

# Prediction of properties of biodiesel-diesel blends using spectrofluorimetry and multivariate calibration

## Research Article

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**Abstract:** Regressions based on fluorescence spectroscopy were developed to provide relatively inexpensive and rapid measurements of the concentration, viscosity, and specific gravity of biodiesel-diesel blends. The methods involved obtaining a mathematical model from spectrofluorimetric data and data from a given property (concentration, dynamic viscosity, or specific gravity) using partial least squares (PLS) regression, which was then applied as a model for predicting properties of interest. The predicted concentrations, dynamic viscosities, and specific gravities of the biodiesel-diesel blends were compared with actual values and agreed reasonably well with the obtained results. The models showed high correlation between real and predicted values. The R-square values near 1 indicated excellent model accuracy for predicting concentrations, specific gravities, and dynamic viscosities of biodiesel-diesel blends. The residual distribution did not follow a trend with respect to the predicted variables, indicating an excellent fit to the data.

**Keywords:** Concentration • Specific gravity • Viscosity • Spectrofluorimetry • Multivariate calibration

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## 1. Introduction

Biodiesel has attracted considerable interest as an alternative to diesel fuel [1]. Biodiesel blends are advantageous for several reasons. For example, biodiesel is non-toxic, it contains no aromatics or sulfur, it biodegrades faster than fossil diesel, it is less polluting to water and soil, and it helps to reduce both the greenhouse effect and our dependence on petroleum [2]. Biodiesel is miscible with diesel in any proportion; however, the suitability of biodiesel blends as fuels is influenced by biodiesel's physical properties. The concentration of biodiesel in biodiesel blends has significant effects on performance and efficiency of biodiesel-powered machines. Therefore, the careful

control of biodiesel concentrations is important. The use of biodiesel blends at concentrations below 20% helps to maintain the engine due to the inherent lubricity of the fuel. Biodiesel blends at concentrations higher than 20% dissolve rubber components, and their use requires changes in the engines of some vehicles [3].

Viscosity is the resistance offered by a fluid deformed by one force, such as, shear or tensile stress. Dynamic or absolute viscosity is more common measure of this property. Kinematic viscosity is the value found by dividing the dynamic viscosity by density of the fluid. In some fluids, viscosity has a constant value over a wide range of shear rates. These fluids are called Newtonian fluids. Fluids without a constant viscosity cannot be described by a single value and are called non-

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Newtonian fluids. Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate. Viscosity is measured with either viscometers or rheometers. In general, viscometers are used for Newtonian fluids, and rheometers are used for non-Newtonian fluids. Vegetable oils and animal fats tend to cause problems when used directly in diesel engines due to their high viscosity [4]. If the oils and fats are first transesterified, however, the resulting biodiesels have viscosities that are closer to diesel [5-7], although the viscosities of monoesters tend to be higher than the viscosity of petroleum-based fuel [8]. The ability to control viscosity in fuels promotes optimal atomization. Viscosity values below an established lower limit may lead to excessive injection system wear, fuel pump leaks and piston damage. Viscosity values above the upper limit may lead to an increased workload of the fuel pump. Additionally, exceptionally high viscosities provide poor fuel atomization and incomplete combustion with a subsequent increase in smoke and particulate matter emission. Viscosity values that are too high may lead to ineffective engine operation [8].

The specific gravities of biodiesels and diesels depend on their composition and purity. The composition of biodiesel depends primarily on the composition of the mixed esters. The composition of diesel can also change, depending on the refinery feedstock and day-to-day variability of the blending streams in the diesel fuel boiling range. The specific gravities of hydrocarbons, and therefore of diesel, are strongly affected by temperature [4].

Multivariate calibrations are increasingly used to extract relevant information from different types of spectral data to predict properties of complex samples [9-15]. Recent works have shown the viability of spectroscopy associated with multivariate calibration for predicting certain properties of fuel. Multivariate near-infrared (NIR) spectroscopy models have been used successfully for the prediction of several physical and operating properties of oil fractions and diesel fuels [16], concentrations and specific gravities of biodiesel-diesel blends [17], methanol and water content [18] as well as iodine value, kinematic viscosity, density and cold filter plugging point in biodiesel [19]. The NIR and NMR have been used to determine blend levels of biodiesel-diesel mixtures [20]. Multivariate NIR and middle infrared spectrometry (MIR) models have been developed to predict quality parameters of biodiesel-diesel blends (density, sulfur content and distillation temperatures) [21], to monitor transesterification reactions [22-24], to determine total sulfur in diesel [25] and to determine several gasoline properties [26,27].

In addition, multivariate NIR spectroscopy models have also been employed to monitor the quality of oils for biodiesel production [28]. Spectrofluorimetry has been used to determine the adulteration of biodiesel-diesel blends with residual oil [29,30] and stability oxidation [31,32].

In this work, multivariate calibration methods based on spectrofluorimetric data were developed to provide relatively inexpensive and rapid measurements of the concentrations, specific gravities and viscosities of biodiesel-diesel blends. Multivariate analysis methods allow the simultaneous use of all variables for the interpretation of data resulting from chemical analyses. Chemometric techniques are currently important tools in diverse technological areas, such as in the analysis of food, pharmaceutical, agricultural, environmental and industrial chemistry.

There are several methods of multivariate analysis used for very different purposes. The most common are principal component analysis (PCA) and partial least squares (PLS) analysis. PCA analysis allows for a reduction in the number of variables to a few principal components that are responsible for explaining most variation associated with the original set. PCA analysis provides tools to identify the most important variables in the principal components space in addition to classifying samples according to their similarities.

With PLS, it is possible to find a mathematical relationship between one variable (the dependent variable) and the remainder of the variables that describe the system (independent variables). PLS analysis then finds a function that describes the variables X and Y by maximizing the correlation between them. PLS is chiefly applied to the prediction of analytical results for a dependent variable in the presence of independent variables.

## 2. Experimental procedure

The data set consisted of blends prepared using biodiesel and diesel samples supplied by Petrobras. The two types of biodiesel used in this study were soy and cottonseed biodiesel. Mixtures of biodiesel and diesel were made with concentrations of biodiesel ranging from 0 to 100%, as shown in Table 1.

Viscosity measurements of soy and cottonseed biodiesel-diesel blends (Table 1) were made using an MCR 501 rheometer Anton Paar at 25°C with a shear rate ranging from 10-100 s<sup>-1</sup>. All analyses of viscosity were performed in 20 replicates and their average values were calculated. The data showed in Table 1 are the average values.

**Table 1.** Concentrations, viscosities and specific gravities of biodiesel-diesel blends at 25°C.

Samples	Biodiesel in diesel (%)	Soy biodiesel-diesel blend Viscosity (cP)		Cottonseed biodiesel-diesel blend Viscosity (cP)		Soy biodiesel-diesel blend specific gravity		Cottonseed biodiesel-diesel blend specific gravity	
		M	s	M	s	M	s	M	s
1	0	3.6015	0.06418	3.5915	0.06409	0.821	0.004	0.823	0.004
2	5	3.6635	0.06675	3.6835	0.05650	0.824	0.004	0.828	0.001
3	10	3.6650	0.06525	3.6870	0.07610	0.832	0.004	0.830	0.002
4	15	3.7300	0.06489	3.7120	0.07736	0.834	0.005	0.832	0.002
5	20	3.7545	0.06509	3.7785	0.06499	0.836	0.002	0.834	0.002
6	25	3.7995	0.06245	3.8435	0.07450	0.838	0.004	0.841	0.002
7	30	3.8580	0.06437	3.8875	0.09408	0.851	0.011	0.842	0.003
8	35	3.9375	0.05981	3.9740	0.07783	0.844	0.002	0.846	0.002
9	40	3.9980	0.06229	4.0170	0.06929	0.851	0.003	0.852	0.002
10	50	4.1550	0.0338	4.1280	0.10938	0.852	0.001	0.858	0.002
11	60	4.2555	0.06278	4.3080	0.08727	0.865	0.013	0.863	0.002
12	70	4.3910	0.07188	4.4630	0.10058	0.867	0.011	0.867	0.004
13	80	4.5330	0.06868	4.6655	0.05680	0.876	0.012	0.875	0.007
14	90	4.6865	0.05958	4.8505	0.07156	0.887	0.016	0.883	0.002
15	100	4.8000	0.06262	5.0460	0.06012	0.898	0.030	0.885	0.002

*M = Mean; s = standard deviation*

Specific gravities were determined by dividing the mass of 5 mL of each sample by the mass of the same volume of distilled water at room temperature (25°C). The samples were weighed on an analytical balance (precision of 1 mg) and the volumes were measured with a micropipette. All analyses of specific gravities were performed in 3 replicates and their average values were calculated. The data showed in Table 1 are the average values.

Fluorescence measurements were performed with a spectrofluorimeter constructed in-house that was equipped with a light-emitting diode (LED) and quartz cells with 1 cm optical paths. The fluorescence emission spectra of the samples were obtained by exciting the samples with the ultra-violet LED and capturing the emission from 350 nm to 1000 nm with 1 nm increments (total of 651 emission wavelengths). The spectra were arranged into a general matrix of 15×651 (samples versus emission wavelengths), processed using mean centering and then analyzed using PLS.

In this study three regression models were developed for each type of biodiesel. One model was for determining the concentration of biodiesel in biodiesel-diesel blends, a second model was for determining specific gravity, and the third was for estimating the viscosity of biodiesel-diesel blends. Each multivariate calibration model was developed using PLS regression

with regions previously established using PCA. The calibration models were constructed using the PLS regression technique with the software Unscrambler® 10.0.1. The number of latent variables for PLS was determined based on the validation error using the default software. The general matrixes (15×651) were used to construct the mathematical models using PLS. By adding one column for the property measurement, each final matrix had the dimensions 15×652.

Each PLS model was built using mean-centered fluorescence spectra as independent variables and the measured corresponding values of concentration, specific gravity, or viscosity as the dependent variables. For the calibration step using PLS, the relationship between the spectra and property measurement was estimated from a set of reference samples of mixtures of soy and cottonseed biodiesel in diesel (Table 1). In this study, we used the method of cross-validation leave-one-out as a strategy for validation. This strategy involves using a single observation from the data set as the validation data, and the remaining observations as the training data. This is repeated such that each observation in the data set is used once as the validation data. In each figure, blue points and curves represent calibration data and red points and curves represent validation data.

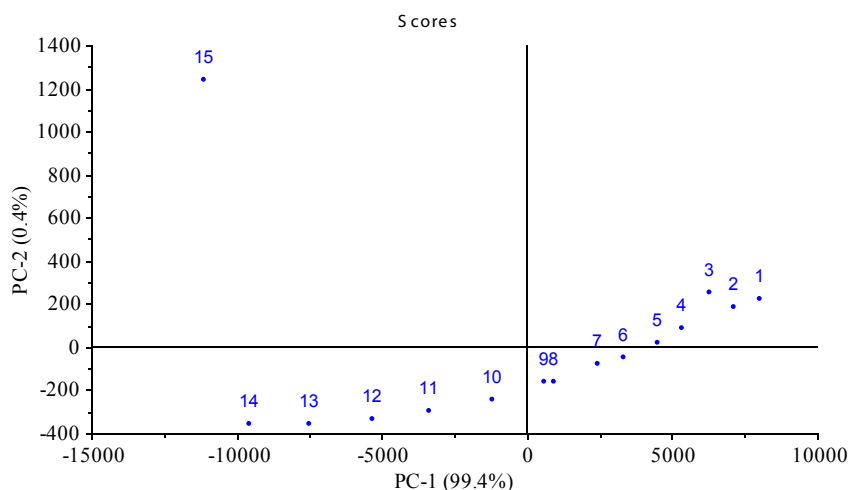
### 3. Results and discussion

The PCA built using entire fluorescence of soy biodiesel-diesel blends as variables showed that two principal components (PC1 and PC2) were responsible for capturing 99.8% of the variance being 99.4% for PC1 and 0.4% for PC2 (Fig. 1). For cottonseed biodiesel-diesel blends, the PCA built with entire fluorescence showed that PC1 and PC2 were responsible for capturing 99.9% of the variance being 99.5% for PC1 and 0.4% for PC2 (Fig. 2).

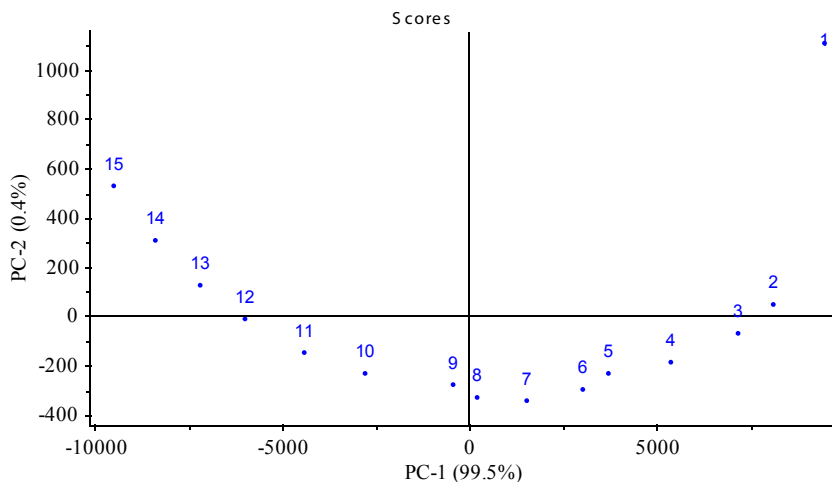
Initially each PLS model was built with all data and were then evaluated in order to detect outliers. Then models were rebuilt with the remaining set of samples. Sample 7, with 30% of soy biodiesel in diesel, was detected as an outlier and removed from the dataset in developing the PLS models for determining

concentration, specific gravity, and viscosity of soy biodiesel-diesel blends (Figs. 3, 7 and 11). Similarly, sample 15 with 100% of cottonseed biodiesel in diesel was detected as outlier and removed from the dataset in developing the PLS model for determining concentration of cottonseed biodiesel-diesel blends (Fig. 4).

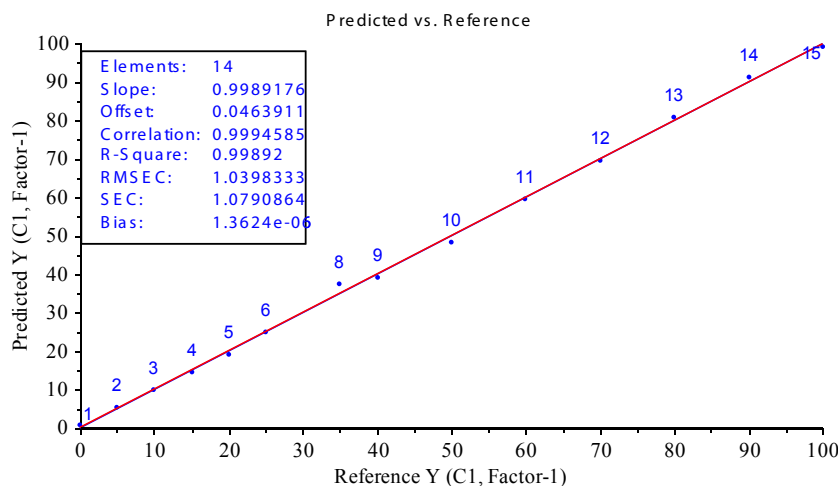
The PLS models were evaluated by examining the calibration parameters: the correlation, the coefficient of determination ( $R^2$ ), and the residual distribution. The correlation shown the strength of the linear relationship between actual values and values predicted by the calibration model. The correlation values can vary in the range from  $-1$  to  $+1$ , and values closer to  $+1$  suggest higher correlation between data. The  $R^2$  is defined as the proportion of variability in  $y$  that may be attributed to the variability in  $x$ , and it indicates the accuracy of the model to predict answers to new observations.



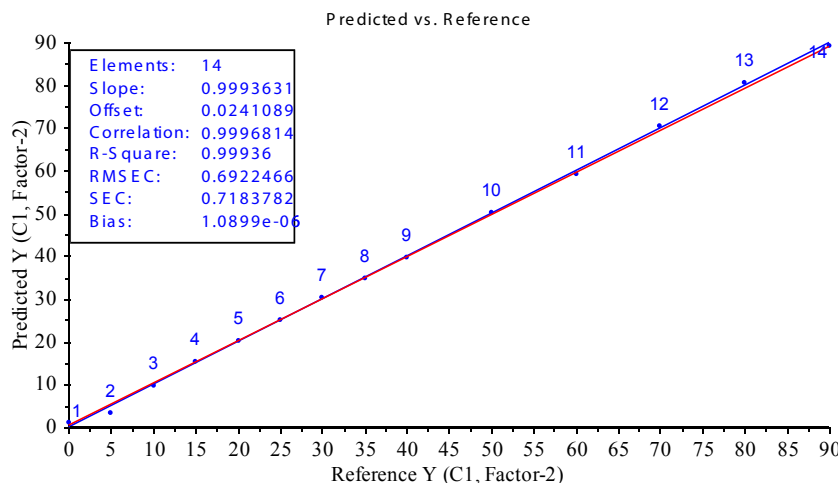
**Figure 1.** PCA of fluorescence spectra for samples of soy biodiesel.



**Figure 2.** PCA of fluorescence spectra for samples of cottonseed biodiesel.



**Figure 3.** Reference versus predicted concentrations for soy biodiesel samples. Blue line represents calibration data and red line represents validation data.



**Figure 4.** Reference versus predicted concentrations for cottonseed biodiesel samples. Blue line represents calibration data and red line represents validation data.

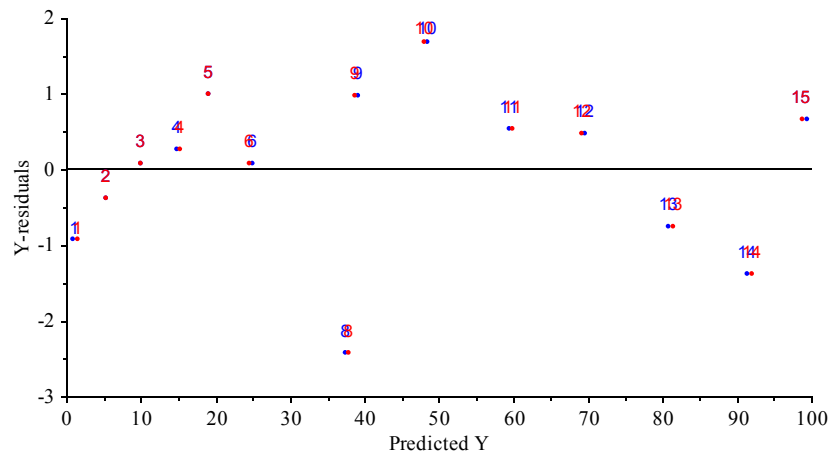
The residual distribution is the distribution of differences between calculated and observed values over the observed values of the studied response. The residual distribution indicates the quality of the fits. The fits are good quality when the residual distribution does not follow a trend with respect to the predicted variables.

For soy and cottonseed biodiesel-diesel blends, the models were shown to be practical for predicting changes in concentration based on fluorescence spectral variances. Figs. 3 and 4 show plots of reference versus predicted concentration values for soy and cottonseed biodiesel-diesel blends, respectively. Correlations of 0.99946 and 0.99968 for soy and cottonseed biodiesel-diesel blends, respectively, indicated a strong association of the observed data for the two variables. An  $R^2$  of 0.99892 and 0.99936 for soy and cottonseed

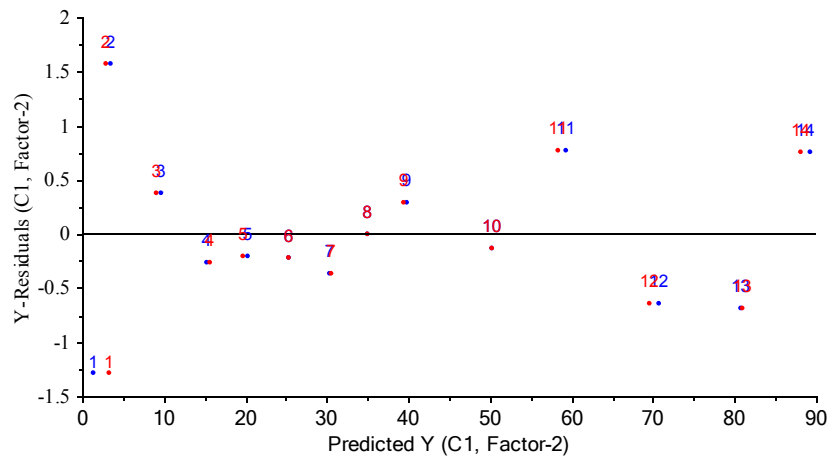
biodiesel-diesel blends, respectively, demonstrated the efficiency of the models for predicting concentrations.

Figs. 5 and 6 show plots of the residual distributions of the models built with concentration values for soy and cottonseed biodiesel-diesel blends, respectively. All of the residuals in the two curves are less than 2.5%, which indicates that the models adequately represented the concentrations for soy and cottonseed biodiesel-diesel blend samples, respectively, over the studied experimental range.

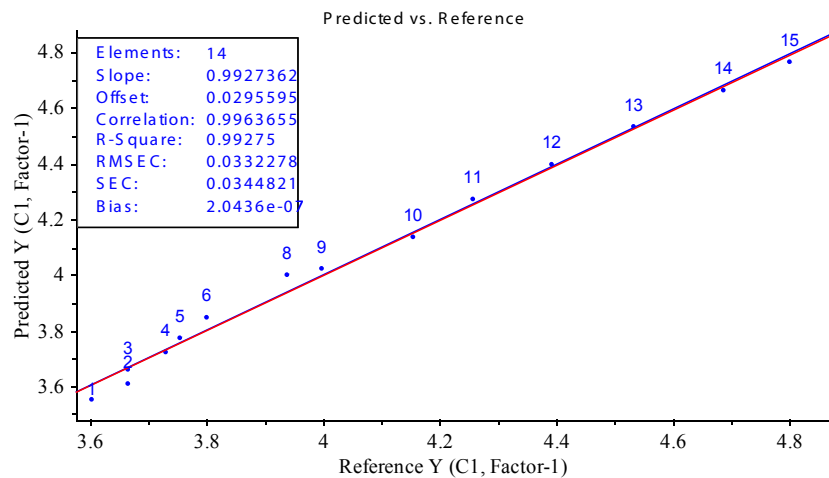
Multivariate calibration models for viscosity were then developed for soy and cottonseed biodiesel-diesel blends using fluorescence as the independent variables for each biodiesel and viscosity values as the dependent variables (Table 1). Figs. 7 and 8 show plots of the reference versus predicted viscosity values for soy



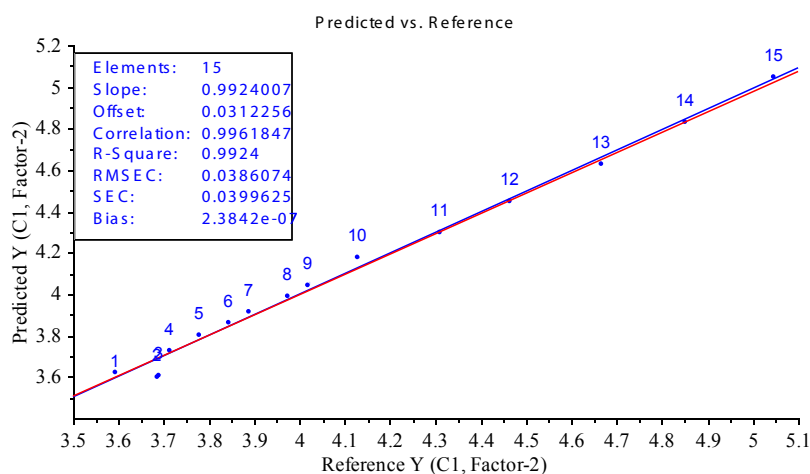
**Figure 5.** Plot of the residuals for the model built with concentration values for soy biodiesel-diesel blends. Blue points represent calibration data and red points represent validation data.



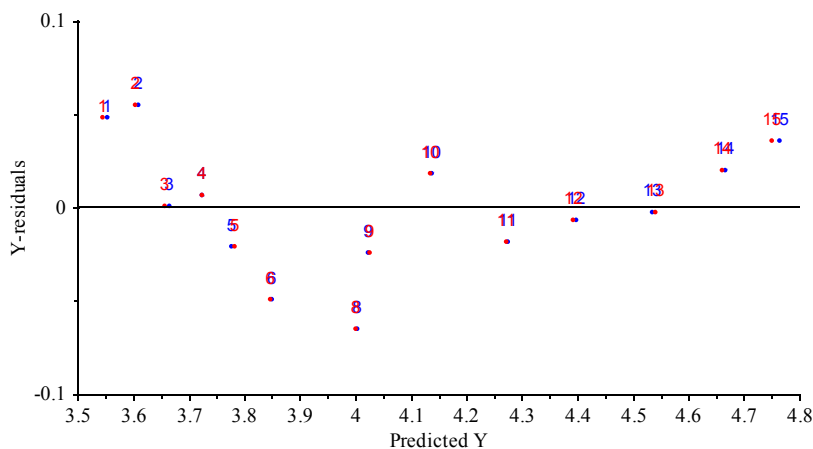
**Figure 6.** Plot of the residuals for the model built with concentration values for cottonseed biodiesel-diesel blends. Blue points represent calibration data and red points represent validation data.



**Figure 7.** Reference versus predicted viscosity values for soy biodiesel-diesel blends at 25°C. Blue line represents calibration data and red line represents validation data.



**Figure 8.** Reference versus predicted viscosity values for cottonseed biodiesel-diesel blends at 25°C. Blue line represents calibration data and red line represents validation data.



**Figure 9.** Plot of the residuals for the model built with viscosity values for soy biodiesel-diesel blends at 25°C. Blue points represent calibration data and red points represent validation data.

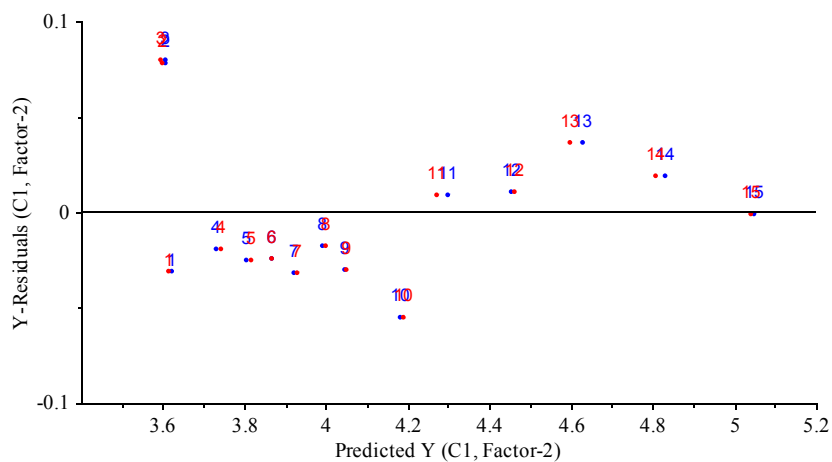
and cottonseed biodiesel-diesel blends, respectively. Correlations of 0.996365 and 0.996185 for soy and cottonseed biodiesel-diesel blends, respectively, indicated good correlation between the fluorescence spectra and viscosity values. The efficiency of the PLS models for predicting viscosity was confirmed with  $R^2$  values of 0.99275 and 0.9924 for soy and cottonseed biodiesel-diesel blends, respectively.

Figs. 9 and 10 present plots of the residual distributions of the models built with viscosity values for soy and cottonseed biodiesel-diesel blends, respectively. All of the residuals from the two curves are less than 0.10%, which indicates that the models adequately represented the viscosity for soy and cottonseed biodiesel-diesel blend samples over the studied experimental range.

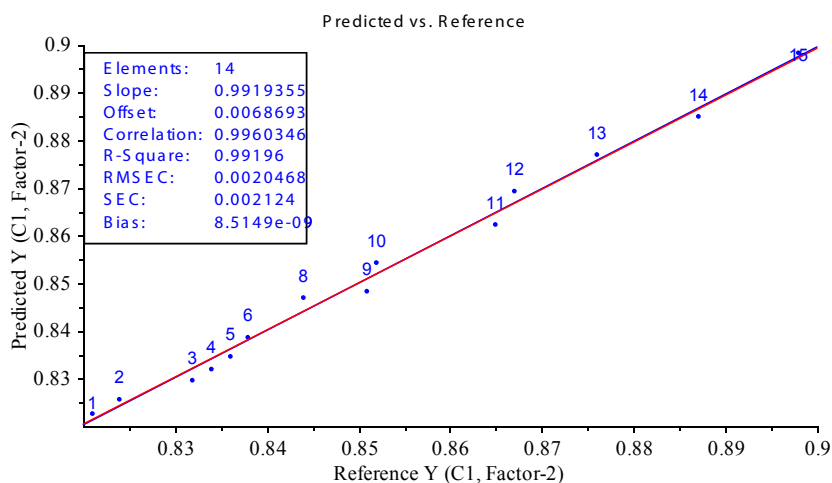
Multivariate calibration models for specific gravity were next developed for soy and cottonseed biodiesel-

diesel blends using fluorescence as the independent variables for each biodiesel and specific gravity as the dependent variables (Table 1). Figs. 11 and 12 present plots of the reference versus predicted specific gravity values for soy and cottonseed biodiesel-diesel blends, respectively. Correlations were 0.99603 and 0.98812 for the soy and cottonseed biodiesel-diesel blends, respectively. The  $R^2$  values were 0.99196 and 0.97652 for soy and cottonseed biodiesel-diesel blends, respectively. Both correlations and  $R^2$  values near 1 indicated good correlation between the fluorescence spectra and specific gravity values, and they demonstrated the ability of the PLS model to accurately predict specific gravity.

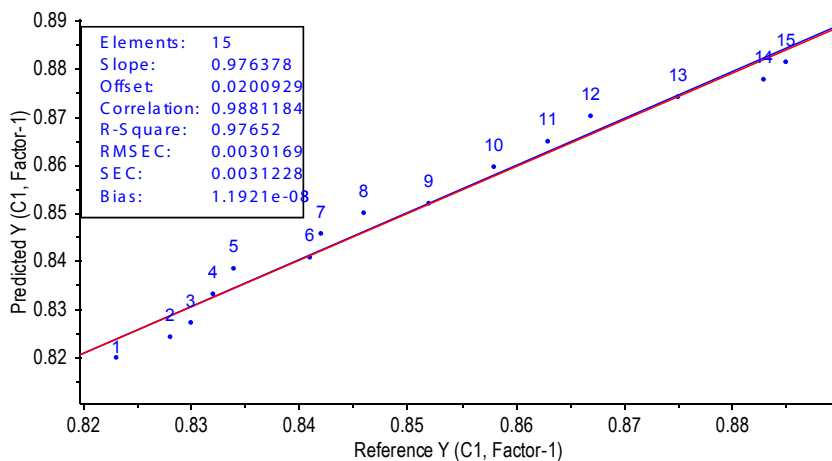
Figs. 13 and 14 show plots of the residual distributions for the models built with specific gravity values for soy and cottonseed biodiesel-diesel blends, respectively. All of the residuals from the two curves



**Figure 10.** Plot of the residuals for the model built with viscosity values for cottonseed biodiesel-diesel blends at 25°C. Blue points represent calibration data and red points represent validation data.

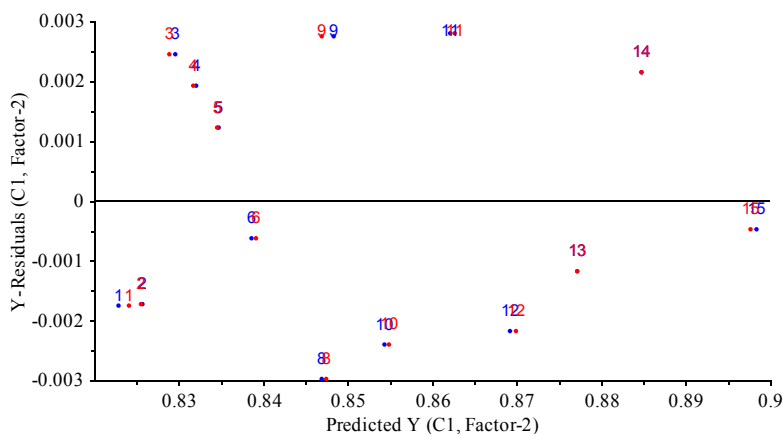


**Figure 11.** Reference versus predicted specific gravity values for soy biodiesel-diesel blends at 25°C. Blue line represents calibration data and red line represents validation data.

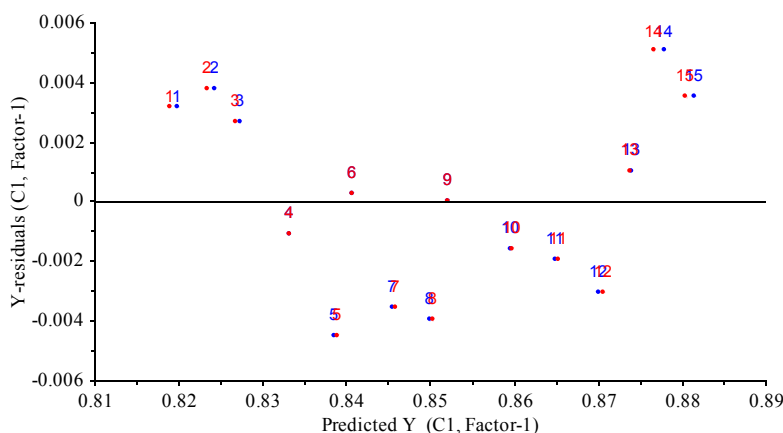


**Figure 12.** Reference versus predicted specific gravity values for cottonseed biodiesel-diesel blends at 25°C. Blue line represents calibration data and red line represents validation data.





**Figure 13.** Plot of the residuals for the model built with specific gravity values for soy biodiesel-diesel blends at 25°C. Blue points represent calibration data and red points represent validation data.



**Figure 14.** Plot of the residuals for the model built with specific gravity values for cottonseed biodiesel-diesel blends at 25°C. Blue points represent calibration data and red points represent validation data.

were less than 0.01%, which indicated that the models adequately represented the specific gravity for soy and cottonseed biodiesel-diesel blend samples over the studied experimental range.

The root mean square error of the calibration (RMSEC) and root mean square error of the validation (RMSEV) were calculated to evaluate the models. For soy biodiesel-diesel blends, the RMSEC values (using two factors) were 1.0398, 0.0332 and 0.0020 for calibration models developed for concentration, viscosity and specific gravity, respectively. The RMSEV values (using two factors) were 1.347, 0.0362 and 0.0025 for validation models developed for concentration, viscosity, and specific gravity, respectively.

For cottonseed biodiesel-diesel blends, the RMSEC values (using two factors) were 0.692, 0.0386 and 0.0030 for calibration models developed for concentration, viscosity, and specific gravity, respectively, from soy biodiesel-diesel blends. The RMSEV values (using two factors) were 1.351, 0.0479 and 0.0036 for validation

models developed for concentration, viscosity, and specific gravity, respectively. The RMSEC and RMSEV results exhibited acceptable levels of error for determinations of concentration, viscosity and specific gravity of both soy and cottonseed biodiesel-diesel blends.

## 4. Conclusions

In conclusion, advantages of fluorescence spectroscopy, such as simplicity, speed, low cost, and ability to implement on-line monitoring systems, suggest that this method is a powerful analytical tool. The association of spectrofluorimetry with the PLS calibration developed in this study was proven perfectly suitable as an analytical method to simultaneously predict concentration, viscosity, and specific gravity of biodiesel-diesel blends. The prediction of these quality parameters displayed good agreement with the results

obtained empirically. The models for soy biodiesel-diesel blends exhibited  $R^2$  values of 0.99892, 0.99275 and 0.99196 for concentration, viscosity and specific gravity, respectively. The models for cottonseed biodiesel-diesel blends exhibited  $R^2$  values of 0.99936, 0.9924 and 0.97652 for concentration, viscosity and specific gravity, respectively. These  $R^2$  values were all nearly 1, which demonstrated the accuracy and efficiency of the models for making predictions.

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