Use of a spectrophotometer for biodiesel quality sensing

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Abstract. Biodiesel from different feedstocks have different properties. ASTM standard D6751 specifies the minimum biodiesel quality requirements and National Biodiesel Accreditation Committee has a BQ-9000 certification program for the manufacturers who maintains ASTM D6751 standard. Even after biodiesel meeting ASTM specifications, biodiesel from different feedstock shows different cold weather and emission properties. The test procedures to assure ASTM biodiesel quality are not being widely implemented because of the lengthy procedures and laboratory equipment requirements. A critical need in the increasingly emerging biodiesel industry right now is a reliable, affordable and rapid test method for determining the blends of biodiesel in diesel fuel. As an effort to explore a reliable and rapid method, a spectrophotometer was used to scan the blends of #2 fossil diesel and biodiesel for spectrums in the wavelength range of 190-1100 nm. Biodiesel from four different feedstocks: Rapeseed, soybean, mustard and waste vegetable oil were investigated. The shape of the spectrum curve was found to be different for different biodiesel feedstock where as relative absorbance and characteristic peaks of absorbance curve was attenuated with increasing

amount of diesel in the blend. Shape characteristics were fed into neural network to predict the biodiesel feedstock and blend level in biodiesel-diesel mixture. Different level of coloring pigmentation showed a promise in characterizing biodiesel with this approach.

Keywords. Biodiesel, oil, quality, neural network, spectrophotometer, sensor.

Introduction

All vegetable oils and animal fats are primarily constituted of triglycerides (triacylglycerols) which are esters of fatty acid. Biodiesel is produced by transesterification reaction of triglycerides with alcohol usually methanol or ethanol. Chemically speaking biodiesel is mono-alkyl esters of the fatty acids. Triglycerides are esters of glycerol with long-chain fatty acids. The composition of vegetable oil varies with the plant source (Van Gerpen et al., 2005). Since biodiesel is made primarily from vegetable oil, its property also depends on fatty acid profile and other constituents. Biodiesel from different feedstock have different properties in terms of their cold weather properties and emission characteristics (Peterson et al., 2000).

Average composition of crude oil contains about 95% of triacylglycerols, 2% of phospholipids, 1.5% of unsaponifiable matter, 0.5% of free fatty acid, and 1% trace metal. Composition of crude soybean and rapeseed oil are shown in table 1.

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

Components	Soybean	Rapeseed
Triacylglycerols (%)	93-99.2	91.8-99.
Phospholipids (%)	Up to 4.0	Up to 3.5
Free fatty acids	0.3-1.0	0.5-1.8
Unsaponifiable matter (%)	0.5-1.6	0.5-1.2
Tocopherols (ppm)	1700-2200	700-1000
Phytosterols (%)	0.33	-
Chlophyll (ppm)	Trace	5-55
Sulfur (ppm)	Nil	5-35

The color of the oil is mainly due to chlorophyll and phytosterol which are the constituents of the major parts of oil pigments and composition of varies for processed oil from crude oil. Chlorophyll content of rapeseed and canola are similar and hence the oil colors for these two feedstocks also look similar. However, the chlorophyll and phytosterols content of soybean and rapeseed are different and it is expected that the light absorption pattern of these two oils in visible spectrum will be different.

Glycerol, mono- di- and triglycerides, free fatty acids, residual alcohol and catalysts may remain in biodiesel as contaminants in the final biodiesel product. When using biodiesel the higher level of some contaminants can lead to severe engine problems, such as engine deposit formation or filter clogging (Knothe, 2001a). Quality of biodiesel depends on the amounts of these contaminants. The high quality of the product is important for consumers to assure that they purchase biodiesel which is not harmful for their engines. Biodiesel must meet the ASTM specification D 6751 (ASTM, 2003) which also defines the test methods for each of the specified biodiesel properties. The most important biodiesel specification is total glycerin. If the fuel fails this specification, then no other properties matter (Van Gerpen, 2005).

ASTM standard D6751 specifies the minimum biodiesel quality requirements and National Biodiesel Accreditation Committee has a BQ-9000 certification program for the manufacturers and distributors who maintain ASTM D6751 standard. The test procedures are not being widely implemented because of the lengthy procedures and laboratory equipment requirements. A critical need in the increasingly emerging biodiesel industry right now is a reliable and rapid test for determining the blends of biodiesel in diesel fuel. Engine manufacturers would benefit from assessing biodiesel fuel use from potential warranty claims to determine if the fuel is within the vehicle manufacturer's guidelines. Consumers would benefit from having a method whereby

they could determine that the fuel purchased contained percentage of biodiesel that they expected and had paid for.

When light is transmitted through a liquid such as biodiesel, it is noted that the light is absorbed at specific wavelengths due to the presence of certain characteristics within the liquid. By monitoring the light absorption at particular known wavelengths, it is possible to identify the presence of certain types of chemical bonds and this can be used to determine whether a specific compound is present. This technique could potentially be used to determine biodiesel quality. Currently, quality must be determined through a complex and expensive series of procedures using a gas chromatograph. Most biodiesel producers do not have the funding to purchase the equipment or to keep an experienced chromatographer on staff. Sending the sample to outside laboratories can take days to receive results.

Some work has been done in the past to determine the biodiesel blend level using near infrared and refractive index. The transesterification reaction which yields the methyl esters can be monitored for completion by near-infrared (NIR) spectroscopy using a fiber-optic probe (Knothe, 2001b). Addition of biodiesel into diesel fuel alters emission characteristics. Particularly while biodiesel reduces CO, PM and HC emission, it increase the NOx emission. NOx emission can be partially corrected by delaying fuel ejection timing. (Tat and Van Gerpen, 2001) has designed a fuel composition detector, which can be used to adjust the engine timing.

With recent development in information technology and availability of low cost optical sensing technology it may be well worth to explore the usability of visible and near UV wavelengths that could provide a means to measure biodiesel properties such as total glycerol (reaction completeness), biodiesel blend level and residual alcohol level.

The objective of this paper is to investigate the use of visible absorption spectrum of biodiesel to detect the biodiesel feedstock, composition of biodiesel in biodiesel-diesel blend and, quantification of total glycerol, the most important biodiesel property determining the usability of biodiesel.

Some biodiesel parameters including density, cetane number and content of sulfur are not influenced by the production and purification methods but mainly depend on the choices of vegetable oil (Mittelbach, 1996). If we manage to tell about the kind of biodiesel from its absorption spectra we can correlate this data with some of its general parameters.

Materials and methods

The absorption spectra of biodiesels, biodiesel blends with diesel and chemical standards were measured using: Beckman Coulter DU520 (Fullerton, CA) General Purpose UV/Vis for visible absorption spectra and Hewlett Packard 8453 for ultraviolet and visible absorption measurement.

Pure standards chemical of free fatty acids (stearic, eicosanoic acid), methyl and ethyl esters of fatty acids (methyl ester of oleic, palmitic, stearic, oleic, linolenic, eicosanoic acid), and mono-di-, triglycerides (monoolein, diolein, triolein glycerol) were purchased from Sigma-Aldrich (MO, USA) and NU-CHEK PREP (MN, USA). Spectra of eleven pure chemical standard components diluted in 2-propanol – hexane (5:4, v/v) were measured. The dilution was necessary to achieve the absorption range within the spectrophotometer detection range. Several batches of different types of biodiesel were prepared on site from rapeseed, mustard and soy oils.

In order to achieve a variety of samples with different total glycerol content, five samples of rapeseed methyl ester (RME) were prepared by varying the biodiesel synthesis conditions including amount of catalyst from 0.2 to 0.5%, alcohol from 10 to 25% and reaction time from 20

to 60 min. Free and total glycerin in biodiesel were determined according to test method D 6584 (*ASTM. 2000)* using gas chromatograph GC Chem Station 6890N (Agilent, Palo Alto, CA) with flame ionization detector (GC-FID). GC-FID was equipped with J&W Scientific 123-5711 DB-5HT column, 15m, 319µm, 0.10µm nominal, 400ºC. Chromatographic separations were achieved using an oven initial temperature of 50ºC and linear temperature gradient of 15ºC min^{-1} to 180ºC, 7ºC min^{-1} to 230ºC, and 30ºC min^{-1} to 380ºC. The samples for GC-FID analysis were derivatized with N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) and mixed with 2 internal standards (1,2,4-butanetriol and 1,2,3-tridecanolylglycerol (tricaprin)) according to Test Method D *6584* (ASTM, 2000)*.* Total glycerol content as the sum of free glycerol and mono-, di-, and triglycerides was calculated using internal standard method.

For the experiment to recognize biodiesel feedstock and blends using neural network, the absorption spectra in the range of 350-500 nm of five different biodiesel batches were measured. Out of thee five batches, three batches of RME were made form the same rapeseed oil. Only one batch of MME and one batch of SME were made. Blends of 5, 10, 20, 30, 50, 80% of biodiesel by volume with commercial No. 2 diesel were prepared. The spectra were recorded at interval of every 1 nm. The shape and position parameter of the curve were extracted by fitting a polynomial curve. It was observed that shape and location parameters of a curve could be captured as low as quadratic polynomial. Higher order polynomial did not significantly improved the curve representation. The coefficients of best fit polynomial were used as input to a feed forward neural network to detect the biodiesel feedstock and blend level. Neural network toolbox in Matlab (Mathworks, Natica, MA) was used to build and test the network.

Results and Discussion

Relation between biodiesel absorption spectrum and total glycerol determined by gas chromatography

Five batches of RME were labeled as RME1 to RME5. The total glycerol content of these batches was determined using gas chromatography (Table 1) and absorption spectra of those samples were measured. Despite the differences in the amount of free and total glycerol in RME4 and RME5 sample, their absorption spectra in visible range were not much different from each other. Differences between spectra of RME5 sample which had the least total glycerol, and others were different but the difference was not proportional to the amount of glycerin content. This indicated that pure aliphatic acids, esters, and glycerides being colorless, does not absorb much in visible spectra. It was postulated that the differences in the visible range of absorption spectra of these samples were due to different amounts of lipid soluble pigments retained in the residual of mono-, di- and triglycerides and not by glycerol itself.

Table 2. Properties of different biodiesel samples. RME- rapeseed methyl ester.

Properties [%]	RME1	RME2	RME3	RME4	RME5
Free glycerin	0.22	6.03	2.64	2.23	0.0075
Monoglycerides	0.66	3.12	1.80	1.39	0.2363
Diglycerides	0.39	1.14	0.76	0.64	0.4017
Triglycerides	1.33	1.00	0.73	0.81	0
Bound Glycerin	0.37	1.08	0.65	0.54	0.1210
Total Glycerin	0.59	7.11	3.30	2.70	0.1285

Biodiesel blend level and feedstock sensing from its absorption spectra

In order to identify the contribution of each biodiesel component to overall absorption spectrum, spectra of eleven pure standard chemical of free fatty acids, methyl, ethyl esters and mono-, di-, triglycerides were measured. Since the absorption of all components was below 350 nm, none of those components contributed to characteristic maximum of the biodiesel absorption spectra in a visible range. Pure aliphatic acids, esters, and glycerides are colorless substances and did not exhibit significant absorption in the visible range. Natural fats and oils from plants and animals contain pigments exhibiting visible absorption (O'Connor, 1960). The absorption of vegetable oils in the visible regions is usually due to lipid-soluble pigments such as carotenoids and chlorophylls (Angioni et al., 2002). Therefore, a characteristic absorption of biodiesel in the visible range in Figure 1 is most likely caused by pigments and other impurities.

Different feedstock used for biodiesel production have different amount and kinds of pigments (Table 1). For example, canola seed is known for high content of chlorophyll pigments. Pigments make color of one vegetable oil different from others. Part of those pigment constituents remain in biodiesel as impurity. The shape of absorbance curve in visible range was used to distinguish between biodiesel from different feedstock (fig. 1). Therefore, despite the fact that absorption in the visible range of biodiesel is not from primary constituent aliphatic acids, or esters or glycerides, it is possible to distinguish between different kinds of biodiesel, its blends and some aspects of the quality from the UV-Vis spectrum.
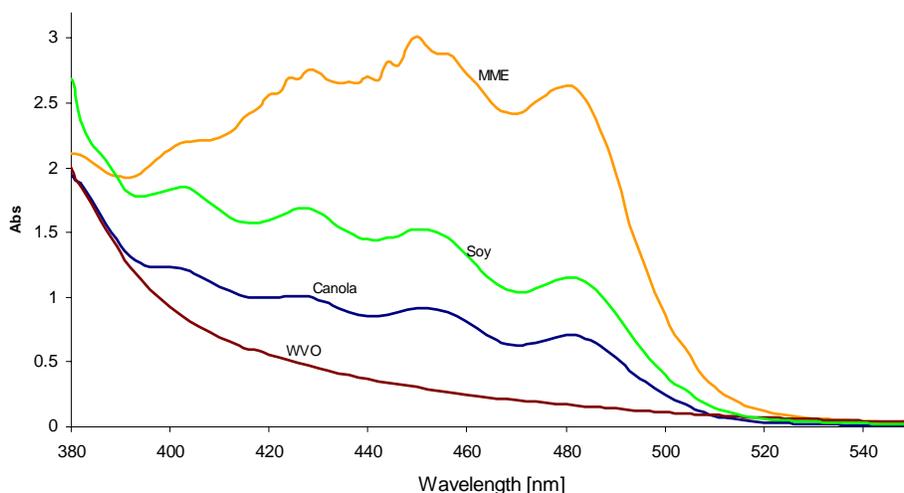
Figure 1. Absorption spectra of different kinds of biodiesel in visible range.

When biodiesel was mixed with diesel in various proportions it was observed that the characteristic shape of the absorbance curve did not change but attenuated in magnitude and characteristic peaks were blended off with main curve as portion of diesel increased in the blend (fig. 2). This indicated that position and magnitude of characteristic peaks can be used to determine the biodiesel blend level.
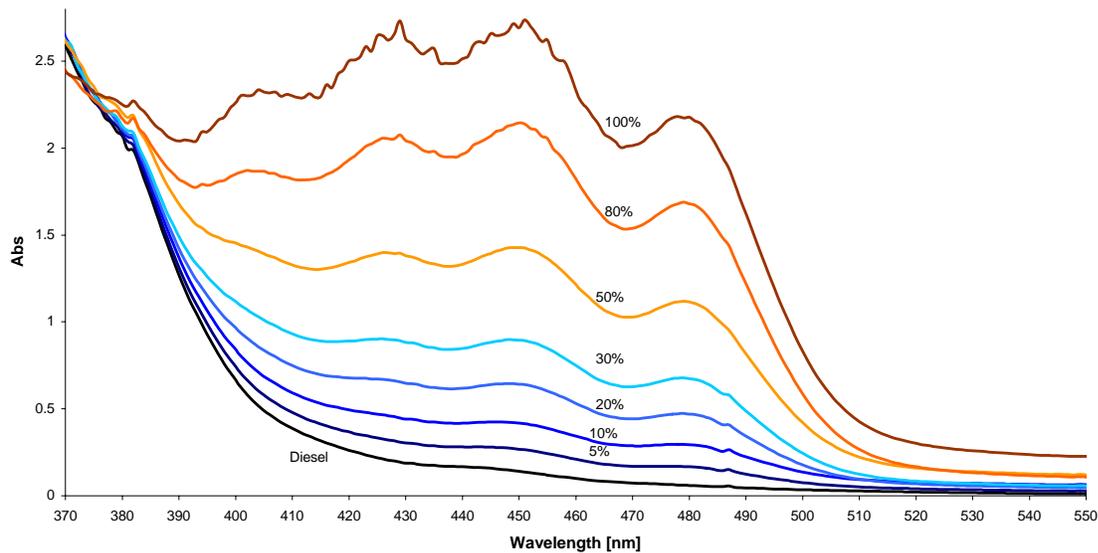
Figure 2. Absorption spectra of mustard methyl ester (MME) with diesel blends

Analysis of biodiesel with application of artificial neural network

Characteristic shapes of biodiesel absorption spectra in visible range indicated that the information can be used to detect the biodiesel feedstock. Differences in position of absorption spectra gave the information about biodiesel blends level with regular diesel. A feed forward neural network was a logical choice to input these spectrum shape and position parameters to identify biodiesel feedstock and blend level.

The three-layer neural network with sigmoidal transfer function in two hidden layers and a linear transfer function in the output layer was employed to distinguish between 3 different kinds of biodiesel blended in different proportion with regular diesel. Each of the five biodiesel batches was blended with diesel in 7 different percentages: B5, B10, B20, B30, B50, B80, B100, where 5, 10, 20, 30, 50, 80, 100 is a percentage of rapeseed (RME), mustard (MME) or soybean methyl ester (SME) in the samples. After measuring absorption spectra of biodiesel and sampling them every five nanometers, shape and position parameters of each curve were enclosed in second degree polynomial coefficients fitted for each curve. Five neurons were used in the first hidden layer and three in the second one. The network had two output neurons since there are two targets: the amount of biodiesel in the sample and the kind of feedstock. The resilient backpropagation algorithm was used for network training in MatLab environment.

The network was trained on the training set of diesel blends with biodiesel from one batch of RME, one of MME and one of SME. Then the values from the second and third batch of RME were applied to verify the network performance. Every time three coefficients, characteristic for each curve, were presented to the net. Initial random weights and biases of the neurons influenced the network performance; therefore, different amount of epoch, usually 1000 or 2000, were used until the regression analysis in Figure 3 was achieved. After training, the network was able to correctly distinguish between B5, B10, B20, B80 and B100 from the second batch of RME and B5, B10 and B100 from the third batch of RME. The regression analysis between the network response and the corresponding targets for the second batch according to procedure in (Demuth and Beale, 1998) was done and is presented in Figure 3. The network outputs are

plotted versus the targets as data points where B5 to B100 corresponding to the percentage of biodiesel in the samples. The best fit linear regression line had slope of 0.9 (±0.18) and intercept of 0.13 (±0.93) with 95% confidence interval. The coefficient of determination (R^2) of the regression line was 0.91. The slope and intercept of the live were not statistically significant from 1 and 0 respectively.
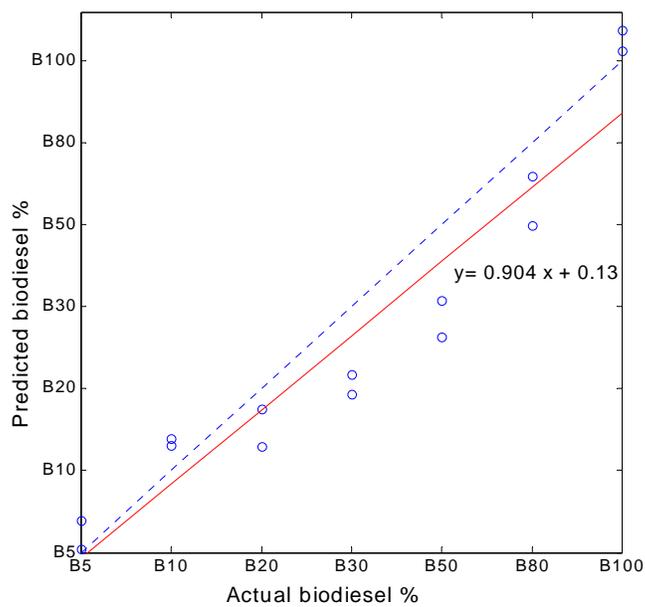
Figure 3. Regression analysis between the network response and the corresponding biodiesel blend levels. The perfect fit (1:1 line) is indicated by a dashed line; the solid line indicates the best linear fit.

Conclusions

The visible absorption spectrum seems not to be suitable for direct sensing of transparent biodiesel impurities such as glycerol, mono-, di- and triglycerides, since the pure components do not have absorption in the visible range. However, the visible range with the combination of ultraviolet range could be appropriate for sensing of some parameters of biodiesel quality and is the subject of future research.

The artificial neural network was used to determine the amount of biodiesel in the samples based on the visible spectra. The used network is one example which structure, learning algorithm and training set could be further modified in order to achieve the optimum solution. The artificial neural network is appropriate tool for the determination of some parameters of biodiesel samples including the amount of biodiesel in the sample and the kind of biodiesel feedstock. Additionally, combining visible absorption spectra with ultraviolet range has a potential for sensing some properties of biodiesel quality enumerated in ASTM specification.

The use of ultraviolet absorption spectrum and its potential application for sensing quality of biodiesel needs additional research. Further use of the UV-Vis spectrum for the determination of biodiesel quality aspects is under investigation.

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