes [2]. Clustering was followed by labeling clusters with appropriate category names from B5 to B80.

Kohonen learning rule was applied to competitive network with six neurons to distinguish between six clusters. Because of unsupervised learning, the output vector was not needed during the learning process.

The eight-dimension input vectors of absorption plot features were presented to the Kohonen network as input data. The training data applied was the same as for the feedforward neural network with LM algorithm. After the training the Kohonen network recognized 6 patterns, but not all B5 and B10 samples were classified correctly from the data set after 1000 iterations. When the unknown samples: B7, B25, and B40 were presented, the network recognized them as the B5, B30, and B50, respectively. When the number of neurons in the competitive layer was increased to 9 and three new input vectors for B7, B25 and B40 were applied, the network was still not able to develop the correct nine blend classes after 3000 iterations. Because of the overlap of the data belonging to distinct clusters, unsupervised training was performed with incorrect classification. The reduction of dimensionality of the input vector from 8 variables to 2 using the principal component analysis did not improve classification. Input vectors in 2 dimensions and neuron's weights after applying Kohonen learning rule are shown in Figure. 4.

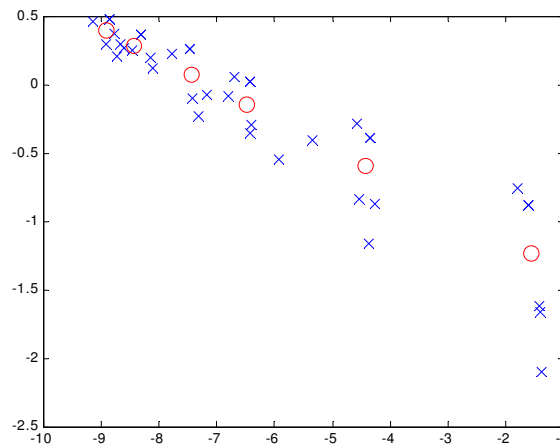


Figure 4. The input vectors appear to fall into clusters representing different biodiesel blend levels. Eight element input vectors were reduced using principal component analysis to two elements represented as “x” markers. Weights of six neurons after applying Kohonen learning rule were represented as “o” markers.

Further modifications of Kohonen network would be possible. In case when more patterns are expected, the additional neurons can be added to the network. The unsupervised training could be performed with an excessive number of neurons, if the final number of patterns is not known. During training not all neurons develop their weights; therefore, such weights are omitted after training. In case of increased dimensionality of patterns, for example higher order of polynomial, the network structure does not need to be changed. Another modification of the winner-take-all

learning rule is possible where both the winners' and losers' weights are adjusted in leaky competitive learning [1]. Such modifications should provide more subtle learning when clusters are hard to distinguish.

Learning Vector Quantization

A learning vector quantization (LVQ) method was chosen to distinguish between biodiesel-diesel blend level in case of overlapping patterns for B5 and B10 (incorrectly classified by Kohonen network). LVQ network has two layers: the first detects subclasses and the second combines subclasses into a single class. LVQ networks combine unsupervised and supervised learning and learn to classify inputs into classes chosen by the user. The input vector used here for this network was the same as in previous simulations. LVQ learning process took longer as compared to the solution with Levenberg-Marquardt algorithm and was very sensitive to the initial weights. The error was decreasing during the initial iterations, for example to 0.046, then stayed stable throughout the remainder of 1000 iterations. After the initial weights and the learning constant were tuned, the network was unable to distinguish patterns correctly when our data were used. The expected results could be brought by training the network on smaller input data set and adjusting the network architecture. This approach is the objective of future research.

Conclusions

The UV absorption spectra were shown to be suitable for sensing the blend level of biodiesel-diesel samples. Two statistical methods allowed to investigate UV absorption spectroscopy as a method to determine the amount of biodiesel in biodiesel-diesel fuel.

The artificial neural network with Levenberg-Marquardt algorithm was applied to estimate the amount of biodiesel in the samples. The selected features of ultraviolet absorption spectra of the samples were used as the input data. The Levenberg-Marquardt algorithm, out of all applied algorithms, was superior to other algorithms with the data set used in this research. The proposed solution and the data preparation approach can be modified; for example, other features of the plots could be extracted and used as data.

The network that used Kohonen learning rule was able to categorize data into clusters. This type of classification could be used when a comparison of several unknown blend samples is needed.

Learning vector quantization rule was shown to be suitable for the categorization of clustered data of unknown samples. However, the conclusions about LVQ application to blend level sensing could be only inferred after additional research is done.

It was shown that blend level could be sensed from ultraviolet absorption spectra of biodiesel-diesel samples uniformly diluted in heptane. The amount of biodiesel was estimated incorrectly when the sample dilution was erroneous. Therefore, the evaluation of ultraviolet absorption plot features as a function of different dilutions is under further investigation.

Also to further enhance the accuracy of blend level estimation, ultraviolet absorption combined with visible absorption range could be used as an input vector for a neural network.

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