Fuel 113 (2013) 546–552

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Application of near infrared spectroscopy to predict the average droplet size and water content in biodiesel emulsions

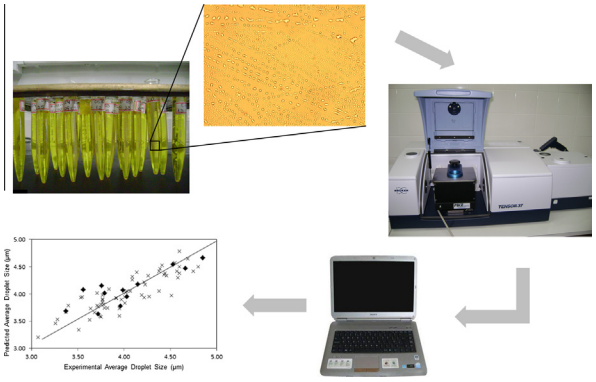
Marlene Bampi, Agnes de P. Scheer, Fernanda de Castilhos *

Department of Chemical Engineering, Paraná Federal University (UFPR), 81531-990 Curitiba, PR, Brazil

HIGHLIGHTS

- Water/biodiesel emulsions were prepared from industrial biodiesel.
- Water content and average droplet size were experimentally determined.
- NIR spectra was collected in order to develop PLS and ANN models.
- PLS model showed better performance compared to ANN model to predict water content.
- To predict the average droplet size, ANN model achieved better results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 March 2013
Received in revised form 13 May 2013
Accepted 29 May 2013
Available online 19 June 2013

Keywords:
Biodiesel
NIR spectroscopy
Emulsion
Droplet size
Water content

ABSTRACT

NIR spectroscopy was used to predict the average droplet size and water content in water/biodiesel emulsions. The emulsions were prepared from industrial biodiesel obtained from soybean oil (85 wt%) and animal fat (15 wt%) by methylic route. NIR spectra was collected in the transmittance mode with the diffuse reflectance technique. Based on the NIR spectroscopy results, it can be pointed out that this methodology has the sensibility to infer the droplet size and water content in the biodiesel emulsions. Two techniques were used to obtain the multivariate models: the partial least squares (PLS) and artificial neural network (ANN) models. Satisfactory values of mean error for the external validation were obtained, with 9.53% to PLS model for average droplet size and 8.79% for water content, since they are close to the experimental standard deviation. The performance of ANN models demonstrated that this technique allowed the prediction of average droplet size and water content with mean errors of 6.10% and 13.20%, respectively. These errors are close to the analytical error associated to the method used indicating that the NIR spectroscopy is a good alternative to be used for this purpose.

1. Introduction

Biodiesel is one of the most promising renewable fuels, proposed as an alternative to replace fossil diesel [1]. The advantages of using biodiesel include biodegradability, low toxicity, domestically produced, good lubricity, higher combustion efficiency and favorable combustion emissions profile, represented by reduced levels of particulate matter and carbon monoxide, despite of the increasing in the nitrogen oxides emission [2–4]. Besides, has a higher cetane number compared to diesel from petroleum and can be used without mechanical modification when used in conventional diesel engines or other combustion engines [3–5].

* Corresponding author. Present address: Chemical Engineering Department, Federal University of Santa Maria, Av. Roraima, 1000, 97105-900 Santa Maria, RS, Brazil. Tel.: +55 (55) 3220 9592.
E-mail address: fernanda.castilhos@ufsm.br (F. de Castilhos).

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http://dx.doi.org/10.1016/j.fuel.2013.05.092

Transesterification or alcoholysis is the most common method to produce biodiesel [5,6]. Most commercial production is alkaline-catalyzed, which is relatively fast, but sensitive to water and free fatty acids contents [6–8]. The content of free fatty acids in the reaction medium must be up to 0.5% and water content up to 0.06% relative to the vegetable oil content that in process conditions are not commonly achieved [4]. Water can hydrolyze the triglycerides in diglycerides producing free fatty acids, reacting in the alkaline catalyst producing soaps [6]. The presence of soap in the reaction increases the viscosity forming gels and stabilizing the emulsion (biodiesel/glycerol), impairing the steps of separation and purification of biodiesel to be conducted [4,6,9,10]. Moreover, it can increase the contaminants in the final product [11].

The water content as a contaminant in the final product as free or emulsified water, with suspended water droplets, depends the utilized feedstock quality, the production process adopted and the water absorption during the storage, that can achieve 1500 ppm [12,9]. Free water is strongly associated with the microorganism proliferation and corrosion in the storage tanks and can affect the stability of the fuel [9,12,13]. The water in oil emulsion stability is influenced by size and distribution of water droplets dispersed in the continuous phase and other parameters as temperature, continuous phase viscosity and volume of dispersed phase [14,15]. Emulsion is considered stable when dispersed droplets remain on the continuous phase for 5 days or more without phase separation [16]. Size distribution of water droplets can be used to explain the formation of stability mechanisms and assist the emulsion separation to a desired condition [17]. The determination of the droplet size distribution is carried out mainly through off-line measurements from different commercial apparatus. The exact values of droplet size are hardly determined, once that different difficulty is related to each one of the usual techniques. Since each analysis technique is based on different physical principles, the results obtained from these analyses may be different. Moreover, laboratory results are generally obtained with delays that may reach some hours. As a consequence, in the context of process control, online and reproducible measurements becomes a fundamental importance [18,19].

Near infrared spectroscopy (NIR) appears as an interesting alternative compared to conventional methods of analysis [2,13]. The NIR spectroscopy associated with multivariate data analysis has been employed in recent studies [2,13,20–22] for biofuels and petroleum analysis. Is an analytic technique based on the absorption of the electromagnetic energy, due to the vibration of the chemical bonds of the molecules in the region from 4000 to 12,800 cm^{-1} (780–2500 nm) [23–25].

This technique allows the multi component analysis in a fast and no destructive method, without requiring a complex sample preparation [2]. Generally, use of NIR spectroscopy is associated with partial least squares model (PLS) and principal component analysis (PCA). But, recently the use of non linear models, as artificial neural networks (ANN), has been reported in the literature with advantages in some cases over PLS models, due to its nonlinearity. An ANN is a parallel processor consisting of simple processing units (neurons), which has the natural propensity for storing experiential knowledge and making it available for use. In a simple form of an ANN, each neuron is connected to other neurons of a previous layer through weights. Neuron receives information from other neurons of the previous layer through its incoming connections. First, this information is added so weighted by the weights associated with the connections and then the result is passed through an activation function to the next neuron [24–30].

Typical NIR applications in biodiesel fuel include the transesterification monitoring and determination of chemical composition and properties, as iodine value, density and stability [24,31–33]. According to the Zhang [33], in recent research, was not found the use of NIR spectroscopy to evaluate the water average droplet size in biodiesel emulsions. In this context, the aim of this paper was to evaluate the use of the NIR spectroscopy with multivariate calibration and artificial neural network models to predict the average droplet size and water content in the soybean and animal fat biodiesel emulsions.

2. Experimental section

2.1. Materials

Industrial biodiesel obtained from soybean oil (85 wt%) and animal fat (15 wt%) by methylic route without biocides were kindly donated by BIOPAR (Usina de Bioenergia do Paraná LTDA, Rolândia, PR, Brazil) were utilized. According to the report emitted by BIOPAR laboratory, biodiesel samples presented a total contamination of 6.9 mg/Kg and a clear aspect. For the emulsions preparation, distilled water and ethanol (MERCK, 99.9%) were used.

2.2. Emulsions preparation and characterization

In a first stage the emulsions were prepared adding 1% (v/v) of ethanol to biodiesel in a heated plate under agitation (FISATOM, model 752 A). The temperature was kept close to 35 °C. In a second stage, a known amount of water (concentration range 840–1.900 mg kg^{-1}) was added slowly to the sample, reaching a final volume 200 mL. The water range was based on the initial concentration of the biodiesel sample and the research of Felizardo et al. [2]. According to these authors, in this water range concentration there is no phase separation in the emulsions. The samples were homogenized during three minutes with five different stirring rates in two homogenizers, in order to obtain different droplet size distributions. A SILVERSON homogenizer (model L4RT) was used at stirring rate of 1500, 5500 and 9500 rpm and a TURRATEC homogenizer (model TE 102), at 14,000 and 22,500 rpm. Seventy-five water/biodiesel emulsions were obtained with fifteen different water contents for each agitation speed.

Droplet size was determined using a microscope (Olympus, model BX 50) linked to a video camera (Sony, model DXC 107a). Two slides were prepared for each sample and two images were captured for each slide with 200× of magnification. The measurements were carried out with the software Olympus microsuite (TM) Basic, for Windows 1991, previously calibrated with 5.0 μm diameter. The water content was performed by titration in a Metronhm 756 titro processor according to the reference method of Karl Fisher.

2.3. NIR spectra acquisition

NIR spectra of seventy-five samples in triplicate in a spectral region from 10,000 cm^{-1} to 4000 cm^{-1} in the transmittance mode with the diffuse reflectance technique were scanned with resolution of 8 cm^{-1}. Thirty-two scans were averaged for each sample spectrum. A FTNIR spectrophotometer (BRUKER, model TENSOR 37) was used at controlled temperature (20 °C). The measurements were carried out in an integrating sphere with are solution of 8 cm^{-1} and the software OPUS 6.0, with Fourier Transform. The spectra were obtained as an average of thirty-two scans for each sample. The first spectrum was collected 1 h after emulsion preparation; the second one, 1 h and 10 min after and the third one, 1 h and 20 min after.

2.4. Multivariate analysis and neural network model

MatLab 7.0.1 software was utilized to develop a multivariate calibration model using principal component analysis (PCA) and the partial least squares (PLS) regression. The method of PLS uses a linear combinations to relate the spectra $\boldsymbol{X}$ with a given property of interest $\boldsymbol{Y}$; in this case, $\boldsymbol{Y}$ is equivalent to the average droplet size and the content of water in the biodiesel [2].

In order to verify the clustering of biodiesel samples by the differences contained in the samples, all spectral regions were treated with principal component analysis (PCA) to compose calibration and external validation groups. Several pre-processing techniques were applied to the data. The pretreatment methods tested was: Mean Centering (MC); Multiplicative Scatter Correction (MSC); Normalize (NL); first order Savitsky–Golay derivative (SG1); second order Savitsky–Golay derivative (SG2) and Orthogonal Signal Correction (OSC); beyond the original spectrum without pre-processing, none (N). Combinations of pre-treatments were also tested as Mean Scattering Correction followed by Mean Centering (MSC + MC); Mean Scattering Correction followed by Normalize (MSC + N); Mean Scattering Correction followed by first order Savitsky–Golay derivative (MSC + SG1) and Mean Scattering Correction followed by second order Savitsky–Golay derivative (MSC + SG2).

The optimal number of principal components for PLS model was determined by leave-on-out cross-validation procedure. Outliers were detected based on leverage and Student residuals values with 95% of confidence. The prediction capability of model was evaluated by root mean square error for external validation group (RMSEP).

The development of neural network models was performed in a home code written in Fortran 90 language. The multilayer perceptron neural networks with only one hidden layer were trained with a training data set of sixty-three patterns and a validation data set of 12 patterns. The root mean square error was the objective function and the Simulated Annealing algorithm [34] was used in the minimization function. Data were normalized between −1 and 1 for hyperbolic tangent transfer function. The architecture of neural network was investigated until seventeen hidden units.

The transmittance values obtained in NIR region in a wavenumbers of 9863, 8803, 8552, 7375 and 7260 cm^{-1} were used as input variables of the neural model. The only output of neural network was the average droplet size. For the content water, the wavenumbers used were 9022, 7680, 6662, 6403 and 4702 cm^{-1} as inputs, the water content was the output of the neural network.

3. Results and discussion

3.1. NIR spectra for the water/biodiesel emulsions

Fig. 1 shows the average of NIR spectra collected in triplicate for all emulsions. The spectra obtained for biodiesel emulsions presented well defined transmittance bands and peaks in the same spectral regions. The regions near to 9610–8650 cm^{-1}, 8260–7290 cm^{-1}, and 6910–6140 cm^{-1} presented higher transmittance values, due to the lower molar absorptivity of medium. The spectral region above 9000 cm^{-1} was excluded in the development of model calibration by partial least squares by presenting noise as verified in Fig. 1.

In order to evaluate the spectrophotometer sensibility in relation to the water droplet size, the spectra of emulsion samples with water content near to 1781 mg kg^{-1} obtained with different stirring rates were compared, as shows in Fig. 2. The different stirring rates used resulted in different droplet sizes. Average droplet sizes 4.55, 4.22 and 3.68 μm were obtained with stirring rates of 1500, 5500 and 9500 rpm, respectively. Is possible observe in Fig. 2 the presence of a discrepancy in the spectra baseline, that can be attributed to the difference in the light scattering by the different water droplet sizes in the emulsions. Since the water content of samples was similar, is possible assume that a higher stirring rate promotes formation of a higher number of water droplets with smaller size, and as consequence, a higher amount of droplets increased the light scattering [18]. This tendency can be confirmed in Fig. 2, where the transmittance decreasing could be noted in the samples with smaller droplet size. Based on the results showed in this figure, we can affirm that the NIR spectroscopy has sensibility to be used to infer the droplet size in biodiesel emulsions.

The spectrophotometer sensibility at different concentrations of water can be verified through the spectra behavior of samples obtained using 5500 rpm as intermediate stirring rate (Fig. 3). In the spectra, is possible to observe a slight change from baseline, where a decreasing of the transmittance peaks in some spectral regions for samples with water concentration 1386 mg kg^{-1} and 1463 mg kg^{-1}. When 1749 mg kg^{-1} of water content was used is possible to observe a larger decrease when compared to the others samples. The transmittance decrease with water content increased. Increasing the water concentration in the medium the absorption

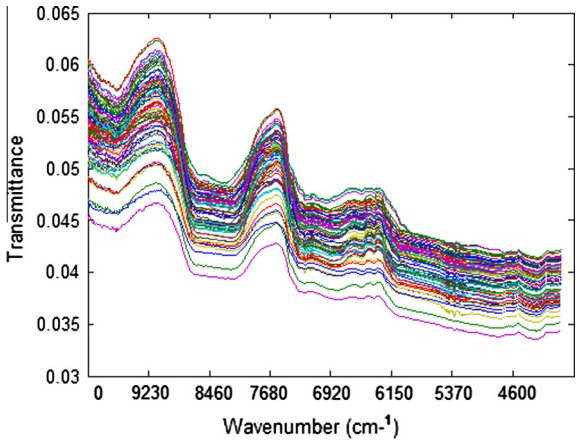

Fig. 1. NIR spectra of seventy-five water/biodiesel emulsions with different droplet sizes and different water contents.

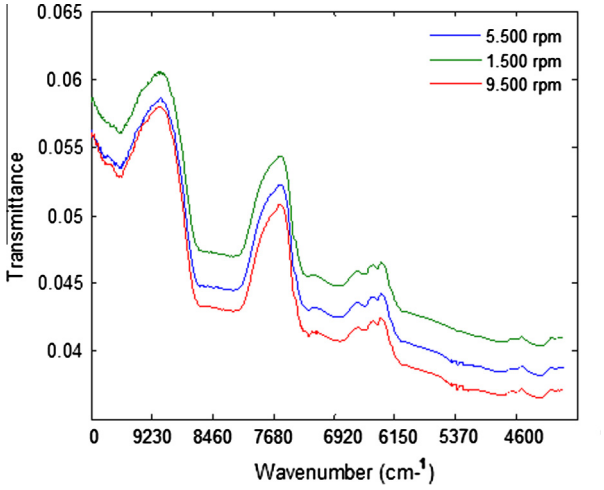

Fig. 2. NIR spectra of emulsion samples with different stirring rates and water content near to 1781 mg kg^{-1}.

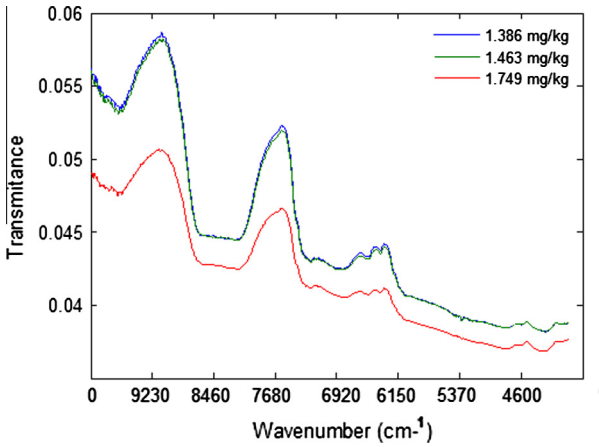

Fig. 3. NIR spectra of emulsion samples with different water contents and speed agitation of 5500 rpm.

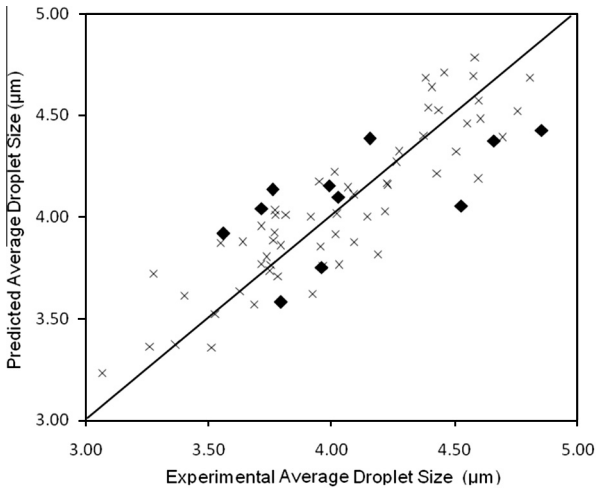

Fig. 4. Correlation between experimental and predicted average droplet size for PLS model ((×) calibration data set; (♦) validation data set).

of electromagnetic energy will increase, and a smaller amount of energy is transmitted, which demonstrates the sensitivity of the equipment to changes in water concentration.

3.2. Models development for the water average droplet size

The pre-processing method in PCA analysis resulted in the best discrimination of samples was the second derivative, where two principal components could explain 69.16% of the total variance of the data. Based on the qualitative results provided by PCA analysis, the model was constructed using 85% of the data in calibration set and 15% in external validation set.

Among the pre-processing methods investigated for PLS model development, the Savisky–Golay second order derivative with a fifteen filter width applied to data set matrix ***X***, and the second polynomial order with Mean Centering applied to the data set matrix ***Y*** presented the best results by comparing the RMSEP values. Analyzing the parameters of leverage and Student residues two outlier samples were detected.

According to Feudale et al. [35], the choice of methodology will depend of the application, because no single method is ideal for all situations. The preprocessing derivative is often used to improve the definitions of bands that are overlapped, removing noise in the same spectral region and/or for correction of the baseline. The derivative aims to give more emphasis to the peaks, allowing an increase in its resolution and eliminate additive effects [36].

For a better evaluation of the minimum number of latent variables, PLS models with 3–6 latent variables were developed with external validation procedure. The performance parameters of these models are presented in Table 1. It can be seen in this table that the root mean square error of calibration set (RMSEC) decreased with the number of latent variables (LVs), while the root mean square error of cross validation (RMSECV) presented a little variation in this latent variables range. It can also be verified that the model with three latent variables presented the lowest RMSEP value and the increase in the number of latent variable resulted in higher RMSEP values, indicating a model overfitting from four latent variable models. Based on these results, the PLS model with three latent variables was considered more adequate to predict the average droplet size. Araujo et al. [18] showed only calibration data set of developed PLS model. They obtained a correlation of 0.995, with four latent variables and, RMSEP of 3.0 μm.

Fig. 4 shows the model performance of the PLS model with three latent variables for calibration and external validation sets, which achieved a satisfactory agreement in the calibration and validation data sets.

Regarding to the development of neural network model, the optimal architecture had eight hidden units in the internal layer. The calibration and external validation data sets used for ANN model were the same used for the PLS model. Fig. 5 presents the ANN model performance for the training and validation data sets. As can be seen in the figure, the predicted values are in a good agreement with experimental data in the calibration and validation data set.

Table 1
Root mean square error for calibration (RMSEC), cross validation (RMSECV) and external validation (RMSEP) steps and determination coefficients (R^2) of calibration and cross validation steps of PLS model for droplet size prediction with different number of latent variables (LVs).

LVs	Calibration R^2	RMSEC (μm)	Cross validation R^2	RMSECV (μm)	RMSEP (μm)
3	0.846	0.235	0.607	0.354	0.455
4	0.904	0.188	0.632	0.346	0.507
5	0.942	0.147	0.636	0.346	0.507
6	0.980	0.088	0.627	0.354	0.510

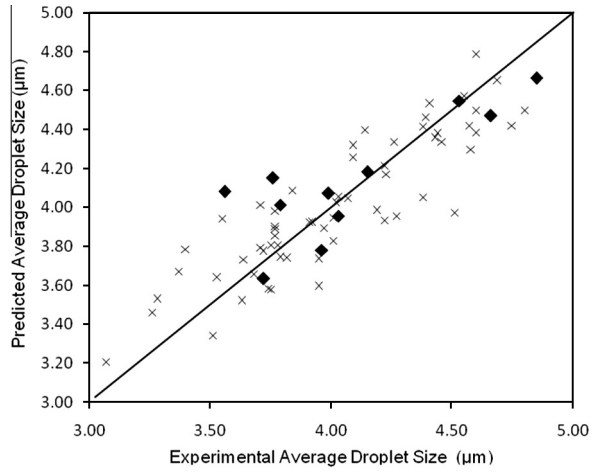

Fig. 5. Correlation between measured and predicted average droplet size for ANN model ((×) calibration data set; (♦) validation data set).

Table 2
Results of partial least squares (PLS) and artificial neural networks (ANN) models for prediction of Average Water Droplet Size.

Model	Calibration R^2	External validation R^2	Mean validation error (%)	Standard deviation
PLS	0.8460	0.6070	9.53	±0.2814
ANN	0.8016	0.7301	6.10	±0.1353

The determination of coefficients for calibration and validation sets, and the average validation error are presented in Table 2 for both models. According to the results the correlation coefficients the performance of ANN model was slightly superior to the PLS model. Although the calibration coefficient of both models was similar, the external validation coefficient showed that ANN model was more robust and performed better in predicting new samples. This result, (Table 2), is corroborated by the comparison of Figs. 4 and 5, which allows verifying the superiority of ANN model. This may be due to the presence of some non-linearity in NIR spectral data, which is not overcome by a linear model like PLS.

For the PLS model the mean error for external validation was 9.53%, which is a satisfactory value, since it is close to experimental standard deviation of 15.64% of these samples. The F statistical test applied between PLS and ANN models not presented significant different at 5% for droplet sizes results. The mean error obtained for validation set by ANN was 6.10%. The performance of ANN model demonstrated that this model allowed the prediction of the average droplet size with similar errors to the associated error to the analytical method used, indicating that NIR spectroscopy may be a good alternative to be used for this purpose.

3.3. Models development for the water content

In the PCA analysis, the pre-processing with better discrimination of samples was the first derivative whereas only two principal components could explain 99.45% the total variance of data. Based on the result of samples distribution the sets calibration were composed with 80% of the data (spectra) and the external validation set with 20% of the data (spectra).

For the calibration model developed by partial least squares (PLS), pre-processing of the first derivative (Savisky–Golay, with a fifteen filter width, second polynomial order) applied to data set matrix ***X*** and Mean Centering applied to data set matrix ***Y*** showed better results when the RMSEP value was compared. By analyzing the parameters of leverage and Student residues four anomalous samples were detected.

The number of latent variables (LVs) used in the construction of model was based on the results of RMSEC, RMSECV and RMSEP. For a better evaluation of the minimum number of latent variable the models were developed with three to eight latent variables. The results of predictive models for water content and predictive errors are shown in Table 3.

Table 3
Root mean square error of calibration (RMSEC), cross validation and (RMSECV) external validation (RMSEP) steps and determination coefficients (R^2) of calibration and cross validation steps of PLS model for water content prediction with different number of latent variables.

LVs	Calibration R^2	RMSEC (mg kg^{-1})	Cross validation R^2	RMSECV (mg kg^{-1})	RMSEP (mg kg^{-1})
3	0.843	158.59	0.809	173.64	212.16
4	0.915	119.14	0.865	148.00	118.03
5	0.940	100.86	0.881	139.86	143.65
6	0.973	68.49	0.885	137.64	146.66
7	0.995	51.47	0.888	136.33	145.55
8	0.993	35.25	0.893	133.51	155.40

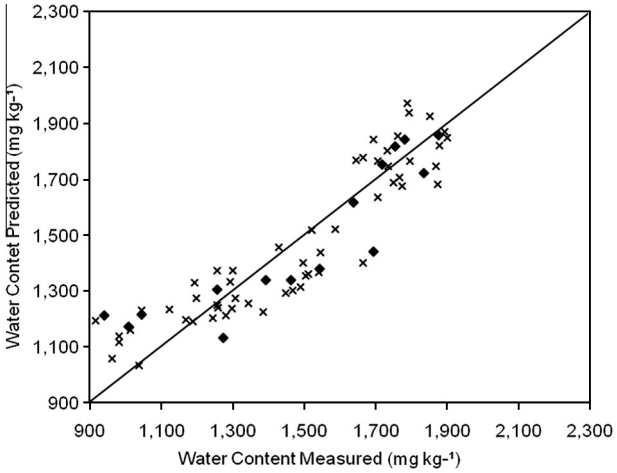

Fig. 6. Correlation between measured and predicted water contents for PLS model ((×) calibration data set; (♦) validation data set).

The parameters most commonly used in stage external validation are the RMSEP or RMSECV. The RMSEP is the most recommended when it is possible to develop a model using a data set for calibration and another for external validation [37].

The model with four latent variables presented better results when RMSEP value was compared. The determination coefficients of calibration, cross-validation and RMSECV value for the model with four latent variables, presented slight variation when compared with the other models. After the fourth latent variable, the RMSEP value increased again. Based on the results, PLS model for prediction of water content was built with four latent variables.

For the prediction of water content in W/O emulsions using models developed by PLS, Balabin et al., [24] obtained a RMSEP of 99 ppm, used six latent variables. Araujo et al. [18] obtained a correlation of 0.997 with four latent variables and RMSEP of 0.5% and, Felizardo et al. [2] used four latent variables and obtained RMSEP of 75 mg kg^{-1}.

As exposed above, the performance of the model obtained in this study was in good agreement with the literature, indicating that the model has good predictive ability for the water content. The correlation model for predicting water content was assessed by the graph of predicted values versus experimental values for both calibration set and external validation.

Fig. 6 shows the PLS model performance with four latent variables. The correlation for the calibration set, cross validation and mean error for external validation are presented in Table 4.

The built model showed a good correlation. The predicted values are close to the experimental values, indicating that the model is sensitive and can detect the differences among the samples.

The development of a neural network model to predict the water content followed the same procedures that used to building the model to predict the water average droplet size. The calibration

Table 4
Results of partial least squares regression (PLS) and artificial neural network (ANN) for prediction of water content.

Model	Calibration R^2	Validation R^2	Validation error (%)	Standard deviation
PLS	0.9150	0.8650	8.79	±80.2660
ANN	0.8711	0.5055	13.20	±124.3546

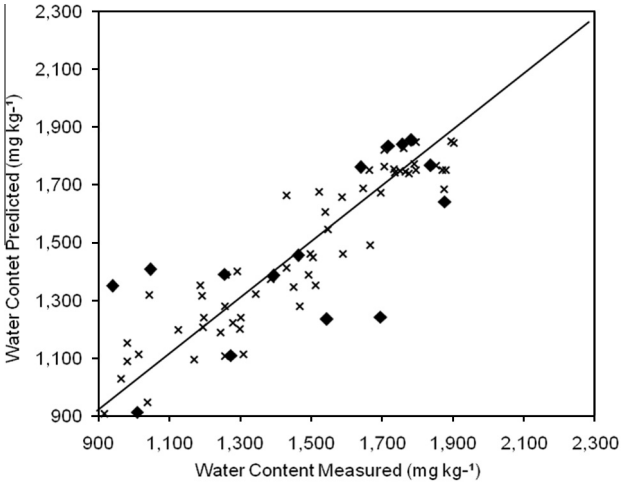

Fig. 7. Correlation between measured and predicted water contents for ANN model ((×) calibration data set; (♦) validation data set).

and external validation data sets used for ANN model were the same used for PLS model. Fig. 7 presents ANN model performance for training and validation data sets. The correlation values of calibration set of cross validation and mean error for the external validation are shown in Table 4.

According to the determination coefficients results (Table 4), the performance of PLS model was superior to ANN model. Although the calibration performance of both models was similar, the external validation showed that PLS performed is better in predicting new samples.

The mean error of PLS model for the external validation was 8.79%, which is a satisfactory value, since it is close to the experimental error 12.2% of these samples. The mean error obtained for the validation set by ANN was 13.20%. The performance of PLS model demonstrated that this model allowed the prediction of water content with a superior error compared to analytical method and ANN model errors. However, the F statistical test applied between the results of PLS and ANN models not presented significantly different at 5% for water content.

4. Conclusions

In this work, NIR spectroscopy was utilized to estimate the average droplet size and water content in water/biodiesel emulsions. The NIR spectra obtained by diffuse reflectance presented reproducibility and sensitivity to the droplet size and water content variations in biodiesel. Both techniques PLS and ANN used to obtain the models showed a satisfactory performance based in the experimental error associated to analytical method.

The model obtained by PLS, based on data from near-infrared spectroscopy, showed good predictive ability of the analyzed properties of biodiesel. In addition, the RMSEP was 9.53% for average droplet size and 8.79% for water content which were lower values than the experimental error for both properties. The ANN model presented a better performance compared to PLS model for droplet size prediction, providing a mean error 6.10% and an inferior performance with a mean error 13.30% for water content in the external validation data set.

NIR spectroscopy showed to be a good alternative to determine the average droplet size and water content in water/biodiesel emulsions with a good potential to application in on-line biodiesel quality control and storage.

Acknowledgments

The authors thank the financial support from ConselhoNacional de Desenvolvimento Científico e Tecnológico (CNPq) and Federal University of Paraná (UFPR) for financial support and scholarships. The authors also thank BIOPAR for the kind donation of the biodiesel samples.

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